

# ECIS 2022

4-9 September 2022  
Chania, Crete, Greece



## Oral Abstract Book

# Table of contents

<b>Plenary and Award Talks</b>	p.1
Christos Likos “Cluster Crystals: from a theorist’s toy model to experimental realization”	p.2
Lorna Dougan “Multiscale Mechanics of Protein Networks”	p.3
Markus Antonietti “Making Polymer Colloids More Sustainable”	p.4
Gijsje Koenderink TU Delft “The material properties of soft living matter”	p.5
John F. Brady “The Mechanics of Active Matter”	p.6
Hans-Jürgen Butt “Electrostatic charging: the source of the missing force on moving drops”	p.7
Patrick Warren “Colloidal diffusiophoresis - a brief history and recent applications”	p.8
<b>Sunday 4th September 2022</b>	p.9
<b>•Satellite Meeting : “Tribological effects on rheology of suspensions: Surface forces, contact effects, and chemical modifications”</b>	p.9
Lars Pastewska “How roughness affects surface forces”	p.10
Lucio Isa “Sliding or rolling? Characterizing single-particle contacts”	p.11
Emmanuel Trizac “Like-charge attraction: old and new”	p.12
Rosa Espinosa-Marzal  “At the intersection between nanorheology and nanotribology of ionic liquids”	p.13
Anwasha Sarkar “Designing biorelevant surfaces for soft tribology across length scales”	p.14
Annie Colin “Solvent role on polymeric bead suspensions”	p.15
Elisabeth Lemaire “Shear-thinning behaviour in non-Brownian suspensions: The role of contact forces”	p.16
Heinrich Jaeger  “Contact forces and surface interactions in dense suspensions”	p.17

Monday 5th September 2022 p.18

---

**•Satellite Meeting : “Tribological effects on rheology of suspensions: Surface forces, contact effects, and chemical modifications”** p.18

---

Jacob Klein

“Colloidal interactions and the viscoelectric effect” p.19

---

Lily Blaiset

“Rheological and frictional behavior of soft particles” p.20

---

Yu-Fan Lee

“Transient microstructure, rheology of shearthickening colloidal suspensions by timeresolved Flow-SANS and relation to nanotribology” p.21

---

Sam Brown

“Surface forces and shear thickening in silica suspensions” p.22

---

Bloen Metzger 

“The Capillarytron: a new rheometer to probe the frictional rheology of colloidal suspensions” p.23

---

Naoyuki Ishida

“Affinity between surface and solvent molecules dominates the interaction forces between surfaces in organic solvents” p.24

---

Lilian Hsiao

“Soft triborheology of elastomers with colloid-laden lubricants” p.25

---

James Richards

“Anomalous stribeck curve exponent for hydrodynamic lubrication of conformal surfaces” p.26

---

Guillaume Ovarlez

“Melting and shear jamming of vibrated suspensions” p.27

---

Meera Ramaswamy

“Universal scaling in shear thickening suspensions” p.28

---

Francisco Rocha

“Shear-thickening suspensions in a large-gap Couette flow: from steadiness to unsteadiness” p.29

---

Simon Scherrer

“Measuring Rolling Friction of Microparticles using Lateral Force Microscopy” p.30

---

<b>•Self-Assembly and Supramolecular Structures</b>	p.31
Martin Buzza	
“Defined core–shell particles as the key to complex interfacial self-assembly”	p. 32
Marco Hildebrandt	
“Core-shell microgels as soft model colloids to study phase behaviour in dense packings via small angle X-ray scattering”	p.33
Marco Laurati	
“Tunable blunt-end interactions drive the assembly of quasi-two-dimensional dispersions of dsDNA coated colloids”	p.34
Frederic Grabowski	
“Asymmetric microgels by supramolecular assembly and precipitation polymerization of pyrazole-modified monomers	p.35
Chiara Moretti	
“Synthesis and self-assembly of colloidal nanoparticles into two-dimensional superlattices”	p.36
Etienne Fayen	
Laboratoire de Physique des Solides “Quasi-crystals in binary (non-)additive hard disk mixtures”	p.37
Janne-Mieke Meijer	
“Shape matters: tuning the self-assembly of colloidal cube superstructures”	p.38
Minghan Hu	
“Multi-compartment supracapsules made from nanocapsules towards programmable release”	p.39
Maria Chiara Di Gregorio	
“Versatile self-assembling nanotubes responding to light stimulus: bio-origin, chirality and stability”	p.40
Patrick Hage	
“Light- and temperature-controlled self-assembly of isotropic and patchy microparticles”	p.41
Karin Schillen	
“Condensed supramolecular helices: the twisted sisters of DNA”	p.42
Stergios Pispas	
“Hyperbranched copolymer colloids”	p. 43
<b>•Wetting Phenomena, Responsive Colloids and Surfaces</b>	p.44
Emilie Verneuil	
“Dramatic slowing down of oil/water/silica contact line dynamics driven by cationic surfactant adsorption on the solid”	p.45
Mugele Frieder	
“Spreading of volatile oils on swelling hydrophobic polymer brush layers”	p.46
Marion Grzelka	
“Spreading of a precursor film on controlled nanorough defects”	p.47
Matthias Karg	
“Optical properties of thermoresponsive microgels:experimental and theoretical insights into the volume phase transition”	p.48

Quinn Besford "Mechanofluorescent polymer brush surfaces that spatially resolve surface solvation"	p.49
Xiaomei Li "How spontaneous charging in sliding drops affects their motion"	p.50
Bjoern Braunschweig, University Muenster "Dynamic wetting of photo-responsive arylazopyrazole monolayers is controlled by the molecular kinetics of the monolayer"	p.51
Tomas Corrales "Nanoscale interaction of water with organic interfaces"	p.52
Xhorxhina Shaulli "dSTORM super resolution microscopy of pNIPAM microgels"	p.53
Matthieu Roche "Droplet dynamics on inclined soft surfaces"	p.54
Christopher Henkel "Describing liquid drops on elastic substrates: Mesoscale model vs. macroscale model and experiment"	p.55
Yoav Tsori "Liquid nucleation around charged particles and electro-rewetting phase lines"	p.56
Periklis Papadopoulos "Wenzel-to-Cassie transition on lubricant-impregnated surfaces"	p.57
Katharina Hegner "Super-amphiphobic surfaces for ultrafast single bubble bursting and bulk defoaming"	p.58
Pawan Kumar "Predicting Contact Angle Hysteresis via Micro-scale Interface Dynamics on Random and Periodic Rough Surfaces"	p.59
Mohammad Abo-Jabal "Coupling between wetting dynamics, Marangoni vortices, and localized hot cells in volatile binary solutions drops"	p.60
Ankur Chattopadhyay "Drying patterns of liquid bridge: coffee ring to scallop shell"	p.61
Alice Pelosse "Probing dissipation length-scale in spreading drops using granular suspensions"	p.62
<b>•Colloidal Dispersions, Colloidal Stability and Surface Forces</b>	p.63
Wuge Briscoe "Centipede" statistical polymer under nano-confinement: surface forces, superlubricity, and transient interfacial gels"	p.64
Yu Zhang "Effect of membrane stability in friction manipulation using electric fields"	p.65
Dong Woog Lee, "Quantification of size-compatible host-guest interactions using a surface forces apparatus"	p.66
J. A. Rivera-Morán On the effect of morphology and particle-wall interaction on colloidal near-wall dynamics	p.67

Max Martens

“Effect of polymer chain stiffness on depletion layers and interactions in colloid–polymer mixtures” p.68

---

Yujie Jiang 

“Colloidal gels with nonsticky dopings” p.69

---

Ramon Castaneda-Priego

“Reversible cluster formation in colloidal dispersions with short-range attractive interactions” p.70

---

Lucas Luciano Cullari

“Kinetically arrested dispersions of carbon allotropes in aqueous solutions” p.71

---

Antara Pal

“Self-assembly and dynamics of colloidal rods” p.72

---

Gabriela Schmidt

“Influence of the hardness on the crystallization behaviour of binary polystyrene microgel systems” p.73

---

Florian Benedetti

“Combining force inference and holographic microscopy to measure colloidal interactions” p.74

---

Khushboo Suman 

“Anomalous rheological aging of a model thermoreversible colloidal gel following a thermal quench” p.75

---

Georg Papastavrou

“The random sequential adsorption model revisited: Elucidating the substrate influence by potentiostatic control of an electrode” p.76

---

Joe Bradley

“Sizing multimodal systems with differential dynamic microscopy” p.77

---

Michael Kappl

“Controlling supraparticles shape and structure by tuning colloidal interactions” p.78

---

Catherine Amiel

“Tailoring nanoparticle clustering by adsorption of poly(methacrylic acid) onto differently charged silica nanoparticles” p.79

---

Marius Otten

“Optical characterization of complex core-shell copolymer microgels” p.80

---

Magdaleno Medina-Noyola

“Non-equilibrium dynamic arrest diagram of SALR fluids” p.81

---

<b>•Colloids at Interfaces, Membranes and Biointerfaces, Emulsions and Foams</b>	p.82
Valerie Ravaine	
“Responsive microgels at drop surfaces: from Pickering emulsions to colloidosomes”	p.83
Lea Waldmann	
“Thermo-induced inversion of water-in-water emulsion stability by bis-hydrophilic microgels”	p.84
Marcel Rey	
“On the breaking mechanism of temperature-responsive emulsions”	p.85
Sebastian Stock	
“Incorporation of hydrophilic microgel at water in oil emulsion interface stabilized by hydrophobic nano-spheres”	p.86
Jacopo Vialetto	
“Controlling the three-dimensional shape of soft particles at fluid interfaces and how this affects their two-dimensional assembly”	p.87
Alexander Petrunin	
“Ultra-low crosslinked nanogels combine polymer and particle properties as emulsion stabilizer”	p.88
<b>•Polymers, Polyelectrolytes, Gels and Liquid Crystals</b>	p.89
Oleg Rud	
“Water desalination using polyelectrolyte hydrogel. Gibbs ensemble modelling”	p.90
Emmanouil Glynos	
“Single-ion electrolytes composed of polyanionic polymer particles”	p.91
Barbara Capone	
“Design smart polymeric materials for controlled selective and reversible adsorption at the nanoscale”	p.92
Patrick Guenoun	
“Phase separation of concentrated polymer solutions for making porous filtration membranes”	p.93
Rachel Yerushalmi-Rozen	
“Modification of acid-base equilibria of weak polyelectrolytes in complex fluids”	p.94
Vitaly Kocherbitov	
“Activity of water absorbed in hydrophilic glassy polymers”	p.95

Tuesday 6th September 2022

**•Colloids at Interfaces, Membranes and Biointerfaces,  
Emulsions and Foams**

Cecile Monteux

“Leaching foams”

p.96

p.96

Olivier Diat

“Stabilization of non-ionic foam with nano-ions”

p.97

p.98

Laurence Talini

“Mechanisms responsible for the longer lifetimes of bubbles and foams in binary liquid mixtures”

p.99

Boubakar Sanogo

“Surface-active agent’s impact on bubble break-up: from single bubble to process-scale liquid foam”

p.100

Tetiana Mukhina

“Phase behavior and miscibility in lipid monolayers containing glycolipids”

p.101

Larissa Braun

“Why do polyelectrolyte / surfactant mixtures form extended structures at the air / water interface?”

p.102

Emanuel Schneck

“Investigating biomembrane models at fluid interfaces - from bacteria surfaces to glycolipid domains to RNA delivery”

p.103

Hannah Boyd

“MUC5B mucin films under mechanical confinement: A combined neutron reflectometry and atomic force microscopy study”

p.104

Marco Fornasier

“Probing alpha-synuclein interactions with lipid membranes via fluorescence techniques”

p.105

Gergana Georgieva

“Biocidal action of Ag and soap against staphylococcus aureus”

p.106

Marie Pierre Krafft

“Perfluorocarbon nanoemulsions activatable in microbubbles for biomedical Imaging: methods of preparation and characterization”

p.107

Noémie Coudon

“Stabilization of water-in-water emulsions with fatty acid bilayers”

p.108

Alexandros Koutsoumpas

“A closer look at the softening of phospholipid membranes by the adhesion of silica nanoparticles”

p.109

Elena Mileva

“Nanostructured Materials and Coatings Based on Synthetic Four-Antennary Peptides”

p.110

Ivan Lesov

“Flow reactor for the preparation of lipid nanoemulsions and nanosuspensions via temperature variations”

p.111

Saul Hunter

“Long-term stability of Pickering nanoemulsions prepared using diblock copolymer nanoparticles: effect of nanoparticle core crosslinking, oil type and the role played by excess copolymer”

p.112

Dilek Gazolu-Rusanova

“Essential oil micro- and nano-emulsions formation, assisted by food grade preservatives”

p.113

Felix Plamper 

“Adjustable viscoelasticity of gelled liquid-liquid interfaces caused by interfacial transformations of block copolymer micelles”

p.114

<b>•Polymers, Polyelectrolytes, Gels and Liquid Crystals</b>	p.115
Rossana Pasquino	
“On the inverse quenching technique applied to gelatin solutions”	p.116
Vincenzo Ruzzi	
“Phase behavior, microscopic dynamics and microrheological properties of a thermosensitive gel-forming polymer”	p.117
Thomas Hellweg	
“Responsive polyacrylamide-based core-shell microgels”	p.118
Hamed Almohammadi	
“Shape and structural relaxation of colloidal liquid crystalline tactoids”	p.119
Daria Noferini	
“Hydrogen dynamics in PHEMA hydrogels - How neutron spectroscopy can help in preserving precious artefacts and designing new drug delivery systems”	p.120
Rajam Elanchelian	
“The importance of charges in the volume phase transition of PNIPAm microgels”	p.121
Holger Frey	
“Watching” the formation of multiblock copolymers with up to 10 Blocks: sequences, morphology, mechanical properties”	p.122
Michael Gradzielski	
“Self-Assembly of thermo-responsive BAB copolymers and their functioning as rheological modifiers”	p.123
Lisa Tran	
“Helfrich-Hurault-like undulations in cholesteric liquid crystals induced by anchoring transitions”	p.124
Pierre Bauduin	
“Polymeric surfactant P84/polyoxometalate $\alpha$ -PW12O <sub>40</sub> 3- A model system to investigate the interplay between chaotropic and hydrophobic effects”	p.125
Pavlik Lettinga	
“Uncovering Log Jamming in semidilute suspensions of quasi-ideal rods”	p.126
Kostas Daoulas	
“Mesoscopic modeling of highly-ordered polymer sanidics and comparison with scattering data”	p.127
Manos Anyfantakis	
“Green synthesis of thin poly(cyanoacrylate) films: patterned coatings, liquid packaging, and gas encapsulation”	p.128
Edwin Johnson	
“Dumbbell’ polymer brushes: understanding the origins of non-monotonic structures”	p.129
Irene Adroher-Benitez	
“Modeling adsorption and stability of polymer coatings on heterogeneous surfaces”	p.130
Rui A. Gonçalves	
“Facile control of surfactant packing and adsorption behavior”	p.131
Miroslav Štěpánek	
“Structure of a comb copolymer-surfactant coacervate elucidated by DOSY NMR and neutron spin echo spectroscopy measurements”	p.132
Asia Matatyaho Ya'akobi	
“Electron Microscopy Study of Boron Nitride Nanotubes Processed into Macroscopic Fibers”	p.133

<b>•Colloidal Systems in External Fields</b>	p.134
Ahmet Faik Demirörs	
“External fields for assembly and manipulation at micro- and macro-scales”	p.135
Carlo Rigoni	
“Ferrofluidic aqueous two-phase system with ultralow interfacial tension and micro-pattern formation”	p.136
Luigi Gentile	
“Out-of-equilibrium multi-lamellar vesicles induced by shear flow”	p.137
Yannick Hallez	
“Shear-induced glass-to-crystal transition in anisotropic clay-like suspensions”	p.138
Fabio Giavazzi	
“The Yielding Transition in Soft Amorphous Solids Under Oscillatory Shear: From Microscopic Rearrangements to Macroscopic Failure.”	p.139
Abraham Mauleon-Amieva	
“Yielding in amorphous solids: an interparticle force determination”	p.140
Junbai Li	
“Molecular Assembly of Peptide and Motor Proteins based Biomimetic Systems”	p.141
Erick Sarmiento-Gomez	
“Dynamical regimes and stochastic transitions of colloids”	p.142
Iman Abdoli	
“Odd-Diffusive Systems”	p.143
Vincent Niggel	
“Measuring 3D rotation of colloidal particles from 2D images”	p.144
Maria L. Jimenez	
“Anomalous rotational diffusion of non-spherical particles in viscoelastic fluids”	p.145
Guillermo Iglesias Salto	
“Magnetic gold nanoparticles under double external stimulus: magnetic field and laser irradiation”	p.146
Matteo Milani	
“Drying drop of colloidal suspension”	p.147
Jérôme J. Crassous	
“Drying of responsive microgels”	p.148
Dominik Horinek	
“Two types of liquid-liquid phase separation induced by centrifugation”	p.149
Nicolas Moreno Gomez	
“Tunable payload release from antibubbles using low-intensity ultrasound”	p.150
Romain Borde	
“Contactless measurement of surface tension on single droplet using acoustic levitation and machine learning”	p.151
Christopher Klein	
“Non-linear rheology and rheo-combined methods applied on colloidal systems”	p.152

<b>•Theory and Multi-scale Modeling of Colloids and Interfaces</b>	p.153
Eva Noya	
“Icosahedral quasi-crystals made of patchy colloids”	p.154
Alvaro Dominguez	
“Colloidal monolayers: bridging the gap between two and three spatial dimensions”	p.155
Remco Tuinier	
“Does the Gibbs phase rule apply to the phase behaviour of colloid-polymer mixtures?”	p.156
Maisa Vuorte	
“Modelling colloidal adsorption in bio-oils: effect of molecular chemistry, surface geometry and hydration”	p.157
Erin Koos	
“Yielding of capillary suspensions”	p.158
Rita Dias	
“Polyelectrolyte-nanoparticle mutual charge regulation and its influence on their complexation”	p.159
Joachim Dzubiella	
“Multi-scale modeling of rates and transport of colloidal nanoreactors”	p.160
Thomas Zemb	
“An explicit multi-scale evaluation of the Gibbs energy of transfer of electrolytes in liquid-liquid extraction”	p.161
Jean-Francois Dufreche	
“Multiscale modelling of the adsorption of pheromone molecules at the water-air interface”	p.162
Raffaele Pastore	
“Fickian non-Gaussian diffusion in the presence of static and dynamic heterogeneity”	p.163
Tom Höfken	
“Changes in the form factor and size distribution of nanogels in crowded environments”	p.164
Terpsichori Alexiou	
“Bottom-up coarse-grained modelling of DNA minicircles”	p.165
Gerhard Naegele	
“Clustering and dynamics in quasi-two-dimensional dispersions of proteins with competing interactions”	p.166
Julian Gerhäuser	
“Analysis of the ice surface structure after binding of an antifreeze protein and its correlation with the Gibbs-Thomson equation”	p.167
Sonya Tsibranska-Gyoreva	
“Monitoring freezing at surfactant-stabilized hexadecane/water interface by molecular dynamics”	p.168
Ivan Palaia	
“Like-charge attraction at the nanoscale: ground-state correlations and water destructuring”	p.169
Joao Maia	
“Confinement vs rigidity and its influence on the structure development of semi-dense and dense suspensions”	p.170
Primož Zihelr	
“Bronze-mean hexagonal quasi-crystals”	p.171

Wednesday 7th September 2022

p.172

**•Chinese-European Symposium**

p.172

Xi Zhang

“Supramolecular polymerization at interfaces”

p.173

Dayang Wang 

“Counterion effect on the water wettability of polycationic surfaces”

p.174

Xu Deng 

“Multi-dimensional manipulation of solid-liquid interaction”

p.175

Matthias Barz

“Peptomicelles in cancer immune therapy”

p.176

Jingcheng Hao 

“Basic study on colloid dispersed systems stimulates chemical industrialization”

p.177

Zhenhui Qi

“Structural water and crown ether: new functional supramolecular assemblies”

p.178

**•Design and Synthesis of Colloidal Systems and Nanoparticles**

p.179

Andrij Pich

“Functional microgels with non-covalent crosslinks: Towards soft adaptive colloidal systems”

p.180

Fabien Dutertre

“Chitosan-based hydrogels: Influence of crosslinking strategy on rheological properties”

p.181

Selin Bulut

“Synthesis of biocompatible dextran-based microporous microgels via microfluidics”

p.182

Viktória Varga

“Encapsulation of neuroactive drugs in desolvated serum album nanoparticles”

p.183

Linda Rozenberga

“Fluorescence and sensor properties of colloidal europium-based metal organic framework nanoparticles”

p.184

Rory McBride

“Synthesis of high molecular weight water-soluble polymers as low-viscosity latex particles in salty media”

p.185

**•Active and Bioinspired Colloidal Systems**

p.186

Saskia Lindhoud

“Separation by complexation”

p.187

Gerald Fuller

“In-situ magnetic microrheology of airway mucus”

p.188

Lukas Zeininger

“Active soft colloids for the transduction of bio-chemical information”

p.189

Diana Cholakova

“Drop self-shaping, self-bursting and swimming: simple non-living system which enlivens upon temperature variations”

p.190

H.J. Jonas

“Viscoelastic patchy particle architectures as models for living matter” p.191

---

Anna Schenk

“Hydration responsive strain-induced self-rolling of mesostructured bio-inspired mineral sheets” p.192

---

**•Composite Materials and Nanostructures** p.193

---

Peter Olmsted

“Diffusion in a realistic simulated model for the stratum corneum” p.194

---

Eric Hill

“Templated colloidal growth of semiconductors toward heterostructured nanomaterials” p.195

---

Lilian Okello

“Design of soft homocomposite silicone gels for 3D printed architectures with magneto-capillary reconfiguration” p.196

---

Alexander Tesler

“Metallic nanoparticle-on-mirror: multiple-band light harvesting and efficient photocurrent generation under visible light irradiation” p.197

---

Theodora Krasia-Christoforou

“Fabrication of electrospun organic-inorganic fibrous nanocomposites starting from highly stable colloidal solutions” p.198

---

Diane Rebiscoul

“Colloidal sol-gel route for the synthesis of mixed actinide oxides” p.199

---

Thursday 8th September 2022 p.200

---

**•Chinese-European Symposium** p.200

---

Jiaying He  
“Lowering ice and gas hydrate adhesion” p.201

---

Tommy Nylander  
“Lipid assembly morphological changes induced by changes of the solution conditions” p.202

---

Zihan Tan  
“An efficient multiparticle collision dynamics approach to membrane protein diffusion” p.203

---

Liu Jie   
Institute of Chemistry Chinese Academy of Sciences “Durable liquid-repellent poly(dimethylsiloxane) coating with anti-fouling and anti-icing performances” p.204

---

Lan Yang   
“Bumpy colloids: synthesis and their applications” p.205

---

Xurui Zhang   
“Tunable mobility of bubble surface and inward flow in ethanol-NaCl aqueous solution” p.206

---

**•Colloids at Interfaces, Membranes and Biointerfaces, Emulsions and Foams** p.207

---

Martin Haase  
Utrecht University “Separating chemicals in nanostructured, fluid-bicontinuous gels” p.208

---

Job Thijssen  
“The University of Edinburgh “Bicontinuous soft solids with a gradient in channel size” p.209

---

Chandra Shekhar   
“Rheological characterization of aqueous two-phase emulgels” p.210

---

Cheng Cheng  
“Understanding the early growth of gold films to provide thin impermeable metal films onto emulsions” p.211

---

Yanyan Liu  
“Diffusion across particle-laden interfaces in Pickering emulsions” p.212

---

Raj Tadi  
“No silver bullet: compositional ripening in water-in-oil systems” p.213

---

Pierre Haas  
“Theory of shape-shifting droplets” p.214

---

Luigi Cristofolini  
“Droplet dynamics and emulsion ageing in microgravity by DWS experiments onboard the international spaces station” p.215

---

Léa Delance  
“Uptake kinetics of spontaneously emulsified microdroplets at an air interface” p.216

---

Eli Sloutskin  
“Self-positioning of colloids and fluorophores on interfacially-frozen alkane-in-water liquid spheres” p.217

---

Katherine Lefroy   
“‘Hydrophobic’ cellulose microgels: the influence of particle size on water-in-oil emulsion stability” p.218

---

Julian Wailliez  
“Probing surfactant dynamics through interfacial surface tension using millifluidic elongational flow” p.219

---

<b>•Colloids in Biomaterials and Biomedical Applications</b>	<b>p.220</b>
Moshe Gottlieb	
“Peptide decorated silica nanoparticles as phosphate binders for the treatment of Hyperphosphatemia”	p.221
Vasileios Koutsos	
“Microbubble agents for biomedical applications: Soft Nano/Micromechanics at the Interface”	p.222
Peter Schurtenberger	
“Charge effects on stability and self-assembly of antibodies in solutions – a colloid approach”	p.223
Javier Reguera	
“Morphological control in multifunctional iron oxide: gold nanoparticles for theranostics”	p.224
Valentina Nigro	
“Thin films of PNIPAM microgels for biocompatible nuclear track detectors in radiobiology”	p.225
Dominik Braunmiller	
“Pre-programmed rod-shaped microgels to create multi-directional Anisogels for 3D tissue engineering”	p.226
Aristotelis Xenakis	
“Nanodispersions as effective vehicles for drug delivery”	p.227
Davide Orsi	
“Nanostructures for X-ray photodynamic therapy characterized by direct detection of singlet oxygen during radiotherapy”	p.228
Fernando Giacomelli	
“Engineering of pH-triggered nanoplatfoms based on novel poly (2- methyl-2-oxazoline)-b-poly[2-(diisopropylamino) ethyl methacrylate] copolymers with tunable morphologies for biomedical applications”	p.229
Beatrice Lucia Bona	
“Nanotherapeutics for cardiac pathologies: from NP development to their biological behaviour comprehension”	p.230
Pavel Švec	
Universal lipid nanoparticles for nucleic acid delivery”	p.231
Gerardo Palazzo	
“Unusual gold nanoparticle-antibody interactions”	p.232
Jiankang Song	
“Depletion interaction mediated micronization of proteins”	p.233
Simona Sennato	
“A novel approach for the determination of number concentration of liposomes by Laser Transmission Spectroscopy”	p.234
Dorota Matyszewska	
“Factors determining the interactions of drugs used to treat chronic obstructive pulmonary disease with model lung surfactants”	p.235
Marta Szczęch	
“Polymeric-based nanocarriers for the treatment of the central nervous system disorders”	p.236
Charaf Eddine Merzougui	
“Small-angle X-ray scattering (SAXS) to explore blood proteins interactions with polymers”	p.237
Nihal Aydogan	
“Synergistic Therapy of Breast Cancer by NIR-Responsive Nanostructured Lipid Carriers Containing Gold Nanorods”	p.238

<b>•Composite Materials and Nanostructures</b>	p.239
Markus Retsch “Thermal transport in self-assembled materials: From high anisotropy to high temperatures”	p.240
Gerardino D’Errico “Bio-inspired phenolic polymers in composite materials: from the nanostructure to the multifunctionality”	p.241
Marco Lattuada “Preparation of structured biomimetic composite materials through magnetic control of sol-gel phase transitions”	p.242
Anastasia Rissanou “Conformations and dynamics of polymer chains in cis and trans polybutadiene/silica nanocomposites through atomistic simulations”	p.243
Loic Hilliou “Dispersion mechanism of organogel in a polymer nanocomposite studied by in-extruder rheo-optical characterization”	p.244
Oren Regev Ben-Gurion University of the Negev “Compression-enhanced thermal conductivity of carbon loaded polymer composites”	p.245
<b>•Self-Assembly and Supramolecular Structures</b>	p.246
Roland Kádár “Cellulose nanocrystals in simple and not-so-simple flows”	p.247
Faniry Andriamiseza “From wet spinning to 3D printing of carbohydrate supramolecular hydrogels”	p.248
Franziska Gröhn “Self-Assembled nano-objects for solar energy conversion: Photocatalysis and switchability in aqueous solution”	p.249
Chlo Guzelot “Development of cross-linked porous materials for membrane filtration: polymerization of microemulsions using non-polymerizable surfactants”	p.250
Maeva Lafitte “Self-assembled nano-colloidal resonators for advanced metasurfaces”	p.251
Lucie Laporte “Influence of lead driers on oil paints’ properties: Correlating supramolecular organization and rheology”	p.252
Ronit Bitton “Tuning the properties of multicomponent polysaccharide/peptide self-assembled macroscopic membranes”	p.253
Cosima Stubenrauch “Transition from a sponge-like to a foam-like nanostructure in water-rich L3 phases”	p.254
Ilan Shumilin “Modifying macrocycle stability and supramolecular chemistry in a deep eutectic solvent”	p.255
Otto Glatter “Inverse internally self-assembled particles (ISAsomes)”	p.256
Marco Manca University of Fribourg “Optical tweezer platform for the characterization of pH-triggered colloidal transformations in the oleic acid / water system”	p.257
Julia Sabadini  “Morphological transition in ethoxylated coacervate core micelles”	p.258

<b>•Advanced Colloid Science for Applications and Products</b>	p.259
Krassimir Velikov “Advanced structuring technologies at micro- and nano-scale for product functionality control”	p.260
Yanshen Zhu “Utilising inorganic perovskite quantum dots as a 2D high-sensitivity optical heat flux meter”	p.261
Peter Mario Worsch “Rheo-SAXS study of lamellar-to-onion structure changes”	p.262
Rut Besseling “Spatially resolved dynamic light scattering: characterizing colloids over unprecedented ranges of turbidity and flow”	p.263
Marek Bekir “Potential filtration technique for microparticles of equal size but different surface modifications”	p.264
Tamas Szabo “Langmuir-Blodgett and LbL deposition of graphene based conductive semitransparent coatings”	p.265
Andrew Clarke “A microstructural investigation of an industrial attractive gel at pressure and temperature”	p.266
Nicolas Bremond “Shaping alginate hydrogel and tuning its properties for the design of a tubular bioreactor”	p.267
Ignacio Martin-Fabiani “The role of polymer rheology modifiers in the assembly of drying binary colloidal dispersions”	p.268
Werner Kunz “Organic reactions and radical polymerizations in surfactant-free, mesostructured liquids”	p.269
Gergana Radulova “Rheological properties of micellar solutions and bicontinuous micellar phases”	p.270
Jesus F. Ontiveros “Dynamic phase inversion as a tool to track the “optimal formulation” of microemulsions. Practical applications”	p.271
<b>•Design and Synthesis of Colloidal Systems and Nanoparticles</b>	p.272
Spyridon Varlas “Polymerization-induced self-assembly and disassembly during the synthesis of thermo-responsive ABC triblock copolymer nano-objects in aqueous solution”	p.273
M. Ali Aboudzadeh “Design of photosensitizer-based core-shell latex particles by PISA in alcoholic dispersion polymerization”	p.274
Claire Council “Extrusion: A new method for rapid formulation of high-yield, monodisperse nanobubbles”	p.275
Csilla Gyorgy “RAFT dispersion polymerization of methyl methacrylate in mineral oil”	p.276
Nicole Janoszka “Mesoporous multicompartiment microparticles of semi-crystalline triblock terpolymers”	p.277
Shaghayegh Hamzehlou “Monte Carlo simulation of the microstructure of bio- versus petroleum-based (meth)acrylates synthesized by emulsion polymerization”	p.278

Friday 9th September 2022 p.279

---

**•Colloids in Biomaterials and Biomedical Applications** p.279

---

Zahari Vinarov

“Colloids and interfaces: the missing link in understanding how advanced oral formulations improve drug absorption” p.280

---

Radiom Milad

“Genetic or chemical conjugation influences the nanomechanics of virus-like particle (VLP) vaccines” p.281

---

Andreas Stadler

“Effect of red blood cell shape changes on hemoglobin interactions and dynamics: a neutron scattering study” p.282

---

Aneta Michna

“Adsorption kinetics of neurotrophins on polyelectrolyte multilayers- the impact of films on neuroblastoma cell viability” p.283

---

Kevin Roger

“Assessing suspension and infectivity times of virus-loaded aerosols involved in airborne transmission” p.284

---

Agata Baryzewska

“Dynamic Janus emulsions as foodborne bacteria sensors via targeting exoenzyme production” p.285

---

**•Design and Synthesis of Colloidal Systems and Nanoparticles** p.286

---

Benjamin Abecassis

“Persistent nucleation and size dependent attachment kinetics produce monodisperse PbS nanocrystals” p.287

---

Martin Reifarth

“Multi-functional patchy SiO<sub>2</sub> particles: Fabrication via microcontact printing and directed self-assembly” p.288

---

Maria Karayianni

“Development of double hydrophilic block copolymer/porphyrin ion complex micelles towards photofunctional nanoparticles” p.289

---

Kornelia Gawlitza

“Fluorescent molecularly imprinted polymer particles for direct detection of glyphosate in organic solvents and water” p.290

---

Krzysztof Szczepanowicz

“Sequential adsorption of charged nanoobjects as a method of functionalization of drug delivery systems” p.291

---

Fabian Sobotta

“Polymerization-induced electrostatic self-assembly” p.292

---

**•Active and Bioinspired Colloidal Systems** p.293

---

Joost De Graaf

“Understanding enhanced rotational dynamics of active probes in rod suspensions” p.294

---

Arturo Moncho-Jorda

“Controlling the structure, phase behavior and dynamics of soft colloids by active interaction switching” p.295

---

Edward Yong Xi Ong

“Can activity in a 3D dense suspension of Quincke rotors cause thickening or dethickening?” p.296

---

Antoine Deblais

University of Amsterdam “Chromatographic separation of active polymer-like worm mixtures by contour length and activity” p.297

---

Andreas Zöttl

University of Vienna “Role of self-generated fluid flows in active colloids moving through polymer networks” p.298

---

Mihail Popescu

“Understanding the non-equilibrium interactions governing the tracer response near chemically active confined Janus particles” p.299

---

**•Advanced Colloid Science for Applications and Products** p.300

---

Anne-Laure Fameau

“Non-aqueous foams stabilized by crystalline particles: from design to applications” p.301

---

Eva Judy

“Mechanistic aspects of drug encapsulation in colloidal assemblies” p.302

---

Mingyu Yuan

TU Berlin “In-situ investigation of Ca<sup>2+</sup> effects on humic acid aggregation with polyelectrolyte for water treatment” p.303

---

Igor Siretanu

“Facet-dependent surface charge and hydration of colloidal nanoparticles at variable pH” p.304

---

Georgios Bokias

“Novolac-based microcapsules containing isocyanate reagents for self-healing applications” p.305

---

Maud Save

“Design of colloidal molecularly imprinted polymer colloids as biomimetic sorbent for recognition and separation of nonylphenol pollutant” p.306

---

ECIS 2022

Plenary and Award Talks

# Cluster Crystals: from a theorist's toy model to experimental realization

*Christos N. Likos<sup>1</sup> and Emmanuel Stiakakis<sup>2</sup>*

*<sup>1</sup>University of Vienna, Austria*

*<sup>2</sup>Forschungszentrum Jülich, Germany*

Crystals are orderly states of matter in which particles with sizes ranging from sub-nanometer to micron are arranged in a periodic lattice. Crystalline solids epitomize the notion of rigidity, lying at the antipode of fluidity that is embodied by liquids. Accordingly, hybrid, exotic phases that combine crystallinity with (super-)fluidity have fascinated researchers both in the classical realm of soft matter physics and in the quantum domain. In usual crystals, the lattice constant  $a$  and the particle concentration  $c$  obey the proportionality  $a \sim c^{-1/3}$ , dictated by the condition that the (conventional) unit cell be populated by a fixed number of particles determined by the lattice geometry. Cluster crystals, a newer concept, are unconventional states of matter whose lattice sites are occupied by clusters of fully or partially overlapping particles rather than single ones. In these states, the number of overlapping particles within a cluster, the lattice-site occupancy  $N_{occ}$ , is a fluctuating quantity, with its expectation value scaling with concentration as  $N_{occ} \sim c$  and thus resulting in a concentration-independent lattice constant, the latter being the salient structural characteristic of both cluster crystals and cluster quasicrystals.

In this talk, I will briefly review 20 years of theoretical work that led to a recent, theory-informed, experimental discovery of this new state of matter.

## Multiscale Mechanics of Protein

*Lorna Dougan*

*School of Physics and Astronomy, University of  
Leeds, UK*

Proteins are bionanomachines. These workhorses of the cell are responsible for a vast array of biological functions. Acting in isolation or as part of complex machinery, they perform their function through structural and mechanical changes. Inspired by their specific mechanical properties and diverse functionality, globular folded proteins are versatile nanoscale building blocks for creating responsive biomaterials. However, a major challenge is to construct a theory that connects the mechanical properties of an individual protein and the collective response of a protein network. Here, I will describe our recent efforts to modulate the nanoscale mechanics of single proteins to control their unfolding during protein network formation. We exploit the chemical and mechanical responsiveness of single functional proteins to provide an important route to finely tune the architecture, mechanics, and dynamic relaxation of protein networks. Such predictive control will be advantageous for future smart biomaterials for applications which require responsive and dynamic modulation of mechanical properties and biological function.

### References

- 1) Hughes, M. D. G., Cussons, S., Mahmoudi, N., Brockwell, D. J. & Dougan, L. , Tuning Protein Hydrogel Mechanics through Modulation of Nanoscale Unfolding and Entanglement in Postgelation Relaxation, *ACS Nano*, 2022
- 2) MDH Hughes, BS Hanson, SE Cussons, N Mahmoudi, DJ Brockwell, L Dougan Control of Nanoscale in situ Protein Unfolding Defines Network Architecture and Mechanics of Protein Hydrogels, *ACS Nano*, 2021, 15, 11296
- 3) BS Hanson, L Dougan Intermediate Structural Hierarchy in Biological Networks Modulates the Fractal Dimension and Force Distribution of Percolating Clusters, *Biomacromolecules*, 2021 10, 4191
- 4) A Aufderhorst-Roberts, MDG Hughes, A Hare, DA Head, N Kapur, DJ Brockwell L Dougan, Reaction Rate Governs the Viscoelasticity and Nanostructure of Folded Protein Hydrogels, *Biomacromolecules*, 2020, 21:4253
- 5) BS Hanson, L Dougan Network Growth and Structural Characteristics of Globular Protein Hydrogels, *Macromolecules*, 2020, 53: 7335
- 6) MDH Hughes, SE Cussons, N Mahmoudi, DJ Brockwell, L Dougan Single molecule protein stabilisation translates to macromolecular mechanics of protein network, *Soft Matter*, 2020, 16: 6389

## Making Polymer Colloids more Sustainable

Markus Antonietti

*Max Planck Institute of Colloids and Interfaces, Potsdam, Germany*

Polymer Colloids are everywhere. From advanced Suspension Stabilizers to polymer paints and glues, from microencapsulation to nanocomposites: In all these modern products polymer colloids are omnipresent. However, it turned out that many of these products, when released into the environment, are rather persistent, accumulate in the food chain, or contribute to the more general phenomenon of microplastic. I will report on the current trend of making such systems bio-based and biodegradable. I will introduce the concept of biorefinery and present some “forgotten” reactions within these biomass transformation cascades to complement a sustainable toolbox for solving also advanced technology problems. From a larger view of time, colloid technology started about 15000 years ago with natural compounds, e.g. soaps, which are still largely based on oils and fats, and it is time to reactivate this “ancient knowledge” to serve the new imperative of sustainability.

**Keywords:** biobased colloids, sustainability, biorefinery, circular economy

## The material properties of soft living matter

*Gijsje Koenderink*

*Department of Bionanoscience, Kavli Institute of Nanoscience Delft, Delft University of Technology, Netherlands*

Cells and tissues are highly dynamic but at the same time need to withstand large mechanical loads. This paradoxical mechanical behavior is governed by fibrous protein scaffolds known as the cytoskeleton and the extracellular matrix. Fibrous networks have many advantageous mechanical properties: fibers can form space-filling elastic networks at low volume fractions and they reversibly stress-stiffen, which provides protection from damage. However, it is still poorly understood how biopolymer networks can combine these features with the ability to dynamically adapt their structure and mechanics. I will summarize recent insights in this question obtained via quantitative measurements on reconstituted cytoskeletal and extracellular matrix networks. We perform these measurements from the macroscopic scale (using rheology) all the way down to the molecular scale (using optical tweezers, in situ small-angle- X-ray scattering, and atomic force microscopy). I will furthermore highlight connections to applications in bottom-up synthetic biology and for tissue (re)generation.

## **The Mechanics of Active Matter**

*John Brady*

*California Institute of Technology, Department of Chemical Engineering,  
Pasadena, USA*

A distinguishing feature of many living systems is their ability to move – to be active. Through their motion living systems are able self-assemble: birds flock, fish school, bacteria swarm, etc. But such behavior is not limited to living systems. Recent advances in colloid chemistry have led to the development of synthetic, nonliving particles that are able to undergo autonomous motion by converting chemical energy into mechanical motion and work. This intrinsic activity imparts new behaviors to active matter that distinguish it from equilibrium systems. Active matter generates its own internal stress, which can drive it far from equilibrium, and by so doing active matter can control and direct its own behavior and that of its surroundings. In this talk I will discuss our work on active matter and on a new source of stress – the swim pressure – that is responsible for self-assembly and pattern formation in active matter systems. The role of confinement and flow on active systems will be discussed.

**2022 Overbeek Gold Medal of the European Colloid & Interface Society**

**Electrostatic charging: the source of the missing force on moving drops**

*Hans-Jürgen Butt*

*Max Planck Institute for Polymer Research, Mainz, Germany*

Although wetting phenomena have been studied for more than 200 years, many fundamental questions are not fully understood. For example, the speed of a water drop moving down an inclined plane cannot be predicted. Still significant progress has been made in the last decade, in particular with respect to dynamic wetting. The aim of the presentation is to draw attention to some new developments, in particular on the influence of charging.

**2022 Solvay Prize of the European Colloid & Interface  
Society**

**Colloidal diffusiophoresis - a brief history and recent  
applications.**

*Patrick B Warren*

*STFC Hartree Centre, Sci-Tech Daresbury, Warrington, UK.*

Diffusiophoresis is a potent and ubiquitous non-equilibrium transport mechanism for micron-sized colloidal particles. The biggest effects arise in electrolyte solutions, where chemiophoresis in concentration gradients combines with electrophoresis in the diffusion potential to drive particles at speeds of 1–10  $\mu\text{m/s}$ , propelling them over large distances in time scales of minutes. An additional peculiarity in binary electrolytes is that the speed is logarithmically dependent on the salt concentration, leading to persistent effects such as osmotic trapping and long-lived particle removal. Since diffusiophoresis is effective at ousting particles from dead-end channels, in the context of laundry detergency it can operate as a previously unsuspected pore-scale particulate soil removal mechanism during rinsing. This offers a possible resolution of the decades-old so-called stagnant core paradox. Moreover, with the surfactant solution playing the role of an electrolyte, there arises an unexpected dependence on the counterion mobility which is verified experimentally. I will discuss my work in this area, which was done in collaboration with Sangwoo Shin and Howard Stone in Princeton.

Sunday 4th September 2022

**•Satellite Meeting :**  
**“Tribological effects on rheology of suspensions:  
Surface forces, contact effects, and chemical modifications”**

# How roughness affects surface forces

Lars Pastewka<sup>1,2</sup>

<sup>1</sup>*Department of Microsystems Engineering, University of Freiburg, Germany*

<sup>2</sup>*Cluster of Excellence livMatS, University of Freiburg, Germany*

Presenting author's e-mail: [lars.pastewka@imtek.uni-freiburg.de](mailto:lars.pastewka@imtek.uni-freiburg.de)

Macroscopic objects interact via surface forces. Traditional models for surface forces assume that interfaces are smooth, but roughness affects interaction by limiting the area of intimate atomic contact. This talk will describe recent developments in computer simulations and theoretical models for surface interactions that take roughness into account. The basic underlying idea is that during rough contact, interfaces need to deform to conform, requiring elastic energy [1]. For soft adhesive interfaces, the balance between spent elastic and gained interfacial energy then determines an effective work of adhesion, which can be quantitatively computed if the surface roughness is known at all scales [2]. Force-distance curves for such soft interfaces are often hysteretic because the adhesive contact line is pinned at surface heterogeneities [3]. For hard interfaces, surface interactions are determined by the perimeter of fractal contacting patches [4]. Such models for soft and hard interfaces can be regarded as generalizations of the famous Johnson-Kendall-Roberts (JKR) and Derjaguin-Muller-Toporov (DMT) models, respectively, for the contact of smooth spheres.

**Keywords:** Roughness, adhesive contact, surface forces, JKR model, DMT model

## References

- [1] Persson, B. N. J. & Tosatti, E. The effect of surface roughness on the adhesion of elastic solids. *J. Chem. Phys.* 115, 5597 (2001)
- [2] Dalvi, S. et al. Linking energy loss in soft adhesion to surface roughness. *Proc. Natl. Acad. Sci. U. S. A.* 116, 25484–25490 (2019)
- [3] Sanner, A. & Pastewka, L. Crack-front model for adhesion of soft elastic spheres with chemical heterogeneity. *J. Mech. Phys. Solids* 160, 104781 (2022)
- [4] Pastewka, L. & Robbins, M. O. Contact between rough surfaces and a criterion for macroscopic adhesion. *Proc. Natl. Acad. Sci. U. S. A.* 111, 3298–3303 (2014); Pastewka, L. & Robbins, M. O. Contact area of rough spheres: Large scale simulations and simple scaling laws. *Appl. Phys. Lett.* 108, 221601 (2016)

# Sliding or rolling? Characterizing single-particle contacts

Lucio Isa

Laboratory for Soft Materials and Interfaces, Department of Materials, ETH Zurich,  
8093 Zurich, Switzerland

Presenting author's e-mail: [lucio.isa@mat.ethz.ch](mailto:lucio.isa@mat.ethz.ch)

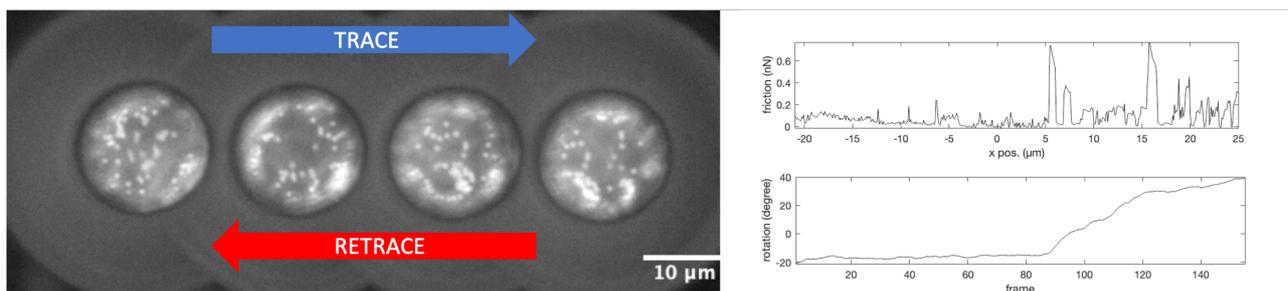
The characterization of contact forces between particles has received increasing attention in recent years due to the role that they are believed to play in determining the rheology of dense suspensions. In particular, lateral force microscopy (LFM) has enabled measuring sliding friction at the single-particle level by measuring the torsion of an atomic force microscopy cantilever onto which a particle is glued and made to slide onto a counter-surface as a function of normal load [1]. A broad range of experimental, numerical and theoretical studies has linked the presence of sliding friction to the onset of discontinuous shear thickening in dense suspensions, making it a necessary parameter to describe their rheology [2].

However, in addition to pure sliding, particles in a fluid are also free to rotate relative to one another, but the characterization of rolling friction at the single-particle level remains practically unexplored, even though its role in shear thickening is being called into question [3,4]. Key to the measurement of rolling friction is the possibility to measure the relative rotation between particles while simultaneously measuring lateral forces as a function of normal load.

Here, I will describe an upgrade to LFM, which uses nanofabricated probes to measure sliding and rolling friction among microparticles as a function of their surface properties. The particles have fluorescent asperities, which enables tracking their rotation during LFM. I will explain the details of the technique and report results for particles of different surface roughness.

This new tool offers exciting possibilities to expand the well-established characterization of sliding friction via colloidal-probe LFM to the largely-unexplored characterization of rolling friction, as of high interest both in suspensions' rheology and in functional coatings.

**Keywords:** Friction; contact forces; rolling; sliding; dense suspensions.



**Figure 1.** Left: Overlay of microscopy images of a particle with fluorescent asperities while scanning in an LFM measurement. The particle is confined in a nanofabricated “cup”, which allows both rolling and sliding. Right: friction force and particle rotation angle as a function of position during a lateral scan. When friction is low, the particle can slide and shows no rotation, while for higher friction, sliding is no longer possible and the particle starts rolling.

## References

- [1] C.-P. Hsu, S.N. Ramakrishna, M. Zanini, N.D. Spencer and L. Isa, Proceedings of the National Academy of Sciences, 2018, 115 (20), 5117-5122
- [2] M. M. Denn, J. F. Morris and D. Bonn, Soft Matter, 2018,14, 170-184.
- [3] B.M. Guy, J.A. Richards, D.J.M. Hodgson, E. Blanco and W.C.K. Poon, Physical Review Letters, 2018, 121(12), 128001.
- [4] A. Singh, C. Ness, R. Seto, J. J. de Pablo and H. M. Jaeger, Physical Review Letters, 2020, 124, 248005.

## Like-charge attraction: old and new

I. Palaia <sup>1</sup>, A. Goyal <sup>2</sup>, E. del Gado <sup>2</sup>, L. Samaj <sup>3</sup>, E. Trizac <sup>4</sup>

<sup>1</sup>Institute of Science and Technology, Klosterneuburg, Austria

<sup>2</sup>Physics Dpt, Institute for Soft Matter Synthesis and Metrology, Georgetown Univ, USA

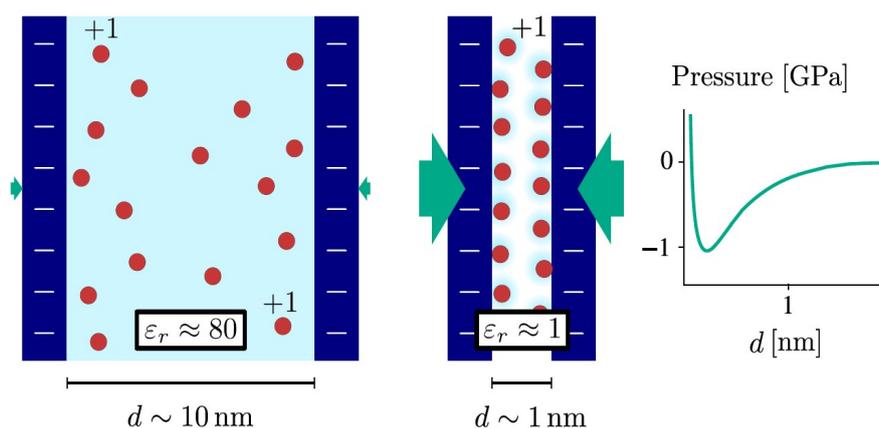
<sup>3</sup>Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovakia

<sup>4</sup>LPTMS, Université Paris-Saclay / CNRS, Orsay, France

Presenting author's e-mail: [emmanuel.trizac@universite-paris-saclay.fr](mailto:emmanuel.trizac@universite-paris-saclay.fr)

Like-charge attraction, driven by ionic correlations, challenges our understanding of electrostatics both in soft and hard matter. It escapes traditional approaches like Poisson-Boltzmann or DLVO theories, and is of importance in a number of phenomena, from DNA condensation to cement cohesion, including colloidal phase separation, vesicle docking, or anomalous bilayer interactions. For two charged planar surfaces confining counterions and water, we prove that even at relatively low electrostatic coupling, the relevant physics is the ground-state one, oblivious of fluctuations. Based on this, we derive a simple and accurate interaction pressure, that fulfills known exact requirements and can be used as an accurate effective potential. We test this equation against implicit-solvent Monte Carlo simulations and against explicit-solvent simulations of cement and several types of clays. We argue that water destructuring under nanometric confinement drastically reduces dielectric screening, enhancing ionic correlations. Our equation of state at reduced permittivity, versatile, explicit and particularly simple, therefore explains the exotic attractive regime reported for these materials, even in absence of multivalent counterions.

**Keywords:** colloidal stability, like-charge attraction, clays, cement



**Figure 1.** Sketch of the geometry considered together with main result

## At the intersection between nanorheology and nanotribology of ionic liquids

*Rosa M. Espinosa-Marzal, Mengwei Han, Xuhui Zhang*

*University of Illinois at Urbana-Champaign, USA*

*Presenting author's e-mail: [rosae@illinois.edu](mailto:rosae@illinois.edu)*

Ionic liquids (ILs) have been recognized as suitable lubricants for harsh conditions. The strongly adsorbed IL layers on solid surfaces are capable of bearing heavy loads and effectively reduce friction. Yet, the literature often mentions the solid-like behavior of ILs under the nanoconfinement provided by two countersurfaces. Here, we have combined nanorheological and tribological studies of five ILs using an extended Surface Forces Apparatus to investigate the behavior of IL thin films under nanoconfinement. We discuss the effects of the chemical structure, water contamination and surface charge on the nanorheological behavior and on friction.

**Keywords:** ionic liquids, nanotribology, nanorheology, confinement

**Acknowledgements:** This material is based upon work supported by the National Science Foundation under CBET 19-16609.

### References

[1] M. Han, S. A. Rogers, and R. M. Espinosa-Marzal. *Langmuir* 2022, 38, 2961.

# Designing biorelevant surfaces for soft tribology across length scales

Anwasha Sarkar

*Food Colloids and Bioprocessing Group, School of Food Science and Nutrition,  
University of Leeds, UK*

Presenting author's e-mail: [A.Sarkar@leeds.ac.uk](mailto:A.Sarkar@leeds.ac.uk)

Soft tribology at multiple length scales [1-5] is emerging as a new frontier in food colloids community to quantify friction and lubrication of food-saliva mixtures in orally relevant surfaces. Tribological assessment is providing mechanistic insights into the physics of oral processing and sensory perception of food. Applications of tribology currently ranges from helping to design healthier foods, create sustainable alternatives without compromising mouthfeel, tackle food counterfeiting and tailor foods for aging populations. However, effective mimicking of the complex features, deformability and motions of oral surfaces to perform tribological experiments and harmonization of such surfaces are crucial to enable the widespread use of oral tribology. For example, frictional properties of biopolymers such as proteins particularly at the nanoscale are rather poorly understood as often hard interfaces are used as model systems unsuitable to represent soft oral contacts [3]. As a first case study, I will discuss the frictional properties of proteins at nanoscale using friction force microscopy in soft-soft contacts (ranging from 150 kPa to 2 MPa) using elastomeric colloidal probes [6]. We found that on bare soft elastomeric surfaces, friction can be described by single asperity models, such as JKR. In contrast, friction on protein-coated surfaces can be described with macroscale models, with protein affinity followed by hydration towards the surface playing a major role on the resulting friction. Surface deformability also had a significant impact on the frictional properties of protein-coated surfaces with higher deformability leading to lower contact pressure and, consequently, decreased friction [6]. In addition, I will present another case study on the recent development of novel 3D soft tribo-surfaces [7] to emulate the highly sophisticated tongue surfaces in terms of deformability, topography of papillae structure and wettability as well as tribological performance and computationally studied mechanosensing. Although there has been a significant progress in this direction on designing novel biomimetic surfaces for tribometer, relating the *in vitro* tribological data to real time *in vivo* sensory data remains as a challenge

**Keywords:** soft tribology; surface; deformability; roughness; nanoscale; 3D printing

**Acknowledgements:** The European Research Council is acknowledged for its financial support (Funding scheme, ERC Starting Grant 2017, Project number 757993) for this work.

## References

- [1] Sarkar A, Soltanamadi S, Chen J, Stokes JR. 2021. Food Hydrocolloids. 117, Art No. 106635.
- [2] Sarkar A, Andablo-Reyes E, Bryant M, Dowson D, Neville A. 2019. Current Opinion in Colloid & Interface Science. 39, pp. 61-75.
- [3] Liasas E, Connell SD, Ramakrishna SN, Sarkar A. 2020. Nanoscale. 12(4), pp. 2292-2308
- [4] Kew B, Holmes M, Stieger M, Sarkar A. 2021. Oral tribology, adsorption and rheology of alternative food proteins. Food Hydrocolloids. 116, Art No. 106635.
- [5] Zembyla M, Liasas E, Andablo-Reyes E, Gu K, Krop EM, Kew B, Sarkar A. 2021. Food Hydrocolloids. 111, , Art No. 106364.
- [6] Liasas E, Connell SD, Zembyla M, Ettelaie R, Sarkar A. 2021. Nanoscale. 13(4), pp. 2350-2367.
- [7] Andablo-Reyes E, Bryant M, Neville A, Hyde P, Sarkar R, Francis M, Sarkar A. 2020. ACS Applied Materials and Interfaces. 12(44), pp. 49371-49385

## Solvent role on polymeric bead suspensions

*Annie Colin<sup>1</sup>, Anh Vu Nguyen Le<sup>2</sup>, Adrien Izzet<sup>2</sup>, and Guillaume Ovarlez<sup>2</sup>*

*<sup>1</sup>ESPCI Paris PSL, CBI 11 rue Vauquelin 75005 Paris, France*

*<sup>2</sup>LOF, CNRS-Université de Bordeaux, 33600 Pessac, France*

*Presenting author's e-mail: [annie.colin@espci.fr](mailto:annie.colin@espci.fr)*

Despite their apparent simplicity, suspensions of hard spheres in a Newtonian fluid show complex non-Newtonian behaviors and remain poorly understood. Recent works have pointed out the crucial role of interparticle contact forces in these behaviors. Here, we show that the same (polystyrene) particles, when immersed in different Newtonian solvents, show different behaviors at both the microscopic and macroscopic scales. Thanks to interparticle force measurements in each solvent together with rheological measurements, we show how the fine details of the pairwise particle interactions impact the macroscopic behavior. The rheological properties (shear thinning, shear thickening, jamming solid fraction value) of the suspensions, made up of same particles, are shown to depend on the nature of the solvent. Here, we highlight several mechanisms at the particle scale: the swelling of polymeric particles in an organic solvent, the role of colloidal repulsive forces and inertia in suspensions with a water solution, and the variation of the friction coefficient as a function of the load for particles immersed in silicone oils. Our study provides new quantitative data to test micromechanical models and simulations. It questions the interpretation of previous experimental works. Finally, it shows the need to systematically characterize the interparticle normal and tangential forces when studying a given suspension of hard spheres in a Newtonian fluid.

# Shear-thinning behaviour in non-Brownian suspensions: The role of contact forces.

*Elisabeth Lemaire<sup>1</sup>, Frédéric Blanc<sup>1</sup>, Laurent Lobry<sup>1</sup> and François Peters<sup>1</sup>*

<sup>1</sup>Institut de Physique de Nice UMR 7010 CNRS/UCA, Parc Valrose, 06108 Nice, France

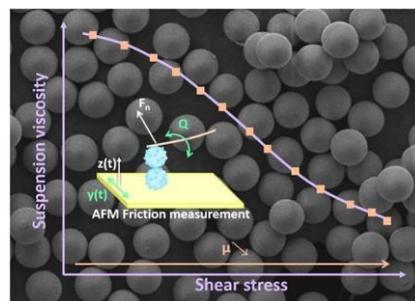
Presenting author's e-mail: [elemaire@unice.fr](mailto:elemaire@unice.fr)

The rheology of concentrated non-Brownian suspensions has undergone a small revolution in the last 15 years when the importance of the role played by solid contacts between particles was realized. Considering these contacts has allowed to explain the continuous or discontinuous shear-thickening in dense suspensions [1] and, more recently, the shear-thinning observed beyond the shear-thickening [2], i.e. in frictional non-Brownian suspensions [3]. In my talk, I will show that this shear-thinning can be explained by variable friction between particles [4].

Considering the low magnitude of the forces experienced by the particles of suspensions under shear flow, it is first argued that rough particles come into solid contact through one or a few asperities. In such a few-asperity elastoplastic contact, the friction coefficient is expected not to be constant but to decrease with increasing normal load. Therefore, since the viscosity has been shown to increase with friction, it is expected that a decrease of the friction coefficient with shear stress leads to a viscosity decrease. Numerical simulations based on the Force Coupling Method provide a model for the shear-thinning and show that the effective friction coefficient is specified by the effective normal contact force which is simply proportional to the bulk shear stress.

This scenario has been validated by coupled experiments of rheology and Atomic Force Microscopy that provide the variation of the pairwise friction coefficient with normal load. It is shown that introducing the experimental friction law into the viscosity model proposed by Lobry et al. [3] enables to fully capture the shear-thinning behavior of suspensions of polystyrene particles (40  $\mu\text{m}$  in diameter) in a Newtonian mixture of water and Ucon oil, at various solid fractions. These results highlight the close links between the microscopic friction properties of the particles and the macroscopic rheological behavior of suspensions.

**Keywords:** mono-contact, friction, shear-thinning, non-Brownian suspensions



**Figure 1.** Picture of the shear-thinning either measured or deduced from the measurement of the friction coefficient.

## References

- [1] R. Mari, R. Seto, J.F. Morris and M.M. Denn, *J. Rheol.*, 2014, 58(6), 1693-1724.
- [2] G. Chatté, J. Comtet, A. Niguès, L. Bocquet, A. Siria, G. Ducouret, F. Lequeux, N. Lenoir, G. Ovarlez and A. Colin, *Soft Matter*, 2018, 14(6), 879-893.
- [3] L. Lobry, E. Lemaire, F. Blanc, S. Gallier and F. Peters, *J. Fluid Mech.*, 2019, 860, 682-710.
- [4] M. Arshad, A. Maali, C. Claudet, L. Lobry, F. Peters and E. Lemaire, *Soft Matter*, 2021, 17(25), 6088-6097.

# Contact forces and surface interactions in dense suspensions

*Heinrich Jaeger*<sup>1</sup>

<sup>1</sup>*James Franck Institute and Department of Physics, University of Chicago, Chicago, Illinois, USA*

Presenting author's e-mail: [h-jaeger@uchicago.edu](mailto:h-jaeger@uchicago.edu)

Concentrated, or dense, suspensions of small particles in a liquid have become an active area of research for the investigation of non-Newtonian flow behavior, where the material's response to shear depends strongly on the intensity of forcing. The talk will discuss how some of the properties of these materials, which enable them to transform reversibly between fluid and solid-like states, arise from frictional contact forces and how these can be tailored by chemically functionalizing the particles' surfaces [1,2] or driving the particles through a glass transition [3]. This opens up new opportunities for designing the dynamic stress response of dense suspensions.

**Keywords:** hydrogen bonds, dynamic covalent bonds

## References

- [1] N. M. James, E. D. Han, R. A. L. de la Cruz, J. Jureller, and H. M. Jaeger, Interparticle hydrogen bonding can elicit shear jamming in dense suspensions, *Nature Materials*, 2018, 17, 965. <http://dx.doi.org/10.1038/s41563-018-0175-5>
- [2] G. L. Jackson, J. M. Dennis, N. D. Dolinski, M. van der Naald, H. Kim, C. Eom, S. J. Rowan, and H. M. Jaeger, Designing Stress-Adaptive Dense Suspensions using Dynamic Covalent Chemistry, preprint, 2022, <https://arxiv.org/abs/2203.12526>
- [3] C. Chen, M. van de Naald, A. Singh, N. D. Dolinski, G. L. Jackson, H. M. Jaeger, S. J. Rowan, and J. J. de Pablo, Leveraging the polymer glass transition to access thermally-switchable shear jamming suspensions, preprint, 2022, [https://assets.researchsquare.com/files/rs-1193286/v1\\_covered.pdf?c=1644600035](https://assets.researchsquare.com/files/rs-1193286/v1_covered.pdf?c=1644600035)

Monday 5th September 2022

**•Satellite Meeting :**  
**“Tribological effects on rheology of suspensions:  
Surface forces, contact effects, and chemical modifications”**

## Colloidal interactions and the viscoelectric effect

*Jacob Klein and Di Jin*

*Weizmann Institute of Science, Israel*

Presenting author's e-mail: [Jacob.klein@weizmann.ac.il](mailto:Jacob.klein@weizmann.ac.il)

Particles in colloidal dispersions frequently carry heterogeneous surface charge, and as they approach to nanometer separations this may result in large electric fields  $\mathbf{E}$  between them; these can modify the viscosity  $\eta$  of the interparticle confined aqueous liquid phase through coupling of the field with the dipoles of the water molecules, though the detailed molecular mechanism is not well understood. Such modification of the viscosity of polar liquids by electric fields is known as the viscoelectric effect. It was first measured for organic polar liquids over 80 years ago, indicating the empirical relation  $\eta(\mathbf{E}) = \eta(1 + fE^2)$  where  $f$  is the viscoelectric constant. For water, however, by far the most ubiquitous and important polar liquid, measuring the viscoelectric effect is much more challenging and has never been carried out directly. Estimates of  $f$  for water, based on different indirect effects such as electrophoretic mobility, mean diffusion coefficients in clay pores or molecular dynamics simulations have been made, but the values of  $f$  estimated from these different approaches vary by over a thousand-fold. We have now (Di Jin et al., PNAS 2022) [1] determined  $f$  in water directly for the first time using a surface force balance (SFB) where the field  $\mathbf{E}$  between the interacting mica and gold surfaces at nanometer separations is varied via a 3-electrode configuration controlling the gold potential, and the resulting viscosity is measured directly through its hydrodynamic modulation of the surface approach dynamics. The value of  $f$  thus measured directly differs by 1 and by 2 orders of magnitude, respectively, from the highest and lowest indirect estimates of its value made over the past 6 decades.

**Keywords:** visco-electric effect; electric-field/viscosity coupling

### References

[1] Jin, D., Hwang, Y., Nir Kampf, N. and Klein, J., 'Direct measurement of the viscoelectric effect in water', Proceeding of the National Academy of Science (PNAS), 2022 Vol. 119 No. 1 e2113690119 <https://doi.org/10.1073/pnas.2113690119>

## Rheological and frictional behavior of soft particles

*Lily Blaiset*<sup>1,2</sup>, *Nicolas Sanson*<sup>2</sup>, *Matthieu Roché*<sup>1</sup>, *Bruno Bresson*<sup>2</sup>,  
and *Elisabeth Guazzelli*<sup>1</sup>

<sup>1</sup>*MSC - Université de Paris, France*

<sup>2</sup>*SIMM - ESPCI, France*

Presenting author's e-mail: [lily.blaiset@espci.fr](mailto:lily.blaiset@espci.fr)

Over the past decades, industrial problems have led to exploring different ways to control the rheology of dense suspensions. Shear thickening or shear thinning can be induced by changing the chemical nature of surfaces which appears as a crucial feature. Recent studies have highlighted the importance of friction in these systems, when particles are non-deformable [1-2].

Much less is known when particles can deform. In this framework, our study focuses on the rheological behavior in water of non-brownian particles with controlled surface properties, and more precisely how surface functionalization impacts particle-particle interactions. We perform alkaline hydrolysis on bare particles of cross-linked poly(methylmethacrylate) (PMMA). During this step, hydrophobic PMMA transforms into a much softer hydrophilic polymer, poly(methacrylic acid) (PMAA) [3]. As the hydrolysis reaction occurs radially from the surface to the core of the PMMA particle, a hydrolyzed layer of controlled thickness of the particle can be obtained, acting as a deformable hydrogel with tunable swelling and surface properties in response to environmental stimuli such as pH, ionic strength, etc.

This surface modification has a great impact on interparticle friction and mechanical properties of the particle itself. The elastic modulus as well as the macroscopic friction of the obtained particles in suspension have been investigated by atomic force microscopy and measure of the angle of repose respectively [4]. Then a correlation has been made with the critical volume fraction of the suspension and with rheological experiments.

We demonstrate that (i) the presence of a hydrogel layer drastically reduces the frictional coefficient compared to non-modified particles (ii) interparticle friction behavior of modified particles strongly depends on physico-chemical properties of the suspending fluid (pH, ionic strength). We believe these parameters affecting their surface properties play a significant role in the deformation of particles, and thus in the macroscopic behavior of the suspension.

**Keywords:** chemical modification, non-brownian particles, hydrolysis, friction, rheology

### References

- [1] Yi. Chen, Y. Zhou, H. Pi and G. Zeng, *RSC Adv.*, 2019, **9**, 3469–3478.
- [2] J. A. Richards, R. E. O'Neill and W. C. K. Poon, *Rheol Acta*, 2020, **60**, 97–106.
- [3] B. C. Thanoo and A. Jayakrishnan, *J. Appl. Polym. Sci.*, 1990, **39**, 1153–1161.
- [4] C. Clavaud, A. Bérut, B. Metzger and Y. Forterre, *Proc Natl Acad Sci USA*, 2017, **114**, 5147–5152.

# Transient Microstructure, Rheology of Shear-Thickening Colloidal Suspensions by Time-resolved Flow-SANS and Relation to Nanotribology

*Yu-Fan Lee<sup>1</sup>, Kevin Whitcomb<sup>1,2</sup>, and Norman J. Wagner<sup>1</sup>*

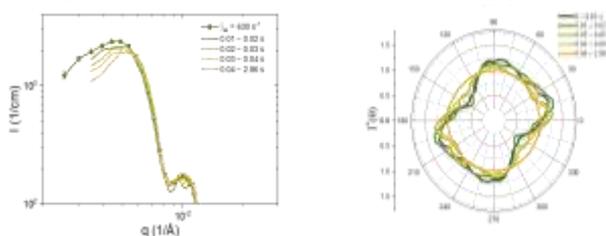
<sup>1</sup>*Center for Neutron Science, Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware, USA*

<sup>2</sup>*TA Instruments, New Castle, Delaware, USA*

Presenting author's e-mail: [yflee@udel.edu](mailto:yflee@udel.edu)

The shear thickening of dense colloidal suspensions is an active area of research aimed to understand the highly nonlinear increase of viscosity under various conditions and how this relates to the nanotribology of the particles comprising the suspension. Efforts in models and experiments have focused on connecting microstructure to the underlying micromechanical mechanism in steady shear rheology, whereas recent theoretical and experimental work shows the ability of transient rheology to distinguish between micromechanical mechanisms (Physics of Fluids. 2021;33(3)). Further, relating this rheology to the nanotribology, such as measured by methods such as lateral force microscopy, provides understanding that can be helpful for formulation of dense suspensions for specific applications (J. Rheology, 2020;64(2):267-82.). While recent studies have focused on the steady-shear microstructure in the shear thickened state, the corresponding measurement of transient microstructure is lacking. Advances in time-resolved flow-small angle neutron scattering (SANS) enable resolving microstructure transients on the scale of 10 milliseconds. In this work, we present measurements of the transient microstructure of a concentrated colloidal suspension of coated silica particles in index matching fluid under shear reversal and shear cessation using time-resolved Flow-SANS in a 1-2 shear cell geometry. To aid in the understanding of the flow reversal experiments, we also present complementary measurements of shear cessation for monitoring transient microstructure recovery by Brownian motion during stress relaxation from the shear thinned and shear thickened states. Rheological measurements of the shear viscosity and first and second normal stress differences along with lateral force microscopy measurements establish this suspension shear thickens due to enhanced lubrication hydrodynamics. Flow reversal experiments demonstrate the persistence of hydroclusters under the entire observation time of shear reversal protocol, indicating the dominance of hydrodynamic interactions for this colloidal suspension of coated particles. These results provide structure and rheology experimental results that can be used to test simulations and theory. Connections and differences between nanotribological measurements and shear rheology are discussed within the Stribeck curve for lubrication.

**Keywords:** colloidal suspensions, microstructure, shear rheology, neutron scattering



**Figure 1.** Transient microstructures at different time frames after shear cessation at a shear rate of  $630 \text{ s}^{-1}$ . left: 1D SANS  $I(q)$  as a function of normalized scattering vector, where symbols represent microstructures measured at a steady shear rate of  $630 \text{ s}^{-1}$ . right: Polar plot of normalized annular average scattering intensity.

# Surface Forces and Shear Thickening in Silica Suspensions

*Sam C. Brown<sup>1</sup>, Wilson C.K. Poon<sup>1</sup>, John R. Royer<sup>1</sup>*

*<sup>1</sup>School of Physics and Astronomy, The University of Edinburgh, King's Buildings, Peter Guthrie Tait Road, Edinburgh EH9 3FD, United Kingdom*

*Presenting author's e-mail: [S.C.Brown-3@sms.ed.ac.uk](mailto:S.C.Brown-3@sms.ed.ac.uk)*

Shear thickening arises in dense suspensions as particles are forced into contact, so that the thickening onset stress  $\sigma^*$  serves as a macroscopic probe of repulsive particle interactions at the nano-scale. In colloidal and surface science, it is commonly assumed one can use the Derjaguin approximation to relate inter-particle forces  $F$  to an interaction free energy per unit area  $W$  for equivalent flat plates. If the Derjaguin approximation holds, for a fixed particle and solvent composition one should expect  $\sigma^* \propto W^*/R$ , with a constant  $W^* \propto F^*/R$  setting the force needed to form frictional contacts,  $F^*$ . Existing literature for suspensions of silica spheres [1,2], where one might expect standard Derjaguin-Landau-Verwey-Overbeek (DLVO) interactions and the Derjaguin approximation to apply, instead suggests  $\sigma \propto 1/R^\alpha$  with  $\alpha$  around 1.5 to 2.

Characterising the rheology silica suspensions over range of particle size and ionic strength, we map the transition from repulsive shear thickening suspensions at low ionic strength to shear thinning yield-stress suspensions at high ionic strength, indicating the transition from repulsive to attractive interactions. At low ionic strength, our results are consistent with  $\sigma^* \propto R^{-1}$  as expected from the Derjaguin approximation. However, this scaling breaks down in our smallest spheres close to the repulsive-attractive transition, potentially reflecting surface roughness effects not accounted for in idealised smooth-sphere interaction models.

**Keywords:** Surface Forces, Silica, DLVO

## References

- [1] B. J. Maranzano and N. J. Wagner, *Journal of Rheology*, 2001, 45, 1205--1222.
- [2] D. Hodgson, PhD thesis, University of Edinburgh, 2016.

# The capillarytron: a new rheometer to probe the frictional rheology of colloidal suspensions

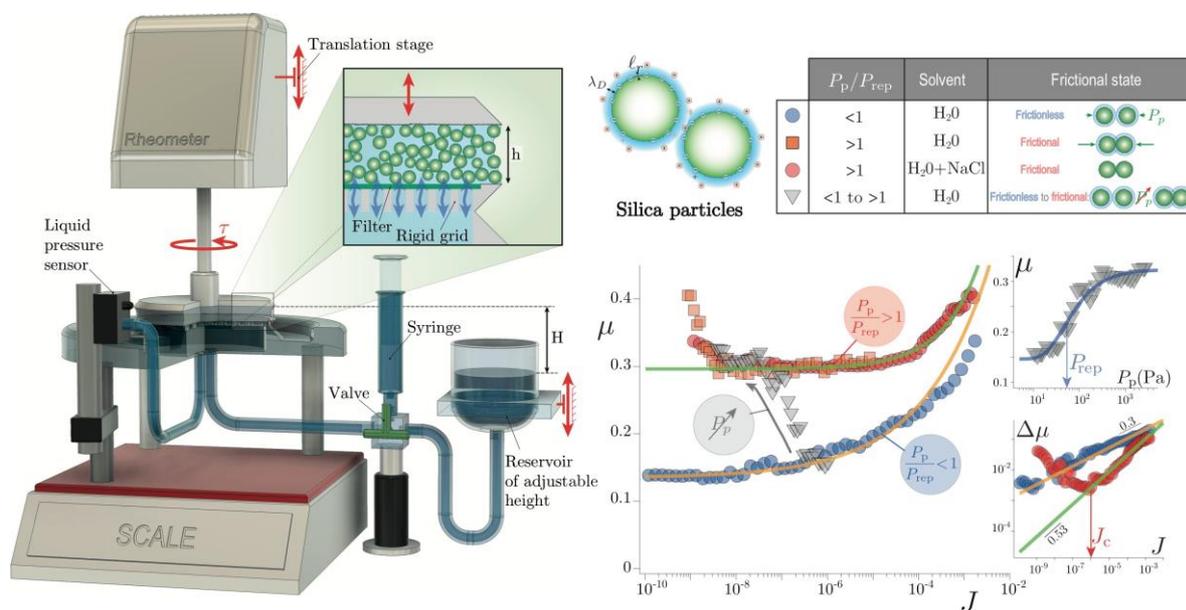
*Bloen Metzger<sup>1</sup>, Bruno Etcheverry<sup>1</sup>, Yoël Forterre<sup>1</sup>,*

*<sup>1</sup>IUSTI-CNRS, Aix-Marseille University, Marseille, France*

Presenting author's e-mail: [bloen.metzger@univ-amu.fr](mailto:bloen.metzger@univ-amu.fr)

A large consensus has recently emerged about the central role played by solid frictional particle contacts in colloidal suspensions. However, no rheological tools exist to characterize the frictional behavior of these suspensions. Here, we develop a new rheometer, which through the control of the particle stress, gives access to the frictional constitutive flow rules of colloidal suspensions. The key idea of this device is to impose the particle stress, not using a rigid grid as in Boyer et al. (2011), but using the air/suspension capillary interface. Based on a new concept in rheometry, the Capillarytron opens the route to pressure-imposed rheology on colloidal and shear thickening suspensions - a potential new frontier in the field and a challenge for industrials.

**Keywords:** shear-thickening, colloidal suspensions, frictional rheology



**Figure 1.** (Left) Sketch of the Capillarytron. (Right) Macroscopic suspension friction coefficient  $\mu(J, P_p/P_{rep})$  versus  $J$  for a colloidal suspension of silica particles of diameter  $d=23$  microns immersed in water, where  $J$  is the viscous number,  $P_p$  is the particle stress and  $P_{rep}$  is the repulsive pressure between particles induced by the electrostatic double-layer.

**Acknowledgements:** ERC Plantmove #647384, ANR ScienceFriction #18-CE30-0024

# Affinity between Surface and Solvent Molecules Dominates the Interaction Forces between Surfaces in Organic Solvents

*Naoyuki Ishida<sup>1</sup>, Akifumi Ohnishi,<sup>1</sup> Shogo Udaka<sup>1</sup> and Koreyoshi Imamura<sup>1</sup>*

<sup>1</sup> *Graduate School of Natural Science and Technology, Okayama University, Okayama, Japan*

Presenting author's e-mail: [n-ishida@okayama-u.ac.jp](mailto:n-ishida@okayama-u.ac.jp)

Suspensions of colloidal particles dispersed in non-aqueous solvents are commonly used in industrial products including paints, cosmetics, ceramics, and electronics. To evaluate and control the stability of such suspensions, it is critical to understand fundamentally the interaction forces between particle surfaces in non-aqueous solvents. However, while the DLVO theory well describes the interaction between surfaces in aqueous solution, the interactions between particles in non-aqueous solvents have been much less understood.

In this study, we conducted direct measurements of the interaction forces between the silica surfaces modified with various coupling reagents with different molecular structures in various organic solvents using atomic force microscopy (AFM). We evaluated how the affinity of the solvent molecules to the surfaces influences the interaction forces.

The repulsive forces acting over a few nanometers were measured between the surface when the particles disperse, whereas only van der Waals attraction was observed when the particles aggregate. This repulsive force was suggested to be the solvation force, arising from the steric hindrance of solvent molecules strongly attached to the surfaces. Complementary solvent relaxation NMR measurements [1] of the suspensions in the organic solvents revealed that the strong interaction between the surface and solvent molecules was seen when the repulsive force acts between the surfaces. These results indicate that the very short-range repulsive force, other than the electrostatic repulsion, can dominate the stability of the suspensions.

**Keywords:** interaction force, atomic force microscope, organic solvents, solvent relaxation NMR, molecular affinity

**Acknowledgements:** We acknowledge financial support by KAKENHI (Grant-in-Aid for Scientific Research (B), Number 21H01639) from the Japan Society for the Promotion of Science (JSPS).

## References

[1] C. L. Cooper, T. Cosgrove, J. S. van Duijneveldt, M. Murray and S. W. Prescott, *Soft Matter*, 2013, 30, 7211.

## Soft triborheology of elastomers with colloid-laden lubricants

*Lilian C. Hsiao<sup>1</sup>, Yug Saraswat<sup>1</sup>, Catherine Hill<sup>1</sup>*

*<sup>1</sup>Department of Chemical & Biomolecular Engineering, North Carolina State University,  
Raleigh NC 27606, USA*

*Presenting author's e-mail: [lilian\\_hsiao@ncsu.edu](mailto:lilian_hsiao@ncsu.edu)*

The friction between two soft surfaces is influenced by the presence of particulates in the interfacial lubricant fluid, which is an important consideration in many technological areas including biotribology, soft robotics, and automotive applications. Here, we connect the tribological behavior of soft elastomer surfaces to the rheological properties of suspensions used to lubricate the tribopairs. The lubricating fluid is composed of smooth hard sphere-like poly(methyl methacrylate) colloids of different diameters ( $2a = 0.43 \mu\text{m}$ ,  $1.5 \mu\text{m}$ , and  $2.8 \mu\text{m}$ ) suspended in squalene at different volume fractions ( $0.05 \leq \phi \leq 0.55$ ), resulting in rheological properties that range from Newtonian to shear thinning and thickening. To synthesize soft elastomers, we crosslink Sylgard 184 to create poly(dimethyl siloxane) tribopairs that are placed in a ball-on-three-plate accessory on a stress-controlled rheometer. Steady shear Stribeck curves are obtained with increasing sliding speeds and a constant normal load. The Stribeck curves for particle-laden suspensions deviate significantly from that of pure squalene, especially in the boundary and elastohydrodynamic regimes. The elastohydrodynamic lubrication friction also demonstrates unique flow transitions and plateaus when the rheology of the lubricant is non-Newtonian. We will develop constitutive relations to link the bulk rheology of the lubricants with elastic deformation and lubrication equations to estimate the film thickness between the tribopairs, which is a strong predictor of the measured interfacial friction coefficients.

**Keywords:** soft tribology, colloids, elastomers, rheology

# Anomalous Stribeck Curve Exponent for Hydrodynamic Lubrication of Conformal Surfaces

*James A. Richards*<sup>1</sup>, *Patrick B. Warren*<sup>2</sup>, *Daniel J. M. Hodgson*<sup>1</sup>, *Alex Lips*<sup>1</sup>,  
and *Wilson Poon*<sup>1</sup>

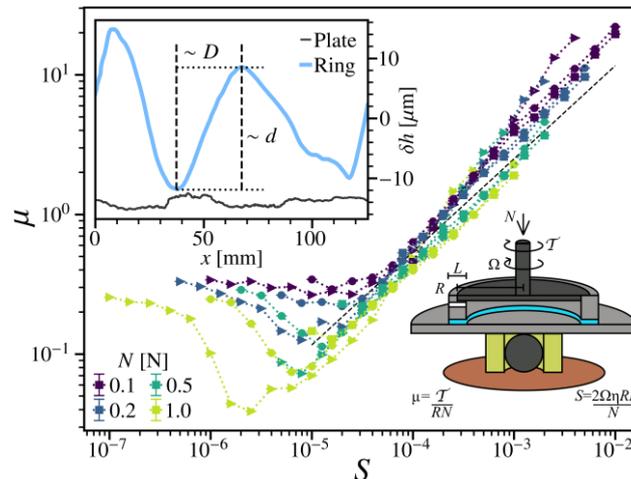
<sup>1</sup>*Edinburgh Complex Fluids Partnership, School of Physics and Astronomy,  
The University of Edinburgh, James Clerk Maxwell Building, Peter Guthrie Tait Road,  
Edinburgh EH9 3FD, United Kingdom*

<sup>2</sup>*STFC Hartree Centre, Sci-Tech Daresbury, Warrington WA4 4AD, United Kingdom*

Presenting author's e-mail: [james.a.richards@ed.ac.uk](mailto:james.a.richards@ed.ac.uk)

The hydrodynamic regime of the Stribeck curve giving the friction coefficient as a function of the dimensionless relative sliding speed (the Sommerfeld number,  $S$ ) of two contacting surfaces,  $\mu(S)$ , is usually considered trivial and well understood. We predict that for conformal surfaces contacting over large areas, a combination of independent length scales, *i.e.*, a surface texture, generically gives rise to  $\mu \sim S^\alpha$  with an anomalous  $\alpha = 2/3$  exponent for a thick lubrication film. Deviations as the film thins superficially resemble the onset of elasto-hydrodynamic lubrication but are due to a cross-over between hydrodynamic regimes. New measurements using a bespoke tribo-rheometer and Newtonian fluid confirm these predictions. Such lightly loaded textured surfaces are common in the use of colloidal complex fluids, from applying consumer formulations to eating food. We show how the hydrodynamic lubrication of conformal surfaces can then be used to measure colloidal fluids in a directly relevant type of flow.

**Keywords:** Rheology, Lubrication, Friction



**Figure 1.** Tribo-rheology experiments using a self-aligning ring-plate geometry. Main plot: Stribeck curves,  $\mu(S)$  at different loads (dark to light with increasing  $N$ ) and silicone oil viscosities (symbols). The dashed line corresponds to a  $\alpha = 2/3$  power-law. Upper inset: circumferential profile for ring and plate. Lower inset: geometry diagram.

# Melting and Shear Jamming of Vibrated Suspensions

Chloé Garat<sup>1</sup>, Sébastien Kiesgen de Richter<sup>2</sup>, Pierre Lidon<sup>1</sup>, Annie Colin<sup>3</sup>, Guillaume Ovarlez<sup>1</sup>

<sup>1</sup>Univ. Bordeaux, CNRS, Solvay, LOF, France

<sup>2</sup>Université de Lorraine, CNRS, LEMTA, France

<sup>3</sup>ESPCI Paris, PSL Research University, MIE-CBI, CNRS, France

Presenting author's e-mail: [guillaume.ovarlez@u-bordeaux.fr](mailto:guillaume.ovarlez@u-bordeaux.fr)

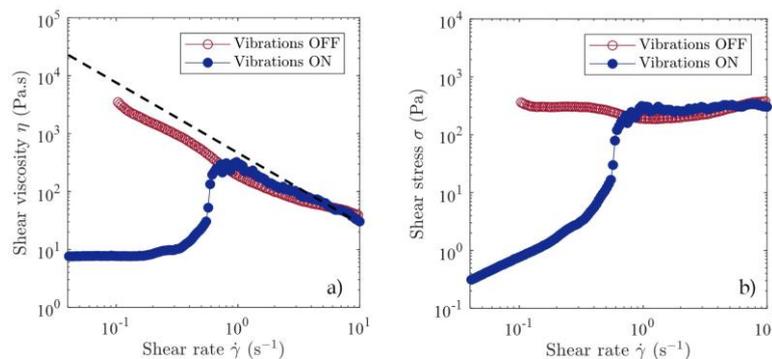
Flows of suspensions can be blocked when the suspended particles are densely packed. This makes their formulation and their transport challenging in the industry. Here, we study the impact of vibrations on the behavior of concentrated suspensions of non-repulsive frictional particles prepared in their jammed state, that is, at volume fraction above their jamming volume fraction, but below the particle assembly random close packing. Our purpose is to see to what extent the material can be unjammed, and to observe in which conditions a re-entrant (shear-)jamming transition can be observed.

We use a non-buoyant jammed suspension, where the material is simply confined by the liquid interface surface tension at rest, and keeps a constant volume fraction throughout the experiments under vibration. We show that, in the absence of vibrations, the prepared suspensions flow only above a yield stress, which is of frictional origin.

By contrast, when vibrations are applied, the yield stress vanishes to give rise to a liquid-like pseudo-Newtonian behavior at low shear rate. Using shear-reversal experiments, we show that these liquid-like vibrated suspensions of frictional particles behave like non-vibrated suspensions of frictionless particles. As the shear rate is increased, we observe a shear thickening of the vibrated suspensions, eventually leading to shear-jamming: the yield stress behavior is recovered and vibrations have no more impact. This transition is tuned by the vibration energy injected into the system, suggesting that vibrations introduce a thermal-like repulsive force.

We finally propose a physical picture based on the competition between contact opening by vibration and contact formation by shear to account for these behaviors. In the framework of the Wyart and Cates (2014) model, vibrations can be seen as introducing a thermal-like repulsive force, yielding a critical stress proportional to the vibration stress introduced by Hanotin *et al.* (2015).

**Keywords:** Suspensions – Shear-jamming – Vibrations



**Figure 1.** Flow curve of a 29 wt% silica suspension with (filled circles, blue) and without (empty circles, red) vibrations: (a) shear viscosity  $\eta$  vs. shear rate  $\dot{\gamma}$ , (b) shear stress  $\sigma$  vs.  $\dot{\gamma}$ . The amplitude and frequency of vibrations are 500  $\mu\text{m}$  and 20 Hz respectively. A dashed line  $\eta \propto \frac{1}{\dot{\gamma}}$  is shown in Fig. 1a to better evidence the plastic behavior of the non-vibrated suspension. Figure from Garat *et al.* (2022).

# Universal Scaling in Shear Thickening Suspensions

*Meera Ramaswamy*<sup>1</sup>, *Itay Griniasty*<sup>1</sup>, *Danilo B. Liarte*<sup>1</sup>, *Abhishek Shetty*<sup>2</sup>, *Eleni Katifori*<sup>3</sup>, *Emanuela Del Gado*<sup>4</sup>, *James P Sethna*<sup>1</sup>, *Bulbul Chakraborty*<sup>5</sup>,  
and *Itai Cohen*<sup>1</sup>

<sup>1</sup> Department of Physics, Cornell University, Ithaca, New York, USA

<sup>2</sup> Anton Paar USA, 10215 Timber Ridge Drive, Ashland, Virginia, USA

<sup>3</sup> Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania, USA

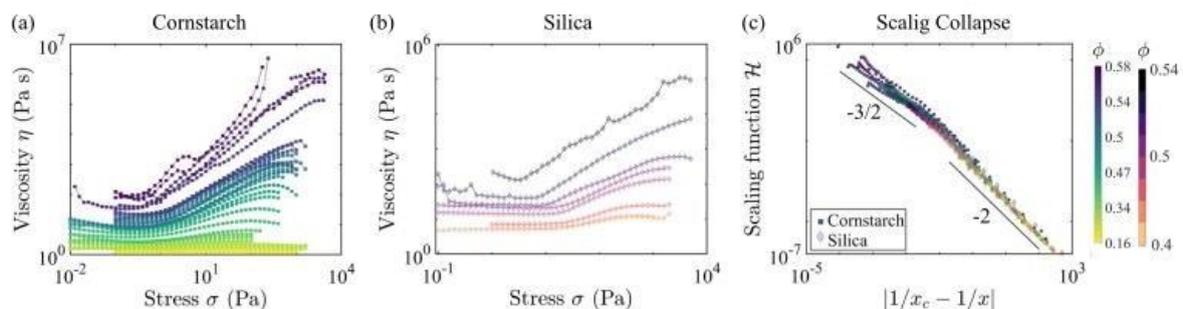
<sup>4</sup> Department of Physics, Georgetown University, Washington DC, USA

<sup>5</sup> Department of Physics, Brandeis University, Waltham, Massachusetts, USA

Presenting author's e-mail: [mr944@cornell.edu](mailto:mr944@cornell.edu)

Nearly all dense suspensions undergo dramatic and abrupt thickening transitions in their flow behaviour when sheared at high stresses. Such transitions occur when the dominant interactions between the suspended particles shift from hydrodynamic to frictional. Here, we interpret abrupt shear thickening as a precursor to a rigidity transition and give a complete theory of the viscosity in terms of a universal crossover scaling function from the frictionless jamming point to a rigidity transition associated with friction, anisotropy, and shear. Strikingly, we find experimentally that for two different systems -- cornstarch in glycerol and silica spheres in glycerol -- the viscosity can be collapsed onto a single universal curve over a wide range of stresses and volume fractions. The collapse reveals two separate scaling regimes corresponding to two different critical points with different critical exponents. The material-specific behaviour due to the microscale particle interactions is incorporated into a scaling variable governing the proximity to shear jamming that depends on both stress and volume fraction. Finally, we illustrate the broad applicability of such a scaling framework by incorporating orthogonal perturbations to the flows into the framework. Specifically, we show that the detickening due to orthogonal shear perturbations (OSP) can be incorporated by simply altering the scaling variable to include a multiplicative term that decreases with the normalized OSP strain rate. This reformulation opens the door to importing the vast theoretical machinery developed to understand equilibrium critical phenomena to elucidate fundamental physical aspects of the shear thickening transition.

**Keywords:** Shear thickening, critical phenomenon, rheology, universal framework



**Figure 1.** Flow curves illustrating the viscosity vs stress over a range of volume fractions for (a) cornstarch and (b) silica suspensions. (c) The scaling collapse using the universal framework. The collapse clearly illustrates the change in exponents.

**Acknowledgements:** The authors acknowledge the Anton Paar VIP program and the following funding sources - NSF CBET awards: 2010118, 1804963, 1509308, 1916877; NSF DMR awards: 1507607, 2026834, 1719490, 1720530, 2026842 and NSF PHY award -1554887

# Shear-thickening suspensions in a large-gap Couette flow: From steadiness to unsteadiness

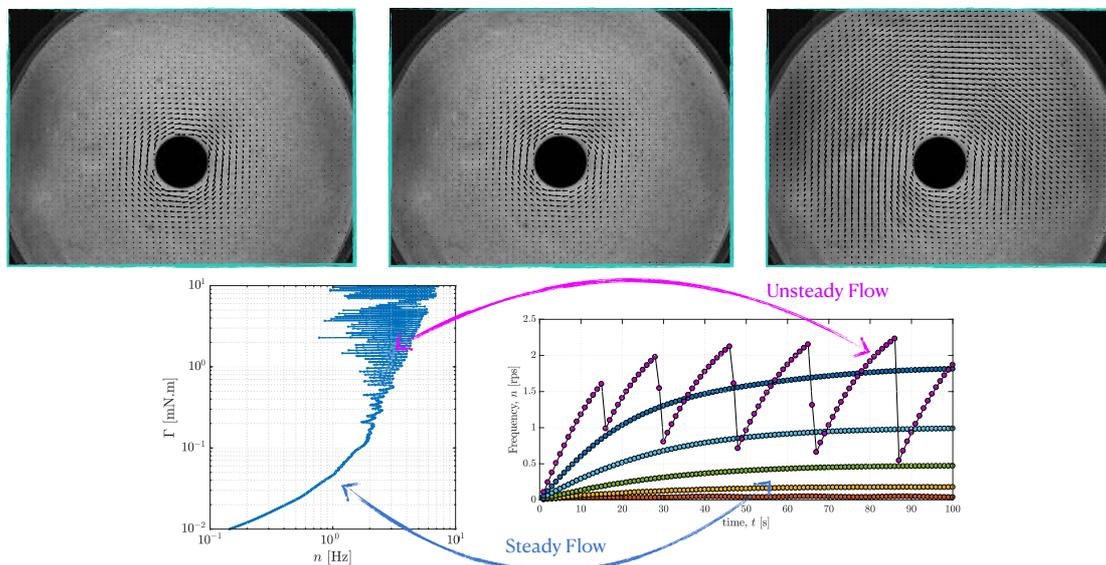
*Francisco Rocha<sup>1</sup>, Henri Lhuissier<sup>1</sup>, Yoël Forterre<sup>1</sup>, and Bloen Metzger<sup>1</sup>*

<sup>1</sup>*Aix-Marseille University, CNRS, IUSTI, Marseille 13453, France*

Presenting author's e-mail: [francisco.rocha@univ-amu.fr](mailto:francisco.rocha@univ-amu.fr)

The question of how shear-thickening suspensions flow has remained largely unexplored outside of rheometers. Here, we consider a floating layer of shear-thickening fluid in a wide-gap cylindrical Couette cell, in which the stress field is highly inhomogeneous. By controlling the torque applied to the inner cylinder and performing fast imaging of the flow, we show that in the frictionless (low stress) regime, the suspension behaves as a quasi-Newtonian fluid, with no sign of shear-induced migration, and the local rheology extracted from the suspension flow field is well captured by the Wyart & Cates flow rules [1]. Moreover, for large solids volume fractions at which discontinuous shear thickening or shear jamming can occur, the flow becomes unstable above a critical shear stress. In contrast to what has been reported previously in the literature, the suspension here neither jams homogeneously [2], nor indefinitely [3]. Instead, we observe the emergence of periodic jamming fronts that propagate anisotropically from the inner to the outer wall, in synchrony with periodic oscillations of the inner cylinder rotation speed (see figure 1). By systematically varying the suspension layer thickness, we show that the steep decelerations of the cylinder result from the angular momentum transferred to accelerate the surrounding suspension as the latter jams.

**Keywords:** Dense suspensions, shear thickening, jamming fronts



**Figure 1.** Flow of a shear thickening suspension in a wide-gap cylindrical Couette cell. The scenario goes from a steady quasi-Newtonian regime to an unsteady regime marked by periodic jamming events.

**Acknowledgements:** ANR ScienceFriction #18-CE30-0024

## References

- [1] Wyart, M. & Cates, M. E. *Physical Review Letters*, 2014, 112 (9), 098302.
- [2] Richards, J. A., Royer, J. R., Liebchen, B., Guy, B. M. & Poon, W. C. *Physical Review Letters*, 2019, 123(3), 038004.
- [3] Peters, I., Majumdar, S. & Jaeger, H. M. *Nature*, 2016, 532 (7598), 214-217.

# Measuring Rolling Friction of Microparticles using Lateral Force Microscopy

*Simon Scherrer<sup>1</sup>, Shivaprakash N. Ramakrishna<sup>1</sup>, and Lucio Isa<sup>1</sup>*

<sup>1</sup>*Soft Materials and Interfaces, ETH Zürich, Switzerland*

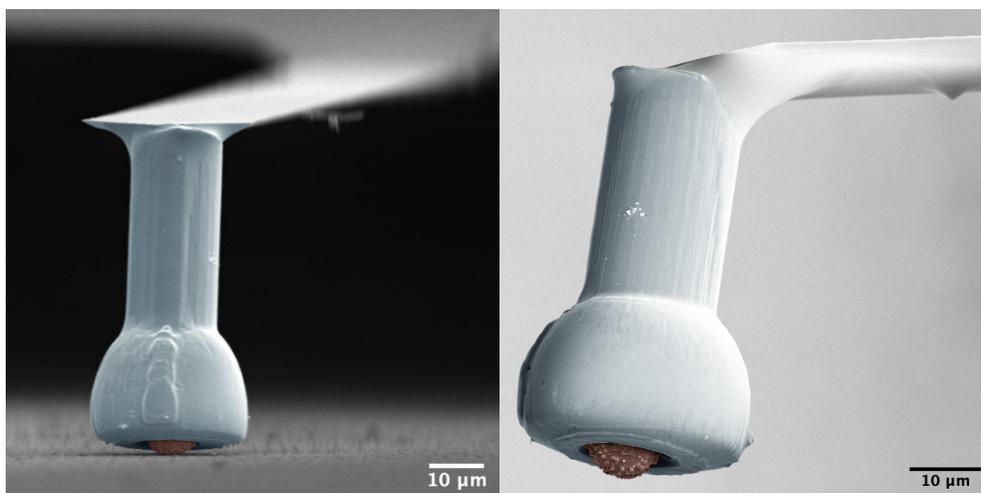
Presenting author's e-mail: [simon.scherrer@mat.ethz.ch](mailto:simon.scherrer@mat.ethz.ch)

The introduction of colloidal probes has expanded the capabilities of atomic force microscopes (AFMs) to allow measuring interactions between particles and surfaces directly. In particular, lateral force microscopy (LFM) provides access to friction coefficient measurements at the nanoscale by determining lateral forces between surfaces as a function of applied load. Typically, experiments are limited to AFM cantilevers with fixed colloids, and thus only enable measuring sliding friction. However, for unconstrained colloidal particles in a fluid, sliding as well as rolling motion is present, but the characterization of the latter remains elusive.

Using two-photon nanolithography, we have developed a colloidal probe that allows free rotation of an encapsulated particle and simultaneous imaging of the contact via fluorescence microscopy. The colloid releases from the cavity when the probe is not in contact with the substrate, making it reusable. Upon lateral spring constant calibration of the cantilever [1], a friction coefficient of the investigated colloid-substrate system can be determined. The three-dimensional rotation of the particle within the cantilever is confirmed by tracking fluorescent markers on the colloid, while simultaneously obtaining the lateral forces acting on it. Direct comparison to a fixed colloidal probe is possible by gluing the particle inside the cavity, therefore restricting any rotational movement and enabling the observation of sliding and rolling friction.

We have first applied our method to a model system of rough, 12  $\mu\text{m}$  silica particles and surfaces with matching asperities [2] and measured friction coefficients of rotating and fixed colloids in HEPES buffer, where the latter is significantly higher. Analysis of the rotational motion correlated with specific features in the friction force signals gives new insights into the behavior of contacting colloids that can be extended to a broad class of systems of direct interest for the study of the rheology of dense suspensions.

**Keywords:** rolling friction, lateral force microscopy, nanotribology, rough particle



**Figure 1.** False colored SEM images of the colloidal probe (blue) with rough silica particle (red).

## References

- [1] M. Varenberg, I. Etsion and G. Halperin, *Review of Scientific Instruments*, 2003, 74, 3362.  
[2] C.-P. Hsua, S. N. Ramakrishna, M. Zaninia, N. D. Spencer and L. Isa, *PNAS*, 2018, 115, 5117-5122.

Monday 5th September 2022

**Self-Assembly and Supramolecular Structures**

# Defined core-shell particles as the key to complex interfacial self-assembly

J. Menath<sup>1</sup>, J. Eatson<sup>2</sup>, R. Brilmayer<sup>3</sup>, A. Andrieu-Brunsen<sup>3</sup>, D.M.A. Buzza<sup>2</sup>, N. Vogel<sup>3</sup>

<sup>1</sup>Institute of Particle Technology, Friedrich-Alexander University Erlangen-Nuernberg, 91058 Erlangen, Germany

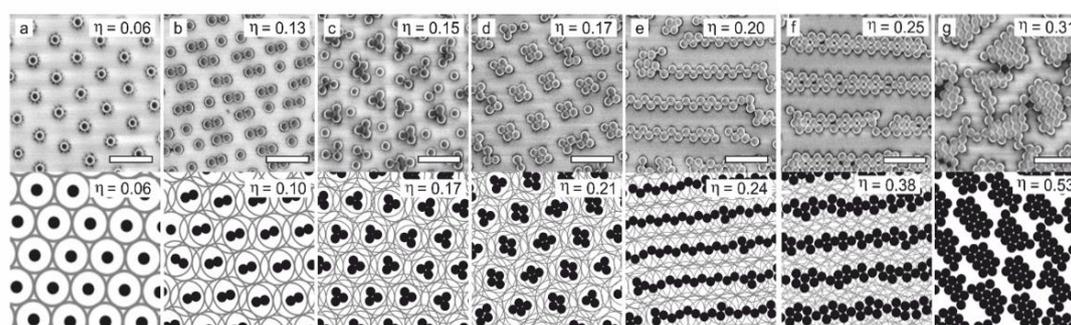
<sup>2</sup>Department of Physics and Mathematics, University of Hull, Hull HU6 7RX, U.K.

<sup>3</sup>Macromolecular Chemistry, Smart Membranes, Technical University of Darmstadt, 64287 Darmstadt, Germany

Presenting author's e-mail: [d.m.buzza@hull.ac.uk](mailto:d.m.buzza@hull.ac.uk)

The two-dimensional self-assembly of colloidal particles serves as a powerful tool to fabricate functional materials and surfaces but the prevalence of hexagonal symmetries in such systems limits its structural versatility. Complex, non-hexagonal phases have been predicted theoretically for decades for spherical particles with a soft repulsive shoulder but have not been experimentally realized up till now. Building on previous work [1], we use controlled radical polymerisation to synthesise defined core-shell particles consisting of a silica core surface functionalized with a non-crosslinked polymer shell. The core-shell particles efficiently spread at a liquid interface to form a two-dimensional polymer corona surrounding the core, and upon interfacial compression, assemble into well-defined dimer, trimer, and tetramer lattices before transitioning into complex chain and cluster phases (Figure 1) [2]. The experimental phase behaviour is accurately reproduced by Monte Carlo simulations and minimum energy calculations, suggesting that the interfacial assembly interacts via a pairwise-additive soft-shell potential. Our study provides a framework to realize unprecedented structural complexity from a simple, one-component system.

**Keywords:** Core-shell particles, self-assembly



**Figure 1** Phase behaviour of defined core-shell particles at an air-water interface upon compression. Representative SEM image of phases observed in experiment (top row) and snapshots of Monte Carlo simulations (bottom) at different area fractions specified in the images (scale bar: 1  $\mu$ m). [2]

## References

- [1] M. Rey, A. D. Law, D. M. A. Buzza, N. Vogel, J. Am. Chem. Soc., 2017, 139, 17464.  
 [2] J. Menath, J. Eatson, R. Brilmayer, A. Andrieu-Brunsen, D. M. A. Buzza, N. Vogel, Proc. Natl. Acad. Sci. U.S.A., 2021, 118, e2113394118

# Core-Shell microgels as soft model colloids to study phase behaviour in dense packings via small angle X-ray scattering

*Marco Hildebrandt<sup>1</sup> and Matthias Karg<sup>1</sup>*

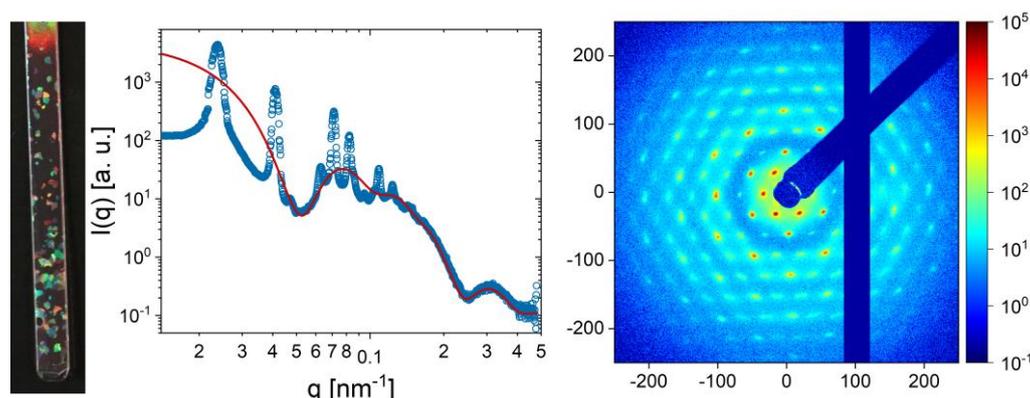
<sup>1</sup>Heinrich-Heine-Universität Düsseldorf, Kolloide und Nanooptik, Physikalische Chemie I, Düsseldorf, Germany

Presenting author's e-mail: [marco.hildebrandt@hhu.de](mailto:marco.hildebrandt@hhu.de)

Microgels made from poly-N-isopropylacrylamide (PNIPAM) have attracted much interest in the past decades due to their thermoresponsive behavior and their soft and deformable character. This makes them an ideal model system to study the behavior of soft colloids. [1] For dense particle dispersions, it is known that microgels tend to assemble in crystalline structures which enables the investigation of soft particle interactions. [2] Due to their small dimensions, the investigation of microgels in dense packings via optical microscopy is nontrivial and scattering techniques can offer much better statistics. The extraction of the structure factors from scattering profiles is often challenging due to interferences between form and structure factor. In small angle X-ray scattering (SAXS), core-shell microgels offer strong contrast differences between the core and the swollen polymer shell which simplifies the extraction of the structure factor and makes such colloids ideal for studying the phase behavior of microgels in dense packings. [3]

In this work we want to study colloidal crystals made from silica core – PNIPAM shell microgels with a silica core and a PNIPAM shell. After a precise annealing procedure of dense core-shell microgel dispersions and storage at low temperatures we were able to produce crystalline structures which exhibit narrow Bragg peaks in UV-Vis absorbance spectroscopy. In SAXS we could detect at least seven orders of distinct Bragg peaks which enables the possibility for detailed analysis of the crystal pattern (fig. 1). Here, the silica cores enhance the contrast of our system for SAXS and support a sufficient decoupling of structure and form factor.

**Keywords:** SAXS, colloidal crystals, microgels, core-shell particles



**Figure 1.** A) Colloidal crystals made from silica-PNIPAM core-shell microgels in a rectangular capillary. B) SAXS profile of dense core-shell microgel dispersion in crystalline structure (blue circles) and a fit describing the particles form factor (red line). C) 2D SAXS pattern of the respective sample.

**Acknowledgements:** We acknowledge Andrea Scotti (RWTH Aachen) and Judith E. Houston (ESS) for synchrotron SAXS measurements

## References

- [1] Bergman, M. J.; Pedersen, J. S.; Schurtenberger, P.; Boon, N.; *Soft Matter* 2020, 16, 2786.
- [2] Brijitta, J.; Schurtenberger, P., *Curr Opin Colloid Interface Sci.* 2019, 40, 87-103.
- [3] Lapkin, D.; Mukharamova, N.; Assalauova, D.; Dubinina, S.; Stellhorn, J.; Westermeier, F.; Lazarev, S.; Sprung, M.; Karg, M.; Vartanyants, I. A.; Meijer, J; *Soft Matter* 2022, 18, 1591.

# Tunable blunt-end interactions drive the assembly of quasi-two-dimensional dispersions of dsDNA coated colloids

Ivany Romero-Sanchez<sup>1,2</sup>, Ilian Pihlajamaa<sup>3,4</sup>, Natasa Adzic<sup>4</sup>, Laura E. Castellano<sup>2</sup>, Emmanuel Stiakakis<sup>5</sup>, Christos N. Likos<sup>4</sup> and Marco Laurati<sup>1</sup>

<sup>1</sup>Dipartimento di Chimica & CSGI, Università di Firenze, 50019 Sesto Fiorentino, Italy

<sup>2</sup>División de Ciencias e Ingenierías, Universidad de Guanajuato, 37150 León, Mexico

<sup>3</sup>Eindhoven University of Technology, NL-5600 MB Eindhoven, The Netherlands

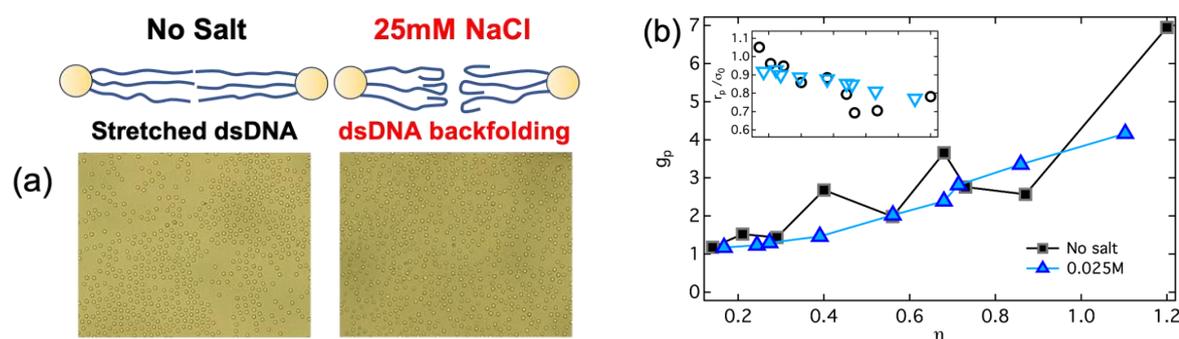
<sup>4</sup>Faculty of Physics, University of Vienna, A-1090 Vienna, Austria

<sup>5</sup>Biomacromolecular Systems and Processes, Forschungszentrum Jülich, D-52425 Jülich, Germany

Presenting author's e-mail: [marco.laurati@unifi.it](mailto:marco.laurati@unifi.it)

We investigate the effects of crowding on the conformations and assembly in quasi-two dimensional confinement of suspensions of colloids grafted with a highly charged and thick brush of double-stranded DNA (dsDNA) fragments. Particle tracking experiments on increasingly dense suspensions reveal nonmonotonic particle shrinking, aggregation, and reentrant ordering. Theory and simulations show that aggregation and reentrant ordering arise from the combined effect of shrinking, which is induced by the osmotic pressure exerted by the counterions absorbed in neighbor brushes, and short-range attractive interactions. An unconventional mechanism gives origin to the short-range attraction: blunt-end interactions between stretched dsDNA fragments of neighboring brushes, which become sufficiently intense for dense and packed brushes. The attraction can be tuned by changes in the number of grafted fragments or by inducing free-end backfolding through the addition of monovalent salt: both effects indeed lead to a reduction of the density of blunt-ends on the surface of the brush. Additionally, particle softness can be modulated through the length of the dsDNA fragments. Our results show that blunt-end interactions provide a mode parallel to hybridization to steer colloidal assembly, in which attractions can be fine-tuned through salinity, grafting density and potentially temperature.

**Keywords:** Colloidal assembly, blunt-ends, DNA, polyelectrolytes



**Figure 1.** (a) Blunt-end attractions between dsDNA fragments drive aggregation. The attraction can be tuned by inducing free-end backfolding through addition of monovalent salt. (b) As a result, with addition of salt reentrant ordering phenomena disappear, as shown by the packing fraction dependence of the first peak height and position of the radial distribution function  $g(r)$ .

## References

- [1] I.C. Romero-Sanchez, I. Pihlajamaa, N. Adzic, L. E. Castellano-Torres, E. Stiakakis, C. N. Likos and M. Laurati, ACS Nano, 2022, 16, 2133.
- [2] I.C. Romero-Sanchez, L. E. Castellano-Torres and M. Laurati, Macromolecules, 2022, accepted.

# Asymmetric Microgels by Supramolecular Assembly and Precipitation Polymerization of Pyrazole-Modified Monomers

*Frédéric Grabowski*<sup>1</sup>, *Vladislav S. Petrovskii*<sup>1</sup>, *Fabian Fink*<sup>2</sup>, *Sonja Herres-Pawlis*<sup>2</sup>, *Igor Potemkin*<sup>1</sup> and *Andrij Pich*<sup>1</sup>

<sup>1</sup>DWI – Leibniz-Institute for Interactive Materials e.V., Aachen, Germany

<sup>2</sup>Chair of Bioinorganic Chemistry, Institute for Inorganic Chemistry, RWTH Aachen University, Aachen, Germany

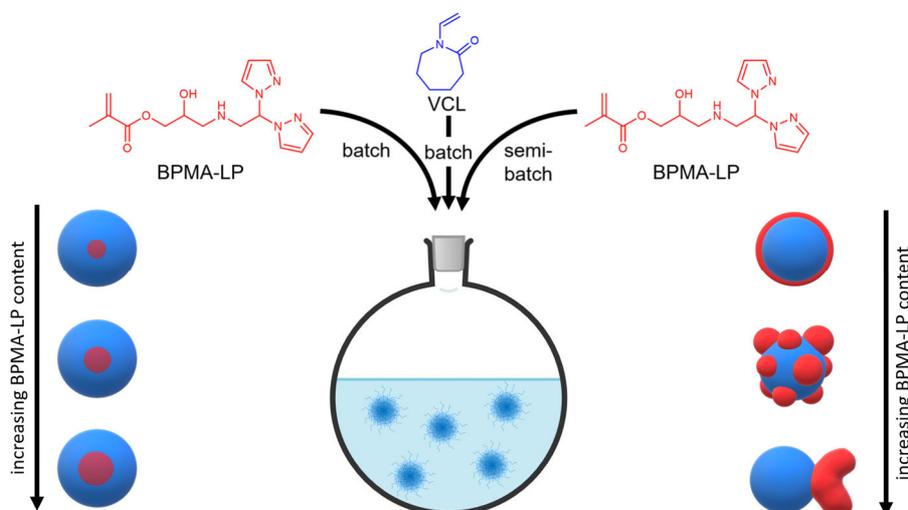
Presenting author's e-mail: [grabowski@dwf.rwth-aachen.de](mailto:grabowski@dwf.rwth-aachen.de)

Nature combines controlled chemical reactions with structure formations by supramolecular, hydrophobic, and electrostatic interactions to design molecular objects with hierarchical structure, controlled shape, size, and chemical composition. Inspired by this fabrication strategy, we developed a facile synthesis approach to stimuli-responsive microgels with asymmetric shapes.

Our synthesis approach combines self-assembly driven by supramolecular interactions and polymerization of pyrazole-modified monomers. Specifically, we first performed computer simulations for series of pyrazole-modified monomers with different numbers of pyrazole groups, different length and polarity of spacers between pyrazole groups and polymerizable group. These allowed us to elaborate the relationship between the chemical structure and ability to undergo  $\pi$ - $\pi$ -stacking behavior in aqueous solutions of the monomers. Based on the results of computer simulations, we synthesized monomers able to undergo  $\pi$ - $\pi$ -stacking and guide the formation of supramolecular bonds between polymer segments during precipitation polymerization, leading to the formation of asymmetric microgels.

We demonstrate that microgel morphologies can be tuned from spherical, raspberry-like to dumbbell-like by the increase of the pyrazole-modified monomer loading (from 5 to 15 mol%) in the shell of the microgels (Figure 1). Our experimental data indicate that the addition mode and concentration of pyrazole-modified monomers in precipitation polymerization process allow programming the shape of microgels.

**Keywords:** pyrazole-modified monomers, supramolecular interactions, self-assembly, precipitation polymerization, asymmetric microgels.



**Figure 1.** Schematic synthesis of PVCL-BPMA-LP microgels with different morphologies via batch and semi-batch polymerization.

**Acknowledgements:** The authors thank the German Research Foundation (DFG) of the Collaborative Research Center SFB 985 “Functional Microgels and Microgel Systems” for financial support.

# Synthesis and self-assembly of colloidal nanoparticles into two-dimensional superlattices

*Chiara Moretti<sup>1</sup>, Claire Goldmann<sup>2</sup>, Benjamin Abécassis<sup>1</sup>*

<sup>1</sup> *Laboratoire de Chimie, ENS de Lyon, 46 allée d'Italie, 69364 Lyon, France*

<sup>2</sup> *Laboratoire de Physique des Solides, Université Paris-Saclay, Orsay 91405, France*

Presenting author's e-mail: [chiara.moretti@ens-lyon.fr](mailto:chiara.moretti@ens-lyon.fr)

Nanoparticles (NPs) can serve as building blocks for the construction of long-range periodic structures (superlattices) which display collective physical properties. Depending on various factors, they can spontaneously assemble into crystalline phases and even more complex structures, including Frank-Kasper [1] or quasicrystalline phases [2]. However, our understanding of the different experimental parameters on the final assembled structure is still incomplete which prevents a predictive approach towards NP superlattices design.

By controlling the NP synthesis and surface chemistry we gain a deep understanding on their self-assembly in superlattices made of one population of given size polydispersity or of a binary mixture. We first have synthesized well-defined hydrophobic colloidal nanoparticles of different shapes and compositions. Using a seed-mediated synthesis strategy, we show that the size of spherical gold nanoparticles can be controlled at the atomic scale in the 2–5 nm size range with very low polydispersity [3]. Secondly, we have studied their two-dimensional self-assembly at the liquid/air interface from the evaporation of a dispersion of colloidal NPs on a liquid surface [4]. We have investigated the self-assembly of one population of NPs and of binary systems composed of spherical NPs or nanoplatelets. Several experimental parameters, such as size, dispersing solvent, coating ligands, and diameter-ratio for binary systems were studied. Many different structures were observed: hexagonal and cubic superlattices, Moiré patterns, binary NP superlattices, and also more complex superlattices, such as Frank-Kasper phases [5]. We have observed a C14 Frank-Kasper phase from the self-assembly of a single population of spherical Au NPs, and a Z phase from the binary self-assembly of spherical Au and Cu<sub>2</sub>S NPs. Our findings help establish a robust and reproducible protocol for film formation and open a route toward building complex nanoparticle superlattices, bringing insights that can be extended to other systems and facilitating the rational design NP superlattices.

**Keywords:** nanoparticle, self-assembly, superlattices, liquid-air interface, Frank-Kasper phases

## References

- [1] S. Hajiw, B. Pansu, J.-F. Sadoc, ACS nano, 2015, 9(8), 8116–8121.
- [2] D. V. Talapin, E. V. Shevchenko, M. I. Bodnarchuk, X. Ye, J. Chen, C. B. Murray, Nature, 2009, 461, 964-967.
- [3] C. Goldmann, C. Moretti, B. Mahler, B. Abécassis, M. Impéror-Clerc, B. Pansu, Chemical Communications, 2021, 57(93), 12512-12515.
- [4] A. Dong, J. Chen, P. M. Vora, J. M. Kikkawa, C. B. Murray. Nature, 2010, 466(7305), 474-477.
- [5] C. Moretti et al., in preparation.

## Quasicrystals in binary (non-)additive hard disk mixtures

*Etienne Fayen<sup>1</sup>, Marianne Impéror-Clerc<sup>1</sup>, Anuradha Jagannathan<sup>1</sup>, Laura Fillion<sup>2</sup>, Giuseppe Foffi<sup>1</sup> and Frank Smallenburg<sup>1</sup>*

<sup>1</sup>*Université Paris-Saclay, CNRS, Laboratoire de Physique des Solides, 91405 Orsay, France*

<sup>2</sup>*Soft Condensed Matter, Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, Netherlands*

Presenting author's e-mail: [etienne.fayen@universite-paris-saclay.fr](mailto:etienne.fayen@universite-paris-saclay.fr)

Over the last few decades, soft quasicrystals, whose relevant building blocks are much larger than atoms, have been observed in an impressive variety of systems, including nanoparticles, colloids, micelles, and block copolymers. These experimental findings suggest that very general principles stabilise quasicrystals in soft matter, although understanding these principles is still a topic of active research.

Here we explore the self-assembly of binary mixtures of non-additive hard disks, a simple 2D model for binary mixtures self-assembling at an interface, where soft quasicrystals are commonly observed. Since interactions are hard, entropy is the only ordering force.

The infinite pressure phase behaviour of this model, which reduces to the geometrical problem of disk packing and entropy arguments, already predicts the stability of dodecagonal quasicrystals, based on random tilings [1, 2].

In addition, we explore the direct self-assembly of quasicrystals in this system at finite pressure. Both the expected 12-fold symmetric quasicrystal and a new octagonal quasicrystal were found to spontaneously self-assemble. The 8-fold symmetric quasicrystal is based on a tiling of the plane by 3 different tiles, whose relative concentrations can be continuously varied by simply changing the composition of the binary mixture. We derive a theoretical prediction for the proportion of each type of tile, and find to remarkably agreement with the measurements on simulated self-assembled structures [3]. Finally, we investigate the stability of the dodecagonal quasicrystal using numerical free-energy calculations.

Our results show that in a system as simple as binary non-additive hard-disk mixture, quasicrystals of symmetry 12 and 8 can consistently self-assemble and demonstrate that geometrical packing constraints and entropy are sufficient ingredients for quasicrystalline order to emerge. Given its simplicity and experimental realisations in colloid mixtures, the binary hard-disks system provide an ideal base model for studies on quasicrystal stability.

**Keywords:** Self-assembly, Quasicrystal, Numerical simulations

### References:

- [1] C. N. Likos and C. L. Henley, *Philos. Mag. B*, 68, 85-113 (1993).
- [2] E. Fayen, A. Jagannathan, G. Foffi and F. Smallenburg, *J. Chem. Phys.* 152, 204901 (2020)
- [3] E. Fayen, M. Impéror-Clerc, L. Fillion, G. Foffi and F. Smallenburg, arXiv:2202.12726

# Shape Matters: Tuning the Self-Assembly of Colloidal Cube Superstructures

*Janne-Mieke Meijer<sup>1,2</sup>*

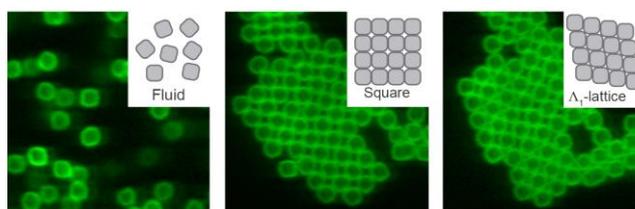
<sup>1</sup> *Soft Matter and Biological Physics, Department of Applied Physics, Eindhoven University of Technology, Eindhoven, The Netherlands*

<sup>2</sup> *Institute for Complex Molecular Systems (ICMS), Eindhoven University of Technology, Eindhoven, The Netherlands*

Presenting author's e-mail: [j.m.meijer@tue.nl](mailto:j.m.meijer@tue.nl)

Colloids with a cubic shape can be prepared on the nano and micron scale and have become of interest for self-assembly of superstructures, with applications in photonics, surface coatings, and solar cells. During the self-assembly processes a distinct coupling appears to occur between the cubic shape, the interparticle interactions and the applied forces. However, the relationship between the cubic colloid properties and the order/disorder in the final self-assembled superstructures remains unclear.

Here, we investigate how the shape of cubic colloids with rounded corners [1], i.e. superballs, and the interparticle interactions influence their self-assembly in- and out-of-equilibrium. Using a combination of small angle x-ray scattering, (optical) microscopy and quantitative image analysis, we study the cubic superstructures formed by different self-assembly methods. For repulsive interactions, we observe a rich behavior for the cubes, including a plastic crystal, dense rhombic packings and solid-solid phase transitions [1]. The phases are driven by excluded volume interactions and are partly in agreement with theory and simulations. When employing solvent evaporation leading to strong immersion capillary forces and fluid flow, we find a distinct coupling between the cubic shape and these forces. Co-existence of the densest packings and switching due to sliding of the cubes is observed [2,3]. In addition, external pressure to organize the cubes in monolayers, distinct order in the direction of the force but increased disorder perpendicular to the force is found [4]. Finally, by employing critical Casimir forces of which the attraction strength can be tuned by temperature, we visualize *in-situ* how the coupling of a cubic shape and short-range attractions occurs [5]. We find that different crystal symmetries including simple cubic to rhombic phases form. Our results provide insight into how finite colloidal shape details influence the self-assembly process and control the superstructure symmetry.



**Figure 1.** Confocal microscopy images of different self-assembled superstructures of cubic colloids.

**Keywords:** cubic colloids, self-assembly, phase transitions, anisotropic colloids, colloidal crystals

## References

- [1] J.M. Meijer *et al.* Nature Commun, 2017, 8, 14352
- [2] J.M. Meijer *et al.* Langmuir, 2012, 28, 7631-7638.
- [3] J.M. Meijer *et al.* Langmuir, 2019, 35, 4946-4955
- [4] D. ten Napel, J.M. Meijer, A.V. Petukhov, Applied Sciences, 11, 5117
- [5] C.L. Kennedy, D. Sayasilpi, P. Schall, J.M. Meijer, J. Phys. Cond. Mat, 2022, 34, 214005

# Multi-compartment supracapsules made from nanocapsules towards programmable release

*Minghan Hu*<sup>1</sup>, *Nico Reichholf*<sup>1</sup>, *Yanming Xia*<sup>2,3</sup>, *Laura Alvarez*<sup>1</sup>, *Xiaobao Cao*<sup>2</sup>, *Shenglin Ma*<sup>3</sup>, *Andrew J. deMello*<sup>2</sup>, and *Lucio Isa*<sup>1</sup>

<sup>1</sup>Laboratory for Soft Materials and Interfaces, Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland

<sup>2</sup>Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 1, 8093 Zürich, Switzerland

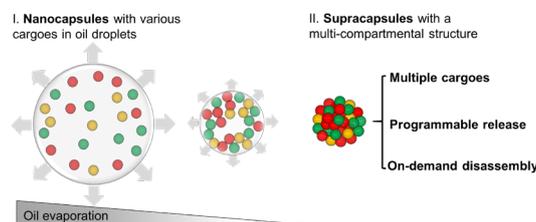
<sup>3</sup>Department of Mechanical & Electrical Engineering, Xiamen University, Xiamen, Fujian, China

Presenting author's e-mail: [minghan.hu@mat.ethz.ch](mailto:minghan.hu@mat.ethz.ch)

Suprastructured assemblies are prominent candidates to advance materials for biomedical science, catalysis, and microrobotics, whereby their architecture enables the enhancement of collective properties and emerging functionalities [1]. Although many structures, including Janus-like and mesoporous ones [2, 3], have been developed to date, the realization of materials with multiple internal compartments remains largely untapped. Multi-compartmentalization, which is inspired by a key structural feature of living cells, involves incorporating two or more distinct units with different cargoes that are spatially resolved and can act in unison. Including multiple compartments within a suprastructure enables both retaining their individual properties and combining them to elicit new functions. However, current multi-compartmentalization strategies require synthetic complexity, hampering their translation towards suprastructured materials.

In this work, we demonstrate a robust and straightforward assembly strategy to create uniform suprastructured assemblies with a multi-compartment architecture. The cornerstone of our approach is to confine nanocapsules within droplets. Solvent evaporation spontaneously triggers the assembly of the nanocapsules into a multi-compartment structure, which we term supracapsules. This strategy presents great control on supracapsule size and flexibility on combinations of different components, which remain spatially separated after assembly. Remarkably, the multi-compartment supracapsules display distinctive and programmable release kinetics compared to the single-compartment nanocapsules. Finally, the suprastructures can be disassembled into single-compartment units by applying ultra-sonication, switching their release to a burst-release mode. These findings open up exciting opportunities to fabricate multi-compartment suprastructures incorporating diverse functionalities for materials with emerging properties [4].

**Keywords:** suprastructures, multi-compartment, evaporating droplets, nanocapsules, supracapsules, programmable release



**Figure 1.** Scheme of supracapsules assembled from nanocapsules

## References

- [1] W. Susanne, T. Granath, M. Oppmann, T. Kister, T. Thai, T. Kraus, N. Vogel, and K. Mandel, *ACS Nano*, 12, 2018, 5093-5120.
- [2] M. Hu, H.J. Butt, K. Landfester, M.B. Bannwarth, S. Wooh, H. Thérien-Aubin, *ACS Nano*, 2019, 13, 3015-3022.
- [3] S. Wooh, H. Huesmann, M.N. Tahir, M. Paven, K. Wichmann, D. Vollmer, W. Tremel, P. Papadopoulos, H.J. Butt, *Adv. Mater.*, 2015, 27, 7338-7343.
- [4] M. Hu, N. Reichholf, Y. Xia, L. Alvarez, X. Cao, S. Ma, A. J. deMello, L. Isa, 2022, submitted.

## Versatile self-assembling nanotubes responding to light stimulus: bio-origin, chirality and stability

*Maria Chiara di Gregorio,<sup>1</sup> Andrea Santilli,<sup>1</sup> Andrea Lapi,<sup>1</sup> Jacopo Cautela,<sup>1</sup> Marco D'Abamo,<sup>1</sup> Cheng Giuseppe Chen,<sup>1</sup> Alessandra Del Giudice,<sup>1</sup> Simona Sennato,<sup>2</sup> Domagoj Belić,<sup>3</sup> Victor Hugo Soto Tellini,<sup>4</sup> Karin Schillén,<sup>3</sup> Luciano Galantini<sup>1</sup>*

<sup>1</sup> Department of Chemistry, Sapienza University, P.le A. Moro 5, Rome, Italy

<sup>2</sup> CNR-Institute of Complex Systems, Sapienza University, P.le A. Moro 5, Rome, Italy

<sup>3</sup> Department of Chemistry, Lund University, Lund, Sweden

<sup>4</sup> Escuela de Química, Universidad de Costa Rica, San José, Costa Rica

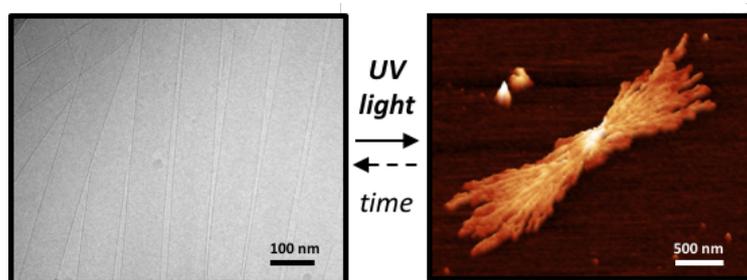
Presenting author's e-mail: [digregoriomariachiara@gmail.com](mailto:digregoriomariachiara@gmail.com)

Self-assembling molecular structures responding to light stimulus are appealing for applications as sensing and drug delivery. Supramolecular nanotubes have a relevant potential in nanotechnology since they are suitable for novel supra-colloidal materials [1] and for specific functions as encapsulation of large molecules. [2] Structural responses of supramolecular nanotubes to non-invasive stimuli are very much desired e.g. to enable controlled release of the encapsulated guests. Yet, the very few reports on such systems indicates that their construction is not trivial. [3,4]

We describe the formation of well-defined tubules that interconvert into twisted ribbons upon UV light exposure in aqueous environment (Figure 1). The structures are provided by self-assembly of an azobenzene substituted cholic acid, a biological surfactant belonging to the family of bile acids. The azobenzene group allows for the light responsiveness of the molecular packing. Concurrently the steroidal moieties assure both chiral features and extensive hydrophobic interactions for time and temperature resistant aggregates. The study crosses microscopy, spectroscopy and theoretical tools for the characterization of the structures.

Innovatively, the molecular design reported in our work allows for encoding in the same light responsive system multiple desirable features (e.g. bio-origin, temperature resistance and chirality of the aggregates). Such combination of properties, never reported before for a single molecule, might be relevant for the realization of robust, stimuli-responsive bio-vectors.

**Keywords:** light responsive system; nano-tubules; bile acid; chirality; stability; self-assembly



**Figure 1.** Microscopy images of the self-assembling structures before and after the light induced transition

### References

- [1] J. Cautela, B. Stenqvist, K. Schillén, D. Belić, L. K. Månsson, F. Hagemans, M. Seuss, A. Fery, J. J. Crassous and L. Galantini, *ACS Nano* 2020, 14, 15748.
- [2] S. Chen, R. Costil, F. K. Leung and B. L. Feringa, *Angew. Chemie* 2021, 133, 11708.
- [3] A. C. Coleman, J. M. Beierle, M. C. A. Stuart, B. Maciá, G. Caroli, J. T. Mika, D. J. Van Dijken, J. Chen, W. R. Browne and B. L. Feringa, *Nat. Nanotechnol.* 2011, 6, 547.
- [4] T. Sendai, S. Biswas and T. Aida, *J. Am. Chem. Soc* 2013, 135, 11509.

# Light- and temperature-controlled self-assembly of isotropic and patchy microparticles

*Patrick Hage<sup>1</sup>, Bas van Ravensteijn<sup>2</sup>, and Ilja Voets<sup>1</sup>*

<sup>1</sup>Laboratory of Self-Organizing Soft Matter, Institute for Complex Molecular Systems, Eindhoven University of Technology, The Netherlands

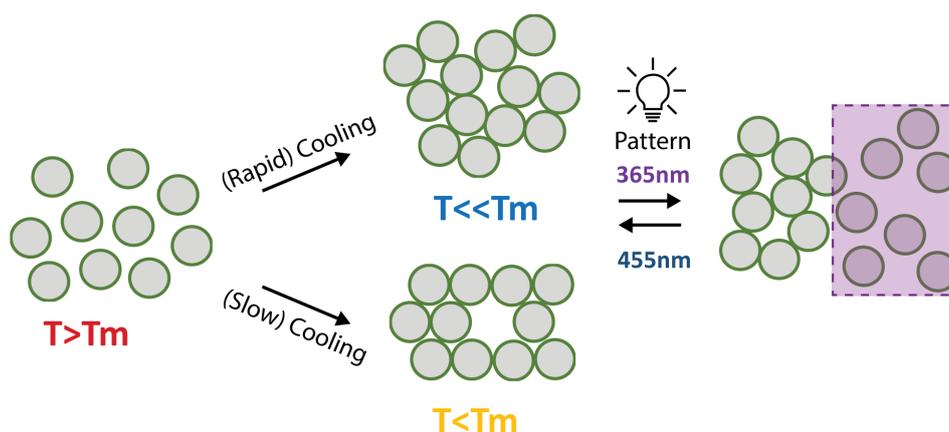
<sup>2</sup>Department of Pharmaceutics, Utrecht Institute for Pharmaceutical Sciences, Utrecht University, The Netherlands

Presenting author's e-mail: [p.a.hage@tue.nl](mailto:p.a.hage@tue.nl)

Supramolecular chemistry offers a wealth of interaction motifs to guide colloidal assembly.[1] Advantageously, the non-covalent interactions between tethered supramolecular moieties can be fine-tuned and regulated with external stimuli, resulting in adaptive and responsive materials. This work focuses on the fabrication, properties, and self-assembly of high-density functionalized (patchy) microparticles equipped with self-complementary DNA sequences. AzoDNA-coated microparticles, responsive to light and temperature, were fabricated upon the incorporation of an azobenzene photoswitch into the DNA strands.

To trigger and study particle (dis)association with both light and temperature, we mounted a digital micromirror device (DMD) onto a confocal microscope. This enables illumination of a large field of view or individual particles, with light to toggle the azobenzene photoswitch between its cis and trans conformation. In combination with precise temperature control, this design offers the possibility to firstly modulate the interaction of microparticles nearly instantaneously from repulsive (cis-state) to attractive (trans-state), and secondly, predetermine the strength of the short range attraction in the trans state by temperature. Deploying this unique adaptivity to trigger colloidal (dis)assembly affords a means to selectively grow colloidal 3D and 2D crystals, in which undesired crystallites or undesired portions of crystallites can be selectively disassembled by UV light illumination. Exotic structures, such as (chiral) chains, can be accessed using patchy instead of spherically isotropic colloids.

**Keywords:** Colloidal assembly, light-switchable, crystallites, supramolecular, high-density



**Figure 1.** Schematic representation showing the dual responsive assembly of DNA oligonucleotides functionalized particles with an azobenzene incorporated into the self-complementary DNA chain. By precise temperature control, colloidal crystallites can be obtained. The use of UV (365 nm) and blue (455 nm) patterned light results in the local isomerization of the azobenzene into the cis- and trans- isomer, respectively. The cis-isomer creates steric hindrance inside the self-complementary DNA helix, which will drastically lower the melting temperature of the particles, resulting in disassembly of the illuminated structures. This process can be reversed by the application of blue light.

## References

[1] Gerth, M. & Voets, I. K., Chem. Commun., 2017, 53, 4414–4428

## Condensed supramolecular helices: The twisted sisters of DNA

*Karin Schillén*<sup>1</sup>, *Guanqun Du*<sup>1</sup>, *Domagoj Belić*<sup>1,5</sup>,  
*Alessandra Del Giudice*<sup>2</sup>, *Viveka Alfredsson*<sup>1</sup>, *Anna M. Carnerup*<sup>1</sup>,  
*Kaizheng Zhu*<sup>3</sup>, *Bo Nyström*<sup>3</sup>, *Yilin Wang*<sup>4</sup>, *Luciano Galantini*<sup>2</sup>

<sup>1</sup>*Division of Physical Chemistry, Department of Chemistry, Lund University, Sweden*

<sup>2</sup>*Department of Chemistry, Sapienza University of Rome, Italy*

<sup>3</sup>*Department of Chemistry, University of Oslo, Norway*

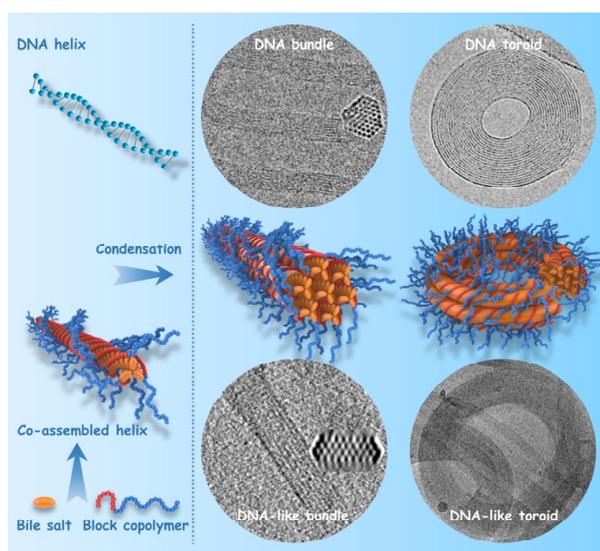
<sup>4</sup>*Institute of Chemistry, Chinese Academy of Sciences, Beijing, China*

<sup>5</sup>*Department of Physics, Josip Juraj Strossmayer University of Osijek, Croatia*

Presenting author's e-mail: [Karin.Schillen@fkem1.lu.se](mailto:Karin.Schillen@fkem1.lu.se)

Condensation of DNA helices into hexagonally packed bundles and toroids represents an intriguing example of functional organization of biological macromolecules at the nanoscale (Figure 1 [1,2]). The condensation models are based on the unique polyelectrolyte features of DNA, however here we could reproduce a DNA-like condensation with supramolecular helices of small chiral molecules, thereby demonstrating that it is a more general phenomenon. We show that the bile salt sodium deoxycholate (NaDC) can form supramolecular helices upon interaction with oppositely charged polyelectrolytes of homopolymer or block copolymers [3]. At higher order, a controlled hexagonal packing of the helices into DNA-like bundles and toroids could be accomplished (Figure 1). The results disclose unknown similarities between covalent and supramolecular non-covalent helical polyelectrolytes, which inspire visionary ideas of constructing supramolecular versions of biological macromolecules. As drug nanocarriers the polymer–bile salt superstructures would get advantage of a complex chirality at molecular and supramolecular levels, whose effect on the nanocarrier assisted drug efficiency is a still unexplored fascinating issue.

**Keywords:** chirality, condensation, DNA-like helix superstructures, hexagonally packed helices, polyelectrolyte–bile salt systems



**Figure 1.** A controlled condensation of the supramolecular NaDC bile salt helices into DNA-like hexagonally packed bundles and toroids can be achieved when using cationic diblock copolymers and increasing the bile salt content (bottom cryo-electron micrographs) [3]. Also displayed are micrographs of polyelectrolyte complex micelles with hexagonal ordering of DNA helices (top, left panel) [1] and  $\lambda$  DNA toroids (top, right panel) [2].

### References

- [1] M. Lueckheide, J. R. Viereg, A. J. Bologna, L. Leon, M. V. Tirrell, *Nano Lett.* 2018, 18, 7111.  
[2] N. V. Hud, K. H. Downing, *Proc. Natl. Acad. Sci.* 2001, 98, 14925.  
[3] G. Du, D. Belić, A. Del Giudice, V. Alfredsson, A. M. Carnerup, K. Zhu, B. Nyström, Y. Wang, L. Galantini, K. Schillén, *Angew. Chem. Int. Ed.* 2022, 61, e202113279.

## Hyperbranched copolymer colloids

Anastasia Balafouti <sup>1</sup>, Dimitrios Selianitis <sup>1</sup>, [Sergios Pispas](#) <sup>1</sup>

<sup>1</sup>Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation,  
48 Vassileos Constantinou Avenue, 11635 Athens, Greece

Presenting author's e-mail: [pispas@eie.gr](mailto:pispas@eie.gr)

Hyperbranched copolymers are a class of polymers that present several intriguing characteristics including tunable internal segment density, composition and globular structures, high number of functional groups, higher solubility, low solution viscosities and better ability to encapsulate species of interest [1].

In this presentation we discuss our results on the synthesis of novel classes of hyperbranched copolymers, prepared by RAFT polymerization, their self-organization into functional colloidal structures, and their co-assembly with hydrophobic drugs, metal nanoparticles and other biorelevant species, with a long-term goal of utilizing them as functional colloids for a range of biomedical applications [2,3]. The hyperbranched copolymers are amphiphilic or double hydrophilic depending on the choice of monomers. According to physicochemical studies, involving the implementation of light scattering, fluorescence spectroscopy and cryo-TEM techniques, the hyperbranched synthetic macromolecules present self-assembly into nanoparticulate structures in response to changes in pH, temperature and ionic strength of their aqueous solutions. Depending on their specific functional groups the hyperbranched macromolecules were found to be effective nanocarriers for anticancer drugs, bioimaging agents and to form hybrid organic-inorganic colloids with magnetic nanoparticles. The studies open ways for the utilization of novel, biocompatible, hyperbranched copolymers for drug/gene delivery, and for the construction of innovative bioimaging agents.

**Keywords:** hyperbranched copolymers, responsive colloids, nanocarriers

### References

- [1] J. A. Alfurhood, P. R. Bachler and B. S. Sumerlin, Polym. Chem. 2016, 7, 3361.
- [2] D. Selianitis and S. Pispas, Polym. Chem. 2021, 12, 6582.
- [3] A. Balafouti and S. Pispas, J. Polym. Sci 2022, doi: 10.1002/pol.20220078.

Monday 5th September 2022

**Wetting Phenomena, Responsive Colloids and Surfaces**

# Dramatic slowing down of oil/water/silica contact line dynamics driven by cationic surfactant adsorption on the solid

*Verneuil Emilie*<sup>1</sup>, *Rondepierre Gaelle*<sup>1</sup>, *Talini Laurence*<sup>1</sup>, *Lequeux Francois*<sup>1</sup>, and *Limat Laurent*<sup>2</sup>

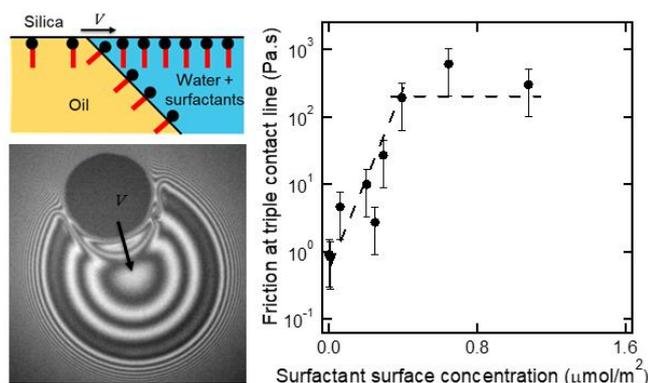
<sup>1</sup>Soft Matter Sciences and Engineering (SIMM), ESPCI Paris, PSL University, Sorbonne Université, CNRS UMR 7615, F-75005 Paris, France

<sup>2</sup>Laboratoire Matière et Systèmes Complexes, Université de Paris, CNRS UMR 7057, 10 Rue Alice Domon et Léonie Duquet, F-75013 Paris, France

Presenting author's e-mail: [emilie.verneuil@espci.fr](mailto:emilie.verneuil@espci.fr)

We report [1] on the contact line dynamics of a triple phase system silica/oil/water. When oil advances onto silica within a water film squeezed between oil and silica, a rim forms in water [2] and recedes at constant velocity. We evidence a sharp (three orders of magnitude decrease of the contact line velocity upon addition of cationic surfactants above a threshold concentration slightly smaller than cmc. We show that, with or without surfactant, and within the range of small capillary numbers investigated, the contact line dynamics can be described by a friction term [3] that does not reduce to pure hydrodynamical effects. In addition, we derive a model that successfully accounts for the selected contact line velocity of the rim. We further demonstrate the strong increase of the friction coefficient with surfactant bulk concentration results from the strongly non-linear adsorption isotherm of surfactants on silica [4]. From the variations of the friction coefficient and of the spreading parameter with surface concentration, we suggest the following picture: adsorbed surfactants that are strongly bound to the silica interface are responsible for the large increase in line friction. Labile surfactants adsorbed through weak interactions desorb as the contact line advances and do not contribute to the friction term.

**Keywords:** wetting dynamics, surfactant adsorption



**Figure 1.** Schematics of wetting by oil onto surfactant-laden silica in water. Microscopy image (500 $\mu\text{m}$ -wide): dark area is oil wetting silica at velocity  $V$ . Graph: Variations of contact line friction with surfactants surface concentration.

**Acknowledgements:** This work benefited from meetings within the French workgroup GDR CNRS 2019 “Solliciter LA Matière Molle” (SLAMM).

## References

- [1] Rondepierre, DeSoete, Passade, Lequeux, Talini, Limat, Verneuil. *Langmuir*. 2021, 37 1662–1673
- [2] Bertrand, E.; Blake, T.; De Coninck, J. *Colloids and Surfaces A*. 2010, 369, 141-147
- [3] Seveno, D.; Blake, T. D.; Goossens, S.; De Coninck, J. *Langmuir* 2011, 27, 14958-14967
- [4] Kékicheff, P.; Contal, C. *Langmuir* 2019, 35, 3087-3107

## Spreading of volatile oils on swelling hydrophobic polymer brush layers

Özlem Kap<sup>1</sup>, Simon Hartmann<sup>2</sup>, Harmen Hoek<sup>1</sup>, Igor Siretanu<sup>1</sup>, Sissi de Beer<sup>3</sup>, Uwe Thiele<sup>2</sup>, Frieder Mugele<sup>1</sup>

<sup>1</sup>University of Twente, Physics of Complex Fluids, PO Box 217, 7500 AE Enschede, Netherlands

<sup>2</sup>Westfälische-Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 9, 48149 Münster, Germany

<sup>3</sup>University of Twente, Sustainable Polymer Chem., PO Box 217, 7500 AE Enschede, Netherlands

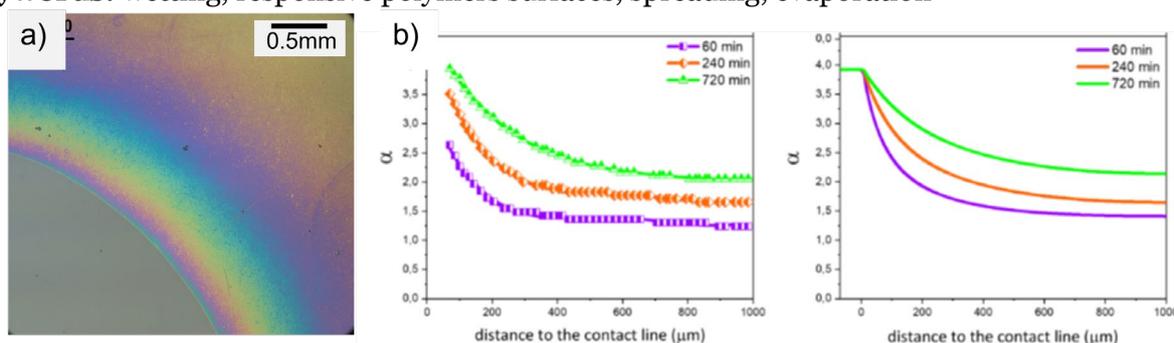
Presenting author's e-mail: [f.mugele@utwente.nl](mailto:f.mugele@utwente.nl)

Polymer brush layers swell fully in good solvents and partly in ambient vapor of good solvents. The spreading of volatile liquids on brush layers is governed by subtle combination of hydrodynamic flow, vapor transport and swelling kinetics. We studied the spreading various alkanes on hydrophobic polymer brush layers of poly-lauryl-methacrylate (PLMA). A rich phenomenology is observed including the formation of a wide halo (see figure) with a gradient of the degree of swelling of the brush layer ahead of the slowly advancing contact line. Drop radius and halo width follow algebraic scaling laws for this system with a macroscopic contact angle of less than 1°. Depending on thickness and grafting density of the brush layer, advancing contact lines can also display a contact line instability. In general, contact line profiles evolve over many hours before achieving a steady state configuration that seems to be stabilized by continued very gradual evaporation of the reservoir drop. Experiments with variable connectivity of the substrate, controlled vapor concentration fields, as well as variable vapor pressure (variable chain length) demonstrate the relevance and relative importance of viscous flow, diffusive transport within the brush layer, as well as evaporation-condensation as competing solvent transport mechanisms.

Numerical calculations using gradient dynamics support the qualitative scenario and reproduce in a semi-quantitative manner the time-dependent swelling profiles in the halo region as extracted from interferometry measurements. In particular, the calculations confirm the relevance of a continuous evaporative flux for stabilizing the halo structure and for setting the degree of swelling far from the contact line. Matching of experiments and calculations allows to estimate solvent transport coefficients within the brush layers and at the brush-vapor interface.

We discuss potential applications of responsive oleophobic polymer brush layers as controlled oil transport layers in advanced grease-lubricated bearings.

**Keywords:** wetting, responsive polymers surfaces, spreading, evaporation



**Figure 1.** Spreading drop of hexadecane on PLMA brush layer with halo ahead. a) white light top view. b) experimental (left) and numerical (right) halo thickness profiles as a function of distance from contact line after 60, 240 and 720min.

# Spreading of a precursor film on controlled nanorough defects

*Grzelka Marion<sup>1</sup> and Bonn Daniel<sup>1</sup>*

<sup>1</sup>*Van der Waals-Zeeman Institute, IoP, University of Amsterdam, Science Park 904, 1098XH, Amsterdam, the Netherlands*

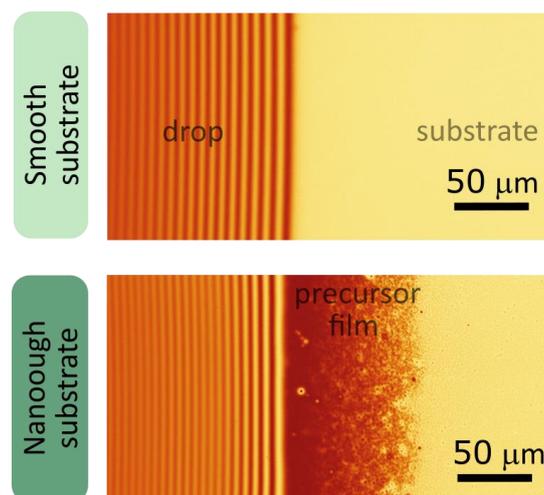
Presenting author's e-mail: [m.grzelka@uva.nl](mailto:m.grzelka@uva.nl)

A drop of coffee spreading on a table, inkjet drops emerging from a printer head, raindrops sliding down a window: many daily situations illustrate the situation where a liquid covers a solid surface. This phenomenon, known as dynamic wetting, has many applications in industrial processes such as painting, coating, or oil recovery. Because of its ubiquity, wetting has been extensively studied for centuries and at the macroscopic scale, we have an effective description that works well, but needs a phenomenological ‘fix’ at the microscale. This and the emergence of micro- and nano-fluidic technologies now require having a better understanding of dynamics of wetting phenomena at small scales, and how it connects to macroscopic phenomena.

The key example is that if one looks at the edge of a drop on a surface at the nanometric scale, a nanometer-thick layer of fluid – the precursor film- connects the drop and the surface. This precursor film remains incompletely understood. In particular, how does nanometric roughness affect its formation and dynamics?

Here, we follow the dynamics of spreading of silicone oils on nanorough substrates with optical profilometer. Playing on the density and the size of the nanodefects, we probe which parameters control the formation and dynamics of spreading of this precursor film. We compare our results to both hemiwicking phenomenon and classical precursor film spreading.

**Keywords:** Wetting, dynamics, nanoscale, roughness, polymers



**Figure 1.** Optical images of a drop of silicone oil spreading on a “smooth” and a “nanorough” substrates. The nanoroughness of the substrate initiates the formation of an precursor film

# Optical properties of thermoresponsive microgels: Experimental and theoretical insights into the volume phase transition

*Ekaterina Ponomareva*<sup>1</sup>, *Ben Tadgell*<sup>2</sup>, *Paul Mulvaney*<sup>2</sup>, *Matthias Karg*<sup>1</sup>

<sup>1</sup>*Physical Chemistry I: Colloids and Nanooptics, Heinrich-Heine-University Düsseldorf, 40225 Düsseldorf, Germany*

<sup>2</sup>*ARC Centre of Excellence in Exciton Science, The University of Melbourne, School of Chemistry, Parkville, VIC 3010, Australia*

Presenting author's e-mail: [karg@hhu.de](mailto:karg@hhu.de)

Responsive microgels are polymeric objects with an internal gel-like structure that react on external stimuli like temperature, pH or ionic strength.[1] For poly-*N*-isopropylacrylamide (PNIPAM based microgels the degree of swelling can be conveniently adjusted by temperature. Typical PNIPAM microgels possess a fuzzy sphere like structure in the swollen state because of the gradient like distribution of cross-links with higher cross-link densities in the interior and a loose outer periphery. During the volume phase transition (VPT a significant volume reduction is observed and the internal mass distribution becomes more homogeneous. The VPT is accompanied by a significant increase in light scattering (turbidity as the microgels collapse. Surprisingly, these changes in optical properties in relation to the microgel structure have not been investigated so far.

We utilize core-shell microgels with small gold nanoparticle cores and much larger PNIPAM shells as an ideal model system to study the structure-property relation of microgels. Importantly, the cores are small enough to not influence the basic physical properties of the microgels and mostly serve as high contrast markers.

Using absolute intensity SAXS and SANS measurements, we were able to determine quantitative, radial polymer density profiles that could be converted into refractive index profiles. Supported by theoretical simulations, we show that the increase in light scattering during the collapse is related to the structural transition from fuzzy spheres to rather homogeneous but still relatively low contrast spheres that behave more like Rayleigh-Debye-Gans scatterers.[2]

Our experimental results reveal a direct correlation between changes in microgel size and changes in turbidity. This correlation was used to study the kinetics of the VPT of microgels of different sizes and cross-linker densities using temperature-jump spectroscopy.[3] Our findings deepen the understanding of structural transitions in microgels and underline the potential of core-shell microgels as ideal model system for soft and deformable objects.

**Keywords:** thermoresponsive microgels, turbidity, temperature-jump spectroscopy

**Acknowledgements:** We acknowledge financial support from the German Academic Exchange Service (DAAD through its Thematic Network Bayreuth-Melbourne Colloid/Polymer Network, sponsored by funds of the Federal Ministry of Education and Research (BMBF).

## References

[1] M. Karg, et al., *Langmuir*, 2019, 35, 6231.

[2] E. Ponomareva, B. Tadgell, M. Hildebrandt, M. Krüsmann, S. Prévost, P. Mulvaney and M. Karg, *Soft Matter*, 2022, 18, 807.

[3] B. Tadgell, E. Ponomareva, M. Karg and P. Mulvaney, *J. Phys. Chem. C*, 2022, 126, 4118.

# Mechanofluorescent Polymer Brush Surfaces that Spatially Resolve Surface Solvation

Quinn A. Besford<sup>1</sup>, Petra Uhlmann<sup>1</sup>, Andreas Fery<sup>1</sup>

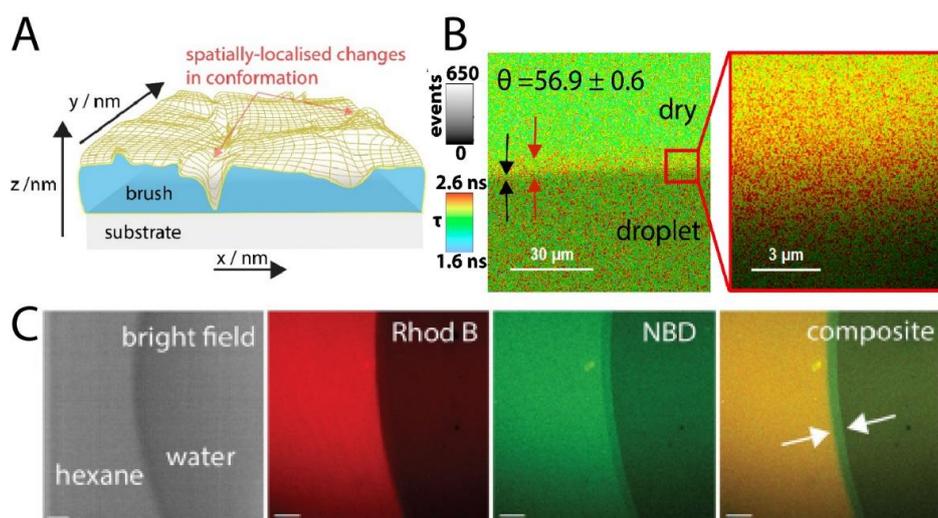
<sup>1</sup>Leibniz-Institut für Polymerforschung, 01069 Dresden, Germany

Presenting author's e-mail: [besford@ipfdd.de](mailto:besford@ipfdd.de)

Surfaces that exhibit switchable properties can be leveraged as new *smart* materials for chemo- and mechanosensing applications. In this pursuit, polymer brush surfaces are key candidates towards realising new surface-based sensing capabilities, stemming from their ability to exhibit rapid and sharp transitions in conformation under applied stimuli. In our work, we look towards spatially-identifying polymer brush conformation (Figure 1A) by integrating fluorescent dye molecules within polymer brush layers in such a way that fluorescent output is correlated to brush conformation.

Our methods are two-fold, and include (1) integrating Förster resonance energy transfer (FRET) dye molecules into diblock random copolymer brush architectures [1], and (2) integrating single-fluorophore dyes into random copolymer brushes that leverage self-quenching effects between dye molecules [2]. For system (1), the dyes produce FRET as the brushes undergo conformational changes due to applied stimuli and solvation, which could be monitored in high spatial resolution by confocal laser scanning microscopy. This identified interesting swelling behaviour at the hexane-water interface (Figure 1C). For system (2), the dye molecules were integrated at specific concentrations within the polymer brushes so that the collapse transitions enhanced the effective concentration towards the self-quenching regime. This self-quenching reduced the fluorescence lifetime of the dye molecules, which could then be monitored by fluorescence lifetime imaging microscopy (FLIM). This was used as a basis to study the solvation of the polymer brush surface from outside of an aqueous droplet (Figure 1B). Our systems provide a non-invasive lateral optical measure of changing polymer brush conformations, which has the potential to be leveraged towards greater surface-based sensing capabilities at intricate interfaces.

**Keywords:** polymer brushes, FRET, mechanofluorescence



**Figure 1:** A) Schematic describing spatially-localising polymer brush conformation, B) FLIM images of the air-liquid interface of a water droplet on a single-fluorophore integrated polymer brush surface, and C) bright field and CLSM images of the hexane-water interface on FRET polymer brush surfaces.

## References

- [1] Q. A. Besford, H., Yong, H., Merlitz, A. J., Christofferson, J. U., Sommer, P., Uhlmann, A., Fery, *Angewandte Chemie*, 2021, 60, 16600-16606.  
 [2] Q. A., Besford, H., Merlitz, Schubotz, S., H., Yong, S., Chae, M. J., Schnepf, A. C. G., Weiss, G. K., Auernhammer, J. U., Sommer, P., Uhlmann, A., Fery, *ACS Nano*, 2022, 16, 3383-3393.

## How spontaneous charging in sliding drops affects their motion

Xiaomei Li<sup>1</sup>, Pravash Bista<sup>1</sup>, Amy Z. Stetten<sup>1</sup>, Henning Bonart<sup>1,2</sup>, Maximilian T. Schür<sup>2</sup>, Steffen Hardt<sup>2</sup>, Francisco Bodziony<sup>3</sup>, Holger Marschall<sup>3</sup>, Alexander Saal<sup>1</sup>, Xu Deng<sup>4</sup>, Rüdiger Berger<sup>1</sup>, Stefan A. L. Weber<sup>4,5</sup> and Hans-Jürgen Butt<sup>1</sup>

<sup>1</sup>Max Planck Institute for Polymer Research, Mainz, Germany

<sup>2</sup>Institute for Nano- and Microfluidics, Technische Universität Darmstadt, Darmstadt, Germany

<sup>3</sup>Computational Multiphase Flows, Technische Universität Darmstadt, Darmstadt, Germany

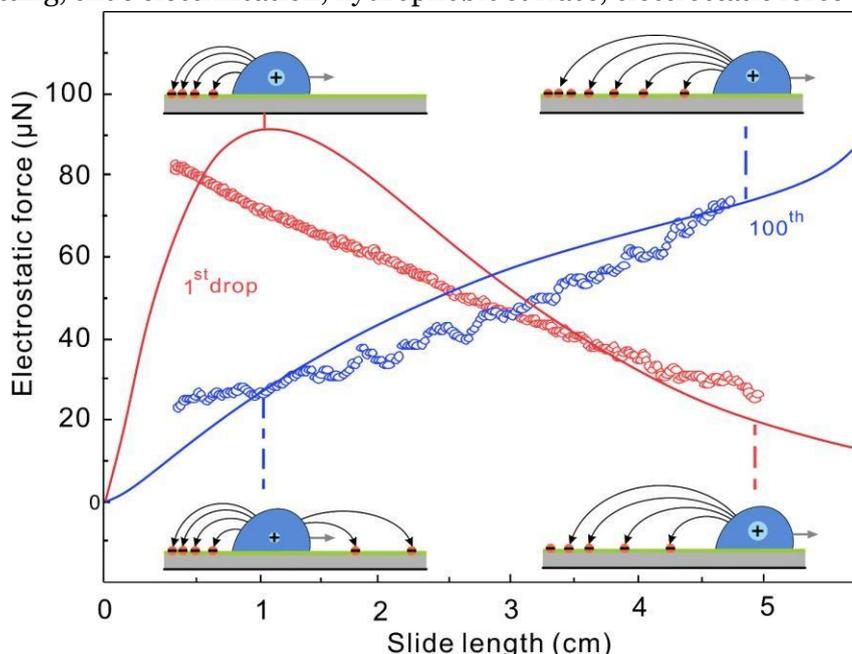
<sup>4</sup>Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu, China

<sup>5</sup>Institute of Physics, Johannes Gutenberg University, Mainz, Germany

Presenting author's e-mail: [lix2@mpip-mainz.mpg.de](mailto:lix2@mpip-mainz.mpg.de)

Water drops moving on surfaces are an everyday phenomenon seen on windows, in laboratories, and in industries around the world. Up to now, it was consensus that drop motion on surfaces is dictated by the interplay of gravitational forces, viscous dissipation and by capillary forces, which are given by the difference in the contact angles at the front and rear of moving drops. Here, we demonstrate that these effects cannot fully explain the complex trajectories of sliding drops. Drop motion on low-permittivity substrates is significantly influenced by electrostatic forces. We analyzed trajectories of drops sliding down a tilted surface and compared results to numerical modelling. This comparison, confirms that electrostatics must be taken into consideration for water, aqueous electrolyte and ethylene glycol on all hydrophobic surfaces [1]. Our finding will improve control of drop motion in many applications such as printing, microfluidics, water management and triboelectric nano-generators.

**Keywords:** wetting, slide electrification, hydrophobic surface, electrostatic force



**Figure 1.** Comparison between experimental results (red and blue data points) and a theoretical model of electrostatic force (continuous lines).

### References

[1] X. Li, P. Bista, A. Z. Stetten, H. Bonart, M. T. Schür, S. Hardt, F. Bodziony, H. Marschall, A. Saal, X. Deng, R. Berger, S. A. L. Weber, H.-J. Butt. *Nature Physics* 2022. <https://doi.org/10.1038/s41567-022-01563-6>

# Dynamic Wetting of Photo-Responsive Arylazopyrazole Monolayers is Controlled by the Molecular Kinetics of the Monolayer

Christian Honnigfort<sup>1</sup>, Leon Topp, Natalia García Rey, Andreas Heuer and Björn Braunschweig<sup>1</sup>

<sup>1</sup>Institute of Physical Chemistry, Corrensstraße 28/30, 48149 Münster, Germany

Presenting author's e-mail: [braunschweig@uni-muenster.de](mailto:braunschweig@uni-muenster.de)

Smart surfaces that can change their wettability on demand are interesting for applications such as self-cleaning surfaces or lab-on-a-chip devices. We have synthesized arylazopyrazole phosphonic acids (AAP) as a new class of photoswitchable molecules for functionalization of aluminum oxide surfaces. AAP monolayers were deposited on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) and showed reversible E/Z photo-switching that can trigger contact angle changes of up to  $\sim 10^\circ$ . We monitored these changes on the macroscopic level by recording the contact angle while the monolayer was switched in situ. On the molecular level, time-dependent vibrational sum-frequency generation (SFG) spectroscopy provided information on the kinetic changes within the AAP monolayer and the characteristic times for E/Z switching. In addition, vibrational SFG at different relative humidity indicates that the thermal stability of the Z configuration is largely influenced by the presence of water which can stabilize the Z state and hinder E/Z switching of the AAP monolayer when it is wetted with H<sub>2</sub>O. Having established the switching times on the molecular scale, we additionally measured the dynamic contact angle and show that the time scales of the substrate and droplet dynamics can be extracted individually. For that, we report on a relaxation model, that is solved analytically and is verified via a comparison with simulations of a Lennard Jones system and with experimental data. The slower E to Z switching in the presence of the droplet as compared to the vapor phase is rationalized in terms of specific interactions of water with the exposed AAP moieties.

**Keywords:** Molecular kinetics, dynamic wetting, photo-responsive, SFG spectroscopy

**Acknowledgements:** The authors gratefully acknowledge funding projects 422792175 by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) within the priority program SPP 2171 Dynamic Wetting.

## References

[1] C. Honnigfort, L. Topp, N. García Rey, A. Heuer and B. Braunschweig, J. Am. Chem. Soc., 2022, 144, 4026-4038.

## Nanoscale Interaction of Water with Organic Interfaces

*Tomas P. Corrales<sup>1</sup>, Filipe Natalio<sup>2</sup>, Sydney Cohen<sup>2</sup>, Irit Rosenhek-Goldian<sup>2</sup>, Diego Diaz<sup>3,4</sup>, Patrick Huber<sup>5</sup>, Ulrich Volkmann<sup>3</sup>, Robert Meissner<sup>5</sup>*

<sup>1</sup>*Universidad Técnica Federico Santa María, Chile*

<sup>2</sup>*Weizmann Institute of Science, Israel*

<sup>3</sup>*Pontificia Universidad Católica de Chile, Chile*

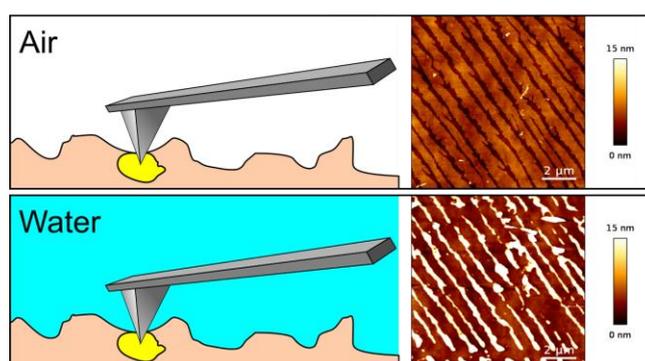
<sup>4</sup>*Max Planck Institute for Polymer Research, Germany*

<sup>5</sup>*Technical University of Hamburg, Germany*

Presenting author's e-mail: [tomas.corrales@usm.cl](mailto:tomas.corrales@usm.cl)

The interaction of water with organic interfaces is an omnipresent phenomenon in biology and of profound relevance in several industrial processes. Here we present new insights on the nanoscale interaction between water and organic interfaces, mainly using Atomic Force Microscopy (AFM). We have studied two different systems, and how they change before and after they are immersed in water. The first system consists of organic micro-inclusions entrapped in silicious rock formations, e.g., flint. Using contact resonance AFM, we have shown that these organic inclusions exhibit a Young's modulus of around 30 GPa when they are dry. When the same inclusion is measured while immersed in water, we obtain a Young's modulus of around 1 GPa. This softening of the micron-sized inclusion is accompanied by swelling, that is seen as a change in height of around 40 nm when exposed to water. The softening and swelling of micro-inclusions is consistent with its biological origin, which we confirm using a suite of complementary techniques<sup>[1]</sup>. In a second system, we study films of n-alkanes that are physisorbed onto silicon. Using AFM in air and then liquid conditions we see that the molecules re-organize into a stable configuration, which involves a stacking of molecules. We observe that in dry conditions, the film is composed of one layer of molecules that are perpendicular to the substrate, and that after water immersion, the molecules stack on top of each other forming 4 perpendicular layers. Using complimentary molecular dynamic simulations we observe the first stages of this water-induced stacking, confirming the effect. Furthermore, we have correlated this molecular rearrangement with the macroscopic contact angles<sup>[2]</sup>.

**Keywords:** Organic Interface, Nano-mechanics, AFM, Liquid Interaction



**Figure 1.** Comparison of AFM images in air and liquid of an n-alkane nanopattern.

**Acknowledgements:** TPC thanks funding grant Fondecyt Regular 1211901 and MPG190023.

### References

- [1] F. Natalio *et al.*, "Characterization of Eocene flint," *Chem. Geol.*, p. 120427, 2021.
- [2] D. Díaz *et al.*, "How water wets and self-hydrophilizes nanopatterns of physisorbed hydrocarbons," *J. Colloid Interface Sci.*, vol. 606, pp. 57–66, 2022.

## dSTORM super resolution microscopy of pNIPAM microgels

*Xhorxhina Shaulli*<sup>1</sup>, *Rodrigo Rivas-Barbosa*<sup>2</sup>, *Maxime Jolisse Bergman*<sup>1</sup>, *Nicoletta Gnan*<sup>2</sup>  
*Emanuela Zaccarelli*<sup>2</sup> and *Frank Scheffold*<sup>1</sup>

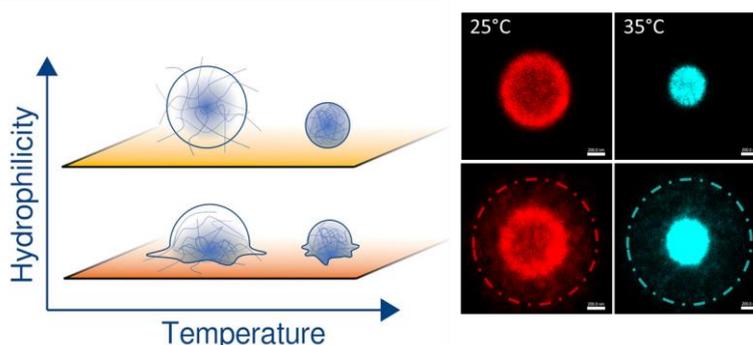
<sup>1</sup>*Department of Physics, University of Fribourg, Chemin du Musée 3, 1700, Fribourg, Switzerland*

<sup>2</sup>*Department of Physics, Sapienza University of Rome, Piazzale Aldo Moro 2, 00185 Roma, Italy*

Presenting author's e-mail: [xhorxhina.shaulli@unifr.ch](mailto:xhorxhina.shaulli@unifr.ch)

The ability to observe microgel morphologies at nanometer scale and its response to temperature changes opens exciting opportunities to design and precisely control the behavior of microgels for various applications [1]. In this context, super resolution microscopy is a well-established tool used to investigate colloidal systems e.g. poly(N-isopropylacrylamide) (pNIPAM) microgels [2]. An important role when performing advanced microscopy experiments on such particles plays the interface where the microgels are established, as they have to be fixed during the experiment. We use super resolution microscopy and molecular dynamic (MD) simulations to investigate how individual microgels anchored on hydrophilic and hydrophobic surfaces change morphology with temperature. Super resolved images of individual microgel particles at different collapsing stages are analyzed and their density profiles are obtained. The results suggest that the anchoring parts of the microgel stick to the surface as the temperature is increased. For these surfaces the experimental data and the MD simulations are in very good agreement. Such study is relevant to establish a technique for the investigation of more complex systems along lower critical solution temperature (LCST), where molecules of interest can be encapsulated in the microgel network and controllably released with temperature.

**Keywords:** super resolution microscopy, dSTORM, interface, pNIPAM microgels.



**Figure 1.** Schematic representation (left) and averaged dSTORM images (right) of microgels below and above LCST (left to right) and at two different surface treatment (bottom to top).

**Acknowledgements:** The authors acknowledge funding from H2020 Marie Curie Actions of the European Commission (ITN SUPERCOL, Grant Agreement 860914)

### References

[1] Scheffold, F. *Nat Commun* 2020, 11, 4315.

[2] Conley, G. M., Nöjd, S., Braibanti, M., Schurtenberger, P., & Scheffold, F. *Physicochemical and Engineering Aspects* 2016, 499, 18–23.

## Droplet dynamics on inclined soft surfaces

Mathieu Oléron<sup>1</sup>, Laurent Limat<sup>1</sup>, Julien Dervaux<sup>1</sup>, and Matthieu Roché<sup>1</sup>

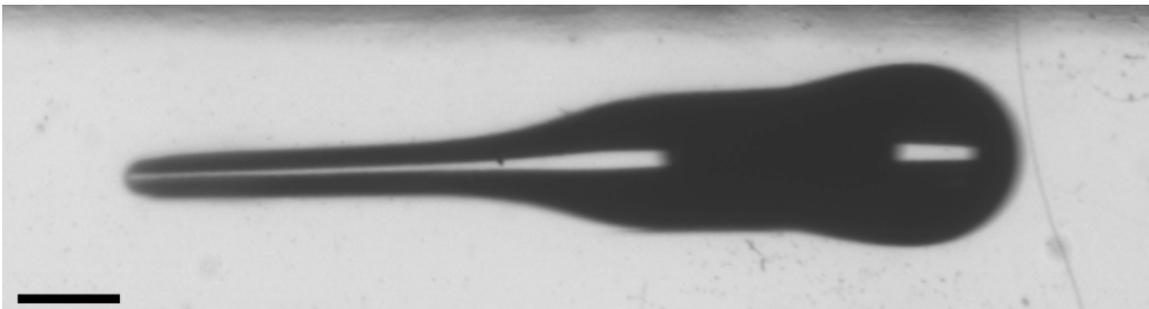
Université Paris Cité, CNRS UMR 7057, Laboratoire Matière Et Systèmes Complexes,  
F-75013 Paris, France

Presenting author's e-mail: [matthieu.roche@u-paris.fr](mailto:matthieu.roche@u-paris.fr)

The motion of a droplet on the surface of a rigid solid can be described by accounting for the mechanical and capillary properties of the liquid and the surface energy of the solid. The same observation on the surface of a soft solid shows that the mechanical properties of the solid also contribute to the dynamics. In most experiments up to now, the mechanics of these elastomers actually dominate that of the liquid.

Here, I will describe recent work in our group that combines experiments and theory to explore how changes in the partition of energy dissipation between the liquid and the soft solid, represented by a dimensionless number, translate into the shape and motion of droplets moving down inclined soft surfaces. I will show that observations in the case where dissipation in the liquid dominates are close to those of the case where the droplet moves on the rigid substrate. Details show however that the latter cannot help describe the former. As the solid becomes the major energy dissipater, I will describe the new regimes of motion that we observe. Both the droplet- and the contact-line-scales contain interesting information, and I will discuss these in the light of a recent model that we proposed.

**Keywords:** wetting, elastomers



**Figure 1.** It must not exceed the limit of 17cm wide. Do not wrap the text around any of the graphics.

**Acknowledgements:** The authors acknowledge support from Agence Nationale de la Recherche (ANR), under grant ANR-17-CE30-0016 (project GelWet).

### References

[1] J. Dervaux, M. Roché, and L. Limat, *Soft Matter* **16**, 5157 (2020).

## Describing liquid drops on elastic substrates: Mesoscale model vs. macroscale model and experiment

*Christopher Henkel*<sup>1</sup>, *Martin H. Essink*<sup>2</sup>, *Ambre Bouillant*<sup>2</sup>, *Uwe Thiele*<sup>1,3</sup>, *Jacco H. Snoeijer*<sup>2</sup>

<sup>1</sup>*Institut für Theoretische Physik, Westfälische Wilhelms-Universität Münster,  
Wilhelm-Klemm-Str. 9, 48149 Münster, Germany*

<sup>2</sup>*Physics of Fluids Group, Faculty of Science and Technology, Mesa+ Institute,  
University of Twente, 7500 AE Enschede, The Netherlands*

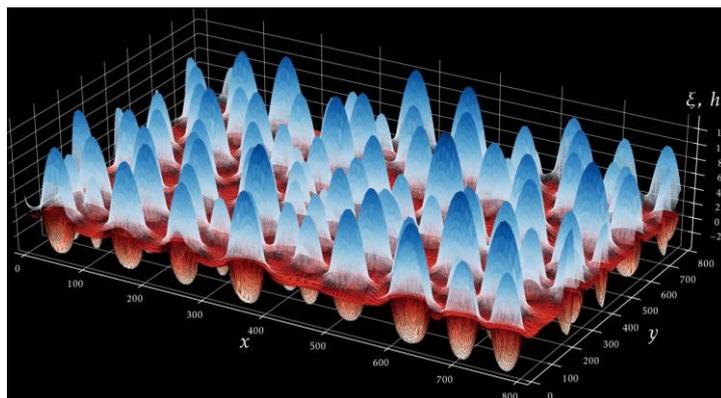
<sup>3</sup>*Center for Nonlinear Science (CeNoS), Westfälische Wilhelms-Universität Münster,  
Corrensstr. 2, 48149 Münster, Germany*

Presenting author's e-mail: [c\\_henko8@uni-muenster.de](mailto:c_henko8@uni-muenster.de)

We investigate the behavior of liquid drops on soft viscoelastic substrates employing mesoscopic and macroscopic models as well as experiments. First we introduce a simple mesoscopic gradient dynamics model and show that it recovers the known double-transition in contact angles with increasing softness and that it is well suited to study multi-drop problems like the dependence of drop coarsening on softness [1].

Second, we incorporate the Shuttleworth effect and compare the mesoscopic results with a macroscopic neo-Hookean model with proper treatment of bulk elasticity in a large-deformation framework [2]. Finally, we present experiments showing that condensation of drops on substrates of different softness results in distinctive breath figures / drop ensembles that indicate softness dependent nucleation probabilities. Extending the mesoscopic model to incorporate condensation allows us to predict the dependence of nucleation probability on softness and compare it with experimental results.

**Keywords:** wetting, fluid-dynamics, elasticity



**Figure 1.:** snapshot of the time simulation of a coarsening drop ensemble on a soft substrate.

### References

- [1] C. Henkel, J. H. Snoeijer, U. Thiele, 2021, Gradient-dynamics model for liquid drops on elastic substrates. *Soft Matter* 17, 10359-10375, DOI: 10.1039/d1sm01032h.  
[2] C. Henkel, M. H. Essink, T. Hoang, G. J. van Zwieten, E. H. van Brummelen, U. Thiele, J. H. Snoeijer, 2022, Soft wetting with (a)symmetric Shuttleworth effect. arXiv:2201.04228.

# Liquid nucleation around charged particles and electro- prewetting phase lines

Roni Kroll <sup>1</sup> and Yoav Tsori <sup>1,2</sup>

<sup>1</sup>Department of Chemical Engineering, Ben-Gurion University of the Negev, Israel

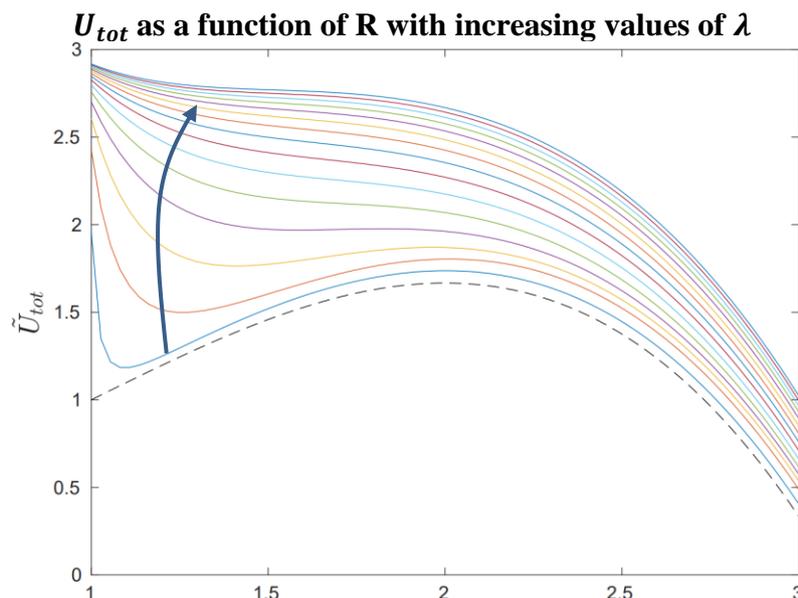
<sup>2</sup> Department of Physics, Ben-Gurion University of the Negev, Israel

Presenting author's e-mail: [tsori@bgu.ac.il](mailto:tsori@bgu.ac.il)

We look at the nucleation of liquid from a vapor as induced by charged spherical particles. The system's energy, accounting for the presence of dissociated ions, generalizes two known limits: (i) when the Debye length is much smaller than the particle size, the electrostatic energy is equivalent to effective interfacial energy between the surface and the liquid. (ii) In the opposite limit, the Thomson nucleation model is retrieved.

We further study "electro-prewetting" and examine the mere existence of a vapor-liquid interface. We calculate the equilibrium density profile at arbitrary temperatures, particle charges, and vapor densities. In contrast to classical nucleation theory, here, both liquid and vapor phases are different from the bulk phases because they are spatially nonuniform. In addition, the theory applies to both sharp and diffuse interfaces and allows the calculation of the surface tension self-consistently. We find that the adsorption at the particle changes discontinuously at a first-order phase transition line. This line becomes a second-order phase transition at a "surface critical point". Like in prewetting, the adsorption diverges at the binodal phase boundary. We construct a phase diagram indicating changes in the binodal, spinodal, and critical temperature. The results are relevant to droplet nucleation around charged particles in the atmosphere and could possibly explain deviations from expected nucleation rates.

**Keywords:** classical nucleation theory, electrowetting, prewetting, phase transitions.



**Figure 1.** The total energy of a charged colloid  $U_{tot}$  as a function of the liquid-vapor interface location  $R$  (scaled by the colloid size). Dashed curve is the classical  $U_{tot} = (...)R^2 - (...)R^3$  behavior. Colored lines show  $U_{tot}$  with increasing Debye length  $\lambda$  (see arrow). At a certain value of  $\lambda$  the nucleation barrier disappears.

# Wenzel-to-Cassie transition on lubricant-impregnated surfaces

*Dimitrios Tzitzilis<sup>1</sup>, Ioannis Ntakoumis<sup>1</sup>, Charalambos Tsekeridis<sup>1</sup>,  
and Periklis Papadopoulos<sup>1</sup>*

<sup>1</sup>*University of Ioannina, Greece, Department of Physics*

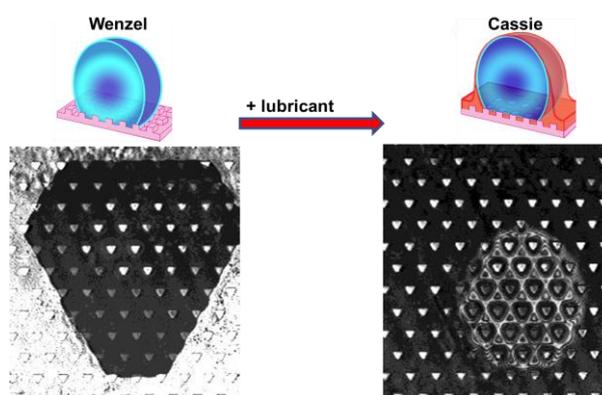
Presenting author's e-mail: [papadopo@uoi.gr](mailto:papadopo@uoi.gr)

Slippery surfaces, a combination of nanostructured surfaces with an immiscible liquid acting as a lubricant, improve various aspects of superhydrophobic surfaces, such as low critical penetration pressure, and condensation of drops and ice inside the structures. However, this is true only when the drops are either in the Cassie state (lubricant cushions under the drop) or the Floating state (no contact between the drop and the solid surface). In contrast, when the drop is in the Wenzel state (full contact with the solid surface) it exhibits strong adhesion forces and does not move easily.

In the present work we investigate the possibility of a transition from the Wenzel to the Cassie state through the injection of lubricant into microstructured hydrophobic surfaces with a liquid drop which is already in the Wenzel state. The "key" to the transition from Wenzel to Cassie is the change of the microscopic contact angle of the drop. We imaged the lubricant layer with Reflection Interference Contrast Microscopy, using a custom-made confocal microscope. When the drop is in the Wenzel state there is only one interface between the drop and the solid, giving rise to a weak, homogeneous reflection. In contrast, the surrounding air-solid interface has a higher refractive index mismatch and reflects strongly. In the Cassie state, there are two nearly parallel interfaces, the drop-lubricant and the lubricant-solid interface. The two reflections give rise to a complex interference pattern (Figure 1).

We investigated the requirements of surface geometry for the transition to take place. By varying the spacing between protrusions and their height we found that it is necessary to have stricter limits than the ones required to prevent the spontaneous Cassie-to-Wenzel transition. We ran simulations to investigate the shape of the drop-lubricant interface. Finally, we constructed a phase diagram showing the favorable geometric configurations of the surface.

**Keywords:** Cassie, Wenzel, interference



**Figure 1.** Reflection Interference Contrast Microscopy images from a drop on a microstructured surface. (Left) The drop is in the Wenzel state. (Right) After the addition of lubricant around the drop, the drop transitioned to the Cassie state. The interference pattern proves the existence of two, nearly parallel, interfaces.

## References

[1] D. Tzitzilis, I. Ntakoumis, C. Tsekeridis, P. Papadopoulos (in preparation).

# Superamphiphobic surfaces for ultrafast single bubble bursting and bulk defoaming

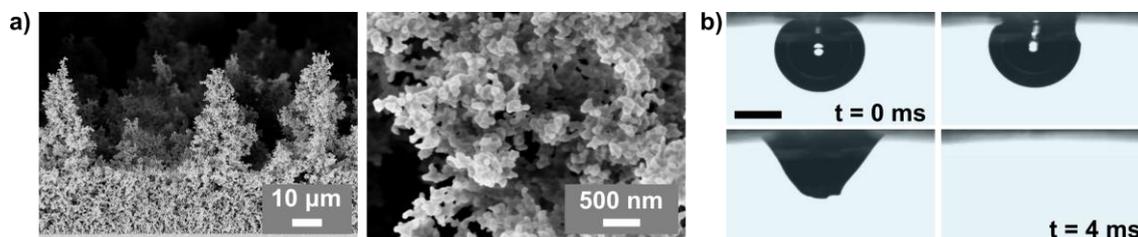
*Katharina I. Hegner<sup>1</sup>, William S. Y. Wong<sup>1</sup>, Doris Vollmer<sup>1</sup>*

<sup>1</sup> *Max Planck Institute for Polymer Research, Mainz, Germany*

*Presenting author's e-mail: hegner@mpip-mainz.mpg.de*

Bubble and foam formation may challenge a variety of industrial sectors including food processing, flotation in mineral mining, and waste-water treatment. Circumventing the need for chemical additives by passive, surface-induced bubble bursting and defoaming is highly desirable. Here, we demonstrate how the speed of bubble bursting can be controlled via the morphology of super-liquid-repellent surfaces.[1] Optimized coatings are prepared using liquid flame spray. Superamphiphobicity was verified by low sliding angles ( $2^\circ \pm 1^\circ$ ) for hexadecane ( $\gamma = 27.5 \text{ mN m}^{-1}$ ) drops. The versatile, easily scalable fabrication method allows simultaneous tuning of nano- and microscale structures. We identify the parameters required to achieve ultrafast bubble bursting: the nanoprotusions should be as small as possible (diameters below 100 nm) and assembled into porous, rough microscale features (Figure 1a). By optimizing the surface morphology, bubble bursting can be induced within 2 ms in water. After only 4 ms the released air is fully absorbed by the Cassie-state's plastron layer (Figure 1b). The coatings demonstrate long-term ultrafast bubble rupturing and chemical and mechanical stability even in the presence of surface-active species. Furthermore, superamphiphobic surfaces are able to increase defoaming rates and inhibit foam formation.[2] The design principles were applied to passively control surfactant-rich bubbles and improve the material collection efficiency in froth flotation.

**Keywords:** aerophilic surfaces, bubble rupturing, liquid flame spray, flotation



**Figure 1.** a) SEM images of particulate superamphiphobic structures prepared by liquid flame spray. b) Images acquired by a high-speed camera show a single air bubble rupturing immediately upon contacting the surface in water (scale bar is 1 mm).

## References

- [1] K.I. Hegner, W.S.Y. Wong, D. Vollmer, *Advanced Materials*, 2021, 33, 2101855.  
[2] W.S.Y. Wong, A. Naga, L. Hauer, P. Baumli, H. Bauer, K.I. Hegner, M. D'Acunzi, A. Kaltbeitzel, H.J. Butt, D. Vollmer, *Nature Communications*, 2021, 12, 5358.

## Predicting Contact Angle Hysteresis via Micro-scale Interface Dynamics on Random and Periodic Rough Surfaces

*Pawan Kumar*<sup>1</sup>, *Paul Mulvaney*<sup>2</sup>, and *Dalton J. E. Harvie*<sup>1</sup>

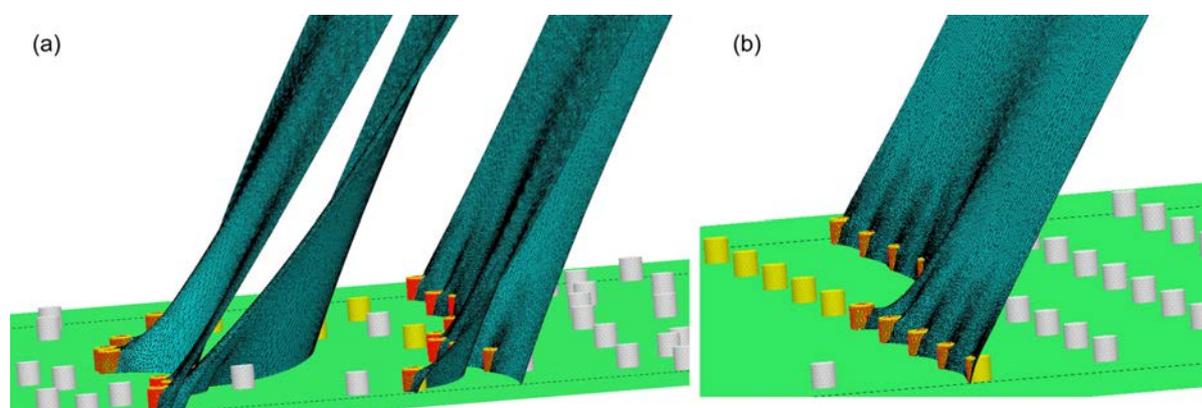
<sup>1</sup>*Department of Chemical Engineering, The University of Melbourne, Australia*

<sup>2</sup>*School of Chemistry, The University of Melbourne, Australia*

Presenting author's e-mail: [pawank@student.unimelb.edu.au](mailto:pawank@student.unimelb.edu.au)

Surface wetting refers to the phenomena of spreading of a liquid on a solid in the presence of another immiscible liquid or gas. Separation of metal ores, water repellent surfaces, enhanced oil recovery etc., are some of the applications where surface wetting plays an important role. On rough surfaces, the wetting exhibits a hysteresis in the static contact angle (CAH). With advancements in microfabrication techniques, hysteresis on surfaces possessing structured roughness has been explored to some extent, however the wetting behaviour on randomly structured surfaces remains largely unexplored. Here we measure the CAH for de-ionized water droplet on surfaces having randomly distributed and hexagonally arranged cylindrical pillars (10-micron diameter and unit aspect ratio) with different area fractions. To ensure that the inherent surface is chemically homogeneous and hydrophobic, a monolayer of octadecanethiol (ODT) is deposited before measurement. Experimental findings are also compared against a unique numerical model that is based on a novel roughness scale mechanical energy balance. The numerical model is developed in the open-source software Surface Evolver and utilizes the concept of free energy minimization. We find that for both randomly distributed and periodic pillars, the macroscopic advancing contact angle increases with pillar area fraction, showing a logarithmic dependence that is in good agreement with the experiments. Further, for a given area fraction a randomly structured surface generally produces a lower advancing contact angle than a structured surface. Extending our results, we also show numerically that on a hexagonal surface (or a structured surface in general), the contact angle is different depending upon the direction of interface advance relative to the orientation of the roughness structure, suggesting the potential of the tool for designing directional wetting surfaces. This combined experimental and numerical study shows that contact angle hysteresis can be quantitatively predicted on surfaces with known roughness topography.

**Keywords:** Contact Angle Hysteresis, Random Surfaces



**Figure 1.** (a) Shows four equilibrium interface morphologies of a liquid/gas interface as it advances over a surface textured with randomly distributed cylindrical pillars. (b) Liquid/gas interface advancing with a zipping contact line motion on a surface with hexagonally arranged cylindrical pillars. For both cases the (flat) Young's angle is 112 degrees, the area fraction of pillars is 0.02 and their aspect ratio is 1.

# Coupling Between Wetting Dynamics, Marangoni Vortices, and Localized Hot Cells in Volatile Binary Solutions Drops

*Mohammad Abo-Jabal, Ekhlash Homede, Anna Zigelman and Ofer Manor*

*Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa  
3200003, Israel*

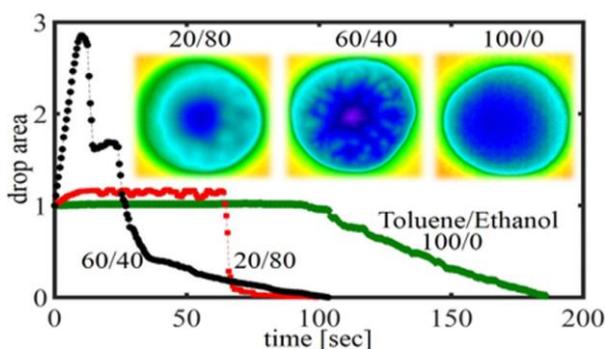
*Presenting author's e-mail: [mohammad.aj@gtiit.cn](mailto:mohammad.aj@gtiit.cn)*

Evaporation of a sessile drop comprising a mixture of volatile solvents supports spatial variations in interfacial energy, driven by the concentration gradients which gives rise to solutal Marangoni flow. Both the Marangoni flow and evaporation bring about a dance of concurrent and inter-connected phenomena: internal Marangoni vortices, localized hot cells, and complex wetting dynamics.

Here we investigate the intimate connection between these phenomena. We employ Particle Image Velocimetry and Infra-Red Microscopy to visualize Marangoni vortices, temperature variations, and the wetting dynamics of drops of toluene and ethanol mixtures.

We observe and confirm the connection between Marangoni vortices and the formation of localized hot cells. Moreover, the drops initially expand on the solid in response to Marangoni flow, then contract due to evaporation; between these dynamic wetting regimes, we further observe a regime of periodic wetting/de-wetting cycles at low toluene concentrations. The intensity of the measured vorticity, temperature variations, and spreading area is found to vary concurrently in time and in like manner accordingly with the initial composition of drops. In particular, we observe maximum intensity levels when the initial toluene proportion in the drops is 60%, and none of these phenomena are in the case of pure toluene. Our findings demonstrate that the initial composition is the key parameter to regulating the internal flow and the wetting dynamics of volatile binary mixtures. We attribute this to thermodynamic effects i.e., non-ideal mixing, which will be our main future research interest.

**Keywords:** wetting dynamics, Marangoni vortices, internal flow, volatile binary drops.



**Figure 1.** Temporal variations of the normalized areas of evaporating drops with different initial compositions, and the corresponding instantaneous temperature variations.

**Acknowledgements:** We acknowledge support of this research by the German Israel Foundation for Scientific Research and Development (GIF) under Grant No. I-1361-401.10/2016, and the support of the Neubauer Family Foundation to M.A.

# Drying patterns of liquid bridge: coffee ring to scallop shell

*Ankur Chattopadhyay*<sup>1</sup>, *Srinivas Rao S*<sup>2</sup>, *Omkar Hegde*<sup>2</sup> and *Saptarshi Basu*<sup>2</sup>

<sup>1</sup>*Department of Applied Physics, Aalto University, Finland*

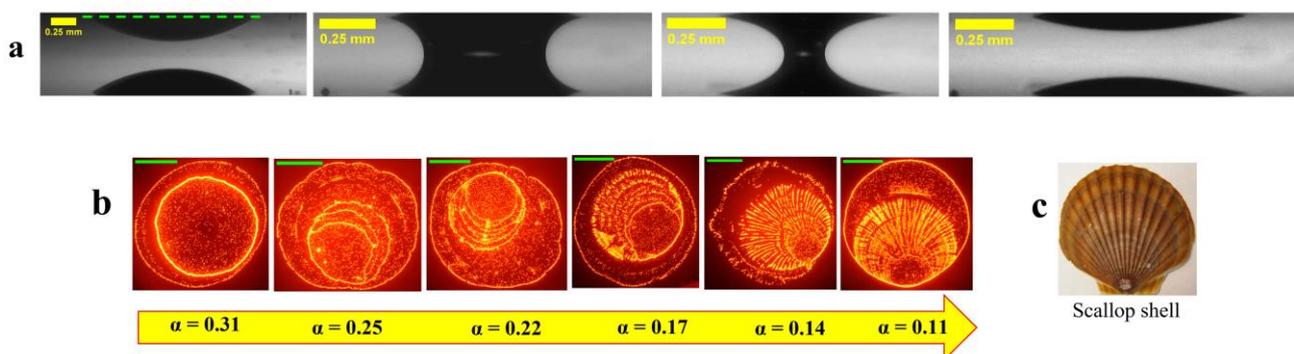
<sup>2</sup>*Department of Mechanical Engineering, Indian Institute of Science, India*

Presenting author's e-mail: [ankur.chattopadhyay@aalto.fi](mailto:ankur.chattopadhyay@aalto.fi)

The present study attempts to generate distinct patterns, different from well-known coffee rings, from the evaporated colloidal droplets in a liquid bridge (LB configuration). A few articles [1,2] have reported evolution of diverse patterns from evaporating colloidal LBs. However, from existing literature, it remains unclear how the interplay of heat and mass transport within a colloidal liquid bridge leads to formation of the distinguished precipitates.

To understand the fundamental contact line (CL) dynamics during evaporation and the physical deposition mechanisms of particles that yield a specific pattern, we study the evaporation of colloidal liquid bridges (LB in parallel plate configuration (fig. 1a). We experimentally demonstrate how the commonly observed “coffee ring” can be turned into differently orientated patterns (fig. 1b). For a given particle concentration, reducing the confinement distance ( $\alpha$ ) (the gap between the solid surfaces leads to systematized nano-particle agglomeration that yields spokes-like patterns similar to those found on scallop shells instead of circumferential edge deposition (figs. 1b, 1c). We observe, altering the confinement distance modulates the geometry of the meniscus of liquid vapor interface that results in varied evaporation flux across the curvature and subsequently influences the flow patterns within the LBs. Analysis reveals lower confinement distances result in the quasi continuous dewetting of the CL. However, the relatively stretched LBs exhibit pinned behaviors. We infer that a drying liquid thin film (height  $\leq O(10^{-7}\text{m})$  present during dewetting near the three-phase contact line is responsible for the aligned deposition of particles. The confinement distance determines the characteristic length scales of the thin film formed near the contact line, and its theoretical estimations are validated against the experimental observations using reflection interferometry, further exhibiting reasonable agreement (in order of magnitude).

**Keywords:** colloid, liquid bridge, dewetting, confined droplet



**Figure 1.** (a) Transient dynamics of colloidal liquid bridges, (b) patterns of different confinement distances ( $\alpha$ ), (c) image of a scallop shell, copyright belongs to [3].

## References.

- [1] Mondal, R. and Basavaraj, M.G., 2020. *Soft Matter*, 16(15),3753-3761.
- [2] Upadhyay, G. and Bhardwaj, R., 2021. *Langmuir*, 37(41), pp.12071-12088.
- [3] Siddon, C.E., Smith, Q.T., McNeel, K., Oxman, D. and Goldman, K.J., 2017. Protocol for Estimating Age of Weathervane Scallops *Patinopecten caurinus* in Alaska. Alaska Department of Fish and Game, Division of Sport Fish, Research and Technical Services.

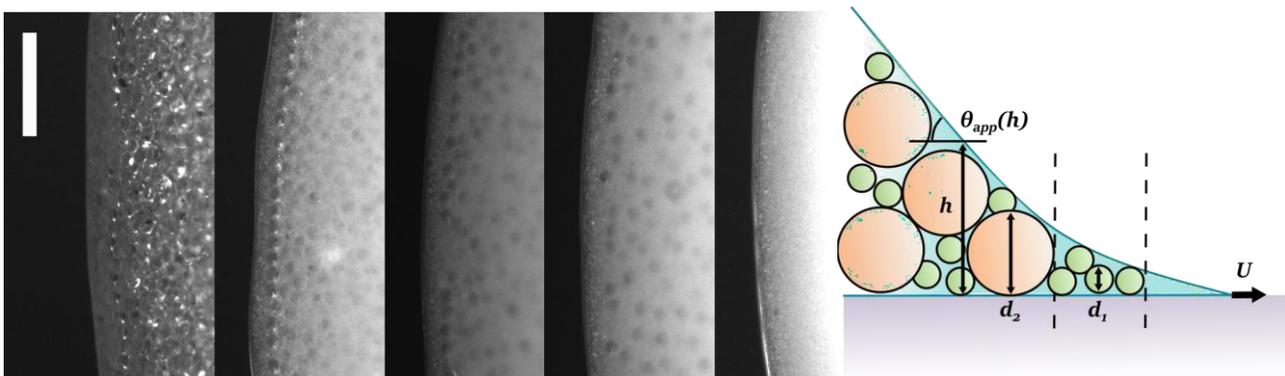
# Probing dissipation length-scale in spreading drops using granular suspensions

*Alice Pelosse<sup>1</sup>, Matthieu Roché<sup>1</sup>, Elisabeth Guazzelli<sup>1</sup>*

*<sup>1</sup>Université Paris Cité, CNRS, Matière et Systèmes Complexes (MSC) UMR 7057, Paris, France*

Presenting author's e-mail: [alice.pelosse@u-paris.fr](mailto:alice.pelosse@u-paris.fr)

Granular suspensions are used to gain a better understanding of the multiscale physics of spreading drops. In a previous work<sup>1</sup>, monomodal granular suspensions were shown to obey the classical Cox Voinov<sup>2, 3</sup> law which relates the capillary number,  $Ca = \eta U / \gamma$ , to the dynamical contact angle,  $\theta_{app}$ , provided one uses an apparent viscosity,  $\eta_w$ . Contrary to the bulk viscosity of monomodal suspensions which solely depends on particle volume fraction,  $\phi$  the wetting viscosity,  $\eta_w$ , extracted from the experiments was shown to depend both on  $\phi$  and the particle size: it is maximum for the smallest particles and decrease to almost the suspending fluid viscosity above a cut-off diameter of 150  $\mu\text{m}$ , even for  $\phi \geq 40\%$ . In the present work, the origin of this cut-off size is investigated and linked to the dissipation length-scale of this multiscale problem. Tuning dissipation can be achieved by using the confinement constraint of the particles by the contact line. Ordering of the particles under confinement is also observed in this region and is shown to affect the wetting dynamics reflected in the effective wetting viscosity. Interestingly, systems that are more complex, consisting of bimodal suspensions offer new insights into the wetting dynamics and provide evidence of the interplay between confinement and bulk effects during the spreading of a granular suspension on a solid.



**Figure 1.** (left) Top view of drops of bimodal suspensions consisting of 10 and 80 microns particles with (from left to right) 0, 25, 50, 75 and 100% of small particles in the solid blend. Snapshots taken at equivalent contact angles. Scale bar: 500  $\mu\text{m}$ . (right) Sketch of the vicinity of the contact line during spreading of bimodal suspension drops.

**Keywords:** Drop spreading dynamical wetting, granular suspensions

## References

- [1] Zhao, M. et al. Spreading of granular suspensions on a solid surface. *Physical Review Research* 2,022031 (2020).
- [2] Voinov, O. Hydrodynamics of wetting. *Fluid dynamics* 11, 714–721 (1976).
- [3] Cox, R. The dynamics of the spreading of liquids on a solid surface. part 1. viscous flow. *Journal of fluid mechanics* 168, 169–194 (1986).

Monday 5th September 2022

**Colloidal Dispersions, Colloidal Stability and Surface Forces**

# “Centipede” statistical polymer under nano-confinement: Surface forces, superlubricity, and transient interfacial gels

Nicholas M. Taylor<sup>1</sup>, Peter J. Dowding,<sup>1,2</sup> Brian Vincent<sup>1</sup> and Wuge H. Briscoe<sup>1</sup>

<sup>1</sup>School of Chemistry, University of Bristol, Cantock’s Close, Bristol BS8 1TS, UK

<sup>2</sup>Infinium UK Ltd, Milton Hill Business and Technology Centre, Abingdon, OX13 6BB, UK

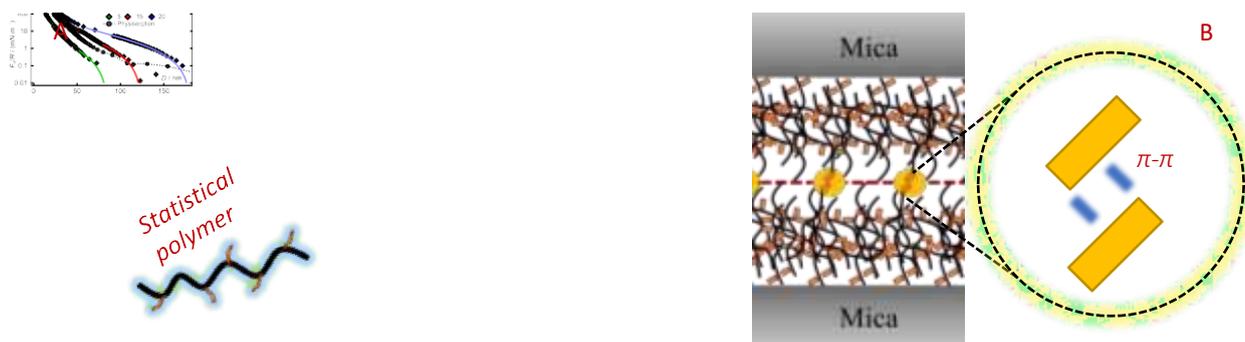
Presenting author’s e-mail: [wuge.briscoe@bristol.ac.uk](mailto:wuge.briscoe@bristol.ac.uk)

Understanding polymer-mediated surface forces and friction is critically important to colloidal stability, biological processes, and industrial applications. Such interactions depend sensitively on the polymer conformation at the interface (e.g. end-anchored brushes, surface aggregates, or loops and trails [1-5]), which in turn depends intimately on the polymer molecular architecture.

Here we report surprising interfacial behavior, through direct measurement of surface forces and friction mediated by a functionalized statistical copolymer in *n*-dodecane using the surface force apparatus (SFA). The bespoke-architecture polymer has an olefin backbone decorated with a statistical distribution of polar-aromatic functional side-groups, with a structure that we term as “centipede” (Fig.1A inset). The polymer is anchored on the mica surface in SFA through either physisorption or using the classic Langmuir-Blodgett (LB) method, i.e. transferred from the air-water interface of an LB trough with the polymer nanofilm thickness and density controlled via the transfer surface pressure  $\Pi$ .

As the LB-polymer layers are brought into nano-confinement in the SFA, the surface forces ( $F_n$ ) observed can be described by the classic Alexander–de Gennes theory (solids lines, Fig.1A), with the onset surface separation for the surface force far exceeding the thickness of an LB-polymer-monolayer. This is confirmed by complementary synchrotron X-ray reflectivity measurements, indicating a *multilayer* structure. Compared to adsorbed polymer layers, the LB polymer layers can mediate *superlubricity* (with a friction coefficient as low as 0.0002, comparable to that found in human articular joints). We propose that molecular arrangement upon LB compression leads to the multilayer nanofilm with a structure akin to an *interfacial gel*, with the *transient crosslinking* facilitated by the intra- and inter-molecular interactions between the functional groups (Fig.1B).

**Keywords:** Surface forces, friction, statistical polymers



**Figure 1.** A) SFA results with FOCF shown in inset; B) Proposed interfacial gel structure mediated by sticky groups.

## References

- [1] W.H. Briscoe, in: D. Berti, G. Palazzo (Eds.), Colloidal Foundations of Nanoscience (Second Edition), 2022, pp. 125, Elsevier, Amsterdam.
- [2] I.E. Dunlop, W.H. Briscoe, S. Titmuss et al., J Phys Chem B (2009) 113(12) 3947.
- [3] M. Chen, W.H. Briscoe, S.P. Armes, J. Klein, Science (2009) 323(5922) 1698.
- [4] J.E. Bartenstein, X. Liu, K. Lange, P.M. Claesson, W.H. Briscoe, JCIS (2018) 512 260.
- [5] C. Redeker, W.H. Briscoe, Langmuir (2019) 35(48) 15739.

# Effect of Membrane Stability in Friction Manipulation Using Electric Fields

Yu zhang<sup>1</sup>, Di Jin<sup>1</sup>, Nir Kampf<sup>1</sup>, Jacob Klein<sup>1</sup>

<sup>1</sup>Weizmann Institute of Science, Rehovot, 7610001, Israel

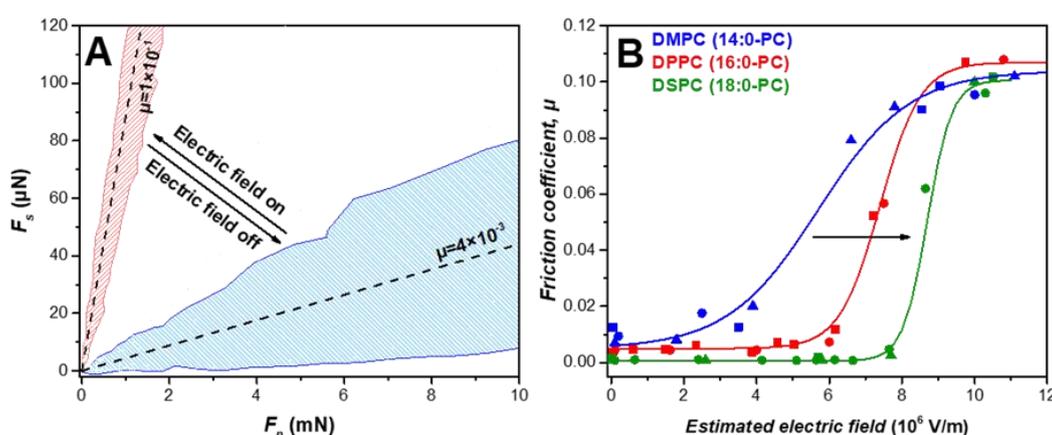
Presenting author's e-mail: [yu.zhang@weizmann.ac.il](mailto:yu.zhang@weizmann.ac.il)

Manipulation of frictional energy dissipation is an emergent topic due to the dual character of friction. Various methods have been used to control the friction, in which external stimuli, such as pH, ionic strength, temperature, electric potential (field) etc., are attractive as they are easy to apply. The surface chemical structures are designed accordingly to enable the change of surface properties through which the friction is manipulated. Based on this principle, the highly hydrated phosphatidyl choline (PC) lipids should respond to the external transmembrane electric field, through which friction could be manipulated.

Here in this work, we present that, by using a three-electrode modified surface force balance (SFB), the friction coefficient between lipid-covered gold and mica surface could be tuned reversibly by applying electric field across the confined lipids, from low friction regime due to hydration lubrication[1], to high friction regime, as shown in Figure 1A. The distribution of friction coefficient against the estimated electric field shows that the critical electric field (at which friction coefficient increases to 50% of the maximum) increases with the alkyl chain length (Figure 1B). The distribution indicates that the friction manipulation is probably achieved by the reversible electroporation, during which transmembrane pores forms in the lipid membrane[2], leading to the friction coefficient increase. The energy requirement that indicated by the critical electric field increases with alkyl chain length of lipid molecules, as the lipid membrane stability increases with the hydrophobic chain length of PC-lipids.

This work shows, for the first time in our knowledge, the manipulation of friction in PC-covered surfaces using electric field, of which the mechanism is probably electroporation.

**Keywords:** hydration lubrication, friction manipulation



**Figure 1.** Manipulation of friction coefficient using electric field (A) and friction coefficient distribution versus electric field (B). Different friction regimes are indicated by different colors with the dashed line showing average values for each regime. The measured friction coefficients in (A) are plotted against electric field, as shown in B, indicating the increasing critical electric field. These data suggest that the friction change could be attributed to electroporation.

## References

- [1] S. Jahn, J. Seror, J. Klein, Annual Review of Biomedical Engineering, 2016, 18, 235.
- [2] E. Cunill-Semanat, J. Salgado, The Journal of Membrane Biology, 2019, 252, 241.

# Quantification of size-compatible host-guest interaction using a surface forces apparatus

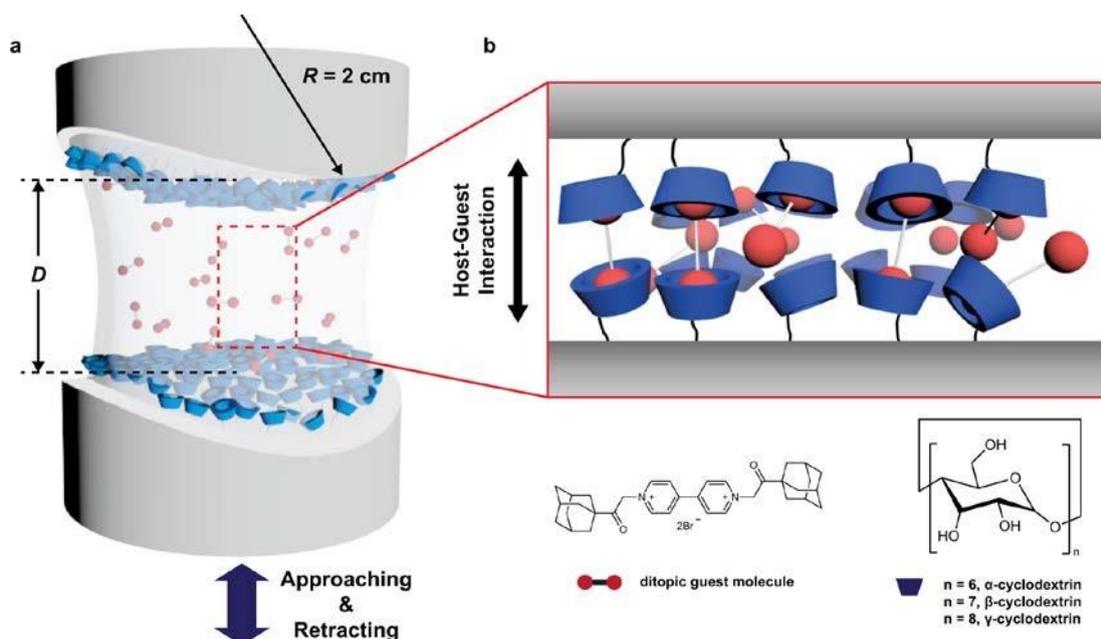
*Dong Woog Lee*<sup>1</sup>, *Jintae Park*<sup>1</sup>, *Jinwoo Park*<sup>1</sup>, *Jinsoon Lee*<sup>1</sup>, and *Chanoong Lim*<sup>1</sup>

<sup>1</sup>*School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), South Korea*

Presenting author's e-mail: [dongwoog.lee@unist.ac.kr](mailto:dongwoog.lee@unist.ac.kr)

The supramolecular host-guest (H-G) interaction has been widely used to the biomedical areas such as hydrogel, bio-glue, and drug delivery. Especially, the H-G complex of cyclodextrin (CD) with adamantane (Ad) are emerging due to their inertness and compatibility in biological system. Despite the considerable interests, the relation of forces to thermodynamic energy of H-G complexes still remain ambiguous. Herein, we directly measured the interaction between CD surface and ditopic Ad (di-Ad molecule in aqueous solution using a surface forces apparatus (SFA) depending on the cavity size of CD and the concentration of di-Ad [1]. The adhesion forces were measured only between the  $\beta$ -CD surface in presence of di-Ad, which showed a drastic increase with increasing the concentration of di-Ad and gradually decreased after reaching complete H-G complex. Moreover, the molecular adhesion energy of a single host-guest inclusion complex was evaluated to be  $\sim 9.69$  kT. This approach has potential for quantifying fundamental information toward furthering the understanding of supramolecular chemistry and its applications, such as molecular actuators, underwater adhesives, and biosensors, which require precise tuning of specific host-guest interactions.

**Keywords:** Supramolecular Chemistry, Host-Guest interaction, Surface Forces Apparatus, Interaction Forces



**Figure 1.** a Surface forces apparatus (SFA) setup for interaction force measurements. b Graphical illustration showing the host-guest pairs between symmetric host (CD)-modified surfaces and ditopic guest molecules (DA).

## References

[1] J. Park, J. Park, J. Lee, C. Lim, D. W. Lee, Nature Communications, 2022, 13, 112.

## On the effect of morphology and particle-wall interaction on colloidal near-wall dynamics

*J. A. Rivera-Morán*<sup>1</sup>, *Y. Liu*<sup>1</sup>, *S. Monter*<sup>1,2</sup>, *C.-P. Hsu*<sup>3</sup>, *P. Ruckdeschel*<sup>4</sup>, *M. Retsch*<sup>4</sup>, *M. Lisicki*<sup>5</sup> and *P. R. Lang*<sup>1</sup>

<sup>1</sup> *Forschungszentrum Jülich, Biomacromolecular Systems and Processes IBI-4*

<sup>2</sup> *Universität Konstanz, Germany*

<sup>3</sup> *Technische Universität München, Germany*

<sup>4</sup> *Universität Bayreuth, Germany*

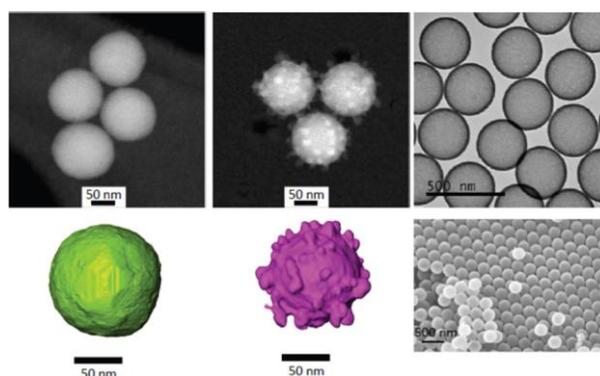
<sup>5</sup> *University Warsaw, Poland*

Presenting author's e-mail: [j.rivera.moran@fz-juelich.de](mailto:j.rivera.moran@fz-juelich.de)

In this contribution, we discuss the influence of the surface-shape of suspended colloidal particles onto their static interaction with a flat solid surface and the resulting effect on the near-wall dynamics. Experimentally, we investigated the near-wall Brownian dynamics of different types of colloidal particles (Figure 1 using evanescent wave dynamic light scattering (EWDLS, specifically, dilute suspensions of silica spheres (SSi and porous hollow shells (HSi with a smooth surface and silica particles with controlled surface roughness (RSi).

While the theoretical predictions for hard sphere colloids [1-2] describe the experimental data of the SSi particles rather well, we found experimentally that the near wall dynamics of RSi and HSi particles appear to be slower than expected [3]. The latter finding is at conflict with hydrodynamic theory. To further investigate this contradiction, we implemented numerical calculations considering both, hydrodynamic and static particle-wall interactions. These show that particle morphology strongly affects the static interaction potential between the colloids and the wall [4-6], leading to a nonuniform particle density distribution along the wall normal, which eventually causes the apparent slowing down of the RSi and HSi particles.

**Keywords:** surface-shape, colloids, near-wall dynamics, colloid-wall interaction



**Figure 1.** TEM images and 3D-reconstructions from TEM tomography of the colloidal silica particles.

### References

- [1] A. J. Goldman, R. G. Cox and H. Brenner, *Chem. Engineering Science*, 1967, **22**, 637-651.
- [2] H. Brenner, *Chem. Engineering Science*, 1961, **16**, 242-251.
- [3] J. A. Rivera-Morán, Y. Liu, S. Monter, C.-P. Hsu, P. Ruckdeschel, M. Retsch, M. Lisicki and P. R. Lang, *Soft Matter*, 2021, **17**, 10301-10311.
- [4] S. Lin and M. R. Wiesner, *Langmuir*, 2010, **26**, 16638-16641.
- [5] J. Y. Walz, *Particles on Surfaces*, 2002, **7**, 151-169.
- [6] S. Bhattacharjee, C.-H. Ko and M. Elimelech, *Langmuir*, 1998, **14**, 3365-3375.

# Effect of polymer chain stiffness on depletion layers and interactions in colloid–polymer mixtures

*Max Martens<sup>1</sup>, Stijn van Leuken<sup>1</sup>, Joeri Opdam<sup>1</sup>, Mark Vis<sup>1</sup>, Remco Tuinier<sup>1</sup>*

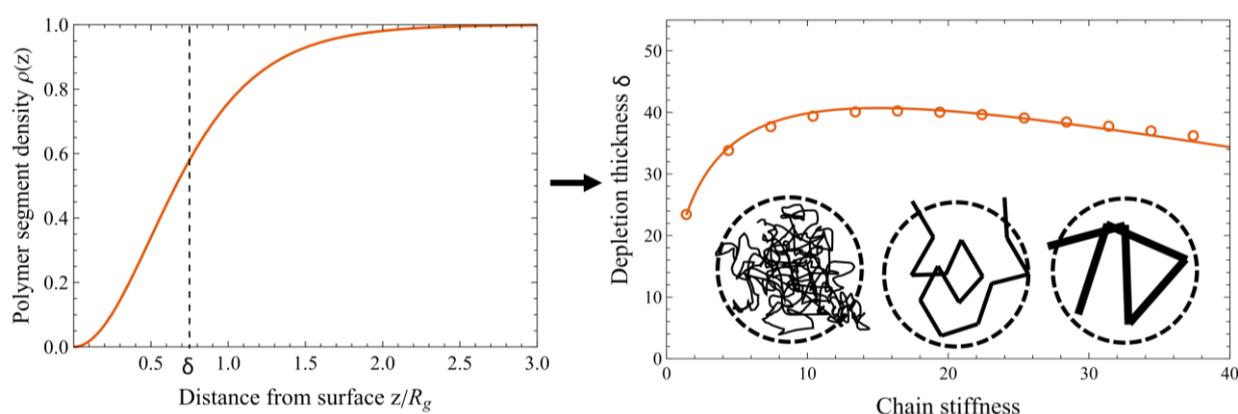
<sup>1</sup> *Laboratory for Physical Chemistry, Eindhoven University of Technology, Eindhoven, Netherlands*

Presenting author's e-mail: [c.m.martens@tue.nl](mailto:c.m.martens@tue.nl)

Mixtures of colloidal particles with non-adsorbing polymers are ubiquitous both in science and in industry. The non-adsorbing polymers induce an effective attraction between the colloidal particles, known as the depletion interaction, and as a result colloid–polymer mixtures display rich physics. Theoretical descriptions of such systems historically assumed the polymer chains to be fully flexible coils, while in reality many polymers have a certain degree of chain stiffness. The effect of this stiffness on the depletion interaction and the resulting phase behavior of these mixtures is as of yet poorly understood, even though it is highly relevant for describing realistic systems.

We present a new analytical theory [1] that describes the concentration profile and depletion thickness of a solution of non-adsorbing semiflexible polymers next to a flat surface. Our theory covers both the dilute and semidilute regime. For fixed polymer radius of gyration, increasing the chain stiffness leads to a decrease in the depletion thickness in dilute conditions. However, in the semidilute regime, a remarkable finding is that there is a maximum in the depletion thickness as a function of the chain stiffness. Furthermore, we present an extension of the theory towards semiflexible polymer solutions around spherical colloids, yielding insights into the phase stability of colloid–polymer mixtures. The analytical expressions are in quantitative agreement with numerical self-consistent field calculations.

**Keywords:** Depletion interaction, Colloidal stability, Polymer-Colloid mixtures, Chain stiffn



**Figure 1.** The depletion thickness in the semidilute concentration regime at constant polymer radius of gyration has a maximum as a function of chain stiffness. Points: numerical self-consistent field computations; curve: our newly developed analytical theory.

**Acknowledgements:** We gratefully acknowledge funding from the Dutch Ministry of Economic Affairs of the Netherlands, the Netherlands Organization for Scientific Research (NWO), and the InScite HiperBioPol project.

## References

[1] C. M. Martens et al., Physical Chemistry Chemical Physics 24 (2022) p. 3618–3631.

## Colloidal Gels with Non-Sticky Dopings

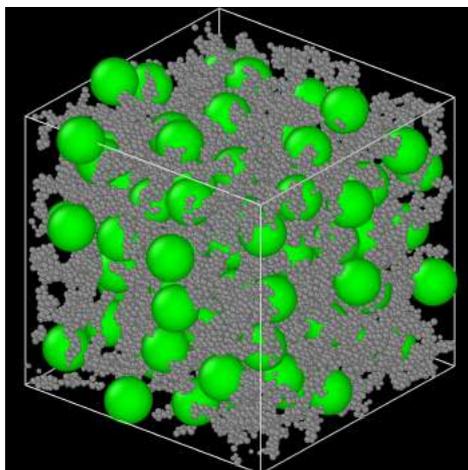
*Yujie Jiang<sup>1</sup>, Ryohei Seto<sup>1</sup>*

<sup>1</sup> *Wenzhou Institute, University of Chinese Academy of Sciences, China*

Presenting author's e-mail: [yujiejiang\\_1994@outlook.com](mailto:yujiejiang_1994@outlook.com)

Attractive colloids aggregate and form a ramified spanning network which responds like a soft solid, i.e. the colloidal gel [1]. Due to the special rheological character, colloidal gels are widely applied in our daily life, e.g. pesticides and foodstuffs. While there has been massive work on pure gels of monodispersed sticky colloids, most realistic systems contain multiple components which coexist with the gel part. A typical class consists of non-sticky grains suspended in a gel matrix, with examples ranging from personal-care products to Li-ion battery slurries [2,3]. Such grain-gel mixtures, or here termed as doped gels (see Fig. 1, receive increasing attention [4,5], and recent work unveils interesting behaviors therein [6].

Yet still, the understanding on such system remains limited. In this work, we use numerical simulation to dope a gel of sticky colloids with non-sticky particles and systematically investigate the effect of doping on gelation dynamics and rheological property. Below dense regime, we find that large doping particles accelerate the gelation process and results in strengthening, while doping of small particles drastically increases the gelation time and produces a gelled state much weaker than the pure gel. Such effect depends on the detailed composition and is consistent with experiments. These results not only shed light on the industrial processing of multi-component systems in general, but are also insightful in tuning properties of colloidal gels.



**Figure 1.** A schematic of colloidal gel with non-sticky doping..

**Keywords:** Colloidal Gel, Composite Materials, Rheology

### References

- [1] Zaccarelli E, Journal of Physics: Condensed Matter, 2007, 19(32): 323101.
- [2] Harich R, Blythe T W, Hermes M, et al. Soft Matter, 2016, 12(19): 4300-4308.
- [3] Wei T S, Fan F Y, Helal A, et al. Advanced Energy Materials, 2015, 5(15): 1500535.
- [4] Ferreiro-Córdova C, Foffi G, Pitois O, et al. Soft Matter, 2022,18, 2842-2850.
- [5] Mohraz A, Weeks E R, Lewis J A, Physical Review E, 2008, 77(6): 060403.
- [6] Jiang Y, Makino S, Royer J R, et al. arXiv preprint arXiv:2111.06019, 2021.

# Reversible cluster formation in colloidal dispersions with short-range attractive interactions

Ramón Castañeda-Priego<sup>1</sup>

<sup>1</sup>*Division of Science and Engineering, Campus León, University of Guanajuato. Loma del Bosque 103, 37150, León, Mexico*

Presenting author's e-mail: [ramoncp@fisica.ugto.mx](mailto:ramoncp@fisica.ugto.mx)

Particle aggregation or clustering is an obligatory step for the initiation of the phase separation or the large-scale formation of materials that exhibit a heterogeneous structure, such as gels and porous media. Nevertheless, even though the macroscopic structure of such materials depends on the shape and size of the resulting clusters or aggregates, the cluster formation at equilibrium and its corresponding morphology are not fully understood.

Combining molecular simulations, experimental characterizations, and theoretical calculations, we conclusively demonstrate that the cluster morphology in short-ranged attractive colloidal systems at and around equilibrium conditions can be uniquely determined by the reduced second virial coefficient [1]; our findings link the reversible colloidal aggregation with the extended law of corresponding states [2].

**Keywords:** colloids, reversible aggregation, short-range interactions

**Acknowledgements:** Author thank financial support provided by DAIP (UG) and Conacyt (Grant. No. A1-S-9098).

## References

- [1] F. Soto-Bustamente, N. E. Valadez-Pérez, Y. Liu, R. Castañeda-Priego and M. Laurati, *Journal of Colloid and Interface Science*, 2022, 618, 442.  
[2] N. E. Valadez-Pérez, Y. Liu, R. Castañeda-Priego, *Physical Review Letters*, 2018, 120, 248004.

# Kinetically arrested dispersions of carbon allotropes in aqueous solutions

*Lucas Luciano Cullari*<sup>1</sup>, *Gennady Ziskind*<sup>3</sup>, *István Furó*<sup>4</sup>, and *Oren Regev*<sup>1,2</sup>

<sup>1</sup>*Department of Chemical Engineering,*

<sup>2</sup>*Ilse Katz Institute for Meso and Nanoscale Science and Technology,*

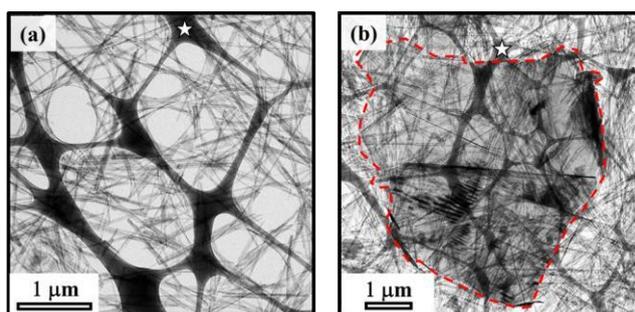
<sup>3</sup>*Department of Mechanical Engineering, Ben Gurion University of the Negev, Beer-Sheva, Israel.*

<sup>4</sup>*Department of Chemistry, Division of Applied Physical Chemistry, KTH Royal Institute of Technology, Stockholm, Sweden.*

Presenting author's email: [Cullari@post.bgu.ac.il](mailto:Cullari@post.bgu.ac.il)

Carbon-based nanomaterials such as graphene are usually produced industrially as powder-like materials. Harnessing the incredible potential of these nanocarbons (e.g., high electrical and thermal conductivities) in various applications (e.g., conductive inks and heat transfer fluids) requires their dispersion. However, when the highly hydrophobic graphene sheets are dispersed in water, they tend to aggregate and precipitate due to gravity and strong van-der-Waals attraction. We disperse graphene in water by adding fibrous clay mineral - sepiolite - a negatively charged particle, which kinetically arrests the system (Figure 1. a). The “trapped” graphene sheets cannot re-aggregate and precipitate (Figure 1. b). The trapping mechanism makes it possible to disperse high graphene concentration (1 wt%) with large lateral size (>5  $\mu\text{m}$ ). [1] Rheological study of these dispersion correlates between the network strength and the dispersion efficiency. Moreover, we demonstrate that the network is disrupted in flow and heals when the system is at rest. This approach applies to all three dimensionalities of carbon, that is, 1D-carbon nanotubes, 2D-graphene and 3D-graphite. The thermal conductivity (TC) of liquids, an essential parameter in heat dissipation applications, is enhanced by 31% via loading graphene as a filler material. [2] The proposed dispersion approach is filler independent and could be employed to stably disperse various particles for diverse applications.

**Keywords:** Kinetic arrest, dispersions, graphene.



**Figure 1.** RT-Transmission electron micrographs of: (a) sepiolite fibers and (b) trapped graphene within the sepiolite network. Dashed lines indicate the graphene contour. Stars: holey carbon support grid.

## References

- [1] L.L. Cullari, T. Masiach, S. Peretz-Damari, S. Ligati-Schleifer, I. Furó and O. Regev, *ACS Appl. Mater. Interfaces*, **2021**, *13*, 6879-6888.  
[2] L.L. Cullari, S. Ligati-Schleifer, G. Ziskind and O. Regev, *ACS Appl. Mater. Interfaces*, **2022**, *14*, 9844-9854.

## Self-assembly and dynamics of colloidal rods

Arif Kamal <sup>1</sup>, Thomas Zinn <sup>2</sup>, T. Narayanan <sup>2</sup>, Peter Schurtenberger <sup>1,3</sup>, Antara Pal

<sup>1</sup> Division of Physical Chemistry, Lund University, Lund, Sweden

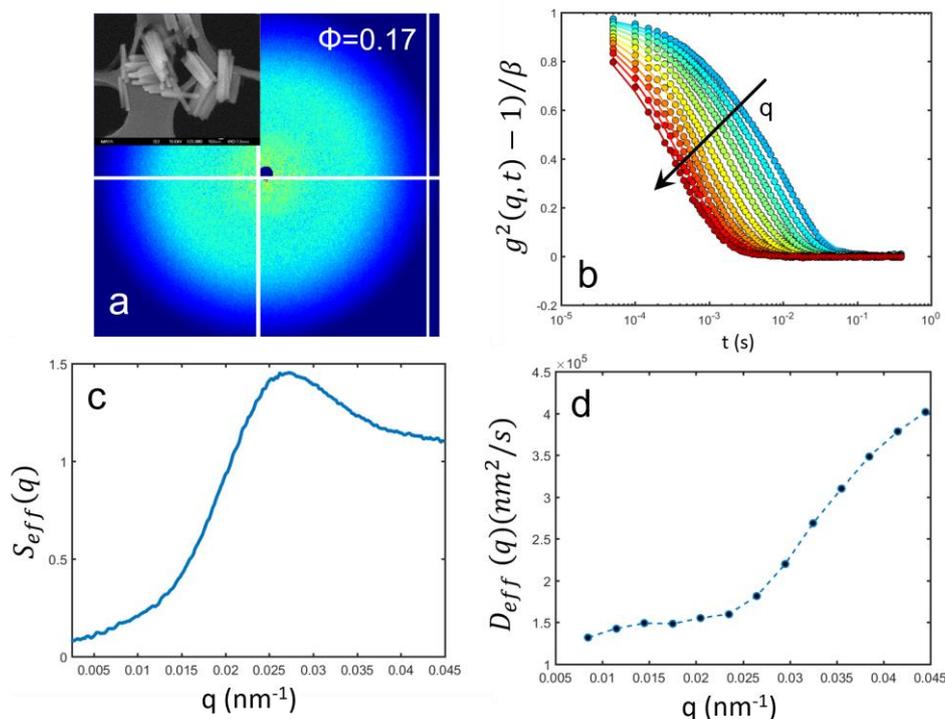
<sup>2</sup> ESRF—The European Synchrotron, 38043 Grenoble, France

<sup>3</sup> Lund Institute of advanced Neutron and X-ray Science LINXS, Lund University, Lund, Sweden

Corresponding author e-mail: [antara.pal@fkem1.lu.se](mailto:antara.pal@fkem1.lu.se)

Anisotropic colloids are known to exhibit a rich phase behavior. In addition to the usual gas, liquid, crystal and glassy states found for spherical particles, anisotropic particles such as rods are known to exhibit additional liquid crystalline phases. Here we present the self-assembly and (an)isotropic dynamics of colloidal rods for aspect ratio,  $\rho \sim 8.0$ . The self-assembly and (an)isotropic dynamics of these particles at the nearest neighbor length scale were investigated over a wide concentration range using SAXS and multispeckle ultrasmall-angle X-ray photon correlation spectroscopy (USA-XPCS). At low concentrations, the self-assembled phase as well as dynamics are isotropic. However, beyond a certain critical concentration a nematic and a smectic phase are formed, which makes the dynamics anisotropic. We have also explored the relation between the resulting diffusion coefficients and the structure factor of the self-assembled structures. The results indicate that the particle dynamics strongly depends on the structure factor. Further, the diffusion coefficients at the nearest neighbor length scale slow down considerably at high concentrations and the system approaches a kinetic arrest.

**Keywords:** Anisotropic dynamics, Colloids, XPCS



**Figure 1.** (a) 2D diffraction pattern of colloidal rods (inset) at volume fraction  $\phi=0.17$ . (b) correlation functions for different scattering vectors  $q$ . (c) Effective structure factor and (d) corresponding effective diffusion coefficient.

# Influence of the hardness on the crystallization behaviour of binary polystyrene microgel systems

*Gabriela Schmidt*<sup>1,2</sup> and *Eckhard Bartsch*<sup>1,2</sup>

<sup>1</sup>University of Freiburg, Institute of Physical Chemistry, Freiburg, Germany

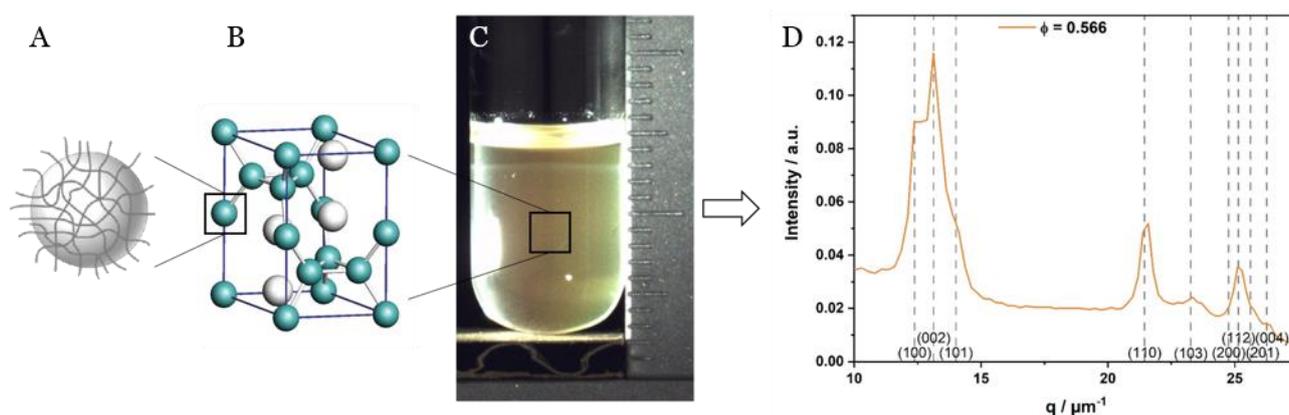
<sup>2</sup>University of Freiburg, Institute of Macromolecular Chemistry, Freiburg, Germany

Presenting author's e-mail: [gabriela.schmidt@physchem.uni-freiburg.de](mailto:gabriela.schmidt@physchem.uni-freiburg.de)

Polystyrene (PS) microgel colloids can be used as model systems for hard spheres (HS) and were widely used to study the glass transition [1]. Recently it was shown for the first time that binary PS microgel systems crystallize near the glass transition volume fraction already in case of purely repulsive interactions [2]. Static light scattering (SLS) revealed the crystal structure of the binary system to be  $MgZn_2$ , a Laves phase of the type  $AB_2$ , with an axial ratio consistent with the ideal axial ratio of  $c/a = 1.633$ . Such Laves phases are of great interest as precursors for the preparation of photonic band gap materials [3].

To further investigate the crystallization behavior of binary PS microgel systems, we varied the hardness of the PS particles via crosslinking [4] and compared crystallization results to theoretical predictions [5,6]. Therefore, we prepared and analyzed bimodal systems with different hardness of the small (S) and large (L) component. By analyzing the crystallization behavior of the different compositions, we found that Laves phases can only be observed if the hardness of the binary system is decreased compared to our previous study [2], confirming theoretical calculations [6]. By changing the hardness of the components separately, we found that Laves phases can only be observed if L is the hard and S is the soft component. We further found that softer particles show faster crystallization, detecting first reflexes within days.

**Keywords:** Laves phases, colloids, crystallization, light scattering



**Figure 1.** Steric stabilized PS microgel colloids (A) crystallize in Laves phases (e.g.  $MgZn_2$ , B,C). SLS is used for crystal structure analysis (D, dashed lines indicate Bragg reflexes of the  $MgZn_2$ -structure).

## References

- [1] T. Eckert, E. Bartsch, Faraday Disc., 2003, 123, 51
- [2] N. Schaertl, D. Botin, T. Palberg and E. Bartsch, Soft Matter, 2018, 14, 5130.
- [3] F. Stein and A. Leineweber, J. Mater Sci, 2021, 56, 5321
- [4] J. Schneider, M. Wiemann, A. Rabe and E. Bartsch Soft Matter, 2017, 13, 445
- [5] A.-P. Hynninen, L. Fillion, M. Dijkstra, J. Chem. Phys., 2009, 131, 064902
- [6] R. A. LaCour, C. S. Adorf, J. Dshemuchadse and S. C. Glotzer, ACS Nano, 2019, 13, 13829

# Combining force inference and holographic microscopy to measure colloidal interactions

*Florian Benedetti*<sup>1</sup>, *Tayebe Sagaheh*<sup>2</sup>, *Peter D. J. van Oostrum*<sup>2</sup> and *Emanuela Bianchi*<sup>1,3</sup>

<sup>1</sup>*Institut für Theoretische Physik, Technische Universität Wien, Austria*

<sup>2</sup>*Institute for Biologically Inspired Materials, Universität für Bodenkultur Wien, Austria*

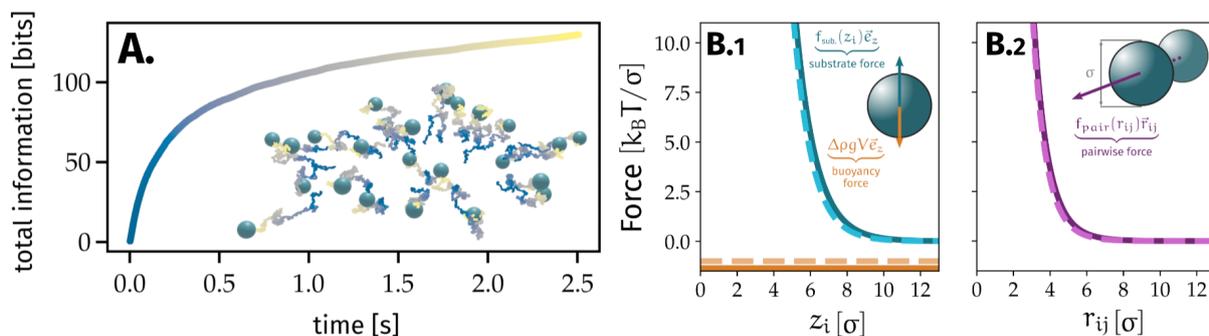
<sup>3</sup>*CNR-ISC, Uos Sapienza, Roma, Italy*

Presenting author's e-mail: [emanuela.bianchi@tuwien.ac.at](mailto:emanuela.bianchi@tuwien.ac.at)

There are two types of methods to extract the forces acting on colloids: equilibrium-distribution and drift-diffusion methods [1-3]. While the former can only be used when the system is in thermodynamic equilibrium, drift-diffusion methods relying on displacement measurements do not require this condition. Alas, because of the solvent agitation, deterministic displacements caused by the forces are tangled with Brownian motion and when this thermal noise is heterogeneous, particles are subject to a noise-induced spurious force that adds another layer of complexity [4-5].

Recently, a novel method based on information and communication theory was introduced to infer force-fields and diffusion from high dimensional stochastic trajectories [6]. Within this approach, we develop a framework for the analysis of trajectories of individual colloids: we first validate our approach with molecular dynamics simulations and we then successfully apply it to three-dimensional trajectories of individual colloids measured using a modified version of 3D-phase contrast holographic microscopy [7]. Within this framework we are able to infer the one-body and two-body interactions as well as the diffusion and spurious force in different solvents. Our method also allows to investigate the measurement error to optimize the acquisition protocol.

**Keywords:** colloids, force inference, external field, pair interactions



**Figure 1.** Force inference result for a system of 25 homogeneously charged particles simulated using Brownian Dynamics. **A.** Temporal evolution of the total amount of information on the forcefield contained in the displayed trajectories. **B.** Comparison between the inferred (continuous) and exact (dashed) forces : **B.1** one-body forces – buoyancy and substrate interaction, **B.2** two-body force – repulsive pairwise radial interaction.

## References

- [1] T. Brettschneider, G. Volpe, L. Helden, J. Wehr, and C. Bechinger, Phys. Rev. E, 2011, 83, 041113.
- [2] A. E. Stones, R. P. A. Dullens, and G. A. L. Aarts, Phys. Rev. Lett, 2019, 123, 098002.
- [3] I. C. Jenkins, J. C. Crocker and T. Sinno, Soft Matter, 2015, 11, 6948-6956.
- [4] A. S. Serov, F. Laurent, C. Floderer, K. Perronet, C. Favard, D. Muriaux, N. Westbrook, C. L. Vestergaard and J-B Masson, Sci Rep., 2020, 10(1), 3783.
- [5] G. Volpe and J. Wehr, Rep. Prog. Phys., 2016, 79, 053901.
- [6] A. Frishman and P. Ronceray, Phys. Rev. X, 2020, 10, 021009.
- [7] F. C. Cheong, C. C. Wong, Y. Gao, M. H. Nai, Y. C. S. Park, L. J. Kenney and C. T. Lim, Biophys. J., 2015, 108, 1248-1256.

# Anomalous rheological aging of a model thermoreversible colloidal gel following a thermal quench

*Khushboo Suman<sup>1</sup> and Norman J Wagner<sup>1</sup>*

<sup>1</sup> *Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, USA*

Presenting author's e-mail: [ksuman@udel.edu](mailto:ksuman@udel.edu)

We investigate the aging behavior in a well-studied model system comprised of a colloidal suspension of thermoreversible adhesive hard spheres (AHS) but thermally quenched below the gel transition to much larger depths than previously studied. The aging behavior in the model AHS system is monitored by small amplitude oscillatory shear rheology measurements conducted while rapidly quenching from liquid state at 40°C to a temperature below the gel temperature and new, anomalous aging behaviors are observed. Shallow quenches lead to monotonic development of the elastic modulus with time, consistent with prior reports for the development of a homogeneous gel [1]. However, for deeper quenches, a unique and new phenomenon is reported – namely after an initial rise in the modulus, a reproducible drop in the modulus is observed, followed by a plateau in the modulus value. This drop can be gradual or sudden, and the extent of the drop, both depends on the quench depth. After this drop in modulus, AHS gel evolves toward a quench-path independent state over the experimental timescale. These effects of the extent of quenching on aging behavior is hypothesized to be a consequence of quenching into different underlying thermodynamic states of colloidal gels and the possible influence of the adhesive glass dynamical arrest for the deepest quenches. The research connects homogeneous gelation with heterogeneous gel formation due to phase separation and shows that the extent of quench can be used as an independent parameter to govern the rheological response of the arrested gel.

**Keywords:** Colloidal gel, thermoreversible, rheology, aging, thermal quench, homogeneous gel, phase separated gel

## References

[1] Melissa B. Gordon, Christopher J. Kloxin and Norman J. Wagner, *Journal of Rheology*, 2017 61, 23.

# The Random Sequential Adsorption Model Revisited: Elucidating the Substrate Influence by Potentiostatic Control of an Electrode

Atsushi Yamaguchi <sup>1,2</sup>, Katharina Otterman<sup>1</sup>, Yannick Jännsch <sup>1</sup>, Sebastian Gödrich <sup>1</sup>,  
Andreas Mark <sup>1</sup>, Nicolas Helfricht <sup>1</sup>, Motoyoshi Kobayashi<sup>2</sup>, and Georg Papastavrou <sup>1</sup>

<sup>1</sup>Department of Physical Chemistry II, University of Bayreuth, Germany

<sup>2</sup> Faculty of Life and Environmental Sciences, University of Tsukuba, Japan

Presenting author's e-mail: [georg.papastavrou@uni-bayreuth.de](mailto:georg.papastavrou@uni-bayreuth.de)

The adsorption of macromolecules, such as polymers or proteins, is of huge importance in biology, environmental sciences or sensorics. The Random Sequential Adsorption (RSA) model, which originates from the field of protein adsorption provides a framework to describe the irreversible adsorption of colloidal particles and macromolecules [1]. In its original form the model is based on a hardcore interaction between the adsorbing species and neglects the influence of the underlying substrate. Inter-particle electrostatic interactions have been incorporated into this model by Adamczyk et al. [2]. However, for small macromolecules, such as dendrimers, significant deviations have been observed to this extended RSA-model [3], which can be attributed to the influence of the substrate [4]. The so-called three-body RSA model includes the substrate [4,5]. Unfortunately, the experimental validation of this model has been restricted to two substrates only, namely mica and silica.

By implementing an electrochemical setup into a quartz microbalance (QCM and optical poor-man's reflectometry), we have been able to determine the adsorbed wet and dry mass in function of the externally applied potential. As model system we studied the adsorption of poly(amido amine) (PAMAM dendrimers of generation G8 and G10 onto gold electrodes. Based on the dependence of the diffuse layer potentials on the applied potential for the gold electrode and the data from previous AFM-based studies for the PAMAM adsorption to mica, no free parameters exist within the three-body model. We find a very good quantitative match between thereby calculated adsorbed mass and the experimental data. In particular, that potential of zero charge (pzc) and minimum adsorbed amount coincide as predicted by the model. An even better agreement with the experimental data can be achieved by including a more realistic model for the electrostatic interaction between the dendrimers. This study provides also an framework for the interpretation of older studies by Kleijn et al [6].

**Keywords:** Adsorption. Interfacial forces. AFM. OCM.

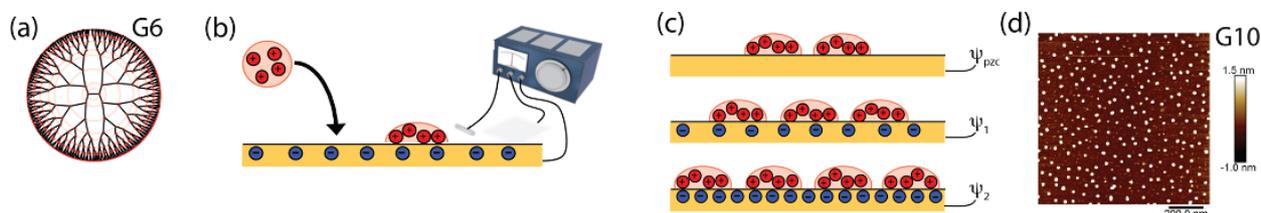


Figure 1.

## References

- [1] J. Feder, *J. Theor. Biol.* 1980, 87, 237
- [2] Z. Adamczyk, P. Warszynski, *Adv. Colloid Interface Sci.* 1996, 63, 41
- [3] R. Pericet-Camara, G. Papastavrou, M. Borkovec, *Langmuir* 2004, 20, 3264.
- [4] R. Pericet-Camara, B. P. Cahill, G. Papastavrou, M. Borkovec, *Chem. Comm.* 2007, 266
- [5] B. P. Cahill, G. Papastavrou, G. J. M. Koper, M. Borkovec, *Langmuir* 2008, 24, 465
- [6] J. M. Kleijn, D. Barten, M. A. C. Stuart, *Langmuir* 2004, 20, 9703

# Sizing Multimodal Systems with Differential Dynamic Microscopy

*Joe Bradley<sup>1</sup>, Vincent Martinez<sup>1</sup>, John Royer<sup>1</sup>, and Wilson Poon<sup>1</sup>*

<sup>1</sup>*University of Edinburgh, UK*

*Presenting author's e-mail: [Joe.Bradley@ed.ac.uk](mailto:Joe.Bradley@ed.ac.uk)*

Particle sizing is vital in both fundamental and applied colloid science. Differential Dynamic Microscopy (DDM) combines real space imaging with analysis in Fourier space to extract the same quantity as dynamic light scattering (DLS, the intermediate scattering function, at considerably lower wavevectors [1]. But, it is based on different physics. Fitting of the ISF yields diffusion coefficients and hence particle size.

However, the limits of DDM in sizing have not been investigated in depth. In particular most studies have focused on monodisperse systems. Using well-characterised multimodal suspensions we study the ability of DDM to size small particles in the presence of large ones. Under both brightfield and phase contrast conditions the DDM signal scales with the sixth power of particle radius (the same as DLS. Nevertheless, we demonstrate that DDM can distinguish distinct populations in the size distribution over a wide range of compositions, and demonstrate advanced analysis techniques for extracting this information with minimal assumptions. Further, by selecting different regions of the real-space images to analyse with a DDM algorithm we were able to isolate the signal from small particles. This allows DDM to extract the size of small particles in the presence of a higher concentration of larger species than DLS.

**Keywords:** Colloids, Characterisation, Size Distribution, DDM, DLS, Experimental.

**Acknowledgements:** Jointly funded by Solvay S.A. and the SOFI2 CDT (EPSRC grant EP/S023631/1)

## References

[1] R. Cerbino and V. Trappe, Physical Review Letters, 2008, 100, 118102.

# Controlling Supraparticles Shape and Structure by Tuning Colloidal Interactions

Wendong Liu <sup>1,2</sup>, Werner Steffen <sup>1</sup>, Hans-Jürgen Butt <sup>1</sup>, Michael Kappl <sup>1</sup>

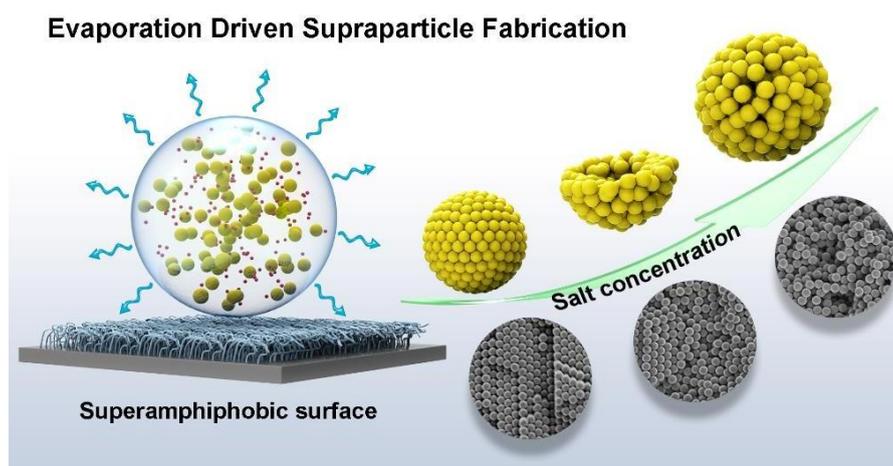
<sup>1</sup>Max Planck Institute for Polymer Research, Mainz, Germany

<sup>2</sup>School of Chemical Engineering, Dalian University of Technology, Dalian, China

Presenting author's e-mail: [kappl@mpip-mainz.mpg.de](mailto:kappl@mpip-mainz.mpg.de)

The evaporation of droplets of colloidal suspension on superhydrophobic surfaces can lead to the formation of supraparticles; supraparticles are assemblies of colloids to larger particles. They have possible applications as photonic crystals, catalysts, capsules or fertilizers. The challenge is to control the structure of supraparticles during the drying process. Here, we demonstrate that both the outer shape and internal structures of supraparticles can be controlled by variation of the salt concentrations. As an example we study suspensions of electrostatically stabilized polystyrene particles. Low salt concentration ( $\leq 100 \mu\text{M}$ ) resulted in highly crystallized spherical supraparticles. The degree of crystallization decreased with increasing salt concentration, leading to a completely amorphous structure above 10 mM salt concentration. For both low ( $\leq 100 \mu\text{M}$ ) and high ( $> 10 \text{ mM}$ ) salt concentrations, final supraparticles had a spherical shape. Nonspherical shapes were observed for intermediate salt concentrations, most likely caused by buckling. We could correlate these changes in shape and structure with the salt-dependent single colloid interaction forces as measured by colloidal probe AFM. Our findings are crucial for understanding the assembly behavior during the drying process and could offer guidance for preparing complex supraparticles to meet specific applications [1].

**Keywords:** supraparticle, evaporation, crystallization, superamphiphobic surface, DLVO force



**Figure 1.** Shape and degree of crystallinity of supraparticles can be tuned by changing the colloidal interactions based on DLVO forces between the colloids varying the salt concentration.

## References

[1] W. Liu, W. Steffen, H.-J. Butt, M. Kappl, *J. Colloid Interface Sci.*, 2022, , 607, 1661.

## Tailoring nanoparticle clustering by adsorption of poly(methacrylic acid) onto differently charged silica nanoparticles

*Amiel Catherine*<sup>1</sup>, *Robin Clément*<sup>1</sup>, *Lorthioir Cédric*<sup>2</sup>, *Fall Abdoulaye*<sup>3</sup>, *Guillaume Ovarlez*<sup>4</sup>, *Le Cœur Clémence*<sup>1</sup>

<sup>1</sup> *Univ Paris Est Creteil, CNRS, ICMPE, UMR 7182, 2 rue Henri Dunant, 94320 Thiais, France*

<sup>2</sup> *Sorbonne Université, CNRS, Laboratoire de Chimie de la Matière Condensée de Paris, 4 Place Jussieu, 75005 Paris, France" Soleil Synchrotron, Gif-sur-Yvette, France*

<sup>3</sup> *Laboratoire Navier (UMR 8205), CNRS, Ecole des Ponts ParisTech, Univ. Gustave Eiffel Cité Descartes-77420 Champs sur Marne, France*

<sup>4</sup> *Univ. Bordeaux, CNRS, Solvay, LOF, UMR 5258, F-33608 Pessac, France*

Presenting author's e-mail: [Catherine.amiel-guenoun@cnrs.fr](mailto:Catherine.amiel-guenoun@cnrs.fr)

Polyelectrolyte addition into aqueous nanoparticle dispersions is often considered as an efficient way to control the nanoparticle clustering as the polymer chains may be at the origin of several kinds of interactions: steric repulsion or bridging attraction due to the adsorbed chains, while the free non-adsorbed chains could induce depletion attraction or electrostatic screening. In this work, silica nanoparticles with different surface modifications providing either negative or positive surface charges have been used with poly(methacrylic acid) (PMAA) as the polyelectrolyte. Adsorption studies have shown that the PMAA/silica interactions could be tuned either by the pH or by the surface modification of the silica nanoparticles, the stronger interactions occurring for amine-functionalized silica nanoparticles at low pH for which PMAA is uncharged. Small-angle X-ray scattering experiments were performed on PMAA/silica dispersions under the condition of saturation adsorption in order to correlate the extent of particle dispersion with polymer/surface interactions. The stronger the polymer/surface interactions, the more compact aggregates are formed. A fine tuning of the polymer/silica interactions may allow tailorable stability of colloidal systems to be achieved.

**Keywords:** polyelectrolyte, adsorption, silica nanoparticles

**Acknowledgements:** The authors acknowledge financial support by the LABEX MMCD

### References

- [1] C. Robin, C. Lorthioir, C. Amiel, A. Fall, G. Ovarlez and C. Le Cœur, *Macromolecules*, 2017, 50, 700-710
- [2] C. Robin, C. Lorthioir, A. Erman, J. Perez, A. Fall, G. Ovarlez, C. Amiel, C. Le Cœur, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 638, 128287, 2022,

# Optical characterization of complex core-shell copolymer microgels

*Marius Otten<sup>1</sup> and Matthias Karg<sup>1</sup>*

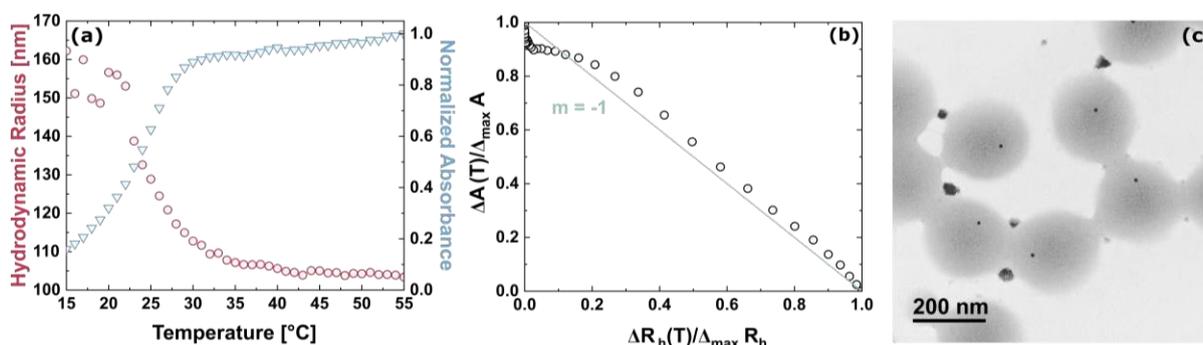
<sup>1</sup>*Institute of Physical Chemistry I: Colloids and Nano-optics, Heinrich-Heine-University Düsseldorf, Universitätsstraße 1, 40225 Düsseldorf, Germany*

Presenting author e-mail: [marius.otten@hhu.de](mailto:marius.otten@hhu.de)

Cross-linking of polymer chains can lead to the formation of micro- or nanometer sized gel-like networks that are known as micro- and nanogels. These soft, deformable particles can react to external stimuli like pH or temperature, which enable microgels to either hold or release the present solvent resulting in a change of the effective size. The respective swelling behavior can further be influenced by variation in the degree of cross-linking and/or implementation of co-monomers.

The incorporation of noble metal nanoparticles into microgel networks can further stabilize and enhance the processability of such systems and therefore experience increased interest in research fields like sensing. The characterization with scattering and microscopic techniques plays an important role to understand the morphology and composition of those systems to further extend the range of possible applications. Noble metal nanoparticle cores can improve the characterization of microgel systems as they, for example, can function as high-contrast marker in SAXS or TEM experiments.

Previously, our group presented an approach for the characterization of core-shell microgel systems by combining the results of temperature dependent dynamic light scattering and absorbance measurements. We revealed a correlation that allows the approximation of microgel size and its temperature-induced changes by conventional absorbance measurements for core-shell microgel systems based on PNIPAM with different sizes and crosslinker degrees.[1] With our recent work we use similar measurements to investigate the behavior of more complex co-polymer microgel systems with and without inorganic nanoparticle cores to verify the validity of our prior findings (**Fig 1 a & b**). We synthesized our investigated PNIPAM-based co-polymer microgels with gold cores in a novel in situ approach as we found that the clever composition of copolymer microgels enables the reliable formation of single gold cores within especially tailored microgels making for a unique system for our studies (**Fig 1 c**).



**Figure 1.** Temperature dependent dynamic light scattering and absorbance measurements at 300 nm (**a**) and normalized absorbance ( $A$ ) at 300 nm as function of normalized hydrodynamic radius ( $R_H$ ) for a PNIPAM-co-AAc-co-AAEM microgel (**b**). TEM image of single gold nanoparticles formed after the in situ synthesis in the respective microgel particles (**c**).

**Keywords:** Microgels, Nanoparticles, Dynamic light scattering, Absorbance spectroscopy, Hybrid materials, Transmission electron microscopy

**References:** [1] K. Ponomareva et al., *Soft Matter*, 2022,18, 807-825.

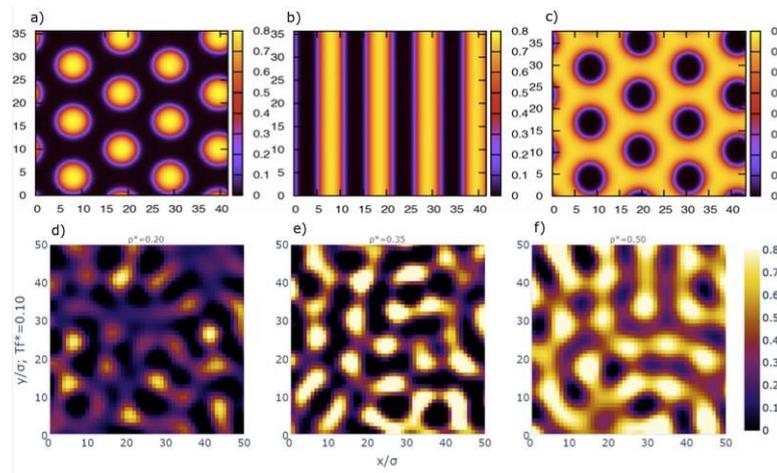
## Non-equilibrium dynamic arrest diagram of SALR fluids

*Magdaleno Medina-Noyola, Gabriela Carretas-Talamantes, Edilio Lázaro-Lázaro, and Jesús B. Zepeda-López*

*Instituto de Física, Universidad Autónoma de San Luis Potosí, Álvaro Obregón 64, 78000 San Luis Potosí, SLP, México.*

Presenting author's e-mail: [medina@ifisica.uaslp.mx](mailto:medina@ifisica.uaslp.mx)

We illustrate the application of the *non-equilibrium self-consistent generalized Langevin equation (NE-SCGLE) theory* [1,2] by describing its predictions for the non-equilibrium phase behavior of the 2D “simple” fluid of hard disks interacting with short-ranged attraction and long-range repulsion (SALR. This is compared with the equilibrium scenario predicted by density-functional theory, summarized by Figs. 1 and 2 of Ref. [3], and represented here by the first row of figure 1, which exhibits the equilibrium spatial distribution of particles of this 2D model fluid, in regular arrays of “clusters”, “stripes” and “bubbles”. If these ordered equilibrium phases are avoided, they may be replaced by the corresponding dynamically arrested phases. The solution of the *NE-SCGLE* equations describes the non-equilibrium relaxation of the structural, dynamical and rheological properties during these processes of dynamic arrest. The upper row of the figure illustrates, for example, the (long-time dynamically-arrested non-equilibrium counterpart of the equilibrium results in the lower row. This work will presents these and other predictions of the *NE-SCGLE* theory, including the aging of this and other related model systems.



**Figure 1.** (a-c): Particle-density profiles in the equilibrium cluster, stripe, and bubble phases, of the 2D SALR model, predicted by density functional theory (reproduced from Fig. 2 of Ref. [3]). (d-e): Non-equilibrium counterparts of (a-c) predicted by the non-equilibrium self-consistent generalized Langevin equation (*NE-SCGLE*) theory [1,2].

**Keywords:** Non-equilibrium theory, SALR systems, clusters, gels, glasses.

### References:

- [1] P. E. Ramírez-González and M. Medina-Noyola, *Phys. Rev. E* **82**, 061503 (2010).
- [2] J. M. Olais-Govea, L. López-Flores, J. B. Zepeda-López, and M. Medina-Noyola, *Scientific Reports* **9**, 16445 (2019).
- [3] A. J. Archer, *Phys. Rev. E* **78**, 031402 (2008).

Monday 5th September 2022

**Colloids at Interfaces, Membranes and Biointerfaces,  
Emulsions and Foams**

## Responsive microgels at drop surfaces: from Pickering emulsions to colloidosomes

Hélène Labie <sup>1</sup>, Yating Qiu <sup>1</sup>, Ritu Ritu <sup>1</sup>, Adeline Perro <sup>1</sup> and Valérie Ravaine <sup>1</sup>

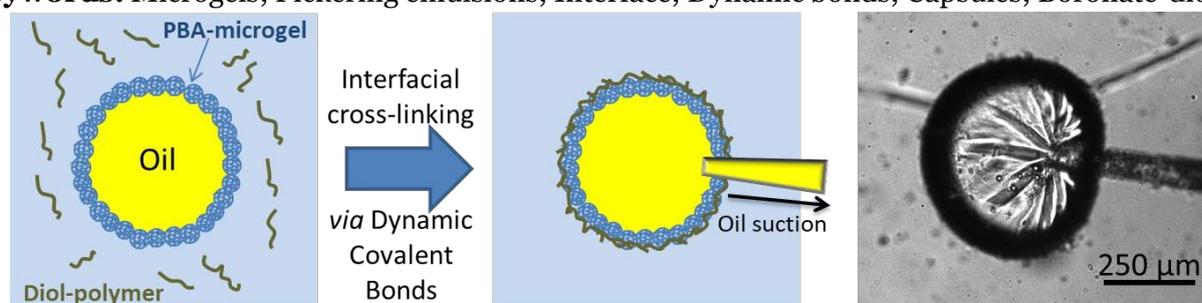
<sup>1</sup>Univ. Bordeaux, CNRS, Bordeaux INP, ISM, UMR 5255, F-33400 Talence, France

Presenting author's e-mail: [vravaine@enscbp.fr](mailto:vravaine@enscbp.fr)

Microgel-stabilized emulsions have gained more attention over the past decade. This class of Pickering emulsions are highly stable at rest but can be destabilized on demand, upon application of a stimulus that can tune the swelling properties of the microgels [1, 2]. The mechanical resistance of such emulsions to an applied stress can be improved by strengthening the interactions between adjacent microgels at the interface. Moreover, these cross-linked polymeric shells can be further transferred to an aqueous environment by removing the oil phase, yielding purely aqueous capsules, with tunable permeability.

In this work, we will present a new strategy to bind microgels with dynamic covalent bonds (DCB) based on reversible binding of phenylboronic acid (PBA) with cis-1,2 or cis-1,3-diol compounds [3]. This reaction occurs under mild conditions, without the need for any catalyst. To achieve this goal, some thermoresponsive microgels based on poly(*N*-isopropylacrylamide) (pNIPAM) are functionalized with PBA moieties. In suspension, a 3-dimensional network is created by inter-crosslinking the microgels with a multifunctional polymer bearing diol units. The whole assembly behaves as a shear-thinning material that can be reshaped. Furthermore, the cross-linking is reversible and the granular assembly can be dissolved by varying the pH or adding a competing diol. This strategy can be applied to bridge the microgels when adsorbed at the interface between oil and water in an emulsion, resulting in a 2D network of chemically interconnected microgels operating as an elastic membrane. The as-stabilized emulsions show highly improved mechanical properties. Upon reduction of the drop volume, the membrane undergoes buckling (Figure 1) [4]. Finally, we will show that microgels can also pack at the surface of water-in-water emulsions [5] or coacervates [6], where they can be further cross-linked to yield colloidosomes. These purely aqueous systems are of great potential to encapsulate fragile water-soluble molecules such as proteins.

**Keywords:** Microgels; Pickering emulsions; Interface; Dynamic bonds; Capsules; Boronate-diol



**Figure 1.** Interfacially-adsorbed microgels are inter-crosslinked by boronate-diol bonds. The oil capsule is mechanically reinforced, buckling is observed upon volume reduction.

### References

- [1] M. Destribats et al., *Soft Matter*, 2011, 7, 7689
- [2] M.C. Tetry et al., *J. Colloid Interface Sci.*, 2021, 589, 96
- [3] D. Tarus et al., *Macromol. Rapid Commun.*, 2014, 35(24) 2089
- [4] H. Labie et al., submitted
- [5] A. Perro et al., *J. Colloid Interface Sci.*, 2019, 548, 275
- [6] T. Merland *et al.* *J. Colloid Interface Sci.*, 2022, 608, 1191

# Thermo-induced inversion of water-in-water emulsion stability by bis-hydrophilic microgels

*Léa Waldmann*<sup>1</sup>, *Théo Merland*<sup>2</sup>, *Anne-Laure Wirotius*<sup>3</sup>, *Véronique Lapeyre*<sup>1</sup>, *Patrick Garrigue*<sup>1</sup>, *Stéphane Arbault*<sup>4</sup>, *Taco Nicolai*<sup>2</sup>, *Lazhar Benyahia*<sup>2</sup>, *Valérie Ravaine*<sup>1</sup>

<sup>1</sup>ISM, Univ. Bordeaux, CNRS, Bordeaux INP, Talence, France;

<sup>2</sup>IMMM, Le Mans Université. 1, Le Mans, France;

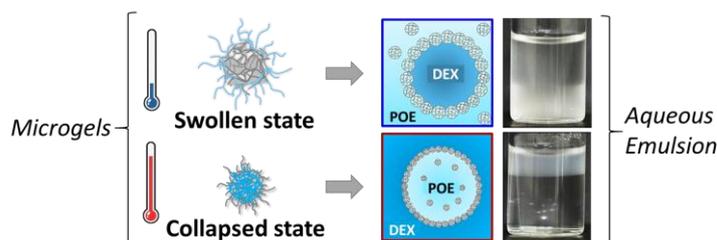
<sup>3</sup>LCPO, Univ. Bordeaux, CNRS, Bordeaux INP, Pessac, France;

<sup>4</sup>CBMN, Univ. Bordeaux, Bordeaux INP, Pessac, France

Presenting author's e-mail: [lwaldmann@enscbp.fr](mailto:lwaldmann@enscbp.fr)

Water-in-water (W/W) emulsions resulting from the separation of two aqueous phases are highly though-after in the area of food science, water purification, bioprocessing or encapsulation, for their ability to spontaneously sequester a large variety of water-soluble molecules [1]. They were more recently recognized as viable compartmentalization strategy to produce biomimetic synthetic cells [2]. The stabilization of water-in-water emulsions is highly challenging, because of the very low interfacial tensions between the two phases and because of the interface thickness extending over several nanometers [3]. In this work, we present a new type of Pickering stabilizers [4], based on bis-hydrophilic and thermoresponsive microgels, able to stabilize the prototypical emulsion composed of dextran (DEX) and poly(ethyleneoxide) (PEO). New microgels incorporating in the same structure poly(*N*-isopropylacrylamide) (pNIPAM) chains having an affinity for the PEO phase and DEX moieties, were synthesized with different DEX/NIPAM ratio. Microgels with a higher DEX content revealed excellent stabilizing properties for the emulsions by adsorbing at the drop surface, thus demonstrating the fundamental role of bis-hydrophilicity. These microgels were swollen below their volume phase transition temperature (VPTT= 32°C) and shrunk above. Nuclear magnetic resonance showed that, below the VPTT, both pNIPAM and dextran chains were hydrated, but the pNIPAM chains became dehydrated above the VPTT. Below the VPTT, coalescence between the droplets of the DEX phase dispersed in PEO phase could be inhibited by adding microgels, whereas the inverse emulsion remained unstable. Above the VPTT the inverse scenario occurred [5]. This stabilization/destabilization on demand of W/W emulsions extends their field of applications and opens new perspectives in the context of recyclability and recovery/delivery of wastes or compounds of interest.

**Keywords:** Water-in-water emulsion, Microgels, Temperature sensitivity, phase inversion.



**Figure 1.** Stabilisation of W/W emulsions with thermoresponsive pNIPAM-DEX microgels and phase-inversion upon volume phase transition temperature of the microgels.

## References

- [1] Y. Chao, H. C. Shum, *Chem. Soc. Rev.*, 2020, 49, 114-142.
- [2] N. Martin, *ChemBioChem*, 2019, 20, 1-17.
- [3] T. Nicolai, B. Murray, *Food Hydrocolloids*, 2017, 67, 157-163.
- [4] V. Schmitt, V. Ravaine, *Curr. Op. Coll. Interf. Sci.*, 2013, 18, 532-541.
- [5] T. Merland, L. Waldmann, O. Guignard, M-C. Tatry, A-L. Wirotius, V. Lapeyre, P. Garrigue, T. Nicolai, L. Benyahia, V. Ravaine, *J. Coll. Interf. Sci.*, 2022, 608, 1191-2001.

## On the breaking mechanism of temperature-responsive emulsions

*Marcel Rey<sup>a</sup>, Jannis Kolker<sup>b</sup>, James A. Richards<sup>a</sup>, Thomas Glen<sup>a</sup>, Denise Li<sup>a</sup>,  
Damian Renggli<sup>c</sup>, Jan Vermant<sup>c</sup>, Andrew B. Schofield<sup>a</sup>, Syuji Fujii<sup>d</sup>,  
Hartmut Loewen<sup>b</sup>, Paul S. Clegg<sup>a</sup>*

<sup>a</sup> School of Physics and Astronomy, The University of Edinburgh,  
Peter Guthrie Tait Road, Edinburgh EH9 3FD, UK.

<sup>b</sup> Institute for Theoretical Physics II: Soft Matter, Heinrich-Heine University Düsseldorf,  
D-40225 Düsseldorf, Germany

<sup>c</sup> Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 5, 8093 Zurich,  
Switzerland

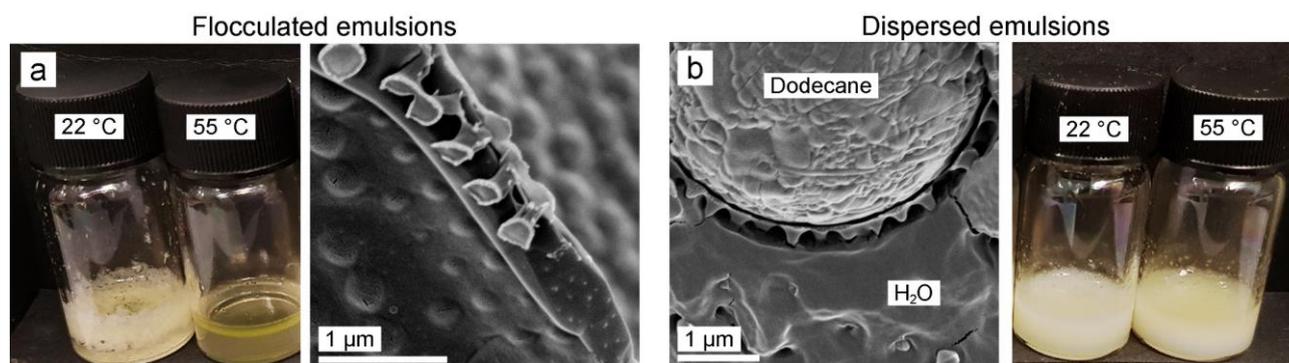
<sup>d</sup> Department of Applied Chemistry, Faculty of Engineering  
Osaka Institute of Technology, 5-16-1 Omiya, Asahi-ku, Osaka 535-8585, Japan

Presenting author's e-mail: [marcel.rey.lfg@gmail.com](mailto:marcel.rey.lfg@gmail.com)

Temperature-responsive microgel-stabilized emulsions combine long-term storage with controlled release of the encapsulated liquid upon temperature increase. The destabilisation mechanism was previously primarily attributed to the shrinkage or desorption of the temperature-responsive microgels, leading to a lower surface coverage inducing coalescence [1,2].

Here, we link the macroscopic emulsion stability to the thermo-responsive behaviour and microstructure of individual microgels confined at liquid interfaces and demonstrate that the breaking mechanism is fundamentally different to that previously anticipated. Breaking of thermo-responsive emulsions is induced via bridging points in flocculated emulsions (Fig. 1a), where microgels are adsorbed to two oil droplets. These bridging microgels induce an attractive force onto both interfaces when heated above their volume phase transition temperature, which induces coalescence. Surprisingly, if such bridging points are avoided by low shear emulsification (Fig. 1b), the obtained emulsion is insensitive to temperature and remains stable even up to 80 °C.

**Keywords:** Emulsions, Interfaces, Microgels



**Figure 1.** Thermo-responsive emulsion behaviour of (a) flocculated and (b) dispersed oil-in-water emulsions. (a) Flocculated emulsions are characterized by bridging points where the stabilizing microgels are shared by two oil droplets. These emulsion break upon temperature increase above the volume phase transition temperature of the stabilizing microgels. (b) Dispersed emulsions are characterized by a defect-free microgel monolayer stabilizing the oil droplets. These emulsions remain unaffected by temperature increase.

### References

- [1] T. Ngai, S. H. Behrens, H. Auweter, Chem. Commun. 2005, 331–333.  
[2] Z. Li, W. Richtering, T. Ngai, Soft Matter 2014, 10, 6182–6191

# Incorporation of Hydrophilic Microgel at Water in Oil Emulsion Interface stabilized by Hydrophobic Nano-spheres

*Sebastian Stock*<sup>1</sup>, *Susanne Röhl*<sup>2</sup>, *Franziska Jakob*<sup>1</sup>, *Kevin Gräff*<sup>1</sup>, *Matthias Kraume*<sup>2</sup>, *Regine von Klitzing*<sup>1</sup>

<sup>1</sup> *Soft Matter at Interfaces, TU Darmstadt, Darmstadt, Germany*

<sup>2</sup> *Chair of Chemical and Process Engineering, TU Berlin, Berlin, Germany*

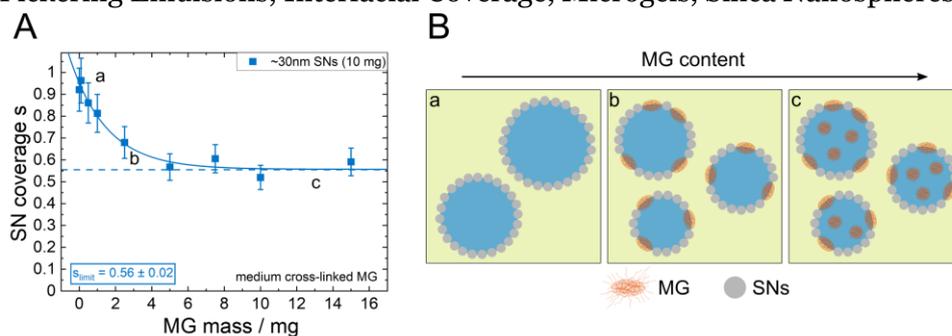
Presenting author's e-mail: [sebastian.stock@pkm.tu-darmstadt.de](mailto:sebastian.stock@pkm.tu-darmstadt.de)

For particle-stabilized emulsions (Pickering emulsions, PEs), the affinity of the particular stabilizers to one or the other liquid decides about the resulting emulsion type [1] - either oil in water (o/w) or water in oil (w/o). Besides specific exceptions, hydrophilic microgel particles (MGs) are only able to stabilize o/w emulsions [2]. However, the w/o emulsion type is preferable in a multitude of applications ranging from the food industry over medicine towards interfacial catalysis. The introduction of a second hydrophobic stabilizer solves this issue without costly and structurally threatening chemical modification of the MGs. The understanding of the interaction of these two or more unequal stabilizers at the interface and clarification of its connection to the resulting emulsion structure remains a challenging task for soft matter science.

For the presented work, we used well-characterized, hydrophobic, positively charged, spherical silica particles (SNs) and hydrophilic, positively charged PNIPAM MGs to stabilize water in 1-dodecene emulsions simultaneously. The thoroughly characterized geometry of the solid particles allows deep insights into the structure formation of the PEs and the calculation of the droplet area occupied by silica and MG, respectively. We have found that the particles are necessary to stabilize the w/o emulsion type and in any case occupy most of the interface. Nevertheless, the MGs claim their own space at the interface and may act as spacers between the silica nano-spheres [3].

This makes this system an ideal candidate for the PE assisted interfacial catalysis, where the w/o type is important for the product separation. The MGs can act as a carrier towards and as protective environment at the interface for the catalyst [4].

**Keywords:** Pickering Emulsions, Interfacial Coverage, Microgels, Silica Nanospheres



**Figure 1.** *W/o emulsions stabilized by hydrophobic SNs and hydrophilic MGs. (a) coverage parameter of the SNs decreases with the present amount of MGs in the system. (b) depiction of the consequence: saturation of the present MG at the interface*

**Acknowledgements:** The authors acknowledge funding from the DFG in form of the SFB transregio 63 subproject B6.

## References:

- [1] B. Binks, *Curr. Opin. Colloid Interface Sci.*, 2002, 7, 21-41
- [2] S. Stock and R. v. Klitzing, *Curr. Opin. Colloid Interface Sci.*, 2022, 58, 101561
- [3] S. Stock et al., *Soft Matter*, 2021, 17, 8258–8268
- [4] S. Stock et al., *PCCP*, 2021, 23 (3), 2355–2367

# Controlling the three-dimensional shape of soft particles at fluid interfaces and how this affects their two-dimensional assembly

*Jacopo Vialetto*<sup>1</sup>, *Shivaprakash N. Ramakrishna*<sup>1</sup> and *Lucio Isa*<sup>1</sup>

<sup>1</sup> *Laboratory for Soft Materials and Interfaces, Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland.*

Presenting author's e-mail: [jacopo.vialetto@mat.ethz.ch](mailto:jacopo.vialetto@mat.ethz.ch)

The confinement of colloidal particles at fluid interfaces holds the key for a broad range of phenomena with applied and fundamental relevance alike, from the stabilization of emulsions and foams, to the creation of model two-dimensional (2D) materials. In the case of hard, mechanically rigid particles of a given shape, all aspects of their adsorption/desorption, dynamics and interactions with and at the interface are influenced by a single parameter, the particle contact angle  $\theta$ . [1] However, if the particle is deformable, it can reconfigure upon adsorption due to interfacial tension ( $\gamma$ ) and to exposure to different solvents. This more complex response is closely connected to the emergence of additional properties and functionalities arising from the 2D phase behaviour of compressible objects.

In this communication, we propose an innovative approach that enables imaging the full three-dimensional (3D) shape of soft particles (poly(N-isopropylacrylamide) (pNIPAM) microgels) adsorbed at oil-water interfaces at high resolution, by using *in-situ* atomic force microscopy (AFM). [2] The technique allows us to: i) reconstruct their 3D shape by complementary imaging from both phases; ii) study the influence of system parameters ( $\gamma$  and  $T$ ) on the resulting particle configuration; iii) investigate how the particle architecture (in terms of crosslinker content and distribution) influences their conformation after adsorption.

Going a step beyond, we provide two examples establishing clear relations between the microgels conformation at the interface, and their structural and mechanical properties in 2D assemblies. In particular, we show how single-particle architectural control during synthesis determines the interfacial behaviour in systems of core-shell microgels undergoing controlled removal of a soft polymeric core. [3] We then discuss the effect of varying the oil polarity and fluid interfacial tension to tune the structural reorganization of the resulting monolayers. [4]

**Keywords:** pNIPAM microgels, atomic force microscopy, mechanical properties, volume phase transition temperature, colloidal particle monolayers

## References

- [1] Vialetto, J.; Zanini, M.; Isa, L. *Curr. Opin. Colloid Interface Sci.* 2022, 58, 101560.
- [2] Vialetto, J.; Ramakrishna, S. N.; Isa, L. Submitted manuscript.
- [3] Vialetto, J.; Camerin, F.; Grillo, F.; Ramakrishna, S. N.; Rovigatti, L.; Zaccarelli, E.; Isa, L. *ACS Nano* 2021, 15 (8), 13105–13117.
- [4] Vialetto, J.; Nussbaum, N.; Bergfreund, J.; Fischer, P.; Isa, L. *J. Colloid Interface Sci.* 2022, 608, 2584–2592.

# Ultra-low crosslinked nanogels combine polymer and particle properties as emulsion stabilizer

*Alexander V. Petrunin<sup>1</sup>, Steffen Bochenek<sup>1</sup>, Walter Richtering<sup>1</sup>, and Andrea Scotti<sup>1</sup>.*

*<sup>1</sup>Institute of Physical Chemistry, RWTH Aachen University, Germany*

*Presenting author's e-mail: [petrunin@pc.rwth-aachen.de](mailto:petrunin@pc.rwth-aachen.de)*

Micro- and nanogels have been widely used to stabilize emulsions that can be broken on-demand by external stimuli, such as temperature or pH. One of the key parameters that determines the stability of such emulsions is the softness of nanogels. In this contribution, we studied how the softest nanogels that can be synthesized by precipitation polymerization of N-isopropylacrylamide (NIPAM), the ultra-low crosslinked (ULC) nanogels [1], stabilize oil-in-water emulsions.

We show that already at low mass concentrations, ULC nanogels can produce emulsions that are relatively monodisperse, non-flocculated, stable against coalescence, and can be broken on-demand by increasing temperature. In terms of polydispersity and resistance to flocculation of emulsion droplets, these emulsions resemble the emulsions stabilized by linear pNIPAM. At the same time, in terms of stability against coalescence and thermo-responsiveness, these emulsions are similar to the emulsions stabilized by regular crosslinked pNIPAM nanogels.

The interfacial viscoelasticity of linear pNIPAM, ULC, and BIS-crosslinked nanogels is very similar and, therefore, cannot be the reason for the mixed properties of the emulsions stabilized by ULC nanogels. Instead the reason for it is that ULC nanogels combine the properties of flexible macromolecules and colloidal particles. We support this idea by estimating the packing density of ULC nanogels at the surface of emulsion droplets and correlating it to the 2D compression states reported in the literature for identical ULC nanogels [2]. The average distance between nanogels that we find is consistent with the value where transition between polymer- and particle-like properties is reported. As a polymer, ULC nanogels can efficiently stretch and cover the interface uniformly preventing the flocculation of droplets. As a regular nanogel particle, they protect emulsions against coalescence by providing a steric barrier and rapidly respond to changes in external stimuli thus breaking the emulsion.

**Keywords:** ultra-low crosslinked nanogels, polymer-particle duality, emulsions.

**Acknowledgements:** The authors acknowledge the financial support from the Deutsche Forschungsgemeinschaft within SFB 985 - Functional Microgels and Microgel Systems (project A3, No. 191948- 804). We thank N. Hazra and J. J. Crassous for the help with the microscopy measurements.

## References

- [1] J. Gao and B. J. Frisken, *Langmuir*, 2003, 19, 5212.
- [2] A. Scotti, S. Bochenek, M. Brugnoli, M.A. Fernandez-Rodriguez, M.F. Schulte, J.E. Houston, A.P.H. Gelissen, I.I. Potemkin, L. Isa and W. Richtering, *Nature Communications*, 2019, 10, 1418.

Monday 5th September 2022

**Polymers, Polyelectrolytes, Gels and Liquid Crystals**

# Water desalination using polyelectrolyte hydrogel. Gibbs ensemble modelling

*Oleg V. Rud<sup>1,2</sup>, Michail Laktionov<sup>2</sup>*

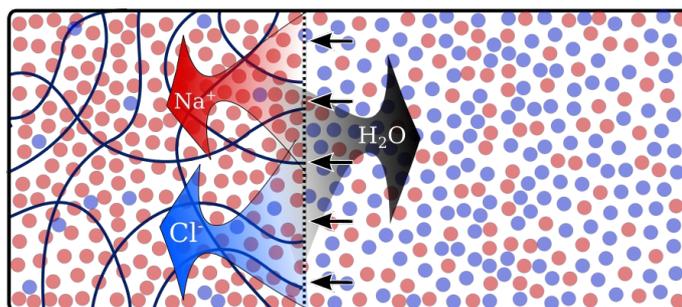
<sup>1</sup>*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Czech Republic*

<sup>2</sup>*Institute of Macromolecular Compounds of Russian Academy of Sciences, Saint-Petersburg, Russia*

Presenting author's e-mail: [helvrud@gmail.com](mailto:helvrud@gmail.com)

Recently polyelectrolyte hydrogels have been proposed as draw agents for reverse osmosis desalination techniques. Indeed, polyelectrolyte hydrogels have the ability to absorb a big amount of water across forward osmosis membrane as a result of their swelling pressure. The insoluble cross-linked network of the gel enables dewatering under the influence of stimuli (thermal and/or mechanical). On the other hand, the network structure of a polymer hydrogel from a thermodynamic perspective is already an osmotic membrane. So hydrogel microparticles may allow to completely avoid the osmotic membranes in forward osmosis and use microfiltration instead. By this article, we present our recent theoretical study of the use of polyelectrolyte hydrogel for water desalination. We modeled the thermodynamic equilibrium of coexistence of the gel and the aqueous salt solution in the so-called closed ensemble, in which the total amount of ions is assumed to be constant. We modeled the compression of the gel and the associated with that release of the solution. We have shown that the squeezed out solution has a little lower salinity than that the gel was equilibrated with. Also, we performed a set of simulations modeling the process of continuous decrease of water salinity up to freshwater concentrations.

**Keywords:** desalination, hydrogel, polyelectrolyte, simulation



**Figure 1.** The compression of the gel affects the salinity of the solution

**Acknowledgements:** This research was supported by the Czech Science Foundation (grant 19-17847Y)

## References

- [1] Rud, O., Borisov, O., Kořovan, P. (2018). Thermodynamic model for a reversible desalination cycle using weak polyelectrolyte hydrogels. *Desalination*, 442, 32–43.
- [2] Rud, O. V., Landsgesell, J., Holm, C., Kořovan, P. (2021). Modeling of weak polyelectrolyte hydrogels under compression – Implications for water desalination. *Desalination*, 506, 114995.

## Single-ion Electrolytes Composed of Polyanionic Polymer Particles

*Emmanouil Glynos<sup>1,2</sup>, Georgia Nikolakakou<sup>1,3</sup>, Christos Pantazidis<sup>4</sup>, Dimitris Kritsiotakis<sup>1,3</sup>, Georgia Sakellariou<sup>4</sup>*

<sup>1</sup>*Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1385, 71110 Heraklion, Crete GR, Greece*

<sup>2</sup>*Department of Materials Science and Technology, University of Crete, 71003 Heraklion, Crete, Greece*

<sup>3</sup>*Department of Chemistry, University of Crete, 71003 Heraklion, Crete, Greece*

<sup>4</sup>*Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece*

Presenting author's e-mail: [eglynos@materials.uoc.gr](mailto:eglynos@materials.uoc.gr)

Despite the considerable research effort in solid-state electrolytes (SPEs), the primary challenge regarding SPEs is the development of materials with a lithium transference number close to unity and good mechanical properties without sacrificing ionic-conductivity. In this talk, we will introduce the use of polyanion polymer particles, composed of poly(styrene-4-sulfonyltrifluoromethylsulfonyl) imide lithium, PSTFSILi, arms that complement longer ion conducting poly(ethylene oxide), PEO, arms, (PSTFSILi)<sub>n</sub>(PEO)<sub>n</sub>, where  $n \approx 22$ , as single-ion SPEs. The degree of polymerization of the PEO arms was kept fixed at 105 while that of PSTFSILi was systematically varied from 5 to 18 approximately, resulting to molar ratios,  $r = [\text{Li}^+]/[\text{EO}]$ , from 0.048 to 0.171, respectively. We will show that the resulted polymer electrolytes showed an astonishingly mechanical, glassy-like behavior (i.e. with  $G' \gg G''$ ), reaching even  $G' \approx 1$  GPa for the (PSTFSILi)<sub>22</sub>(PEO)<sub>22</sub> with the largest volume fraction of PSTFSILi,  $\Phi_{\text{PSTFSILi}}$ . In contrast, ion conductivity decreases monotonically with  $r$  indicating changes in the  $\Phi_{\text{PSTFSILi}}$  (or in  $r$ ) has a non-trivial effect on ion conductivity as the volume fraction of the conductive phase decreases with increasing  $r$ . Our analysis indicates that, due primarily to the core-shell structure of the polyanion polymer nanoparticles, ion transport depends exclusively on Li<sup>+</sup> ion concentration (proportional to  $r$ ), the volume fraction of the conductive phase ( $\Phi_{\text{PEO}}$ ), and the corresponding changes in segmental dynamics of the PEO segments due to the degree and strength of the Li<sup>+</sup>/EO complexation. Noticeably, while (PSTFSILi)<sub>22</sub>(PEO)<sub>22</sub> single-ion electrolytes have ion conductivities less than an order of magnitude lower than the corresponding linear polyanion block copolymers, they possess several orders of magnitudes better mechanical properties. In particular, while linear block copolymers show a liquid like behavior ( $G'' \gg G'$ ), (PSTFSILi)<sub>22</sub>(PEO)<sub>22</sub> are glassy/solids with  $G' \gg G''$ . This feature reveals that the proposed macromolecular design approach offers new means to control and tune the antagonistic properties of ion-conductivity and shear modulus, which currently limits the realization of single-ion polymer electrolytes in lithium metal batteries.

**Acknowledgements:** This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness and innovation, under the call RESEARCH –CREATE –INNOVATE (project code: T1EAK-02576, MIS5033805)



## Design Smart Polymeric Materials for controlled, selective and reversible adsorption at the nanoscale

*Barbara Capone<sup>1</sup>, Sara Del Galdo<sup>1</sup>, Pietro Corsi<sup>1</sup>, Carlo Andrea De Filippo<sup>1</sup>, Luca Stefanuto<sup>1</sup>, Tecla Gasperi<sup>1</sup>*

<sup>1</sup>Science Department, Roma Tre University, Rome, Italy

Presenting author's e-mail: [barbara.capone@uniroma3.it](mailto:barbara.capone@uniroma3.it)

Designing nanomaterials for selective and tunable adsorption/release is a topic of extremely wide interest, with a manifold of possible applications, spanning from biomedical ones, with the realisation of functionalised systems for drug delivery [1], up to more applied materials for selective removal of contaminants in water [2].

The creation of a pipeline leading to the design, and consequent realisation, of the optimal material, requires a multidisciplinary approach, as a multitude of details, from the atomic up to the meso scale, have to be considered.

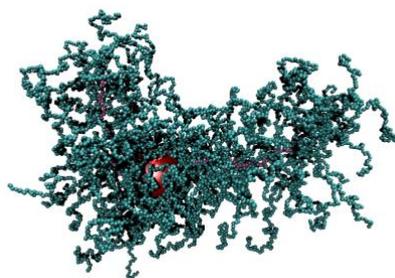
With this talk, we will show a generalised path that, starting from atomistic simulations - tailored on experimental synthesis - passes through a multiscale theoretical and computational process, and finally reaches its final experimental goal, with the realisation of functionalised nanoparticles with fully controllable and tunable properties.

Through a hybrid theoretical and experimental approach, we will show how to choose and tune atomistic details in general classes of polymers to assess the optimal sub-category of polymeric adsorbers. A multiscale strategy will then be implemented to assess how to exploit the selected optimal polymeric classes by assembling them in polymeric macromolecules, and specifically how to unveil the role played by the geometry of the macromolecules in both adsorption and selectivity [3]. We will then show that it is possible to define universal classes of adsorbers just retaining a few microscopic details [4]. Finally, we will present an experimental realisation of a designed nanomolecular adsorber [5,6].

**Keywords:** polymers, selective adsorption, theory, simulations, nanoparticles

### References

- [1] C. P. Reis, *Therapeutic Delivery* 10, 401 (2019).
- [2] Yang J, Hou B, Wang J, et al. *Nanomaterials (Basel)* 9(3):424, 2019
- [3] P. Corsi, A. Gonzalez Garcia, E. Roma, T. Gasperi, and B. Capone, *Soft Matter* 17, 3681 (2021).
- [4] P. Corsi, C. A. De Filippo, S. Del Galdo, B. Capone, *submitted* 2022
- [5] E. Roma, P. Corsi, M. Willinger, N. S. Leitner, R. Zirbs, E. Reimhult, B. Capone, and T. Gasperi, *ACS applied materials & interfaces* 13, 1386 (2021).
- [6] E. Roma, P. Corsi, B. Capone, E. Reimhult, and T. Gasperi, *AIP Conference Proceedings* 2416, 020018 (2021).



*Cylindrical polymeric macromolecule (bottlebrush) adsorbing a predetermined cargo*

## Phase separation of concentrated polymer solutions for making porous filtration membranes

*Guenoun Patrick<sup>1</sup>, Garate Hernan<sup>1</sup>, Mericq Jean Pierre<sup>2</sup>, Manzanarez Hervé<sup>2</sup> and Bouyer Denis<sup>2</sup>*

<sup>1</sup>Université Paris-Saclay, UMR NIMBE, LIONS, CEA Saclay, F-91191

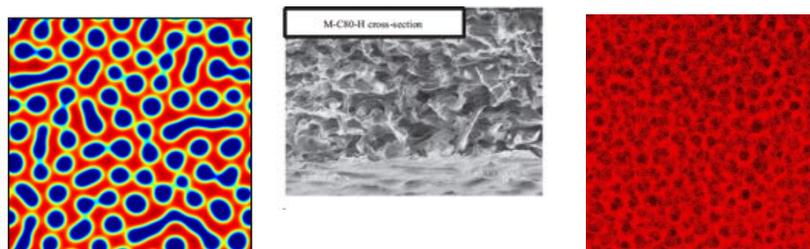
<sup>2</sup>Université de Montpellier IEM, cc047, Place E. Bataillon 34095 Montpellier France

Presenting author's e-mail: [patrick.guenoun@cea.fr](mailto:patrick.guenoun@cea.fr)

Phase separation (PS) of concentrated homopolymer solutions is surprisingly much more complicated than textbook descriptions though it is of practical importance in particular for mastering the process of membranes fabrication. A first complication is the necessity of taking into account the polymer dispersion in size and of reaching a correct description of the mobility dependence with concentration. I will first address these two aspects by describing growth laws of polymer phases thanks to experiments with poly(vinyl alcohol) and phase-field simulations respectively. [1, 2] New kind of porous membranes can be made by PS of water-soluble polymers but many of the latter exhibit anomalous phase diagrams which seem to be closely connected to unusual features of arrested-like PS as evidenced by light scattering and confocal microscopy. I will describe first attempts of membrane making with these polymers avoiding the use of organic solvents as well as numerical approach to describe the process. [3, 4, 5]

The case of polyelectrolytes is also of great interest since the theory is still controversial but polyelectrolytes are important precursors for polyimide membranes. First results will be presented about phase separation upon changes in salt concentration, polymer concentration and temperature.

**Keywords:** phase separation, polymer solutions, membranes



**Figure 1.** From left to right: a simulation of phase separation in polymer solution; a membrane made by phase separation of poly (vinyl alcohol); a phase separation pattern of poly (vinyl alcohol) solution

### References

- [1] O. M'barki, A. Hanafia, D. Bouyer, C. Faur, R. Sescousse, U. Delabre, C. Blot, P. Guenoun, A. Deratani, D. Quemener and C. Pochat-Bohatier, *J. Memb. Sci.*, 2014, **458**, 225–235.; D. Bouyer, O. M'Barki, C. Pochat-Bohatier, C. Faur, E. Petit and P. Guenoun, *AIChE J.*, 2017, **63**, 3035–3047.
- [2] H. Manzanarez, J. P. Mericq, P. Guenoun, J. Chikina and D. Bouyer, *Chem. Eng. Sci.*, 2017, **173**, 411–427.
- [3] A. Hanafia, C. Faur, A. Deratani, P. Guenoun, H. Garate, D. Quemener, C. Pochat-Bohatier and D. Bouyer, *J. Memb. Sci.*, 2017, **526**, 212–220.
- [4] H. Manzanarez, J. P. Mericq, P. Guenoun and D. Bouyer, *J. Memb. Sci.*, 2021, **620**, 118941.
- [5] H. Garate, K. W. Li, D. Bouyer and P. Guenoun, *Soft Matter*, 2017, **13**, 7161–7171.

## Modification of acid-base equilibria of weak polyelectrolytes in complex fluids

*Rachel Yerushalmi-Rozen<sup>1</sup>, Evgenee Yekymov<sup>1</sup>, David Attia<sup>1</sup>, Ronit Bitton<sup>1</sup>, Yael Levi-Kalisman<sup>2</sup>*

<sup>1</sup>*Dept. of Chem. Eng. Ben-Gurion University of the Negev, Beer-Sheva Israel*

<sup>2</sup>*The Center for NanoScience and NanoTechnology and the Institute of Life Sciences the Hebrew University of Jerusalem, Jerusalem Israel*

Presenting author's e-mail: [rachely@bgu.ac.il](mailto:rachely@bgu.ac.il)

Weak polyelectrolytes (WPE) are polymeric molecules comprising covalently linked monomers of a weak acid (or base). Unlike monomeric acids in WPE acid-base balance is not only determined by the bath pH, ionic strength and the dielectric constant of the solvent but also by the polymer's ability to regulate the charge (charge regulation, CR) and modify the local environment due to the complex interplay between the conformational degrees of freedom, solution entropy, electrostatic and excluded-volume interactions.

Practical applications of WPE rely on their utilization in multi-component complex fluid environments, in mixtures of molecular aggregates such as micelles, liposomes and nanoparticles where multiple (often weak) intermolecular interactions are active. In these complex fluids it is often observed that the responsiveness of the WPE to the environmental pH deviates from that predicted from the pKa value measured in single-component solutions of the WPE.

In the presented study we describe significant shifts of the titration curves and the measured pKa (up to about 1 pH unit) of a model WPE, polyacrylic acid (PAA) in solutions of PEO-based micelles of different size (and volume fraction). Titration experiments (potentiometric and FTIR-ATR measurements) in dilute, salt-free solutions of PAA (of a few molecular weights) indicate that micelles of Pluronics block-copolymers and Brij-S20 (Polyethylene glycol octadecyl ether) modify the acid-base equilibria of PAA, with only a minor effect on the acid-base behavior of monomeric acids (propionic acid). TEM and SAXS characterization reveal correlation between the pKa shift and the spatial re-organization of the PEO-based micelles in the presence of PAA at low pH.

The results suggest that coupling between weak hydrogen bonding of protonated PAA to PEO and steric interactions with non-charged micelles modify the charge-regulation of high molecular weight PAA probably due the conformational degrees of freedom of the PAA chains. The study highlights the origins of modified pH responsiveness of WPE in complex fluids.

**Keywords:** Weak polyelectrolytes, steric effect, self-regulation

### References

[1] E. Yekymov, D. Attia, R. Bitton, Y. Levi-Kalisman and R. Yerushalmi-Rozen, *Polymers*, 2022, 14, 1926.

# Activity of water absorbed in hydrophilic glassy polymers

*Vitaly Kocherbitov*<sup>1,2</sup>

<sup>1</sup>*Department of Biomedical Science, Malmö University, Malmö, Sweden*

<sup>2</sup>*Biofilms research center for Biointerfaces, Malmö, Sweden*

Presenting author's e-mail: [Vitaly.Kocherbitov@mau.se](mailto:Vitaly.Kocherbitov@mau.se)

Water sorption isotherms of hydrophilic polymers exhibit a pronounced sorption-desorption hysteresis in the glassy state, which cannot be explained by diffusion limitations [1]. In the glassy state, the water activity values deviate from the expected equilibrium values in both sorption and desorption branches of the isotherms. The hydration enthalpy is negative in the glassy state and in many cases shows relatively complex profiles. The enthalpy behavior was recently explained based on the glass transition properties of the components [2]. To develop this approach further, we derived an expression for water activity in glassy materials, where the deviation from the equilibrium activity values is related to the heat capacity changes of the components of the system [3]. This theory explains in thermodynamic terms the sorption-desorption hysteresis and provides valuable information about the state of water in the glassy matrix. The theory is tested on experimental data on water sorption by polymers and low molecular weight substances [3, 4]. A very good fitting of the experimental data for both sorption and desorption cases is demonstrated. The values of heat capacity changes of the components obtained by fitting water activity data are in agreement with calorimetric data on pure components and can be interpreted in connection to the mobility of water in glassy materials.

**Keywords:** Hydrophilic polymers, Water sorption, Glass transition

## References

- [1] Björklund, S.; Kocherbitov, V. Water vapor sorption-desorption hysteresis in glassy surface films of mucins investigated by humidity scanning QCM-D. *J. Colloid Interface Sci.* (2019), 545, 289-300
- [2] Kocherbitov, V.; Argatov, I. Enthalpy of sorption by glassy polymers. *Polymer* (2019), 174, 33-37
- [3] Kocherbitov, V.; Argatov, I. A thermodynamic theory of sorption in glassy polymers. *Polymer* (2021), 223, 124195
- [4] Bogdanova, E; Millqvist Fureby, A.; Kocherbitov, V. Hydration enthalpies of amorphous sucrose, trehalose and maltodextrins and their relations to heat capacities. *Phys. Chem. Chem. Phys.* (2021), 23, 14433-14448

Tuesday 6th September 2022

**Colloids at Interfaces, Membranes and Biointerfaces,  
Emulsions and Foams**

## Leaching foams

*Trinh Pierre<sup>1</sup>, Bruez Cyriaque<sup>1</sup>, Lefevre Gregory<sup>2</sup>, Monteux Cécile<sup>1</sup>*

<sup>1</sup>*ESPCI Paris, France*

<sup>2</sup>*ENSCP, France*

*Presenting author's e-mail: [cecile.monteux@espci.fr](mailto:cecile.monteux@espci.fr)*

The recovery of metals from WEEE, Waste from Electrical and Electronic Equipment, is a major challenge to preserve natural resources. Hydrometallurgy, which consists in leaching metals is a promising method but generates large amounts of polluting effluents. In this study we design aqueous leaching foams, composed of 90% v/v of gas and 10% v/v of HCl solution to oxidize and dissolve copper. We take advantage of the oxidizing power of the dioxygen (O<sub>2</sub>) present in the air bubbles whose fast transfer through the foams enables an efficient oxidation of copper. Using a forced drainage set up we show that the liquid fraction in the foam controls the transfer of O<sub>2</sub> from bubble to bubble as well as the transfer of the H<sup>+</sup> ions in the continuous phase. Finally we show that it is possible to extend the concept of leaching foams to other metals such as silver (Ag) and to other surfactants that complex cupric ions and help improving the dissolution of the metal. These promising results open new recycling routes for metals contained in WEEE, with a lower environmental footprint.

**Keywords:** foams, oxidation, drainage

### References

[1] Trinh et al, ACS Sustainable Chemistry and Engineering, 9, 42, 14022–14028 (2021)

## Stabilization of non-ionic foam with nano-ions

Lamolinairie Julien <sup>1</sup>, Chiappisi Leonardo <sup>1</sup>, Diat Olivier <sup>2</sup>, Bauduin Pierre <sup>2</sup>, Girard Luc <sup>2</sup>, Pasquier Coralie <sup>2</sup>, Jonchère Alban <sup>2</sup>, Lechevalier Peggy <sup>3</sup> and Bridot Jean-Luc <sup>3</sup>

<sup>1</sup>Institut Max von Laue-Paul Langevin, Grenoble, France

<sup>2</sup>Institut de Chimie Séparative de Marcoule, Marcoule, France

<sup>3</sup>Teclis Scientific, Civrieux-d'Azergues, France

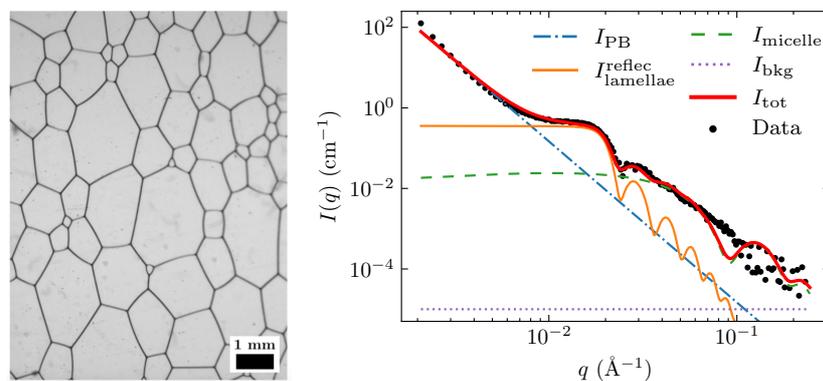
Presenting author's email: [lamolinairie@ill.fr](mailto:lamolinairie@ill.fr)

Very recently, it was shown that the aging of non-ionic foam could be strongly impacted by adding nanometer-sized anions (called nano-ions) due to their superchaotropic property, i.e. their ability to absorb onto a neutral surface and charge the interface which becomes repulsive [1-3].

In order to better understand the physico-chemical factors that affect the aging of foams from the non anionic alkylether BrijO10 surfactant and the silicatungstic acid polyoxometallate as nano-ion at different molar ratio in D2O, it was necessary to develop a new columnar device. It enables the simultaneous data collection at different length scales from a small-angle neutron scattering (SANS) diffractometer, from an optical camera and an electrical conductivity meter.

The volume of the foam, its liquid fraction and the radius of the foam bubbles as a function of time obtained by image analysis and conductivity processing are macroscopic information, necessary for foam lifetime characterization but not sufficient. SANS analysis is known to provide useful information at the nano-scale, on the structure of the inter-bubble film or the surfactant self-assemblies trapped within the foam [3-5]. However, to extract this information over a large structural range and in order to be able to compare the various structural features (the specific surface area, the liquid fraction, the film thickness) determined from different techniques, we have for the first time performed a quantitative analysis - in absolute scale - of the scattering data.

The analysis of nano- and macroscopic information obtained simultaneously enabled us to better understand the correlation between the aging mechanisms of drainage, ripening and coalescence and their effects on the aging of the foam.



**Figure 1 :** *Left* - Picture of a foam for 65 min aging time (free drainage mode). *Right* - Various contributions of the total scattering simulation (red curve) to adjust SANS data from a foam photographs in left picture :  $I_{PB}$  from Plateau Borders,  $I_{micelle}$  from micelles present within the foam and  $I_{lamellae}^{reflec}$  from lamellae.

**Keywords:** Foam stability, Film thickness, SANS analysis

### References

- [1] M. Hohenschutz, I. Grillo, O. Diat and P. Bauduin, *Angew. Chem. Int. Ed.*, 2020, 59, 8084
- [2] T. Buchecker, P. Schmid, S. Renaudineau, O. Diat, A. Proust, A. Pfitzner and P. Bauduin, *Chem. Commun.*, 2018, 54, 1833
- [3] M. Hohenschutz, I. Grillo, C. Dewhurst, P. Schmid, L. Girard, A. Jonchère, O. Diat and P. Bauduin, *J Colloid Interface Sci.*, 2021, 603, 141
- [4] C. Micheau, P. Bauduin, O. Diat, and S. Faure, *Langmuir*, 2013, 29, 8472
- [5] A. Mikhailovskaya, L. Zhang, et al, *Adv. Colloid Interface Sci.*, 2017, 247, 444

# Mechanisms responsible for the longer lifetimes of bubbles and foams in binary liquid mixtures

*Talini Laurence<sup>1</sup>, Tran Hoai-Phuong<sup>2</sup>, and Lequeux François<sup>2</sup>*

<sup>1</sup>*CNRS, Surface du Verre et Interfaces, Aubervilliers, France*

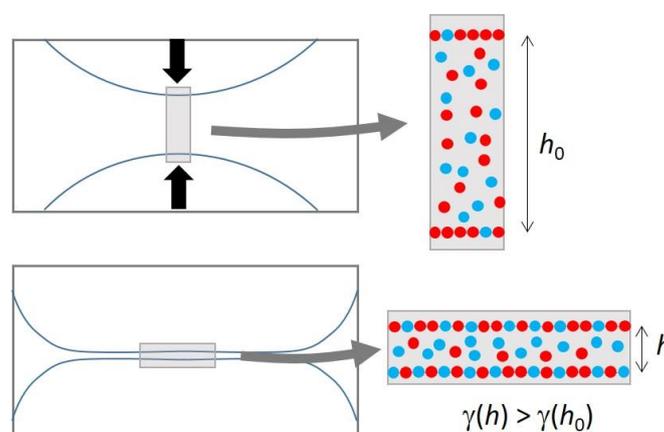
<sup>2</sup>*CNRS, Laboratoire Physico-chimie des Interfaces Complexes, ESPCI, Paris, France*

Presenting author's e-mail: [laurence.talini@cnrs.fr](mailto:laurence.talini@cnrs.fr)

Bubbles formed in pure liquids have very short lifetimes because, in the absence of surfactant, there is no effect to oppose the thinning of liquid films. In contrast, it has been known for a long time that, in liquid mixtures, bubbles or foams persist for times that are four orders of magnitude larger than in pure liquids [1]. We have shown recently that the enhanced stability in binary mixtures results from a surfactant-like effect of one liquid for the other [2], taking its origin in slight concentration differences of the species between bulk and interfaces with air and giving rise to a thickness-dependent surface tension. Here, we report an experimental and theoretical study of the mechanisms responsible for the longer lifetimes of liquid films in mixtures.

Experiments were performed with different binary mixtures: stationary foams were obtained by continuous injection of gas on one hand, and single bubbles were swollen under the surface of a liquid bath on the other hand. Remarkably, the lifetimes measured in both experiments were observed to follow the same variations with mixture composition. Experimental power laws were obtained between lifetimes and the characteristic lengths involved in the thickness-dependent surface tension. In addition, film thicknesses at the onset of bursting were found to vary as a power law with the latter lengths. We suggest that two stages occur between the formation of liquid films and their rupture. We show how their thickness-dependent surface tension allows an equilibrium shape to be reached at the end of a first stretching stage. We give an analytical description of this shape, and show it is fully consistent with experimental findings. We suggest a possible mechanism for final rupture of the film, and discuss it in light of existing theoretical predictions.

**Keywords:** thin liquid films, capillary drainage



**Figure 1.** Schematical representation of the mechanism at the origin of the enhanced stability of liquid films in binary mixtures, resulting from slight concentration differences between bulk and interfaces and giving rise to a thickness-dependent surface tension.

## References

- [1] S. Ross, G. Nishioka, *Journal of Physical Chemistry*, 1975, 795, 1561.  
[2] H.P. Tran et al., *Physical Review Letters*, 2020, 125, 178002.

# Surface-active agent's impact on bubble break-up: from single bubble to process-scale liquid foam

*Boubakar Sanogo<sup>1</sup>, Alain MARCATI<sup>1</sup>, and Christophe VIAL<sup>1</sup>*

<sup>1</sup>Université Clermont Auvergne, CNRS, Clermont Auvergne INP, Institut Pascal, F-63000, Clermont-Ferrand, France

Presenting author's e-mail: [boubakar.sanogo@uca.fr](mailto:boubakar.sanogo@uca.fr)

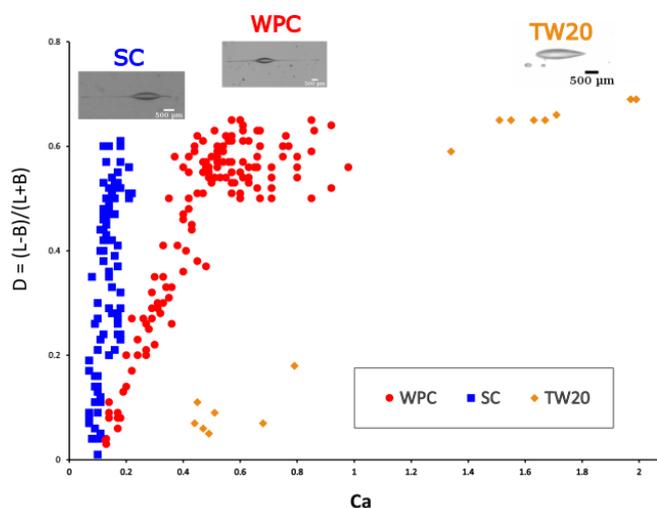
Proteins and surfactants are used to stabilize aqueous foams in food-related applications. There has been a huge number of published papers focused on bubble formation on a large scale in the presence of surfactants and proteins, that is to say on the production and stability of foams. However, there is still a lot to understand regarding the primary break-up of bubbles during the continuous foaming process. The present work aims to study the break-up behavior of gas bubbles stabilized by two different proteins (WPC: whey protein concentrates; SC: sodium caseinate) and a surfactant (TW20: tween 20).

Three Newtonian model solutions (1 Pa.s) consisting of 2% (w/w) surface-active agent (SAA) were prepared (one solution for each SAA). They were used to observe the deformation and break-up behavior of single bubbles in a transparent Couette system. Besides, a continuous foaming operation was carried out with the same solutions using a Rotor-Stator device.

Single gas bubbles subjected to simple shear flow using the Couette device were deformed and the deformation parameter  $D$  was obtained. This parameter was plotted as a function of the Capillary number  $Ca$  (Fig.1), which is the ratio between the viscous stress and the stabilizing Laplace pressure. These results show that protein-stabilized bubbles break by the tips (*tip-streaming*) around  $Ca \sim 0.15$  for SC and 0.5 for WPC. Regarding TW20, even though  $Ca$  reached 2, no break-up was observed, which likely means that this molecule is not very prone to enhance break-up under shearing flows.

In addition, the results of the continuous foaming operation show that TW20 is not a good foaming agent compared to proteins. Regarding proteins, SC needed a lower  $Ca$  to break bubbles, but it was not as good as WPC to produce foam at process scale. These differences between surfactant and proteins, and between WPC and SC, seem to be related to their distinct adsorption mechanisms and to their behavior on bubbles' surface (migration and accumulation at the tips). Gathering information on the way these SAA act on bubble surface is an important tool to better understand foam generation and to reach the long-term goal of predicting a foaming operation result.

**Keywords:** bubble break-up, tip-streaming, protein, surfactant, simple shear flow



**Figure 1.** Deformation parameter ( $D$ ) as a function of the Capillary number ( $Ca$ ) for bubbles stabilized by proteins (whey protein concentrate, and sodium caseinate) and surfactant (tween 20) in simple shear flow.

# Phase Behavior and Miscibility in Lipid Monolayers Containing Glycolipids

*Tetiana Mukhina*<sup>1</sup>, *Gerald Brezesinski*<sup>1</sup>, *Chen Shen*<sup>2</sup> and *Emanuel Schneck*<sup>1</sup>

<sup>1</sup>*Institute for Condensed Matter Physics, Technical University of Darmstadt, Hochschulstraße 8, 64289, Darmstadt, Germany*

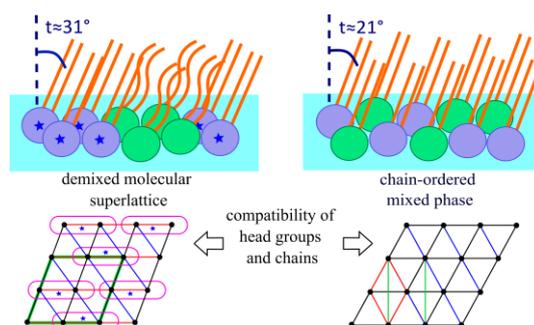
<sup>2</sup>*Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, 22607 Hamburg, Germany*

Presenting author's e-mail: [tetiana.mukhina@pkm.tu-darmstadt.de](mailto:tetiana.mukhina@pkm.tu-darmstadt.de)

Glycolipids in biological membranes are ubiquitous and believed to be involved in the formation of ordered functional domains. However, our current knowledge about such glycolipid-enriched domains is limited because they are inherently difficult to characterize.

We use grazing-incidence x-ray diffraction, isotherm measurements, and Brewster angle microscopy to investigate the phase behavior and miscibility in Langmuir monolayers containing glycolipids with various saccharide headgroups in mixtures with phospholipids and other glycolipids [1,2]. In glycolipid/phospholipid mixtures, glycolipid-enriched domains give rise to distinct diffraction patterns that allow for a systematic structural investigation and reveal a rich phenomenology, ranging from near-complete demixing to the formation of mixed domains with unique features. The phase behavior is governed by the headgroup chemistry and by the length and saturation of alkyl tails. Remarkably, glycolipid-enriched domains can recruit and integrate phospholipids which are otherwise disordered under the imposed conditions. Similarly, glycolipids forming molecular superlattices are able to form similar superlattices containing defined fractions of other glycolipids that do not form superlattices on their own. In other cases, however, a loss of molecular crystallinity was observed in glycolipid mixtures whose components on their own form such superlattices, due to incompatibility between sugar head groups.

Our work may contribute to a better understanding of the still controversial concept of lipid raft formation in biological contexts.



**Figure 1.** Schematic illustration of lipid arrangement at the interphase (top) along with the corresponding lattice structure (bottom)

**Keywords:** glycolipid, phospholipid, Langmuir monolayer, phase diagram, phase behavior, grazing incidence X-ray diffraction

**Acknowledgements:** We thank Deutsches Elektronen-Synchrotron for beamtime allocation. Financial support by the German Research Foundation (DFG, SCHN 1396/1, SCHN 1396/2) is gratefully acknowledge

## References

- [1] T. Mukhina, G. Brezesinski, C. Shen and E. Schneck, *J. Colloid Interface Sci.*, 2022, 615, 786-796.  
[2] C. Stefaniu, V. M. Latza, O. Gutowski, P. Fontaine, G. Brezesinski, E. Schneck, E., *J. Phys. Chem. Lett.*, 2019, 10, 1684-1690

## Why do polyelectrolyte / surfactant mixtures form extended structures at the air / water interface?

*Larissa Braun<sup>1</sup>, Richard A. Campbell<sup>2</sup>, Emanuel Schneck<sup>3</sup> and Regine von Klitzing<sup>1</sup>*

<sup>1</sup>*Department of Physics, Soft Mater at Interfaces, Technische Universität Darmstadt, Darmstadt, Germany*

<sup>2</sup>*Division of Pharmacy and Optometry, University of Manchester, Manchester, UK*

<sup>3</sup>*Soft Matter Biophysics, Department of Physics, Technische Universität Darmstadt, Germany*

Presenting author's e-mail: [larissa.braun@pkm.tu-darmstadt.de](mailto:larissa.braun@pkm.tu-darmstadt.de)

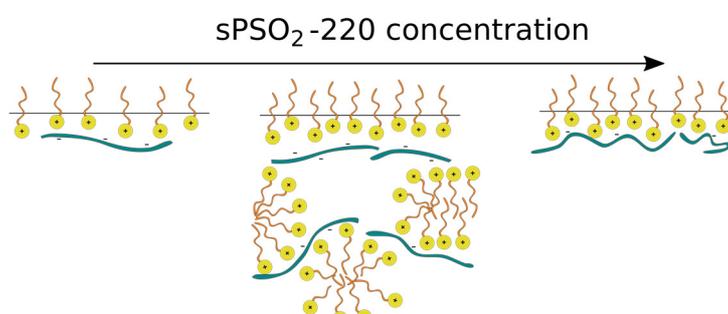
Colloidal dispersions (foams, emulsions) of oppositely charged polyelectrolyte/surfactant (P/S) mixtures are of interest in many applications such as cosmetics, cleaning products and in food technology [1]. For foams, understanding the stability of the foam films, which separates the gas bubbles, is crucial. Thereby, the surface properties of these mixtures play an important role.

Interfacial structures of the P/S mixtures are expected to dominate the foam film stability [2]. Monolayers or extended layers (meaning disordered multilayers of S and P) may form at the interface depending on the P/S ratio. We were curious why these structures form and how we can manipulate their formation. Therefore, we focus on the interfacial structures of two P/S mixtures: either the anionic polyelectrolyte PSS or the stiffer sPSO<sub>2</sub>-220 is mixed with the cationic surfactant C<sub>14</sub>TAB. Using neutron reflectometry including contrast matching, we find the former one forms only monolayers whereas the later one forms extended layers at certain P/S ratios. Moreover, we study the influence of salt on the interfacial structures and find that salt suppress the extended structures.

Considering the monomer structures of the P as well as the influence of salt, we identified the driving force for the formation of extended structures: reaching an optimal ratio at the interface to maximize the gain in entropy.

Furthermore, we will discuss our results in the context of the foam film properties for the sPSO<sub>2</sub>-220 / C<sub>14</sub>TAB mixtures.

**Keywords:** polyelectrolyte/surfactant mixtures, neutron reflectometry, interfacial structure



**Figure 1.** Scheme of the interfacial structures of sPSO<sub>2</sub>-220 / C<sub>14</sub>TAB mixtures in dependence of sPSO<sub>2</sub>-220 concentration. Addition of salt suppress the formation of extended layers.

### References

- [1] Lindmann et al Colloid Journal, 2014, 76, 585-594  
[2] Uhlig et al, Chem. Commun. 2019, 3, 3-6

# Investigating Biomembrane Models at Fluid Interfaces - from Bacteria Surfaces to Glycolipid Domains to RNA delivery

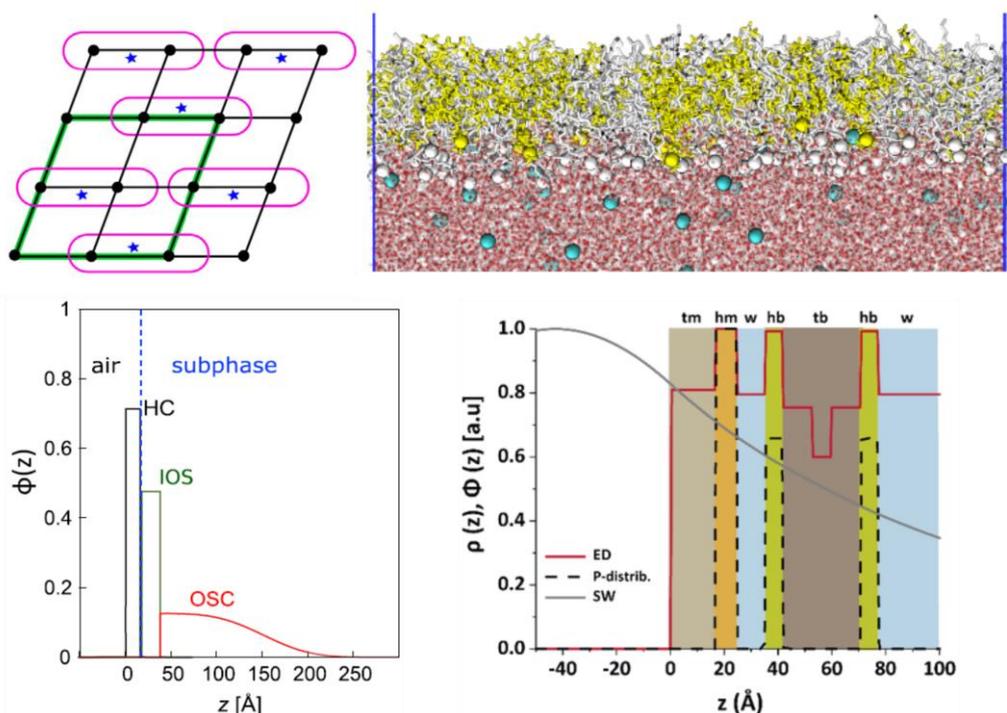
*Emanuel Schneck*

*Institute for Condensed Matter Physics, Technische Universität Darmstadt, Germany*

Presenting author's email: [emanuel.schneck@pkm.tu-darmstadt.de](mailto:emanuel.schneck@pkm.tu-darmstadt.de)

Biological membranes based on lipid bilayers are major components of all living organisms, but lipid layers are also used in many biomedical applications. We use biomembrane models in the form of lipid mono- and bilayers at water/air and water/oil interfaces in order to investigate various biological and biotechnologically relevant phenomena involving lipid layers. These experimental models are comprehensively characterized with numerous surface-sensitive techniques, notably x-ray and neutron scattering/reflectometry and x-ray fluorescence, as well as molecular dynamics simulations. The talk will cover examples from our recent activities, including the conformation of wild-type bacterial lipopolysaccharide layers [1], the formation of glycolipid-enriched ordered lipid domains [2], the characteristics of lipid bilayers adsorbed to functionalized fluid interfaces, and the pH-dependent charge and structural properties of transfection lipid layers for RNA delivery.

**Keywords:** lipopolysaccharides, lipid rafts, transfection lipids, x-ray scattering, x-ray fluorescence, neutron reflectometry



**Acknowledgements:** Allocation of beamtime by Institut Laue-Langevin and by Deutsches Elektronen-Eynchrotron DESY is gratefully acknowledged.

## References

- [1] S. Micciulla, Y. Gerelli, E. Schneck, *Biophysical Journal*, 2019, 116, 1259.
- [2] T. Mukhina, G. Brezesinski, C. Shen, E. Schneck, *J. Colloid Interf. Sci.*, 2022, 615, 786.

## MUC5B mucin films under mechanical confinement: A combined neutron reflectometry and atomic force microscopy study

Hannah Boyd<sup>1,2</sup>, Juan F Gonzalez-Martinez<sup>1,2</sup>, Philipp Gutfreund<sup>3</sup>, Rebecca JL Welbourn<sup>4</sup>, Carolina Robertsson<sup>2,5</sup>, Claes Wickström<sup>2,5</sup>, Thomas Arnebrant<sup>1,2</sup>, Robert M Richardson<sup>6</sup>, Stuart W Prescott<sup>7</sup>, Robert Barker<sup>8</sup>, Javier Sotres<sup>1,2</sup>

<sup>1</sup>*Department of Biomedical Science, Malmö University, Sweden.*

<sup>2</sup>*Biofilms-Research Center for Biointerfaces, Malmö University, Sweden.*

<sup>3</sup>*Institut Laue Langevin, France.*

<sup>4</sup>*ISIS Facility, STFC, RAL, UK.*

<sup>5</sup>*Department of Oral Biology and Pathology, Malmö University, Sweden.*

<sup>6</sup>*School of Physics, University of Bristol, UK.*

<sup>7</sup>*School of Chemical Engineering, University of New South Wales, Australia.*

<sup>8</sup>*School of Physical Sciences, University of Kent, UK.*

Presenting author's e-mail: [Hannah.boyd@mau.se](mailto:Hannah.boyd@mau.se)

Mucins hydrate and protect biological interfaces from mechanical challenges [1]. Mucins also attract interest as biocompatible coatings with excellent lubrication performance [2]. Therefore, it is of high interest to understand the structural response of mucin films to mechanical challenges. Neutron Reflectometry (NR) is an ideal technique to obtain structural information of thin film normal to the surface. Using a novel sample environment [3] that achieves mechanical confinement by means of inflating a flexible membrane against the films within the neutron reflectometry geometries allows any changes in the structure to be observed. Complimentary force spectroscopy (FS) measurements using an atomic force microscope (AFM) also allow investigations of the mucin films under confinement.

NR indicated that MUC5B films were almost completely compressed and dehydrated when confined at 1 bar. This was supported by FS investigations, which also indicated that MUC5B films could withstand mechanical confinement by means of steric interactions for pressures lower than ~ 0.5 bar i.e., mucins could protect interfaces from mechanical challenges of this magnitude while keeping them hydrated. To investigate mucin films under these pressures by means of the employed sample environment for NR, further technological developments are needed. The most critical would be identifying or developing more flexible membranes that would still meet certain requirements like chemical homogeneity and very low roughness.

**Keywords:** MUC5B, confinement, neutron reflectometry, AFM

### References

[1] R.A. Cone, *Adv. Drug Deliv.*, 2009, 61 (2), 75–85.

[2] J. Sotres, and T. Arnebrant, *Lubricants*, 2013, 1, 102.

[3] W.M. de Vos, L.L.E. Mears, R.M. Richardson, T. Cosgrove, R.M. Dalglish, S.W. Prescott, *Rev. Sci. Instrum.*, 2012 83 (11) 113903

## Probing $\alpha$ -synuclein interactions with lipid membranes via fluorescence techniques

Marco Fornasier<sup>1</sup>, Alexandra Andersson<sup>1</sup>, Ricardo Gaspar<sup>1</sup>, Katarzyna Makasewicz<sup>1</sup>, Emma Sparr<sup>1</sup>, Peter Jönsson<sup>1</sup>

<sup>1</sup>Department of Chemistry, Lund University, SE-22000 Lund, Sweden

Presenting author's e-mail: [marco.fornasier@fkem1.lu.se](mailto:marco.fornasier@fkem1.lu.se)

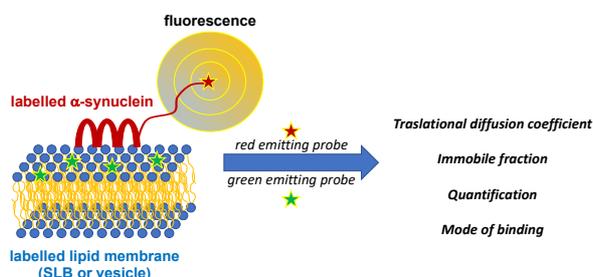
The healthy function of  $\alpha$ -synuclein ( $\alpha$ Syn) *in vivo* is not well understood, and the aberrant aggregation of such protein is related to Parkinson's disease [1,2]. Protein binding to lipid membranes was found to be a common denominator in molecular mechanisms of healthy and pathological  $\alpha$ Syn functions [2].

For this purpose, we studied how (i) fluorescently labelled  $\alpha$ Syn interacts with lipid membranes of different compositions, in the form of vesicles or supported lipid bilayers, and (ii) how the solution conditions affect the binding. The lipid bilayers were composed of the biologically relevant lipids POPC/DOPC (zwitterionic) and the negatively charged DOPS and gangliosides GM1 and GM3.

Fluorescence recovery after photobleaching (FRAP) measurements highlighted that the diffusivity of both the protein and SLBs is media-dependant (e.g., pH, ionic strength). While the lipid mobility does not really change in the different conditions,  $\alpha$ Syn appears to be less mobile at pH 7. Total internal reflection fluorescence (TIRF) microscopy and fluorescence correlation spectroscopy (FCS) were employed to study the binding of  $\alpha$ Syn in different media to SLBs and vesicles, respectively. These techniques showed that the binding strongly depends on the solution conditions and the composition of the membrane. As the protein presents a stronger affinity towards PS-containing membranes, we studied how the negative charge density of the SLBs affects the protein binding, by increasing the DOPS content from 0 to 40 mol %. These results suggested that the protein adsorption reaches a plateau around 25-30 mol % of DOPS. Additionally, the binding showed a positive cooperative behaviour when interacting with membranes containing 30 mol % of PS.

These results may rationalise the effect of media and lipid composition on protein binding, to shed some light on biologically relevant lipid-protein interactions, and to translate such studies into applications *in vivo*.

**Keywords:**  $\alpha$ -synuclein, lipid membranes, fluorescence, microscopy, diffusion



**Figure 1.** Schematic representation of the qualitative and quantitative information of the protein-lipid system.

### References

- [1] K. Makasewicz, S. Wennmalm, B. Stenqvist, M. Fornasier, A. Andersson, P. Jönsson, S. Linse, E. Sparr, *Chemical Neuroscience*, 2021, 12, 2099.
- [2] J.T. Bendor, T.P. Logan, R.H. Edwards, *The function of  $\alpha$ -synuclein*, *Neuron*, 2013, 79.

## Biocidal action of Ag and soap against *Staphylococcus aureus*

*Gergana Georgieva*<sup>1</sup>, *Dimitrina Foteva*<sup>1</sup>, *Nikolay Avramov*<sup>1</sup>, *Yana Goranova*<sup>1</sup>,  
*Tsvetelina Paunova-Krasteva*<sup>2</sup>, *Prem Chandar*<sup>3</sup>, *Joseph Carnali*<sup>3</sup>, *Svetoslav Anachkov*<sup>1</sup>

<sup>1</sup> Dpt. Chemical & Pharmaceutical Engineering, Sofia University, 1164 Sofia, Bulgaria

<sup>2</sup> Institute of Microbiology, Bulgarian Academy of Sciences (BAS), 1113 Sofia, Bulgaria

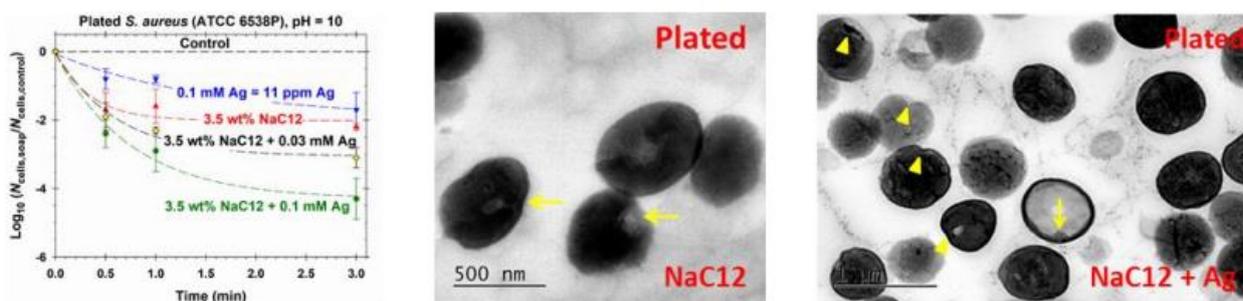
<sup>3</sup> Unilever Research and Development, Trumbull, CT 06611, USA

Presenting author's e-mail: [gerganag@lcpe.uni-sofia.bg](mailto:gerganag@lcpe.uni-sofia.bg)

Microbial pathogens (bacteria, viruses, and fungi), which can cause infections and diseases in humans, are one of the leading causes of death worldwide, namely one-fourth of global deaths annually [1]. Therefore, the control and prevention of microbial infections are of utmost importance. To fight with pathogens, many antimicrobial agents have been developed, such as antibiotics, disinfectants, and antiseptics. However, due to mutations, new strains of antimicrobial-resistant microorganisms are emerging, thus making the search of new biocides a substantial challenge.

In our study, we have tested the biocidal action of soaps and silver ( $\text{Ag}^+$ ) against planktonic and adherent *S. aureus*. Soaps are commonly used in hand-wash formulations and should be able to kill most bacteria within 30-60 s without damaging the skin, however, in many cases they are not very effective alone. We found that the antibacterial properties of soaps improve when their hydrophobicity increases up to 12 carbon atoms. Moreover, when soaps are combined with  $\text{Ag}^+$ , we observed a synergistic effect: increased cell permeability due to soap, resulting into higher silver uptake and enhanced biocidal action. Furthermore, using SEM and TEM, we detected the external and internal defects due to the treatment, thus elucidating the mechanism of biocidal action.

**Keywords:** Bacteria, Biocides, Soaps, Silver



**Figure 1.** Biocidal effect of sodium laurate (NaC12) and/or Ag on plated *S. aureus* – surviving cells and TEM images.

### References

[1] Y. Xue, H. Xiao and Y. Zhang, *Int. J. Mol. Sci.*, 2015, 16, 3626.

**Acknowledgements:** The authors acknowledge the funding from Unilever R&D Trumbull, USA.

# Perfluorocarbon Nanoemulsions Activatable in Microbubbles for Biomedical Imaging: Methods of Preparation and Characterization

Hagop Abadian<sup>1</sup>, Salima El-Yakhlifi<sup>1</sup>, Da Shi<sup>1</sup>, Benjamin Ayela<sup>2</sup>, Marine Rey<sup>2</sup>, Delphine Felder-Flesch<sup>2</sup>, Marc Schmutz<sup>1</sup>, Marie Pierre Krafft<sup>1</sup>

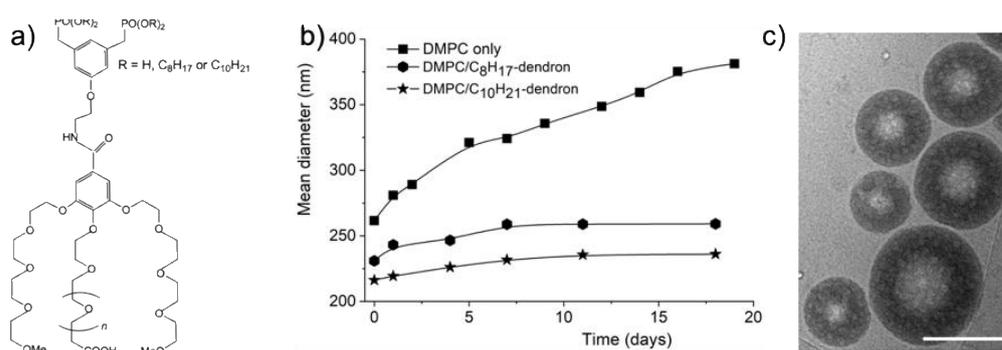
<sup>1</sup>Institut Charles Sadron, Univ. Strasbourg. 23 rue du Loess, 67034 Strasbourg, France

<sup>2</sup>SUPERBRANCHE, Strasbourg, France

Presenting author's e-mail: [krafft@unistra.fr](mailto:krafft@unistra.fr)

Microbubbles (MBs) focus intense interest for biomedical imaging and therapy. In combination with ultrasound technologies, MBs are used in the clinic for cardiovascular imaging and early detection of cancer [1]. Further applications concern molecular and multimodal imaging, cell therapies, treatment of neurodegenerative diseases and potentiation of oxygen-dependent cancer therapies [2]. However, the size of the MBs (a few micrometers in diameter) confines them to the vascular system, and their short lifetime in the circulation limits the scope of their uses. Nanometric droplets (NDs) of a liquid, yet volatile fluorocarbon (PFC), which circulate for much longer times in the vasculature and can accumulate in tumors, can be vaporized on demand at the target site by applying ultrasound, and thus be converted into MBs [2]. PFC NDs represent an attractive approach to the design of imaging agents. We identified a lack of well-defined, biocompatible and versatile amphiphiles tailored for PFC ND stabilization and acoustic droplet vaporization control. Therefore, we developed oligo(ethylene glycol) (OEG) bisphosphonate dendrons [3] (Fig. 1a) that, in combination with phospholipids, provide control over the mean diameter and the stability of perfluorohexane nanoemulsions. These NDs (~200 nm) could be easily converted into MBs (~2 μm) with a half-life (~5 h), five time longer than for reference MBs. We discuss the methods of preparation (sonication vs. high pressure emulsification) and characterization (sedimentation/centrifugation vs. dynamic light scattering) of PFC nanoemulsions (Fig. 1b). Cryo-TEM at various temperatures allowed capture of key intermediates in the phase-shift of the NDs into MBs (Fig. 1c). The efficacy of OEG dendrons as stabilizing agents will be compared to that of semi-fluorinated alkanes (C<sub>n</sub>F<sub>2n+1</sub>C<sub>m</sub>F<sub>2m+1</sub>) used to stabilize PFC nanoemulsions destined for oxygen delivery.

**Keywords:** Phase-shift; dendron; microbubble; fluid interfaces; diagnostics



**Figure 1.** a) The OEG dendrons. b) Variation of the mean diameter of C<sub>6</sub>F<sub>14</sub> (10% v/v) nanoemulsion droplets stabilized by DMPC, or a DMPC/C<sub>8</sub>H<sub>17</sub>- (or C<sub>10</sub>H<sub>21</sub>-) dendron combination (25°C). c) Cryo-TEM image of a C<sub>6</sub>F<sub>14</sub> nanoemulsion stabilized by egg yolk phospholipids (2% w/v) and C<sub>4</sub>F<sub>9</sub>CH=CHC<sub>8</sub>H<sub>17</sub> (scale bar = 200 nm).

## References

- [1] E. Stride, T. Segers, G. Lajoinie, S. Cherkaoui, T. Bettinger, M. Versluis, M. Borden, *Ultrasound Med. Biol.*, 2020, 46, 1326.
- [2] M.P. Krafft, J.G. Riess, *Adv. Colloid Interface Sci.* 2021, 294, 102407.
- [3] A. Parat, C. Bordeianu, H. Dib, A. Garofalo, A. Walter, S. Bégin-Colin, D. Felder-Flesch, *Nanomedicine (Lond.)*, 2015, 10, 977.

## Stabilization of water-in-water emulsions with fatty acids bilayers

Noémie Coudon<sup>1</sup>, Laurence Navailles<sup>1</sup>, Frédéric Nallet<sup>1</sup>, Isabelle Ly<sup>1</sup>, Ahmed Bentaleb<sup>1</sup>,  
Jean-Paul Chapel<sup>1</sup>, Laure Béven<sup>2</sup>, Jean-Paul Douliez<sup>2</sup> and Nicolas Martin<sup>1</sup>

<sup>1</sup>Univ. Bordeaux, CNRS, Centre de Recherche Paul Pascal, UMR 5031, 115 Avenue du Dr. Schweitzer, 33600 Pessac, France

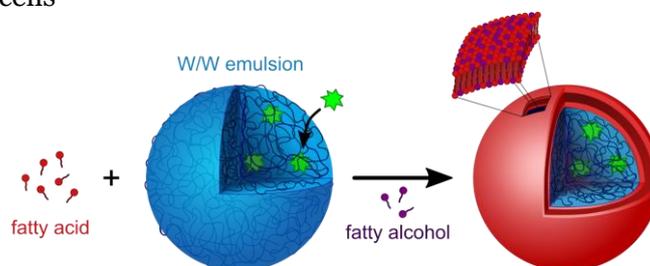
<sup>2</sup>Univ. Bordeaux, INRAE, Biologie du Fruit et Pathologie, UMR 1332, 71 Avenue Edouard Bourlaux, 33140 Villenave d'Ornon, France

Presenting author's e-mail: [noemie.coudon@crpp.cnrs.fr](mailto:noemie.coudon@crpp.cnrs.fr)

Water-in-water (W/W) emulsions produced by liquid-liquid phase separation in aqueous polymer solutions have received increasing attention for micro-encapsulation applications and for the construction of bio-inspired artificial cells [1]. W/W emulsions are indeed easily produced without oil or organic solvents, and spontaneously capture and accumulate various solutes, including fragile biomolecules. However, these emulsions are thermodynamically unstable and rapidly coalesce over time, which limits their use as functional micro-compartments. The stabilization of W/W emulsions against macroscopic phase separation is very challenging due to the large thickness of the water/water interface and associated ultra-low surface tension. Colloidal particles have been used to stabilize W/W droplets as Pickering-like emulsions, but they form a highly permeable shell that only partially restrict the diffusion of encapsulated biomolecules.

To tackle this issue, we recently reported the construction of stable and impermeable W/W droplets via the spontaneous interfacial self-assembly of mixed fatty acid/alcohol bilayers [2]. We used a segregative liquid-liquid phase separation between two neutral polymers, poly(ethylene glycol) (PEG) and dextran, to form W/W droplets enriched in dextran suspended in a PEG-rich continuous aqueous phase. We showed that sodium oleate spontaneously self-assembled as multilamellar bilayers at the surface of the dextran-rich droplets upon addition of 1-decanol, as revealed by freeze-fracture transmission electron microscopy and small-angle X-ray scattering. We further demonstrated the impermeability of this bilayers architecture to oligonucleotides, proteins and also to a low molecular weight dye sequestered in the droplets, so that a strict encapsulation of biomolecules in W/W droplets was achieved. Taken together, our results provide a simple and robust formulation strategy to stabilize W/W droplets with impermeable fatty acid/alcohol bilayers, opening perspectives for the solvent-free self-assembly of functional micro-capsules and artificial cells.

**Keywords:** liquid-liquid phase separation, water-in-water emulsion, fatty acids, interfacial self-assembly, artificial cells



**Figure 1.** Schematic representation of a W/W emulsion stabilized by self-assembly of fatty acid/alcohol bilayer.

### References

- [1] A. Perro, N. Coudon, J.-P. Chapel, N. Martin, L. Béven and J.-P. Douliez, *J. Colloid Interface Sci.*, 2022, 613, 681–696.
- [2] N. Coudon, L. Navailles, F. Nallet, I. Ly, A. Bentaleb, J.-P. Chapel, L. Béven, J.-P. Douliez and N. Martin, *J. Colloid Interface Sci.*, 2022, 617, 257–266.

## A closer look at the softening of phospholipid membranes by the adhesion of silica nanoparticles

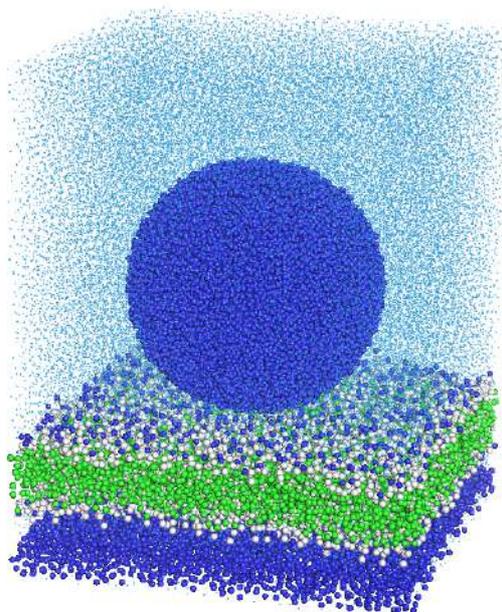
*Alexandros Koutsioumpas*<sup>1</sup>

<sup>1</sup>Jülich Centre for Neutron Science (JCNS) at Heinz Maier-Leibnitz Zentrum (MLZ), Forschungszentrum Jülich GmbH, Lichtenbergstrasse 1, 85748 Garching, Germany

Presenting author's e-mail: [a.koutsioumpas@fz-juelich.de](mailto:a.koutsioumpas@fz-juelich.de)

Interaction of bio-membranes with inorganic nanoparticles presents great interest in relation to practical applications in nanomedicine and nanotoxicology. In a previous Neutron Spin Echo study[1] the surprising finding of phospholipid membrane softening (reduction of bending rigidity) under the binding of silica nanoparticles was reported, although intuitively it might be expected that nanoparticles suppress membrane undulations, especially close to the adsorption site. In the present investigation by a combination of specular neutron reflectivity measurements, theoretical arguments and coarse-grained molecular dynamics simulations we try to elucidate the nanoscopic structural effects that lead to the observed dynamic behavior. Additionally, we discuss the implications for the general case of the interaction of hydrophilic nanoparticles with biological membranes.

**Keywords:** bio-membranes, nanoparticles, scattering, molecular dynamics



**Figure 1.** Snapshot of the molecular dynamics simulation of the supported membrane/nanoparticle system

### References

[1] Hoffmann *et al.* Nanoscale, 2014, 6, 6945.

## Nanostructured Materials and Coatings Based on Synthetic Four-Antennary Peptides

*Elena Mileva<sup>1</sup>, Anna Gyurova<sup>1</sup>, Dimitrinka Arabadzhieva<sup>1</sup>, Kaloyan Berberov<sup>1</sup> and Ljubomir Nikolov<sup>1</sup>*

*<sup>1</sup>Institute of Physical Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., bl. 11, 1113 Sofia, Bulgaria*

Presenting author's e-mail: [mileva@ipc.bas.bg](mailto:mileva@ipc.bas.bg)

The antennary peptides are synthetic substances, obtained as a result of preliminary molecular design. These compounds contain hydrophilic tails of equal lengths (antennae) composed of several glycine units terminated by amine groups. Here we report results about four-antennary peptides, with the antennae attached to C-atom. They are biocompatible and nontoxic to living organisms, and have high potential for biomedical and water-purity-control applications.

The key feature of these substances is that they are capable of forming well-organised nanostructures (tectomers) (bulk hydrophilic nanoplatfoms) in aqueous media, and specific coatings on solid supports. The innate reason for this nanoaggregate formation is the onset of highly cooperative arrangements of intra- and intermolecular hydrogen bonds (Polyglycine II, PG-II) [1]. The tendency to promote PG-II motifs is coupled with various other interaction options among the antennary oligoglycine species themselves, and also include the impact of the other components of the complex aqueous formulations. Thus there is a high potential for fine-tuning of structures and properties through changes of pH, and/or by addition of charged entities (low or high molecular mass substances) [2,3], and via temperature variations. The 'delicate' interplay and competition between the onset of PG-II motifs and the bulk and interfacial interaction options demand 'softer' research approaches. A combined procedure is developed to characterize the bulk self-assemblies and coatings. It is based on the examination of the performance of interfacial layers at solution/air and solution/solid boundaries, studies on drainage and stability of microscopic foam films. The experimental methodology includes also implementation of transmission-electron-microscopy and dynamic-light-scattering measurements.

The emerging application prospects regarding the design of these nanostructured materials and super-regular coatings are identified and commented.

**Keywords:** antennary oligoglycines, tectomers, Polyglycine-II, nanoplatfoms

**Acknowledgements:** The study was funded by Bulgarian National Fund for Scientific Research through Project "Design and Characterization of Soft Nanostructured Materials Based on Antennary Oligoglycines", Grant Number KII-06-H39/5. The support by the European Regional Development Fund within the Operational Programme "Science and Education for Smart Growth", Project CoE "National Center for Mechatronics and Clean Technologies", No. BG05M2OP001-1.001-0008 is also gratefully acknowledged.

### References

- [1] A.Y. Gyurova, A. Michna, L. Nikolov and E. Mileva, *Colloids Surf. A*, 2017, 519, 106.
- [2] A.Y. Gyurova, S.V. Stoyanov and E. Mileva, *Colloids Surf. A*, 2017, 520, 914.
- [3] A.Y. Gyurova, K. Berberov, A.A. Chinarev, L. Nikolov, D. Karashanova and E. Mileva, *Materials*, 2021, 14, 7659.

## Flow reactor for preparation of lipid nanoemulsions and nanosuspensions via temperature variations

*I. Lesov,<sup>1</sup> D. Glushkova,<sup>1</sup> D. Cholakova,<sup>1</sup>  
M.T. Georgiev,<sup>1</sup> S. Tcholakova,<sup>1</sup> S. K. Smoukov,<sup>2</sup> N. Denkov<sup>1</sup>*

<sup>1</sup> Sofia University, 1 J. Bourchier Ave., 1164 Sofia, Bulgaria

<sup>2</sup> Queen Mary University of London, London E1 4NS, U.K.

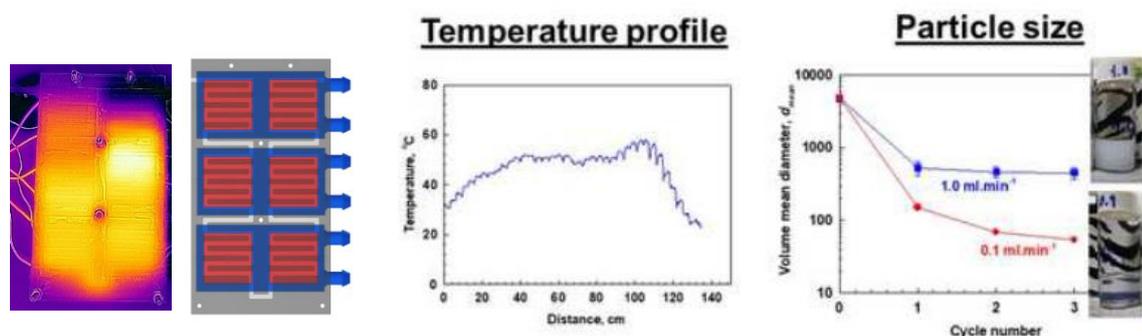
Presenting author's e-mail: [lesov@lcpe.uni-sofia.bg](mailto:lesov@lcpe.uni-sofia.bg)

Lipid nanoemulsions and nanosuspensions are used as flavor carriers and bubble stabilizers in soft drinks and foods, as well as delivery vehicles for lipophilic drugs in pharmaceuticals. Common techniques for their formation are the high-pressure and ultrasonic homogenizers. These techniques dissipate most of the input energy, which results in excessive heating and generation of free radicals that might modify sensitive ingredients. Low energy methods are also used in some applications, but they have specific limitations restricting their universal use.

In the current study[1], we propose an alternative approach - a flow reactor with a variable temperature, which utilizes the lipids' polymorphic transitions to induce spontaneous fragmentation of the lipid microparticles into nanoparticles. The reactor allows us to obtain emulsions or

suspensions with particle diameters tunable between 20 and 800 nm when appropriate surfactants, temperature profiles, and flow rates are applied. The fragmentation is comparable to that in a high-pressure homogenizer at ca. 500 bars or higher, without creating emulsion overheating or cavitation typical for the conventional methods. The flow reactor can be scaled up to industrial applications using simple scaling rules.

**Keywords:** emulsion, flow reactor, lipid nanoemulsions, lipid nanoparticles; infrared temperature optimization



**Figure 1.** Micro and nanoemulsions formation in a flow reactor with temperature variations

**Acknowledgements:** The authors gratefully acknowledge the financial support of the ERC Proof-of-concept grant CoolNanoDrop (# 841827) and by the Operational Program "Science and Education for Smart Growth", Bulgaria, grant number BG05M2OP001-1.002-0012.

### References

[1] I. Lesov, D. Glushkova, D. Cholakova, M.T. Georgiev, S. Tcholakova, S. K. Smoukov, N. Denkov, Journal of Industrial and Chemical Engineering, 2022, *accepted manuscript*

# Long-term stability of Pickering nanoemulsions prepared using diblock copolymer nanoparticles: effect of nanoparticle core crosslinking, oil type and the role played by excess copolymer

*Saul J. Hunter and Steven P. Armes*

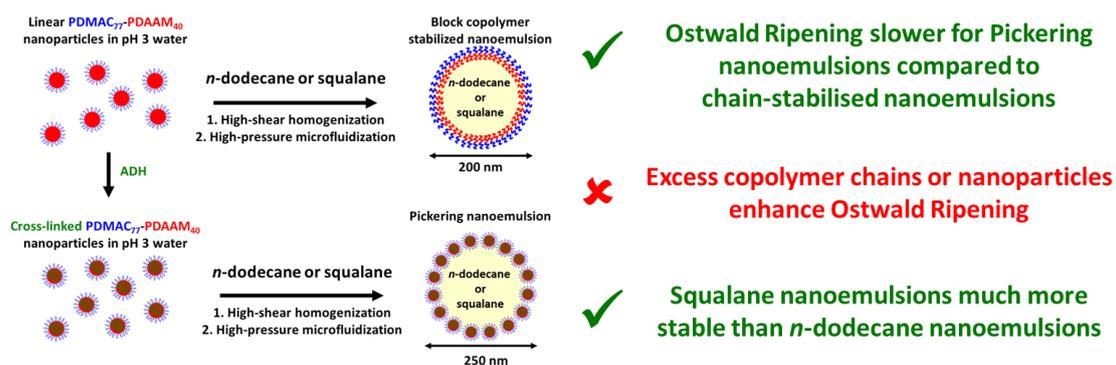
*Department of Chemistry, Dainton Building, University of Sheffield,  
Brook Hill, Sheffield, South Yorkshire, S3 7HF, UK*

Presenting author's e-mail: [s.j.hunter@sheffield.ac.uk](mailto:s.j.hunter@sheffield.ac.uk)

A poly(N,N'-dimethylacrylamide) (PDMAC) precursor is chain-extended with diacetone acrylamide (PDAAM) via reversible addition-fragmentation chain transfer (RAFT) aqueous dispersion polymerization to produce PDMAC<sub>77</sub>-PDAAM<sub>40</sub> spherical nanoparticles with a z-average diameter of  $29 \pm 6$  nm. Post-polymerization core-crosslinking of such nanoparticles was performed at 20 °C using adipic acid dihydrazide (ADH), which reacts with the ketone-functionalized PDAAM chains to form hydrazone bonds. The resulting covalently-stabilized nanoparticles remained intact on exposure to methanol, which is a good solvent for both blocks. The linear and core-crosslinked nanoparticles were each subjected to high-shear homogenization in the presence of n-dodecane to form macroemulsions. Subsequent processing of these macroemulsions via high pressure microfluidization led to the formation of nanoemulsions. When using the core-crosslinked nanoparticles, increasing the copolymer concentration led to a significant reduction in the mean oil droplet diameter, indicating that such nanoparticles adsorb intact at the oil/water interface and hence produce genuine Pickering nanoemulsions with a z-average diameter of  $170 \pm 59$  nm. In contrast, the linear nanoparticles underwent in situ molecular dissociation to afford surface-active diblock copolymer chains, which stabilize oil droplets of  $244 \pm 60$  nm diameter. The long-term stability of these two types of n-dodecane-in-water nanoemulsions towards Ostwald ripening was examined using analytical centrifugation. When prepared at the same copolymer concentration, Pickering nanoemulsions stabilized by core-crosslinked nanoparticles proved to be significantly more stable than the nanoemulsion stabilized by the amphiphilic PDMAC<sub>77</sub>-PDAAM<sub>40</sub> chains. Moreover, increasing the copolymer concentration led to a significantly faster rate of droplet growth. This is attributed to excess copolymer facilitating the diffusion of n-dodecane through the aqueous phase. Finally, analytical centrifugation was used to assess the long-term stability of the analogous squalane-in-water nanoemulsions. These systems proved to be significantly more stable than n-dodecane-in-water nanoemulsions, regardless of whether the copolymer was present in the form of sterically-stabilized nanoparticles or molecularly-dissolved chains.

**Keywords:** Emulsions, Pickering Emulsions, Block Copolymers

## Nanoemulsions stabilised by either diblock copolymer nanoparticles or amphiphilic chains



**Figure 1.** Preparation of nanoemulsions using either linear or core-crosslinked nanoparticles.

## Essential oil micro and nanoemulsions formation, assisted by food grade preservatives

*Dilek Gazolu-Rusanova<sup>1</sup>, Zlatina Mitrinova<sup>1</sup>, Ivan Lesov<sup>1</sup>, and Slavka Tcholakova<sup>1</sup>*

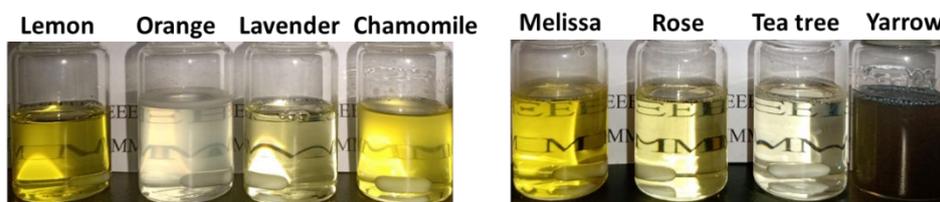
*<sup>1</sup>Department of Chemical and Pharmaceutical Engineering, Faculty of Chemistry and Pharmacy, Sofia University, 1164 Sofia, Bulgaria*

*Presenting author's e-mail: [dg@lcpe.uni-sofia.bg](mailto:dg@lcpe.uni-sofia.bg)*

Essential oils are a key ingredient in foods, beverages, personal care and home care products of various kind. Essential oils are often incorporated as micro or nanoemulsions to lower product costs and to achieve optimal delivery of a scent or a flavor, as well as to enhance their antimicrobial and antifungal activities.

In the current work, we study the formation and stability of micro and nanoemulsions originating from 8 different essential oils and 4 traditional food grade preservatives. Following our previous work [1], we prepared emulsions with lavender, chamomile, yarrow, melissa, tea tree, lemon, orange and rose oils in presence of citric acid, sodium citrate, potassium sorbate and sodium benzoate. Stable transparent nanoemulsions of lemon, lavender, melissa, rose and tea tree oils are formed when citric acid and sodium citrate present in the solutions. Model experiments revealed that bicontinuous phase is formed, which incorporates the essential oil upon heating and facilitates the formation of nanoemulsions upon rapid cooling of the mixture.

**Keywords:** essential oils, nanoemulsions, microemulsions.



**Figure 1.** Pictures of emulsions containing different essential oils, stabilized with Tween 60 in presence of 40 % citric acid + 4.72 % sodium citrate.

**Acknowledgements:** This work was supported by Operational Program “Science and Education for Smart Growth” 2014–2020, co-financed by European Union through the European Structural and Investment Funds, Grant BG05M2OP001- 1.002-0012 “Sustainable utilization of bio-resources and waste of medicinal and aromatic plants for innovative bioactive products”.

### References

[1] B. Ahtchi-Ali, S. Tcholakova, N. Denkov, S. Tsibranska and D. Gazolu-Rusanova, Patent Number: US20210059278A1/03.03.2021

# Adjustable Viscoelasticity of Gelled Liquid-liquid Interfaces Caused by Interfacial Transformations of Block Copolymer Micelles

*Felix Plamper*<sup>1</sup>, and *Quirin Prasser*<sup>1</sup>

<sup>1</sup> *Institute of Physical Chemistry, TU Bergakademie Freiberg, 09599 Freiberg, Germany*

Presenting author's e-mail: [felix.plamper@chemie.tu-freiberg.de](mailto:felix.plamper@chemie.tu-freiberg.de)

Interfacially active components like amphiphilic molecules or particles, which can undergo adsorption to liquid interfaces, are ubiquitous in nature and in technology. However, the observation of reorganization pathways of such amphiphiles at interfaces is often inaccessible. This is especially true for micelles, which could - in principle - adsorb in a pickering-like fashion besides unimeric adsorption. The temporal fate of such surface-attached micelles is often too rapid to follow.

We present a block copolymer system, where the reorganization kinetics is slowed down. It comprises a bishydrophilic poly(ethylene oxide)<sub>110</sub>-*b*-poly{[2-(methacryloyloxy)ethyl]diisopropylmethylammonium chloride}<sub>170</sub> (*i.e.*, PEO<sub>110</sub>-*b*-qPDPAEMA<sub>170</sub> with quaternized poly(diisopropylaminoethyl methacrylate)) and ferricyanide ([Fe(CN)<sub>6</sub>]<sup>3-</sup>), [1] which stimulates a hydrophobic behavior of the polycationic block. In addition, the ferricyanide acts like a dynamic (physical) crosslinker between the cationic sites of the polymer (similarly to the vitrimer case), allowing the investigation of the micellar reorganization kinetics at the water/*n*-decane interface. As a sensitive tool, interfacial shear rheology (ISR) was used to trace the mechanic properties of the interface [2]. The adsorbed micelles provide initially a mere viscous interface. However, the elastic interfacial modulus increases in the course of hours leading to a gel-like behavior. This transition is accompanied with a bursting/flattening of micelles followed by a merging of the resulting rafts toward a network structure, as seen by atomic force microscopy (AFM) after Langmuir-Blodgett transfer at various residence times of the micelles.

In addition, the resulting interconnected monolayers provide additional means to change the rheological properties. Reduction of ferricyanide weakens the polymer/hexacyanoferrate interaction and provides merely viscous interfaces, while the formation of hybrid Prussian blue films stiffens the interfacial film. Hence, the obtained results can give an example of the fine-tuning of the interfacial properties of adsorbed amphiphiles, where viscoelasticity and permeability matter.

**Keywords:** Self-Assembly, Interfacial Rheology, Monolayers, Gels



**Figure 1.** Schematic depiction of monolayer formation, which acts as an interfacial gel (green: physical crosslinks)

**Acknowledgements:** We thank the German Research Foundation DFG for funding (PL 571/4-1).

## References

- [1] Q. Prasser, D. Steinbach, D. Kodura, V. Schildknecht, K. König, C. Weber, E. Brendler, C. Vogt, U. Peuker, C. Barner-Kowollik, F. Mertens, F. H. Schacher, A. S. Goldmann and F. A. Plamper, *Langmuir* 2021, 37, 1073.  
[2] Q. Prasser, D. Steinbach, A. S. Münch, R. Neubert, C. Weber, P. Uhlmann, F. Mertens and F. A. Plamper, *Small* 2022, DOI: 10.1002/smll.202106956

Tuesday 6th September 2022

**Polymers, Polyelectrolytes, Gels and Liquid Crystals**

## On the inverse quenching technique applied to gelatin solutions

*Pietro Renato Avallone, Salvatore Costanzo, Francesco Greco, Nino Grizzuti,  
Rossana Pasquino*

*Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale,  
University of Naples Federico II, P.le Tecchio 80, 80125 Naples, Italy*

Presenting author's e-mail: [r.pasquino@unina.it](mailto:r.pasquino@unina.it)

Gelatin is a biopolymer composed of proteins, mineral, salts and water and it is employed in food, pharmaceutical and biomedical fields due to its gelling properties. Furthermore, it can be used as stabilizer, thickener, and texturizer. Gelatin gels are known to be non-equilibrium systems, due to the continuous growth and shuffling of the junction zones, over a long-time scale. This makes hard to perform rheological experiments on a distinct microstructure characterized by a definite number of junctions. To understand modelling, and predicting the transformation processes of gelatin solutions, it would be crucial to find a relation between the relative degree of crosslinking and macroscopic elasticity. In isothermal conditions, indeed, the density of physical crosslinks evolves indefinitely, and network formation cannot be arrested. Inspired by the *inverse quenching technique* applied in the past to semi-crystalline polymers, we here apply an unusual thermal history to an aqueous solution of gelatin in the semi-concentrated regime 6.67%<sub>wt</sub> pig-skin gelatin, to *freeze* the system in a metastable condition for a time sufficiently long to perform a rheological characterization. The solution, initially kept in the sol-state at 60°C, is rapidly cooled below gelation temperature, and isothermal gelation is started at 10°C. After soaking at this low temperature for a given time, the sample is rapidly heated (inverse quenching) up to a value in the range 24-29°C, where kinetics is monitored. If the waiting time at low temperature and the inverse quenching temperature are suitably chosen, sample elasticity will remain stationary for a relatively large time window, and rheological experiments can then be reliably performed.

**Keywords:** gels, rheology, inverse quenching, gelatin

### References

- [1] Acierno S. *et al*, J. Rheol. 47, 563, 2003
- [2] Avallone P.R. *et al*, Food Hydrocolloids 111, 106248,
- [3] 2021 Avallone P.R. *et al*, J. Rheol. 65, 1081, 2021

# Phase Behavior, Microscopic Dynamics and Microrheological Properties of a Thermosensitive Gel-Forming Polymer

*Vincenzo Ruzzi<sup>1</sup>, Stefano Buzzaccaro<sup>1</sup>, and Roberto Piazza<sup>1</sup>*

*<sup>1</sup>Department of Chemistry, Materials Science, and Chemical Engineering, Politecnico di Milano, 20133 Milano, Italy*

*Presenting author's e-mail: [vincenzo.ruzzi@polimi.it](mailto:vincenzo.ruzzi@polimi.it)*

Soft adaptive networks like polymer gels are promising candidates as surrogates for the extracellular matrix, more so when their rheo-mechanical properties can be carefully tuned. Using dynamic light scattering and photon correlation imaging, we have investigated the phase behaviour, the microscopic dynamics and the microrheological properties of a thermoresponsive network, Mebiol® Gel, extensively used as scaffold for cell growth.

In the dilute limit, Mebiol displays a Newtonian behaviour with a viscosity that decreases with temperature [1], consistent with a peculiar aggregation mechanism characterized by an increase of the molecular weight with a simultaneous reduction of the aggregate size [2]. By increasing concentration and temperature, the polymer solution progressively attains the structure of a percolating network, as witnessed by the logarithmic decay of the intensity correlation functions [2]. Moreover, both the storage and loss moduli shows a nonmonotonic dependence with temperature, with a pronounced peak around the value above which, in the dilute limit, the individual Mebiol chains are fully compacted. Such a distinctive trend persists within the gel, which therefore becomes “softer” above that temperature.

Although when temperature changes are performed adiabatically the transition from the fluid to the gel phase takes place without any apparent discontinuity, a rapid T-jump leads to the formation of a hard gel at a concentration where a low heating rate conversely yields a fluid phase. This behaviour actually mirrors the effect of quenching rate observed in simple glass-forming liquids and it is consistent with a simple model of competition between chain compaction and increase of the crosslinks strength. Indeed, if the heating rate is much faster than this intrinsic restructuring time the chains, already fully entangled at low T, remain frozen in a network having the same topology but with very strong inter-chain bonds, forming a strong gel.

**Keywords:** physical gel, light scattering, microrheology

**Acknowledgements:** We acknowledge funding from the Italian Ministry for Education, University and Research (PRIN Project 2017Z55KCW, Soft Adaptive Networks)

## References

- [1] S. Buzzaccaro, V. Ruzzi, T. Faleo, and R. Piazza, *The Journal of Chemical Physics*, submitted.
- [2] R. Piazza, M. Campello, S. Buzzaccaro and F. Sciortino, *Macromolecules*, 2021, 54, 3897.

# Responsive polyacrylamide based core-shell microgel

*Thomas Hellweg*<sup>1</sup>

<sup>1</sup>*Physikalische und Biophysikalische Chemie, Universität Bielefeld,  
Universitätsstr. 25, 33615 Bielefeld, Germany*

Presenting author's e-mail: [thomas.hellweg@uni-bielefeld.de](mailto:thomas.hellweg@uni-bielefeld.de)

Since nearly 40 years so-called smart microgels are studied and the yearly number of published works on such systems exceeds 500. The most studied type of these colloidal gels is based on poly(N-isopropylacrylamide) (PNIPAM). However, recently also other acrylamides came into focus. All these microgels exhibit a so-called volume phase transition (VPT) at the lower critical solution temperature (LCST) of the respective polymer [1] leading to drastic changes in particle size.

This behavior grants them the adjective “smart” and makes them interesting as actuators or sensors in mesoscale devices or for drug delivery applications. The characteristics of microgels were reviewed recently [2]. The VPT can be rather fast. The determination of the response times of such colloidal gels by stroboscopic SANS will be presented in this talk (collaboration with Thomas Sottmann) [3]. The properties of such microgels can be varied in two ways. One is the use of comonomers e.g. to shift the LCST or to change the response with respect to pH and ionic strength. The second possibility is to change the architecture. The most prominent and most versatile example for this is the use of core shell systems [4].

The talk will focus on our contributions to the study of core-shell microgels. In this context, scattering experiments are of paramount importance and especially neutron scattering provides very important information about the internal structure of colloidal core-shell gels. This is related to the unique possibility to use contrast variation by employing deuterated monomers (collaboration with Julian Oberdisse) [5].

Moreover, also some recent dSTORM results for core-shell microgels will be presented which are in line with the SANS results [6].

**Keywords:** microgels, SANS, dSTORM

## References

- [1] S.Friesen, Hannappel, Y.; Kakorin, S. and Hellweg, T.; *Gels*, 2021, 7(2), 42.
- [2] M. Karg et al.; *Langmuir*, 2019, 35, 6231.
- [3] O. Wrede et al. *Scientific Reports*, 2018, 8, 13781.
- [4] I. Berndt et al.; *Langmuir*, 2006, 22, 459.
- [5] M. Cors, L. Wiehemeier, Y. Hertle, A. Feoktystov, F. Cousin, T. Hellweg, J. Oberdisse; *Langmuir*, 2018, 34 (50), 15403; M. Cors, L. Wiehemeier, O. Wrede, A. Feoktystov, F. Cousin, T. Hellweg, J. Oberdisse; *Soft Matter*, 2020, 16, 1922.
- [6] P. M. Otto, Bergmann, S., Sandmeyer, A., Dirksen, M., Wrede, O., Hellweg, T. and Huser, T. R.; *Nanoscale Adv.*, 2020, 2, 323. A. Name, B. Name and C. Name, *Journal Title*, 2000, 35, 3523.

# Shape and structural relaxation of colloidal liquid crystalline tactoids

*Hamed Almohammadi<sup>1</sup>, Sayyed Ahmad Khadem<sup>2,3</sup>, Massimo Bagnani<sup>1</sup>, Alejandro D. Rey<sup>2,3</sup>, Raffaele Mezzenga<sup>1,4</sup>*

<sup>1</sup>Department of Health Sciences and Technology, ETH Zurich, Zurich, Switzerland

<sup>2</sup>Department of Chemical Engineering, McGill University, Montreal, QC, Canada

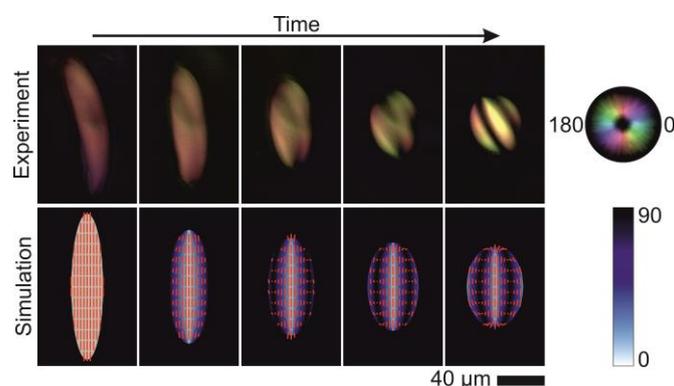
<sup>3</sup>Quebec Centre for Advanced Materials, Canada (QCAM/CQMF), Montreal, QC, Canada

<sup>4</sup>Department of Materials, ETH Zurich, Zurich, Switzerland

Presenting author's email: [hamed.almohammadi@hest.ethz.ch](mailto:hamed.almohammadi@hest.ethz.ch)

Facile geometric-structural response of liquid crystalline colloids to external applied fields [1] enables many technological advances to design novel functional materials. However, disentangling the dynamic behavior of the confining shape from its internal liquid crystalline structure is challenging, so that the relaxation mechanisms for liquid crystalline colloids under mobile boundaries remain still unexplored. In this work, by combining experiments, direct numerical simulations and theory, we describe the shape and structural relaxation of colloidal liquid crystalline micro-droplets, called tactoids, where amyloid fibrils and cellulose nanocrystals are used as model systems, Figure 1 [2]. We show that tactoids shape relaxation bears a universal single exponential decay signature, which is governed by liquid crystalline anisotropic and isotropic contributions. The tactoids structural relaxation shows fundamentally different paths, with first- and second-order exponential decays, depending on the existence of splay, bend and twist orientation structures in the ground state. We derive an analytic expression for the deformation of the liquid crystalline tactoids out of equilibrium and discuss the nature of the structural relaxation of tactoids and shape changes subjected to boundary motion. Our findings offer a comprehensive understanding on the confinement effects in liquid crystalline colloidal systems and may set unexplored directions in the development of technologies based on responsiveness of colloidal systems to external fields.

**Keywords:** Liquid Crystalline Colloids, colloidal Tactoids, Shape Relaxation, Structural Relaxation, Amyloid Fibrils, Cellulose Nanocrystals



**Figure 1.** Shape and director field relaxation of the cholesteric liquid crystalline tactoid.

## References

- [1] H. Almohammadi, M. Bagnani and R. Mezzenga, Nature Communications, 2020, 11, 5416.  
[2] H. Almohammadi, S. A. Khadem, M. Bagnani, A. Rey and R. Mezzenga, Nature Communications, 2022, 13, 2778.

## Hydrogen Dynamics in pHEMA Hydrogels – How Neutron Spectroscopy Can Help in Preserving Precious Artefacts and Designing New Drug Delivery Systems.

*Daria Noferini<sup>1,2</sup>, Antonio Faraone<sup>3</sup>, Marta Rossi<sup>2</sup>, Eugene Mamontov<sup>4</sup>, Piero Baglioni<sup>2</sup>, and Emiliano Fratini<sup>2</sup>*

<sup>1</sup>European Spallation Source ERIC P.O. Box 176, SE-221 00 Lund, Sweden. <sup>2</sup>Department of Chemistry “Ugo Schiff” and CSGI, University of Florence, Via della Lastruccia 3 – 50019 Sesto Fiorentino, Florence, Italy.

<sup>3</sup>NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899-6100, USA.

<sup>4</sup>Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA.

Presenting author’s e-mail: [daria.noferini@ess.eu](mailto:daria.noferini@ess.eu)

Hydrogels with optimal release and confining properties for drugs and detergents are highly relevant for medical and cultural heritage applications [1,2]. Notable examples are hydroxyethylmethacrylate (HEMA) based systems [3]. To optimize their delivery properties, a thorough comprehension of transport phenomena at the molecular level is highly desirable. To this end, we used quasielastic neutron scattering (QENS) with deuteration to investigate the dynamics of the polymer network and the transport properties of the water confined into the hydrogel matrix [4]. In particular, we focused on the effect of crosslinking nature (chemical or physical) and water content. Thanks to the peculiarities of thermal neutrons as a probe, QENS is a very powerful technique to study the dynamics of hydrogenated systems, in time and space ranging from pico- to tens of nanoseconds and from Ångstroms to nanometers, respectively.

The results on the polymer network show a distribution of relaxation processes, mainly related to the side-chains. Water dynamics was found to occur as a hydrogen-bond governed process with a jump-diffusion mechanism. The interaction with the polymer matrix considerably slows the water dynamics with respect to bulk water and water within other confining systems. It also leads to a fraction of water molecules that appear as immobile in the investigated timescale. With a higher hydration level, the mobility of both the water and polymer network increases. At the same water content, the physical gel polymer networks present slower relaxation processes and smaller explored space than their chemical gel equivalents. The water mobility is sensibly reduced in the chemical gels compared with physical gels in the less hydrated gels, whereas at higher hydration the values are similar but with shorter residence times in the chemical gels.

**Keywords:** hydrogels, neutron scattering, dynamics, QENS

### References

- [1] T. R. R. Singh, G. Laverty and R. Donnelly, *Hydrogels: Design, Synthesis and Application in Drug Delivery and Regenerative Medicine*, 2017, CRC Press, Boca Raton, USA.
- [2] P. Baglioni, E. Carretti and D. Chelazzi, *Nat. Nanotechnol.*, 2015, 10, 287.
- [3] O. Wichterle, D. Lím, *Nature*, 1960, 185, 117.
- [4] D. Noferini, A. Faraone, M. Rossi, E. Mamontov, E. Fratini and P. Baglioni, *J. Phys. Chem. C*, 2019, 123, 19183.

# The importance of charges in the Volume Phase Transition of PNIPAm Microgels.

*Rajam Elancheliyan*<sup>1</sup>, *Giovanni Del Monte*<sup>2,3</sup>, *Edouard Chauveau*<sup>1</sup>, *Simona Sennato*<sup>2,3</sup>,  
*Emanuela Zaccarelli*<sup>2</sup> and *Domenico Truzzolillo*<sup>1</sup>

<sup>1</sup>Laboratoire Charles Coulomb, UMR 5221, CNRS-Université de Montpellier, F-3409 Montpellier, France

<sup>2</sup>Department of Physics, Sapienza University of Rome, 00185 Rome, Italy

<sup>3</sup>National Research Council-Institute for Complex Systems (CNR-ISC), Sapienza University of Rome, 00185 Rome, Italy

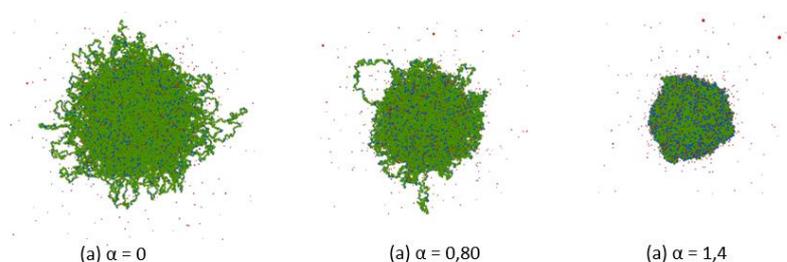
Presenting author's e-mail: [rajam.elancheliyan@umontpellier.fr](mailto:rajam.elancheliyan@umontpellier.fr)

Stimuli responsive microgels are of steadily growing interest due to the plethora of potential applications involving them, ranging from drug-delivery [1] to thermoresponsive sensors [2]. Among them, PNIPAm microgels have the peculiarity of being subjected to a Volume Phase Transition (VPT) close to ambient temperature [3] and they are widely employed for fundamental research purposes. Despite of that, the modifications of their internal structure due to the VPT are not completely understood, especially when it comes to the role of electrostatics [3].

In this study we show, both experimentally and via simulations which are the effects of electrostatic interactions on the PNIPAm microgel deswelling process. In experiments electrostatic charges were mainly introduced into the microgels by embedding acrylic acid co-monomers during the synthesis. Microgel deswelling at varying content of acrylic acid, ranging from 0% to 5% in molar ratio, was studied by means of viscosimetry, static and dynamic light scattering, and electrophoresis. Our study evidences that the addition of acrylate co-monomers not only tends to increase the microgel mass and suppresses the VPT, shifting progressively the microgel collapse to higher temperatures, but also enhances largely the two-step deswelling of the crosslinked networks, with the inner core of the microgels collapsing at lower temperatures than the outer corona.

Numerical simulations performed using a coarse-grained bead-spring model [4] confirm this scenario and point out the impact of the charge distribution within the microgels on the two-step deswelling. Our work shows unambiguously how electrostatic interactions rule the VPT of PNIPAm-based microgels.

**Keywords:** Microgels, PNIPAm-co-AAc, volume phase transition



**Figure 1.** Simulation snapshots of a microgel as a function of its solvophobicity; green spheres represent neutral beads, while blue and red ones represent charged beads and counterions, respectively.

## References

- [1] M.J. Serpe, et al, *Biomacromolecules*, 2005, 6(1), 408-413,
- [2] M.R. Islam, et al, *Sensors*, 2014, 14(5), 8984-8995,
- [3] G. Del Monte, et al, *Proceedings of National Academy of Science*, 2021, 118, 37,
- [4] G.S. Grest, K. Kremer, *Physical Review A*, 1986, 33, 3628.

## “Watching” the Formation of Multiblock Copolymers With up to 10 Blocks: Sequences, Morphology, Mechanical Properties

Holger Frey<sup>\*,1</sup>, Axel H. E. Müller<sup>1</sup>, George Floudas<sup>2</sup>, Markus Gallei<sup>3</sup>, Marvin Steube<sup>1</sup>, Tobias Johann<sup>1</sup>, Eduard Grune<sup>1</sup>, Ramona Barent<sup>1</sup>

<sup>1</sup>Department of Chemistry, Johannes Gutenberg University Mainz, D-55099 Mainz

<sup>2</sup>Department of Physics, University of Ioannina, 451 10 Ioannina, Greece

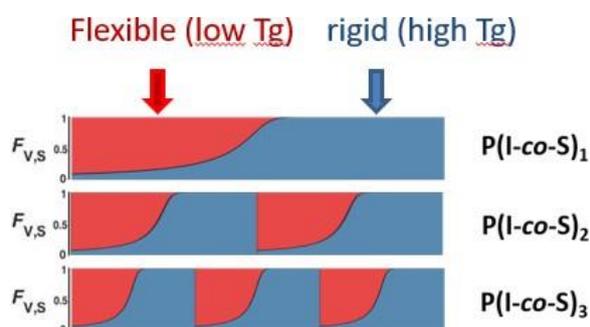
<sup>3</sup>Faculty of Natural Sciences & Technology, Saarland University, D-66123 Saarbrücken

Presenting author's e-mail: [hfrey@uni-mainz.de](mailto:hfrey@uni-mainz.de)

Highly defined multiblock copolymers with 10 (or more) blocks<sup>1</sup> can be obtained by anionic copolymerization of styrene with diene monomers, such as isoprene, myrcene or farnesene, resulting in high molecular weights up to 10<sup>6</sup> g/mol and dispersities  $M_w/M_n$  below 1.15 (commonly <1.1).<sup>2</sup> The multiblock structure can be achieved by repeated statistical copolymerization of styrene/diene mixtures (see figure below), resulting in multiple tapered segments or by alternating, sequential addition of the respective monomers in cyclohexane. This one-pot preparation route requires detailed understanding of the copolymerization kinetics. We have developed *in-situ* monitoring of the chain growth directly by online NMR techniques as well as online NIR (Near Infrared Spectroscopy) methods.

The resulting multiblock copolymers with multiple segments of different flexibility are attractive materials, if the blocks are microphase-segregated. It is obvious that this requires sufficient  $cN$  and consequently rather high degrees of polymerization of the segments within the multiblock chains. Polymers show domain bridging and represent an interesting class of thermoplastic elastomers. It is an intriguing question, which block number leads to highest toughness for such materials. Using SAXS and TEM, relationships between block number, morphology and mechanical properties have been derived.<sup>3</sup> The resulting multiblock copolymers have been routinely prepared on 100g scale. In recent follow-up works, the use of bio-based terpene monomer structures, such as myrcene and farnesene has been investigated, resulting in novel thermoplastic elastomer materials that rely on bio-based monomers.

**Keywords:** multiblock copolymer, copolymerization, thermoplastic elastomer, morphology, biobased



**Figure 1.** Tapered diblock, tetrablock and hexablock copolymers, based on repeated statistical copolymerization of styrene and isoprene (50/50) in cyclohexane (one-pot procedure, 100g scale).

### References

- [1] M. Steube, T. Johann, E. Galanos, M. Appold, C. Rüttiger, M. Mezger, M. Gallei, A. H. E. Müller, G. Floudas, H. Frey, *Macromolecules* **2018**, *51*, 10246.
- [2] C. Wahlen, J. Blankenburg, P. v. Tiedemann, J. Ewald, P. Sajkiewicz, A. H. E. Müller, G. Floudas, and H. Frey, *Macromolecules* **2020**, *53*, 1039.
- [3] Rational Design of Tapered Multiblock Copolymers for Thermoplastic Elastomers. M. Steube, T. Johann, R. D. Barent, A. H. E. Müller, H. Frey, *Prog. Polym. Sci.* **2022**, *124*, 101488.

## Self-Assembly of Thermo-Responsive BAB\* Copolymers and their Functioning as Rheological Modifiers

*Michael Gradzielski*<sup>1</sup>, *Albert Prause*<sup>1</sup>, *Michelle Hechenbichler*<sup>2</sup>, *Artem Feoktystov*<sup>3</sup>, and *André Laschewsky*<sup>2</sup> (12pt Georgia, Italics)

<sup>1</sup>Department of Chemistry, Technische Universität Berlin, 10623 Berlin, Germany

<sup>2</sup>Department of Chemistry, Universität Potsdam, 14476 Potsdam, Germany

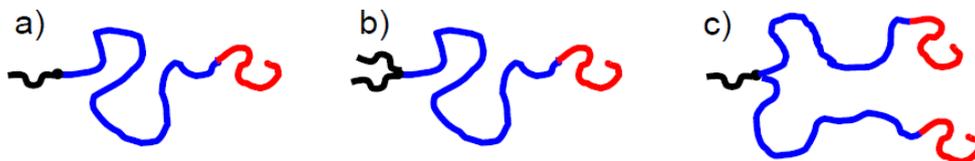
<sup>3</sup>Jülich Centre for Neutron Science (JCNS), 85748 Garching, Germany

Presenting author's e-mail: [michael.gradzielski@tu-berlin.de](mailto:michael.gradzielski@tu-berlin.de)

Amphiphilic copolymers typically self-assemble in aqueous solution. This tendency and the structures formed will strongly depend on the copolymer architecture and the amphiphilic nature of the copolymer. Particularly interesting are copolymers with temperature-responsive blocks, for instance lower critical solution temperature (LCST) blocks that become more hydrophobic with increasing temperature. In our work we synthesised different architectures, depicted in Fig. 1, with a permanently hydrophobic part B, a hydrophilic block A, and an LCST block B\*. For B a dodecyl chain was used, for A poly(N,N dimethylacrylamide, pDMAm), and for B\* the LCST polymers poly(N- isopropylacrylamide, pNiPAm), poly(N-propylacrylamide, pNPAm), and poly(N,N-diethylacryl- amide, pDEAm), which are type I or II LCST polymers and their length was varied systematically. The synthesis was done by RAFT polymerisation leading to well-defined copolymers. [1]

Their assembly behaviour in aqueous solution was studied for various concentrations and in the temperature range of 20-60 °C. The structural characterisation was done by means of static and dynamic light scattering (SLS, DLS), fluorescence measurements, and complementary small-angle neutron scattering (SANS). It is observed that the structure of the formed aggregates depends markedly on the molecular architecture of the amphiphilic copolymers and can be tuned largely via the LCST block. For longer LCST blocks the formation of highly ordered structures is observed above the LCST. The rheological characterisation shows that for sufficiently long LCST blocks interconnection of aggregates takes place which leads to an increased viscosity, where the rheological behaviour can be clearly linked to the structural picture seen by the scattering experiments. In further experiments the same copolymers were employed for controlling the viscosity of microemulsion droplet solutions as a function of temperature. In summary, the studied BAB\* copolymers are an interesting way to exert control over the rheological properties of surfactant formulations with an integrated temperature response.

**Keywords:** amphiphilic copolymers, self-assembly, rheology, SANS, light scattering



**Figure 1.** Examples of different copolymer architectures of BAB\* type with permanently hydrophobic part (black), permanently hydrophilic part (blue), and LCST block (red).

**Acknowledgements:** This work was funded by the DFG as project GR1030/22-1.

### References

[1] M. Hechenbichler, A. Laschewsky, M. Gradzielski, *Colloid Polym. Sci.* 2021, 299, 205.

# Helfrich-Hurault-like undulations in cholesteric liquid crystals induced by anchoring transitions

Maxim O. Lavrentovich<sup>1</sup> and Lisa Tran<sup>2</sup>

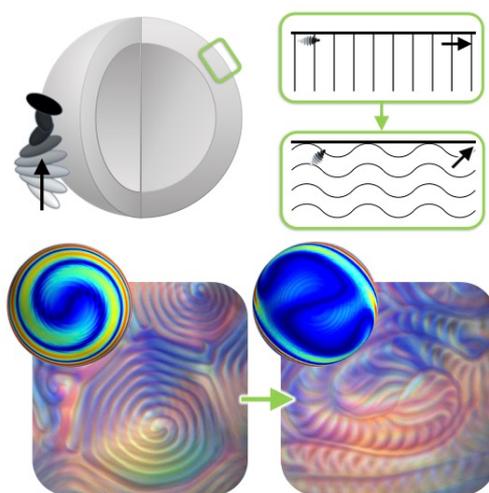
<sup>1</sup> Department of Physics & Astronomy, University of Tennessee, Knoxville, TN, USA

<sup>2</sup> Department of Physics, Soft Condensed Matter & Biophysics, Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, Netherlands

Presenting author's e-mail: [l.tran@uu.nl](mailto:l.tran@uu.nl)

Cholesteric liquid crystals (CLCs) have a characteristic length scale given by the pitch of the twisted stacking of their constituent rod-like molecules. Under homeotropic anchoring conditions where the molecules prefer to orient perpendicular to an interface, cholesteric interfaces exhibit striped phases with stripe widths commensurate with the pitch. Conversely, planar anchoring conditions have the molecules remain in the plane of the interface so that the CLC twists perpendicular to it. Varying the anchoring conditions dramatically rearranges the CLC patterning. We show with experiments and numerical simulations that the stripe patterns undergo an undulation instability when we transition from homeotropic to planar anchoring conditions and vice versa. The undulation can be interpreted as a transient relaxation of the CLC resulting from a strain in the cholesteric layers due to a tilting pitch axis, with properties analogous to the classic Helfrich-Hurault instability [1]. We focus on CLC shells in particular and show that the spherical topology of the shell also plays an important role in shaping the undulations. We end by highlighting that the Helfrich-Hurault mechanism is a generic and often overlooked mode of pattern formation for periodic materials subject to strain [2].

**Keywords:** liquid crystals, anchoring, pattern formation, topological defects



**Figure 1.** Figure 1 – Patterns on a CLC shell undergo an undulatory instability due to changes in the anchoring condition (Top – schematic, Bottom – cross-polarized micrographs, Insets – simulations).

**Acknowledgements:** M.O.L. gratefully acknowledges partial funding from the Neutron Sciences Directorate (Oak Ridge National Laboratory), sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences. L.T. acknowledges support from the Simons Society of Fellows of the Simons Foundation and from the Marie Curie Individual Fellowship project EXCHANGE\_inLCs (Grant No. 892354).

## References

- [1] M.O. Lavrentovich, L. Tran, Phys. Rev. Research, 2, 2, 023128 (2020).  
[2] C. Blanc, et al., arXiv, preprint arXiv:2109.14668 (2021).

# Polymeric surfactant P84/polyoxometalate $\alpha$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> - A model system to investigate the interplay between chaotropic and hydrophobic effects

Philipp Schmid<sup>1,2</sup>, Olivier Diat<sup>1</sup>, Arno Pfitzner, Pierre Bauduin<sup>1</sup>

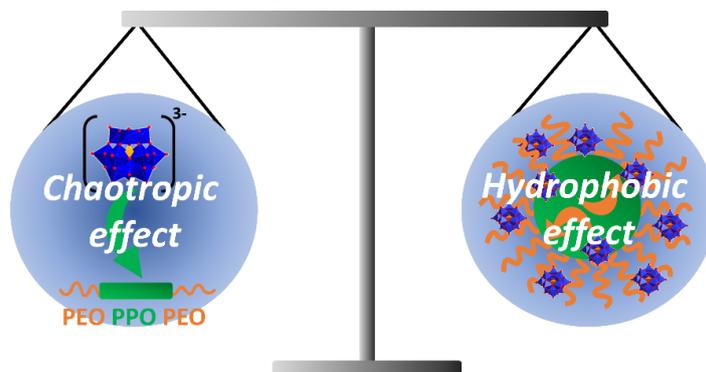
<sup>1</sup> ICSM, CEA, CNRS, ENSCM, Univ Montpellier Marcoule (France)

<sup>2</sup> Institute of Inorganic Chemistry, University of Regensburg (Germany)

Presenting author's e-mail: [pierre.bauduin@cea.fr](mailto:pierre.bauduin@cea.fr)

In the recent years, inorganic ions with a nanometric size and low charge density were shown to bind strongly to neutral hydrated organic matter in aqueous solution.[1] This phenomenon, called the (super-)chaotropic effect, arises from the partial dehydration of both, the nano-ion and the hydrated organic solute, leading to a high gain in enthalpy. Here, we investigate the chaotropic effect of the polyoxometalate (POM)  $\alpha$ -PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> on the polyethoxylated/polypropoxylated triblock copolymer P84: (EO)<sub>19</sub>(PO)<sub>43</sub>(EO)<sub>19</sub>. [2] The combination of phase diagrams, NMR and scattering techniques (SAXS/SANS) reveals that (i) below the micellization temperature of P84, PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> exclusively binds to the propylene oxide moiety of P84 unimers and (ii) above the micellization temperature, PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> mostly adsorbs on the ethylene oxide micellar corona. The preferential binding of the PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> to the PPO chain over the PEO chains suggests that the binding is driven by the chaotropic effect and reinforced by the hydrophobic effect. At higher temperatures, the copolymer micellization leads to the displacement of PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> from the PPO chain to the PEO chains. This study deepens the understanding of the subtle interplay between the chaotropic and the hydrophobic effect in complex salt-organic matter solutions and on self-assembly. The effect of polyoxometalates on other polymers[3] and on shorter amphiphilic (solvent-like PPO) molecules[4] will also be discussed.

**Keywords:** specific ion effect, chaotrope, polymers



**Figure 1.** It must not exceed the limit of 17cm wide. Do not wrap the text around any of the graphics.

## References

- [1] (a) Naskar, B.; Diat, O.; Nardello-Rataj, V.; Bauduin, P., *J. Phys. Chem. C* 2015, 119 (36), 20985. (b) Assaf, K. I.; Nau, W. M., *Angew. Chemie Inter; Ed.* 2018, 57 (43), 13968. (c) Hohenschutz, M.; Grillo, I.; Diat, O.; Bauduin, P., *Angew. Chemie Inter. Ed.* 2020, 59 (21), 8084.
- [2] Schmid, P.; Graß, X.; Bahadur, P.; Grillo, I.; Diat, O.; Pfitzner, A.; Bauduin, P., *Coll. and Interfaces* 2022, 6 (1), 16.
- [3] (a) Buchecker, T.; Le Goff, X.; Naskar, B.; Pfitzner, A.; Diat, O.; Bauduin, P., *Chem. A Eur. J.* 2017, 23 (35), 8434. (b) Buchecker, T.; Schmid, P.; Grillo, I.; Prévost, S.; Drechsler, M.; Diat, O.; Pfitzner, A.; Bauduin, P., *J. Am. Chem. Soc.* 2019.
- [4] Schmid, P.; Buchecker, T.; Khoshsim, A.; Touraud, D.; Diat, O.; Kunz, W.; Pfitzner, A.; Bauduin, P., *J. Coll. Int. Sci.* 2021, 587, 347-357.

# Uncovering Log Jamming in Semidilute Suspensions of Quasi-Ideal Rods

*Pavlik Lettinga<sup>1,2</sup>, Sergey Abakumov<sup>3</sup>*

<sup>1</sup>IBI-4, Forschungszentrum Jülich, Germany

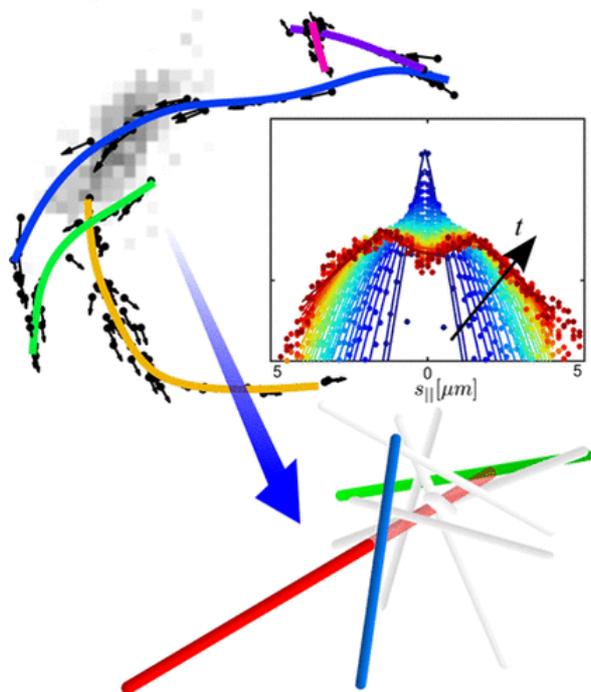
<sup>2</sup>Laboratory for Soft Matter and Biophysics, KU Leuven, B-3001 Leuven, Belgium

<sup>3</sup>Laboratory for Molecular Imaging and Photonics, KU Leuven, B-3001 Leuven, Belgium

Presenting author's e-mail: [p.lettinga@fz-juelich.de](mailto:p.lettinga@fz-juelich.de)

Video microscopy of fluorescently labeled semiflexible, slender, monodisperse colloidal rods in a host dispersion of unlabeled rods reveals a complex skating-type motion. Trajectories of single rods consist of a zig-zag sequence of paths where rods move within a tube set up by the surrounding rods. We show that head-on collisions within the tube affect the dynamics in a fundamental way, leading to a unique anomalous splitting of the distribution of particle displacements. Based on this log jamming process and relatively weak tube confinement, we propose an improved coupling relation between the parallel and perpendicular motion of individual rods within a tube.

**Keywords:** isotropic, anomalous diffusion, rod-like virus



**Figure 1.** Following the trajectory of a rod in the isotropic phase, resulting in anomalous self-van Hove functions

## References

[1] S. Abakumov, O. Deschaume, C. Bartic, C. Lang, O. Korculanin, J.K.G. Dhont, M.P. Lettinga, *Macromolecules*, 2021, 54, 9609-9617.

## Mesoscopic Modeling of Highly-Ordered Polymer Sanidics and Comparison with Scattering Data

Emma Wood <sup>1</sup>, Cristina Greco <sup>1</sup>, Dimitri Ivanov <sup>2,3</sup>, Kurt Kremer <sup>1</sup> and Kostas Daoulas <sup>1</sup>

<sup>1</sup>Max Planck Institute for Polymer Research, Mainz 55128, Germany

<sup>2</sup>Sirius University of Science and Technology, Sochi 354340, Russian Federation

<sup>3</sup>Institut de Sciences des Matériaux de Mulhouse, CNRS, Mulhouse 68057, France

Presenting author's e-mail: [daoulas@mpip-mainz.mpg.de](mailto:daoulas@mpip-mainz.mpg.de)

Functional polymers frequently have board-like shapes due to “flat”, e.g. aromatic, backbones with attached side chains. This shape favors ordering into sanidic mesophases — assemblies of parallel lamellae of stacked backbones, separated by disordered side-chains. Sanidic mesophases vary significantly [1] with respect to polymer order inside their lamellae and are interesting for two reasons. First, they can be technologically useful; for instance, as processing intermediates for manipulating solid-state morphologies of semiconducting polymers. Second, the most ordered sanidics bare similarities to crystals. Therefore, their mesoscopic simulations can offer insights into the properties of (semi)crystalline materials on application-relevant length scales. Such “extrapolative” studies are necessary, because the “genuine” crystalline state is highly sensitive to microscopic details and is therefore challenging to obtain using mesoscopic models.

We develop [2] a generic model of board-like polymers that enables simulations of the most ordered sanidic mesophase  $\Sigma_r$ . We describe polymers by generic hindered-rotation chains and use soft anisotropic non-bonded potentials [3] to represent board-like monomer shapes. In contrast to other generic potentials, such as soft Gay-Berne interactions, our potentials are simple tensorial expressions constructed using straightforward arguments of symmetry.

Using Monte Carlo simulations, we demonstrate that our lamellar mesophase indeed has all basic hallmarks of  $\Sigma_r$  order: within each lamella, polymers are periodically stacked and mutually registered along their backbones. Furthermore, chain positions across different lamellae are correlated. These generic features are robust with respect to variations of model parameters.

The generic character of our model enables us to compare [2] the molecular arrangement in our mesophase with experimental findings in two different polymers: polyesters [1] and polypeptoids [4]. For this purpose we use scattering patterns. Most of the structural features observed in experiments are present in our model. However, our mesophase is closer to the crystalline state because of interlamellar correlations.

**Keywords:** functional polymers, partial order, sanidic liquid crystals, molecular simulations

**Acknowledgements:** We are grateful to Douglas Greer and Ronald Zuckermann for providing the polypeptoid scattering data and useful discussions.

### References

- [1] M. Ebert, O. Herrmann-Schönherr, J. Wendorff, H. Ringsdorf and P. Tschirner, *Liq. Cryst.*, 1990, 7, 63.
- [2] E. Wood, C. Greco, D. Ivanov, K. Kremer and K. Daoulas, *J. Phys. Chem. B*, 2022, 126, 2285.
- [3] C. Greco, A. Melnyk, K. Kremer, D. Andrienko and K. Daoulas, *Macromolecules*, 2019, 52, 968.
- [4] D. Greer, M. Stolberg, S. Xuan, X. Jiang, N. Balsara and R. Zuckermann, *Macromolecules*, 2018, 51, 9519.

## Green synthesis of thin poly(cyanoacrylate) films: patterned coatings, liquid packaging, and gas encapsulation

Manos Anyfantakis<sup>1</sup>, Venkata Jampani<sup>2</sup>, Miha Skarabot<sup>2</sup>, Urban Mur<sup>3</sup>, Miha Ravnik<sup>3</sup>, Ulrich Jonas<sup>4</sup> & Jan Lagerwall<sup>1</sup>

<sup>1</sup>Department of Physics & Materials Science, University of Luxembourg, Luxembourg City, Luxembourg

<sup>2</sup>Condensed Matter Physics Department, Jožef Stefan Institute, Ljubljana, Slovenia

<sup>3</sup>Faculty of Mathematics & Physics, University of Ljubljana, Ljubljana, Slovenia

<sup>4</sup>Department of Chemistry & Biology, University of Siegen, Siegen, Germany

Presenting author's e-mail: [anyfas.com@gmail.com](mailto:anyfas.com@gmail.com)

Thin polymer films are indispensable elements in numerous applications, from coatings to sensing technologies. Their production is typically based on either wet chemistry relying on organic solvents, or chemical vapor deposition involving low pressure and/or high temperature, and elaborate equipment. Here, we discuss a new concept comprising a minimal system and a green method to produce thin films of cyanoacrylates, the main component of superglue and surgical adhesives.

Our system comprises water, ordinary surfactant and cyanoacrylate monomer. Upon exposure of the air-water interface to cyanoacrylate vapor, anionic polymerization is initiated by water. At the same time, water acts as a precipitation solvent for the polymer chains, confining their growth to the fluid interface. The surfactant role is to promote uniform growth, resulting in a homogeneous, thin poly(cyanoacrylate) film. Under appropriate conditions, centimeter-sized films with thickness variations less than 10 nm, are prepared. The thickness is precisely programmed by varying the reaction time; values of 50-500 nm are achieved in a timescale from a few minutes to one hour.

We showcase the application potential of this new technology for making and using thin polymer films on demand with three paradigms. First, by patterning the fluid interface shape and modulating the film thickness, we produce planar films of arbitrary size, shape, and color (arising from thin-film interference). Second, by applying the polymerization scheme to liquid entities of different forms, we demonstrate the *in-situ* packaging and manipulation of chemical and biological samples. Finally, by solidifying soap bubbles, we achieve the *in-situ* encapsulation and handling of various gases.

The unique advantages of this new concept are its simplicity, water-based nature, and its generic applicability to various cyanoacrylates and surfactants. These, in conjunction with the biodegradable and biocompatible nature of poly(cyanoacrylates) may open an avenue for a wide range of packaging, photonics, and biotechnology applications.

**Keywords:** thin polymer films, cyanoacrylate, surfactant, patterning, liquid packaging, gas encapsulation

**Acknowledgements:** M.A. acknowledges support by the Luxembourg National Research Fund (CORE CORELIGHT grant, C18/ MS/12701231).

# 'Dumbbell' polymer brushes: understanding the origins of non-monotonic structures

Edwin Johnson<sup>1</sup>, Josh Willott<sup>2</sup>, Isaac Gresham<sup>3</sup>, Hayden Robertson<sup>4</sup>,  
Timothy Murdoch<sup>2</sup>, Ben Humphreys<sup>2</sup>, Stuart Prescott<sup>3</sup>, Andrew Nelson<sup>5</sup>,  
Wiebe de Vos<sup>2</sup>, Grant Webber<sup>4</sup>, Erica Wanless<sup>4</sup>

<sup>1</sup>Department of Chemistry, University of Sheffield, UK

<sup>2</sup>Membrane Science and Technology, Mesa Institute for Nanotechnology, University of Twente, Netherlands

<sup>3</sup>School of Chemical Engineering, UNSW Sydney, Australia

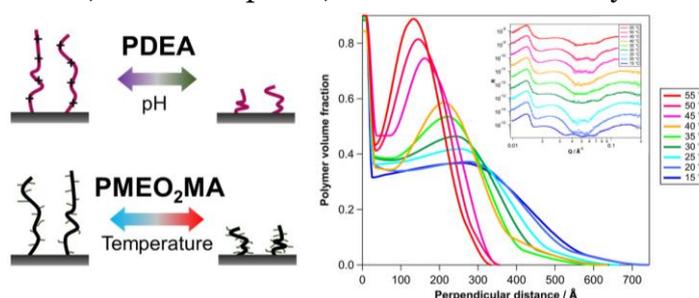
<sup>4</sup>College of Science, Engineering and Environment, University of Newcastle, Australia

<sup>5</sup>ANSTO, Lucas Heights, Australia

Presenting author's e-mail: [e.c.johnson@sheffield.ac.uk](mailto:e.c.johnson@sheffield.ac.uk)

Stimuli responsive polymer brushes offer the ability to modify interfacial properties such as wettability and lubricity as well as control biofouling. Surface-initiated ARGET ATRP has been utilised to synthesise pH and temperature responsive copolymer brushes which were subsequently characterised *in situ* with ellipsometry.[1,2] Neutron reflectometry (NR) revealed depletion regions in the polymer volume fraction profile (PVFP) near the silicon subphase resulting in 'dumbbell' like shaped PVFPs. There is no accepted mechanism through which depletion regions arise in brush conformations. Numerical self-consistent field theory was employed to investigate the role segment configuration along the polymer chain has on the conformation of copolymer brushes. Enrichment of charge segments near the interface was found to be responsible for the increased brush hydration in the depletion regions. Further, copolymer brush thermoresponsive behavior varied considerably in the presence of different salts. The nature of the effect of a given salt could be modulated with pH changes. Neutron reflectometry showed that salts had opposite effects on brush conformation at different distances from the surface, attributed to compositional gradients in the brush structure.[3] Understanding the origins of these unusual surface structures is important to develop relationships between surface structure and other interfacial properties.

**Keywords:** Polymer brushes, stimuli-response, neutron reflectometry



**Figure 1.** Cartoon of the composite homopolymers response to individual stimuli. Polymer volume fractions of a copolymer brush as measured by neutron reflectometry as a function of temperature with near surface depletion region.

## References

- [1] E. Johnson, J. Willott, W. De Vos, E. Wanless and G. Webber, *Langmuir*, 2020, 36, 5765
- [2] E. Johnson, J. Willott, I. Gresham, T. Murdoch, B. Humphreys, S. Prescott, A. Nelson, W. de Vos, G. Webber and E. Wanless, *Langmuir*, 2020, 36, 12460
- [3] E. Johnson, I. Gresham, S. Prescott, A. Nelson, E. Wanless and G. Webber, *Polymer*, 2021, 214, 123287.

## Modeling adsorption and stability of polymer coatings on heterogeneous surfaces

*Irene Adroher-Benítez<sup>1</sup>, Tatiana I. Morozova<sup>2</sup>, Nicolás A. García<sup>3</sup>, Jean-Louis Barrat<sup>1,2</sup>, Gustavo S. Luengo<sup>4</sup> and Fabien Léonforte<sup>4</sup>*

<sup>1</sup>Laboratoire Interdisciplinaire de Physique, UGA-CNRS, Grenoble, France.

<sup>2</sup>Institut Laue-Langevin, Grenoble, France.

<sup>3</sup>Instituto de Física del Sur, UNS-CONICET, Bahía Blanca, Argentina.

<sup>4</sup>L'Oréal Research and Innovation, Aulnay-Sous Bois, France

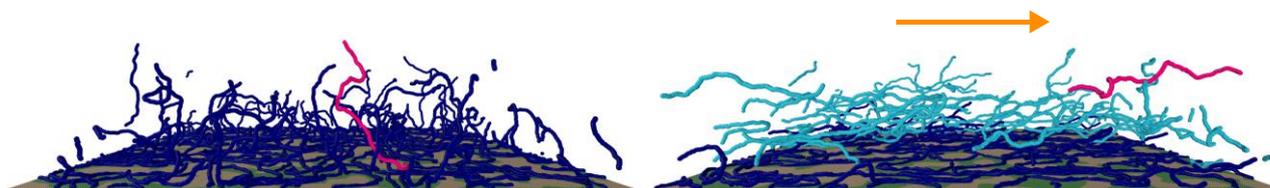
Presenting author's e-mail: [irene.adroher-benitez@univ-grenoble-alpes.fr](mailto:irene.adroher-benitez@univ-grenoble-alpes.fr)

Polymers play a main role in most cosmetic products. In the case of hair care, their cosmetic performance is determined by the way polymers adsorb in the hair surface, which is highly conditioned by the physico-chemical properties of its external structure. For some years now, cosmetic industry has been making a great effort to develop new sustainable products that have better performance and at the same time are truly respectful with the environment. However, despite the large amount of experimental work already done in this direction, it remains to be known which physical quantities play a determining role in polymer adsorption onto hair-like substrates, as well as in the stability of these polymeric coatings.

With this aim, we have analyzed the behavior of polymers of cosmetic interest in realistic surfaces, modeled from actual experimental images of human hair. In particular, in the work presented here we have prepared coarse-grained models for two different families of polymers. First, we have modeled semi-flexible linear chains in which each bead corresponds to a monomer. With this model we aim to study the performance of simple molecules of natural origin. Second, we have created a branched stiff polymer model with 17 beads per monomer. This more complex system is intended to mimic some of the macromolecules currently used in the cosmetic industry.

For these two models we have performed implicit-solvent Molecular Dynamics simulations to study the quantities involved in the polymer adsorption onto a heterogeneous surface. We have analyzed the structure of the resulting coating and compared the results for the two types of polymers. Then, we have used Brownian dynamics simulations to apply a linear shear flow on the adsorbed polymer layer. This way we have tested the stability of the coating and we have analyzed the dynamics of the polymer desorption.

**Keywords:** polymers, coatings, cosmetics, simulations



**Figure 1.** a) Adsorbed polymers on the substrate. b) The same polymer coating under a shear flow. Light blue colored chains have completely detached from the surface. Pink polymer is the same chain in both images.

### Reference

[1] Morozova, T. I.; García, N. A.; Barrat, J.-L.; Luengo, G. S.; Léonforte, F. Adsorption and desorption of polymers on bio-inspired chemically structured substrates. *ACS Applied Materials & Interfaces* **2021**, 13 (25), 30086–30097.

# Facile Control of Surfactant Packing and Adsorption Behavior

Rui A. Gonçalves<sup>1</sup>, Yeng Ming Lam<sup>1</sup>, and Björn Lindman<sup>1,2</sup>

<sup>1</sup>School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

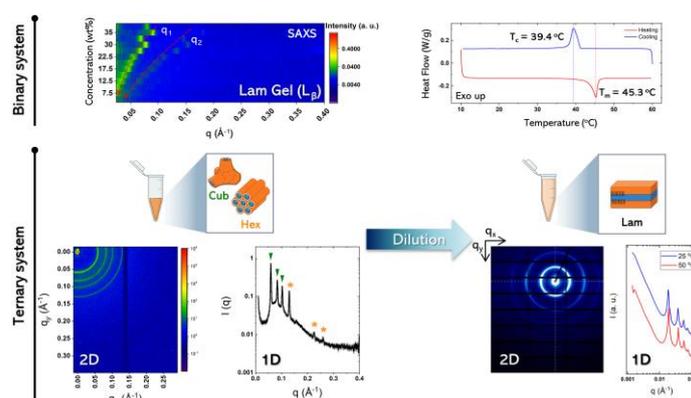
<sup>2</sup>Centre for Chemistry and Chemical Engineering, Department of Chemistry, Division of Physical Chemistry, Lund University, SE-221 00 Lund, Sweden

Presenting author's e-mail: [rui.goncalves@ntu.edu.sg](mailto:rui.goncalves@ntu.edu.sg)

Double-tailed amphiphiles, such as surfactants and lipids, have broad relevance in applications like consumer care and biology. In particular, the cationic dioctadecyldimethylammonium chloride surfactant is well known for its swelling potential [1]. This work investigates the effects of additives of different polarities on the lamellar gel (frozen-like) and liquid-crystalline (fluid-like) phases. Differential scanning calorimetry (DSC) allowed us to identify the gel-to-liquid crystalline phase transition temperature and determine the associated enthalpy. Laboratory-based and synchrotron small- and wide-angle X-ray scattering (SAXS/WAXS) enabled the identification of the self-assembled structures of the surfactant mixtures and to determine the extent of swelling with water of both phases, as well as the water channel dimensions for non-lamellar systems. In-situ null ellipsometry was employed to study the deposition and robustness of the surfactant mixtures on a hair-like model substrate.

The observations suggest a gel phase with unusually tilted and interdigitated alkyl chains. Small polar additives were found to have no significant effect on the phase stability, whereas fatty acids and fatty alcohols have strong effects but quite different depending on the non-polar domain [2-3]. Moreover, it was possible to obtain a fluid-like phase at a significantly lower temperature in the presence of an additive and achieve a frozen-like state by dilution. Hence, robust layers of at least one bilayer-thick were deposited onto the surface and shown to be irreversibly adsorbed due to poor surfactant solvency in water [4].

**Keywords:** double-tailed surfactants, lamellar gel, lamellar liquid crystalline, SAXS, ellipsometry.



**Figure 1.** Surfactant packing in various conditions.

## References

- [1] Marques, E. F., Regev, O., Khan, A., Lindman, B., *Advances in Colloid and Interface Science*, 2003, 100, 83.
- [2] Gonçalves, R. A., Lindman, B., Miguel, M. G., Iwata, T., Lam, Y. M., *Journal of Colloid and Interface Science*, 2018, 528, 400.
- [3] Gonçalves, R. A., Lam, Y. M., Lindman, B., *Molecules*, 2021, 26, 3946.
- [4] Gonçalves, R. A., Naidjonoka, P., Nylander, T., Miguel, M. G., Lindman, B., Lam, Y. M., *RSC Advances*, 2020, 10, 18025.

## Structure of a Comb Copolymer-Surfactant Coacervate Elucidated by DOSY NMR and Neutron Spin Echo Spectroscopy Measurements

*Miroslav Štěpánek<sup>1</sup>, Anastasiia Fanova<sup>1</sup>, Zdeněk Tošner<sup>2</sup>, Ingo Hoffmann<sup>3</sup> and Sylvain Prévost<sup>3</sup>*

<sup>1</sup>*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 8, 128 43 Prague 2, Czech Republic*

<sup>2</sup>*NMR Laboratory, Faculty of Science, Charles University, Hlavova 8, 128 43 Prague 2, Czech Republic*

<sup>3</sup>*Institut Max von Laue-Paul Langevin (ILL), 71 avenue des Martyrs, CS 20156, F-38042 Grenoble Cedex 9, France*

Presenting author's e-mail: [stepanek@natur.cuni.cz](mailto:stepanek@natur.cuni.cz)

In this communication, we report structure and dynamics of coacervate emulsion formed by electrostatic complexation of anionic comb polyelectrolyte poly[methacrylic acid-*stat*-poly(ethylene glycol) methyl ether methacrylate] (PMAA-PEGMA) and cationic surfactant *N*-dodecylpyridinium chloride (DPCl) [1]. The behavior of the PMAA-PEGMA/DPCl system was followed by a combination of diffusion ordered and nuclear Overhauser effect NMR spectroscopies (DOSY and NOESY NMR), small-angle neutron scattering (SANS) and neutron spin echo spectroscopy (NSE). The measurements were conducted for various charge ratios  $Z$  of the number of DPCl positive charges to the number of PMAA-PEGMA negative charges.

NMR spectra showed splitting of signals caused by partitioning of both PMAA-PEGMA and DPCl between the bulk aqueous phase and coacervate particles formed at  $Z > 0.7$ , with much slower diffusion of both polymer and surfactant in the coacervate phase. SANS measurements revealed formation of two types of DPCl micelles forming complex with PMAA-PEGMA in the system: (i) cylindrical micelles and (ii) densely packed spherical micelles. The difference in dynamics between two types of DPCl micelles was confirmed by NSE, showing that apparent diffusion coefficients,  $D_{app}(q)$ , in the high  $q$  region,  $1.1 - 2.0 \text{ nm}^{-1}$ , dominated by scattering from densely packed DPCl micelles were much lower (hydrodynamic radius,  $R_H > 10^2 \text{ nm}$ ) than those in the low  $q$  region,  $0.2 - 1.1 \text{ nm}^{-1}$ , dominated by scattering from cylindrical DPCl micelles ( $R_H$  of ca. 5 nm). NSE measurements confirmed that densely packed DPCl micelles were present in coacervate phase domains, while the scattering between  $0.2$  and  $1.1 \text{ nm}^{-1}$  originated from cylindrical DPCl micelles in the bulk solution.

This study thus demonstrates the usefulness of neutron spin echo spectroscopy and DOSY NMR as techniques for studying dynamics in the case when microheterogeneity of the investigated system makes interpretation of scattering data difficult.

**Keywords:** coacervate; polyelectrolyte-surfactant complex; phase domains; dynamics

**Acknowledgements:** Support from the Ministry of Education, Youth and Sports of the Czech Republic (Project No. CZ.02.1.01/0.0/0.0/15\_003/0000417-CUCAM) is gratefully acknowledged.

### References

[1] A. Fanova, M. Janata, S.K. Filippov, M. Šlouf, M. Netopilík, A. Mariani and M. Štěpánek, *Macromolecules*, 2019, 52, 6303.

## Electron Microscopy Study of Boron Nitride Nanotubes Processed into Macroscopic Fibers

*Asia Matatyaho Ya'akobi*<sup>1</sup>, *Cedric J. S. Ginestra*<sup>2</sup>, *Matteo Pasquali*<sup>2,3</sup>, *Yeshayahu Talmon*<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering and the Russell Berrie Nanotechnology Institute (RBNI), Technion-Israel Institute of Technology, Haifa 3200003, Israel

<sup>2</sup>Department of Chemical and Biomolecular Engineering, The Smalley-Curl Institute 6100 Main Street, MS 369, Houston, Texas 77005, United States

<sup>3</sup>Department of Chemistry, The Smalley-Curl Institute, Rice University, 6100 Main Street, MS 369, Houston, Texas 77005, United States

Presenting author's e-mail: [asiamati@campus.technion.ac.il](mailto:asiamati@campus.technion.ac.il)

The spontaneous molecular dissolution of boron nitride nanotubes (BNNTs) in superacid, e.g., chlorosulfonic acid (CSA), into stable solutions significantly facilitates their assembly into multifunctional macroscopic structures through liquid-phase processing. BNNT/superacid solutions can be thermodynamically described by Onsager and Flory theories of rigid-rod polymer solutions. At the appropriate concentrations, BNNTs exhibit lyotropic liquid crystallinity in solutions, and by that could contribute to achieve neat, highly ordered, and dense macroscopic fibers. Nevertheless, production of BNNT-based fibers is currently hindered by challenges in the mass production of high quality and high purity BNNTs.

BNNTs possess remarkable properties of high mechanical strength and stiffness, excellent thermal conductivity, and low density like carbon nanotubes (CNTs). However, they offer significantly higher thermal stability and oxidation resistance than CNTs, as well as a wide bandgap regardless of the tube diameter and chirality. Due to this unique feature combination, liquid-phase processing of BNNTs into multifunctional fibers is highly desirable. Furthermore, the analogy between CNTs and BNNTs suggests that such processing may be applicable for BNNTs as for CNTs. However, while the fabrication of CNT-based macroscopic assemblies is well advanced, fabrication of BNNT-based macroscopic structures have been rarely reported.

In this study, we use advanced electron microscopy techniques to study the BNNT/CSA system. First, we examine our starting material by room-temperature (RT) high-resolution (HR) transmission electron microscopy (TEM), and compare different batches for their purity, intrinsic properties, and defects. We investigate BNNTs interaction, dissolution, and phase behavior in CSA by cryogenic temperature TEM (cryo-TEM) and cryogenic temperature scanning electron microscopy (cryo-SEM). We show the first direct imaging evidence of the liquid crystalline phase in a BNNT/CSA system, as well as the first BNNTs-based fibers produced from such a system by the wet spinning method.

**Keywords:** Boron nitride nanotubes, chlorosulfonic acid, electron microscopy

Tuesday 6th September 2022

**Colloidal Systems in External Fields**

## External Fields for Assembly and Manipulation at Micro- and Macro- scales

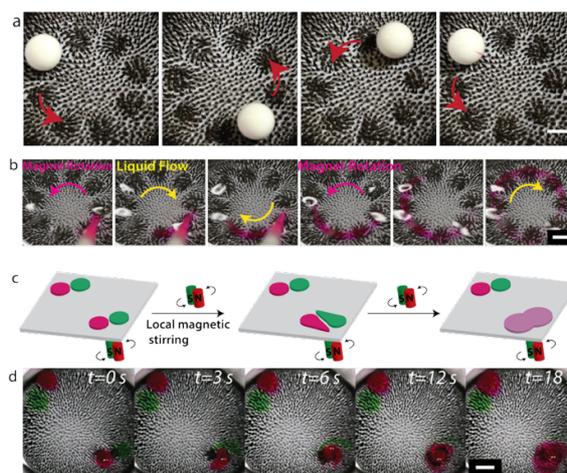
*Ahmet Faik Demirörs<sup>1</sup>*

<sup>1</sup>Complex Materials, Department of Materials, ETH Zurich, 8093 Zurich, Switzerland.

Presenting author's e-mail: [ahmet.demiroers@mat.ethz.ch](mailto:ahmet.demiroers@mat.ethz.ch)

External field gradients are commonly used for separation, contactless manipulation and assembly of nano- and microparticles. Here, we introduce a novel method to transport colloidal matter with the help of external electric and magnetic fields<sup>[1]</sup>. We further show that these principles can be combined with active propulsion to manufacture microrobots<sup>[2]</sup>. In addition, we extend the scale of manipulation with external fields to macro-scale by creating soft magnetic carpets via an easy self-assembly route based on the Rosensweig instability. These carpets can transport liquids, solid objects and droplets that are larger and heavier than the artificial cilia, using a crowd-surfing effect. This amphibious transportation is locally and reconfigurably tuneable by simple micromagnets or advanced programmable magnetic fields with a high degree of spatial resolution<sup>[3,4]</sup>. While our active carpets are generally applicable to integrated control systems for transport, mixing, and sorting, these effects could also be exploited for microfluidic viscosimetry and elastometry.

**Keywords:** Colloidal systems in External Fields, magnetic & electric fields, colloids, soft actuators



**Figure 1.** Soft magnetic carpets explored for the transport of a) solid spheres, b) liquids and functions such as spatially controlled mixing in a milli-fluidic chip.

### References

- [1] A. F. Demirörs, F. Eichenseher, M. J. Loessner, A. R. Studart, *Nat. Commun.* **2017**, *8*, 1872.
- [2] Y. Alapan, B. Yigit, O. Beker, A. F. Demirörs, M. Sitti, *Nat. Mater.* **2019**, *18*, 1244.
- [3] A. F. Demirörs, S. Aykut, S. Ganzeboom, Y. A. Meier, R. Hardeman, J. de Graaf, A. J. T. M. Mathijssen, E. Poloni, J. A. Carpenter, C. Ünlü, D. Zenhäusern, *Adv. Sci.* **2021**, *8*, 2102510.
- [4] A. F. Demirörs, S. Aykut, S. Ganzeboom, Y. A. Meier, E. Poloni, *Proc. Natl. Acad. Sci.* **2021**, *118*, DOI 10.1073/pnas.2111291118.

# Ferrofluidic aqueous two-phase system with ultralow interfacial tension and micro-pattern formation

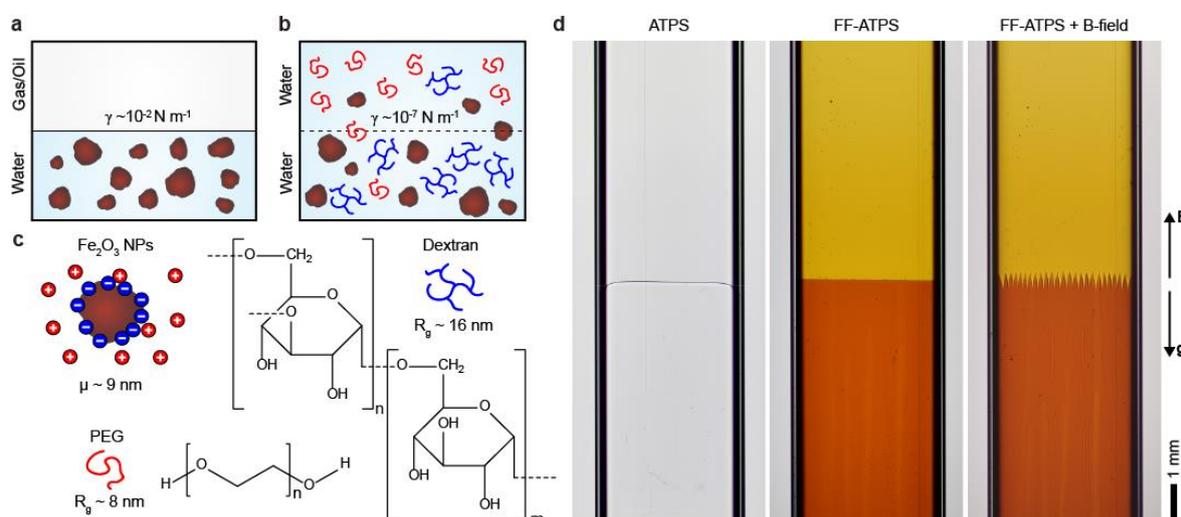
*Carlo Rigoni<sup>1</sup>, Grégory Beaune<sup>1</sup>, Bent Harnist<sup>1</sup>, Fereshteh Sorhrabi<sup>1</sup>, Jaakko V. I. Timonen<sup>1</sup>*

<sup>1</sup>Department of Applied Physics, Aalto University School of Science, Puumiehenkuja 2, 02150 Espoo, Finland

Presenting author's e-mail: [carlo.rigoni@aalto.fi](mailto:carlo.rigoni@aalto.fi)

Ferrofluids are magnetic liquids known for the patterns they form in external magnetic fields. Typically, the patterns form at the interface between a ferrofluid and another immiscible non-magnetic fluid with a large interfacial tension  $\gamma \sim 10^{-2} \text{ N m}^{-1}$ , leading to large pattern periodicities. In this presentation related to a recently accepted publication [1] we show that it is possible to reduce the interfacial tension several orders of magnitude down to ca.  $\gamma \sim 10^{-6} \text{ N m}^{-1}$  by using two immiscible water-based phases based on spontaneous phase separation of dextran (Dex-T500) and polyethylene glycol (PEG 35000) and the asymmetric partitioning of superparamagnetic maghemite nanoparticles into the dextran-rich phase. The system exhibits classic Rosensweig instability in uniform magnetic field with periodicity  $\sim 200 \mu\text{m}$ , significantly lower than in traditional systems ( $\sim 10 \text{ mm}$ ). This system paves the way towards the science of pattern formation at the limit of vanishing interfacial tension and ferrofluid applications driven by small external magnetic fields.

**Keywords:** ferrofluids, interfacial tension, pattern



**Figure 1.** Scheme and experimental realization of a ferrofluidic aqueous two-phase system (FF-ATPS). **a**, A scheme of a regular water-based ferrofluidic system. **b**, A scheme of the FF-ATPS. **c**, Components of the FF-ATPS system and structural formulas of PEG and dextran. **d**, Photographs of a standard PEG-dextran ATPS (left), a maghemite-PEG-dextran FF-ATPS (center) and the same maghemite-PEG-dextran FF-ATPS in a vertical magnetic field of 20.0 mT exhibiting a quasi-1D magnetic instability at the interface (right). All the three images correspond to samples in a glass capillary of thickness 200  $\mu\text{m}$ .

## References

[1] C. Rigoni et al., *Communication Materials*, 2022, accepted.

# Out-of-equilibrium multilamellar vesicles induced by shear flow

*Luigi Gentile<sup>1,2</sup>, Norman J. Wagner<sup>3</sup> and Ulf Olsson<sup>4</sup>*

<sup>1</sup> Department of Chemistry, University of Bari, Via Orabona 4, Bari 70126, Italy

<sup>2</sup> Center of Colloid and Surface Science (CSGI) Bari Unit, via della Lastruccia 3, SestoFiorentino 50019, Italy

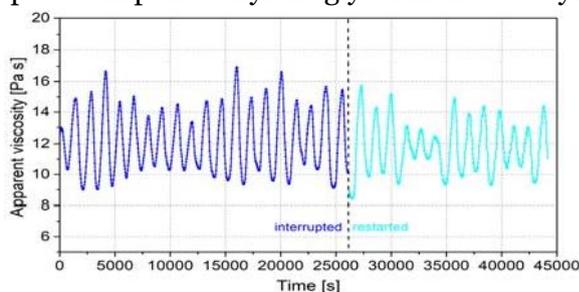
<sup>3</sup> Chemical & Biomolecular Engineering, University of Delaware, 150 Academy Street, Newark, Delaware 19716, USA

<sup>4</sup> Physical Chemistry Division, Kemicentrum, Lund University, Lund 221 00, Sweden

Presenting author's e-mail: [luigi.gentile@uniba.it](mailto:luigi.gentile@uniba.it)

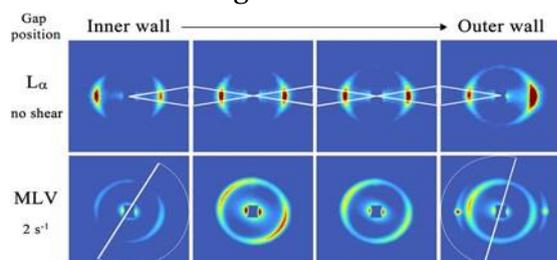
The bending rigidity of the surfactant bilayer is known to play a decisive role in controlling the elastic resistance to curvature of fluid membranes. The lamellar-to-multilamellar vesicles (MLVs) transition under shear flow is related to the low bending rigidity (in the order of  $1-10 k_B T$ ). The transition can be demonstrated by using rheo-small-angle light scattering (rheo-SALS) and rheo-small angle neutron scattering (rheo-SANS). The transition leads to an increase of the apparent bulk viscosity of almost an order of magnitude under a constant shear rate,  $\dot{\gamma}$ .

Surprising stable and regular viscosity oscillations during the lamellar-to-MLVs transition were reported and attributed to the volume fraction fluctuation of the coexisting MLVs and planar lamellae, in the tetraethylene glycol monohexadecyl ether,  $C_{16}E_4/D_2O$ , those oscillations were resilient to shear flow interruption (Fig. 1). [1] Moreover, a lamellar-to-MLVs-to-lamellar transition was reported in pentaethylene glycol monododecyl ether,  $C_{12}E_5/D_2O$  under constant shear rate. [2,3]



**Figure 1.** Evolution of the apparent viscosity at a shear rate of  $2 \text{ s}^{-1}$ . Flow interruption and restarting tests were carried out, during the experiment: no remarkable changes were observed in the viscosity oscillations.

The volume fraction time-fluctuation was detected by time-resolved flow-SANS experiments carried out using a *Couette* geometry in the radial beam configuration, i.e. probing the scattering in the velocity-vorticity (1-3) plane. Here a special-designed *Couette* geometry allowed observing the  $C_{16}E_4/D_2O$  system in the flow(x) and vorticity (z) directions of the neutron-scattered intensity determining a tilting angle of the lamellar layer and of the final vesicles main axis orientation. The *Couette* allows localizing the MLVs-lamellar coexistence at the outer wall of the geometry (Fig. 2).



**Figure 2.** 2D SANS pattern  $40^\circ \text{C}$  of the lamellar phase  $L_\alpha$  before applying shear flow deformation at the 4 gap positions and 2D SANS obtained averaging all time experiments for each position after the MLV formation and under constant shear flow of  $2 \text{ s}^{-1}$ .

Shear-induced MLVs are only kinetically stable after interruption of the external stimuli. However, certain boundary conditions lead to out-of-equilibrium even under constant shear flow.

**Keywords:** lamellar phase, vesicles, rheology, scattering, out-of-equilibrium, shear-induced

## References

- [1] L Gentile, BFB Silva, S Lages, K Mortensen, J Kohlbrecher, U Olsson *Soft Matter*, 2013, 9, 1133.
- [2] L Gentile, CO Rossi, U Olsson, GA Ranieri, *Langmuir*, 2011, 27, 2088.
- [3] L Gentile, MA Behrens, L Porcar, P Butler, NJ Wagner, U Olsson, *Langmuir*, 2014, 30, 8316.

## Shear-induced glass-to-crystal transition in anisotropic clay-like suspensions

Vincent Labalette <sup>1</sup>, Yannick Hallez<sup>1</sup>, Martine Meireles <sup>1</sup>, and Jeffrey F. Morris<sup>2</sup>

<sup>1</sup>Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, France

<sup>2</sup>Benjamin Levich Institute, City College of City University of New York, New York, USA

Presenting author's e-mail: [yannick.hallez@univ-tlse3.fr](mailto:yannick.hallez@univ-tlse3.fr)

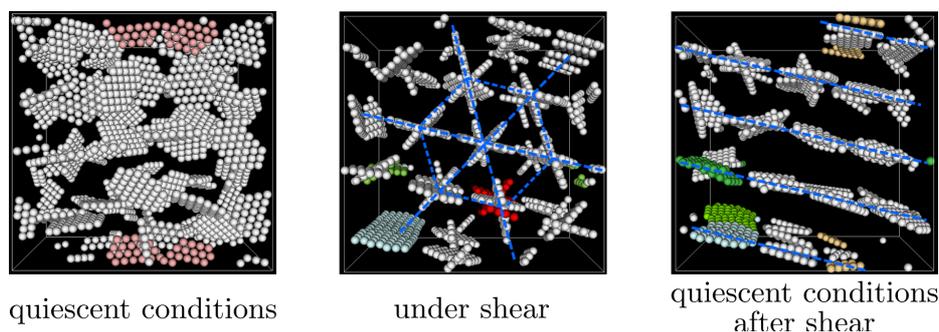
We report and elucidate a rarely observed glass-to-crystal transition happening upon flow cessation, after a period of shear, in a system of anisotropic clay-like colloids.

A new simulation strategy to study the structure evolution and mechanical response of anisotropically charged, plate-like colloids to a shear flow is first presented. Hydrodynamics are computed using an extension of Accelerated Stokesian Dynamics for anisotropic objects, and electrostatics are accounted for with a site model including charge renormalization.

We then briefly present the structures obtained in quiescent conditions as a function of volume fraction and salt concentration, and we confirm previous results obtained on clay-like systems with different numerical methods, in particular the existence of bonded or non-bonded glasses and different gel states.

The main results of this work concern the study of partial orientational and positional ordering of initially glassy suspensions by shear and the subsequent evolution towards a nematic crystal upon flow cessation. The mechanisms at play are elucidated by examining time-resolved statistical information on the structure, hydrodynamic stresses, and electrostatic stresses that develop as shear is started and stopped. Shear-induced partial ordering is made possible by the forced alignment of platelets upon shear startup, which unlocks translational degrees of freedom in the initially arrested state. Hexagonally packed strings of platelets are formed under shear, a structure sufficiently close to the crystal state for the latter to be reached after flow cessation. This mechanism involving a flow-induced weakening of the translation-orientation coupling could be actually quite generic for other suspensions of strongly anisotropic colloids interacting at long range.

**Keywords:** anisotropic colloids, shear, glass, crystal, Stokesian dynamics



**Figure 1.** Platelet suspension during a relaxation/shear/relaxation cycle.

### References

[1] V. Labalette, A. Praga, F. Girard, M. Meireles, Y. Hallez, and J.F. Morris, *Soft Matter*, 2021, 17(11), 3174-3190.

# The Yielding Transition in Soft Amorphous Solids Under Oscillatory Shear: From Microscopic Rearrangements to Macroscopic Failure.

Paolo Edera<sup>1</sup>, Matteo Brizioli<sup>1</sup>, Elie N'Gouamba<sup>2</sup>, Mahnoush Madani<sup>3</sup>, Philippe Coussot<sup>2</sup>, George Petekidis<sup>3</sup>, Fabio Giavazzi<sup>1</sup>, Roberto Cerbino<sup>4</sup>

<sup>1</sup>University of Milan, Italy

<sup>2</sup>Université Gustave Eiffel, France

<sup>3</sup>University of Crete, Greece

<sup>4</sup>University of Vienna, Austria

Presenting author's e-mail: [fabio.giavazzi@unimi.it](mailto:fabio.giavazzi@unimi.it)

Failure of materials under mechanical loading is a widespread phenomenon occurring at very different length scales ranging from the geological ones, as in earthquakes, down to molecular scale, as in the case of fractures occurring in nanomaterials. While the mechanisms leading to failure in crystalline solids are quite well understood and have well-identified structural features [1], a unified picture of the microscopic events leading to yielding in amorphous solids is still missing. In this context, soft materials such as dense colloidal suspensions, concentrated emulsions, clays, or foams, which promptly deform and eventually flow when subject even to relatively small loads, represent a very convenient model system to investigate the mechanical failure and the onset of plasticity in amorphous solids [2].

In this work, we exploit a custom shear-cell coupled to a bright-field microscope to probe the shear-induced dynamics of embedded colloidal tracers in different yield stress materials (polymeric gels and emulsions) when subjected to oscillatory shear deformations. By devising a new acquisition protocol and image analysis scheme [3-4], we are able to accurately monitor shear-induced structural rearrangements within the material, while simultaneously measuring its rheological response.

We find that rare, intermittent, and spatially heterogeneous rearrangement events start occurring in the material even when it is subject to very small amplitude perturbations, well below the threshold of macroscopic yielding. By increasing the amplitude of the perturbation, the structural rearrangement activity becomes more spatially homogeneous and undergoes a dramatic speed-up when approaching the yielding transition. This corresponds to an explosive increase in the mobility of the tracer particles, which display an affective Fickian diffusion with markedly non-Gaussian distribution of displacements, in particular across the yield point.

Our results, by establishing a firm connection between macroscopic non-linear mechanical response and microscopic shear-induced dynamics, represent a promising step forward in the understanding of the yielding transition and support its interpretation in terms of underlying non-equilibrium phase transition [5].

**Keywords:** yielding transition, amorphous solids, non-linear rheology, emulsion

## References

- [1] L.B. Chen *et al.*, Physical Review Letters, 1992, 69(4), 688.
- [2] D. Bonn *et al.*, Reviews of Modern Physics, 2017, 89(3), 035005.
- [3] R. Cerbino and V. Trappe, Physical Review Letters, 2008, 100(18), 188102.
- [4] P. Edera *et al.*, Soft Matter, 2021, 17(37), 8553.
- [5] A.J. Liu and S.R. Nagel, Nature, 1998, 396, 21-22.

## Yielding in Amorphous Solids: an Interparticle Force Determination

*A. Mauleon-Amieva*<sup>1</sup>, *R. Cheng*<sup>1</sup>, *K. Thijssen*<sup>2,3</sup>, *T. B. Liverpool*<sup>4</sup>, *M. Faers*<sup>5</sup>, *R. L. Jack*<sup>2,3</sup>,  
and *C. P. Royall*<sup>6,7,1</sup>

<sup>1</sup> *HH Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, United Kingdom*

<sup>2</sup> *Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom*

<sup>3</sup> *Department of Applied Mathematics and Theoretical Physics, University of Cambridge, Cambridge CB3 0WA, United Kingdom*

<sup>4</sup> *School of Mathematics, University of Bristol, Bristol BS8 1UG, United Kingdom*

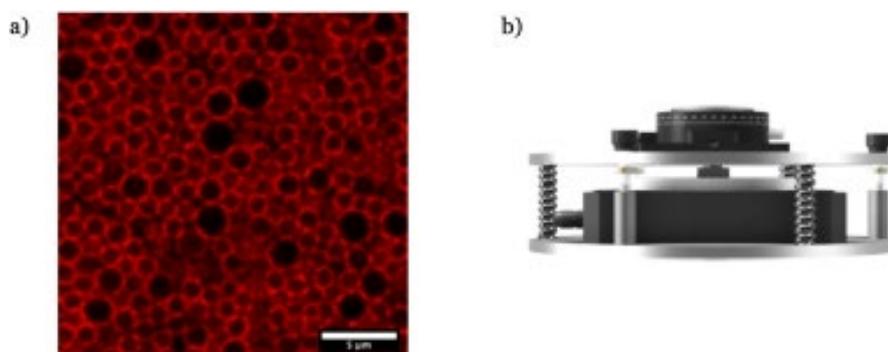
<sup>5</sup> *Bayer CropScience AG, 40789 Monheim am Rhein, Germany*

<sup>6</sup> *Gulliver UMR CNRS 7083, ESPCI Paris, Université PSL, 75005 Paris, France*

<sup>7</sup> *School of Chemistry, Cantock's Close, University of Bristol, BS8 1TS, United Kingdom*

Presenting author's e-mail: [a.mauleonamieva@bristol.ac.uk](mailto:a.mauleonamieva@bristol.ac.uk)

Yielding in amorphous solids dictates the change of the mechanical properties of the material upon loading. That is, the elastic to plastic response due to internal stresses or to imposed shear [1]. For this yield transition, a smooth ductile deformation or a catastrophic brittle failure is determined by the microscopic material properties, e.g. the structural stability [2]. Nonetheless, relating mechanical response to microscopic structure remains challenging. Here we address this challenge by studying the contacts and the interparticle forces, in addition to particle resolved studies [3]. We use a colloidal model system (Fig. 1a), in which forces between particles and local stress can be linked to the microscopic structure [4]. Moreover, simultaneous imposed shear and super-resolution imaging is achieved with a special rheoscope [5] that allows linear and rotational shearing (Fig. 1b). We show the potential of our method for the understanding of the failure mechanisms of soft amorphous solids by determining local stress in a colloidal glass.



**Figure 1.** a) Super-resolution microscopy of our colloidal model. Image shows the contacts between droplets that allows the determination of interparticle forces. b) Schematic representation of the rheoscope used for simultaneous microscopy and imposed shearing

**Keywords:** Colloids, Glass, Yielding

### References

- [1] Bonn, D., et al. Rev. Mod. Phys. 89, 035005 (2017)
- [2] Ozawa, M., et al. PNAS, 6656-6661, 15. (2018)
- [3] Ghosh, A., et al. PRL, 118, 148001. (2017)
- [4] Dong, J, et al. ArXiv, 2203.03757 (2022)
- [5] Lin, N. Y. C., et al. Soft Matter, 10, 1969. (2014)

# Molecular Assembly of Peptide and Motor Proteins based Biomimetic Systems

Yi Jia,<sup>1</sup> and Junbai Li<sup>1,2</sup>

<sup>1</sup>Beijing National Laboratory for Molecular Sciences, CAS Key Lab of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences

<sup>2</sup>University of Chinese Academy of Sciences

Presenting author's e-mail: [jbli@iccas.ac.cn](mailto:jbli@iccas.ac.cn)

Molecular biomimetics is mimicking the structures and functions of biological systems at the molecular scale via molecular assembly of biomolecules or synthetic components. Molecular assembly of biomimetic systems can not only serve as experimental models for guiding research on biological evolution in organisms, but also open up new avenues for the design of multifunctional materials with a wide range of applications. In this lecture, we will introduce our recent progress on the molecular assembly of natural molecular machines “motor proteins” into active biomimetic systems,<sup>1-3</sup> as well as the controlled self-assembly or co-assembly of aromatic dipeptides.<sup>4,5</sup> The biomedical applications of these biomimetic assemblies, including drug delivery and anticancer therapy are highlighted.

**Keywords:** Molecular Assembly, Peptide, Motor Proteins, Biomimetic Systems

## References

- [1] a) X. Xu, J. Fei, Y. Xu, G. Li, W. Dong, H. Xue, J. Li, *Angew. Chem. Int. Ed.* 2021, 60, 7617; b) M. Xuan, J. Li, *Natl. Sci. Rev.* 2021, 8, nwab051; c) Z. Li, X. Xu, F. Yu, J. Fei, Q. Li, M. Dong, J. Li, *Angew. Chem. Int. Ed.* 2022, 61, e202116220.
- [2] a) Y. Jia, J. Li, *Nat. Rev. Chem.* 2019, 3, 361; b) Y. Jia, J. Li, *Acc. Chem. Res.* 2019, 52, 1623.
- [3] a) Y. Xu, J. Fei, G. Li, T. Yuan, X. Xu, J. Li, *Angew. Chem. Int. Ed.* 2019, 58, 5572; b) G. Li, J. Fei, Y. Xu, B. Sun, J. Li, *Angew. Chem. Int. Ed.* 2019, 58, 1110.
- [4] a) A. Wu, Y. Guo, X. Li, H. Xue, J. Fei, J. Li, *Angew. Chem. Int. Ed.* 2021, 60, 2099; b) Y. Jia, J. Li, *Chem. Rev.* 2015, 115, 1597.
- [5] a) T. Yuan, J. Fei, Y. Xu, H. Xue, X. Li, C. Wang, G. Fytas, J. Li, *Angew. Chem. Int. Ed.* 2019, 58, 11072; b) C. Yuan, W. Ji, R. Xing, J. Li, E. Gazit, X. Yan, *Nat. Rev. Chem.* 2019, 3, 567.

## Dynamical regimes and stochastic transitions of colloids in periodic light fields

Iván Guerrero García<sup>1</sup>, Stefan Egelhaaf<sup>2</sup>, Ramon Castañeda Priego<sup>3</sup>, Erick Sarmiento-Gómez<sup>3</sup>

<sup>1</sup>Facultad de Ciencias, Universidad Autónoma de San Luis Potosí, México

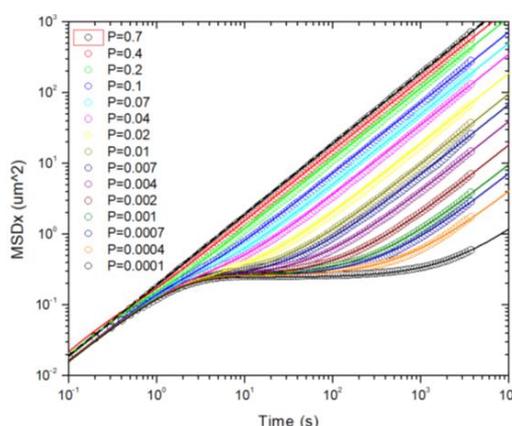
<sup>2</sup>Heinrich Heine University, Dusseldorf Germany, Germany

<sup>3</sup>División de Ciencias e Ingenierías, Universidad de Guanajuato, México

Presenting author's e-mail: [esarmiento@fisica.ugto.mx](mailto:esarmiento@fisica.ugto.mx)

As an inhomogeneous distribution of light interacts with a dielectric colloidal particle, the refraction of light on the particle's surface induces the formation of an external field [1]. If energy density is not high enough, the particle may be capable of overcome the energy barrier, thus escaping from the potential minima. A typical effect of such moderate-trapping potential is the appearance of dynamical regimes in the mean squared displacement, i.e. anomalous diffusion, related with the caging effect induced by the trapping potential, and the thermally activated escape at long times [2]. In this work I will present the main features of the dynamical properties of spherical colloids in periodical fields, including the above-mentioned times regimes and the effect of the competition between direct interactions and the particle-field coupling, from the dilute regime up to a moderated-high concentration. The experimentally found results are compared with Brownian dynamics simulations. By using a simple, yet powerful ray tracing algorithm developed recently, the laser-induced potential can be computed for any cluster formed by spherical particles, and thus the preferred states found by this algorithm will be also discussed [3]. Finally, I present a methodology to simulate the dynamical properties of the experimentally studied systems by using Monte Carlo simulation based in the transition probability to overcome the energy barrier. Such methodology can explain, from a different point of view, the anomalous diffusion found experimentally, but can be also used to predict the dynamical properties of Brownian particles interacting with complex landscapes, such as the case of a trimer in a periodical potential.

**Keywords:** Anomalous diffusion, optical manipulation, dynamical transition.



**Figure 1.** Mean squared displacement of the stochastic simulation as the escape probability decreases.

**Acknowledgements:** ESG and RCP acknowledges CONACYT A1-S-9098 and CF - 102986

### References

- [1] H. Löwen, J. Phys.: Condens. Matter., 13, R415-R432 (2001).
- [2] F. Evers, R. D. L. Hanes, C. Zunke, R. F. Capellmann, J. Bewerunge, C. Dalle-Ferrer, et. al. Eur. Phys. J Special Topics., 222, 2995-3009 (2013).
- [3] E. Sarmiento-Gomez, J. A. Rivera-Moran, J. L. Arauz-Lara, Soft Matter, 14, 3684-3688 (2018).

## Odd-Diffusive Systems

*Iman Abdoli<sup>1</sup>, Jens-Uwe Sommer<sup>1</sup>, Hartmut Löwen<sup>2</sup>, and Abhinav Sharma<sup>1</sup>*

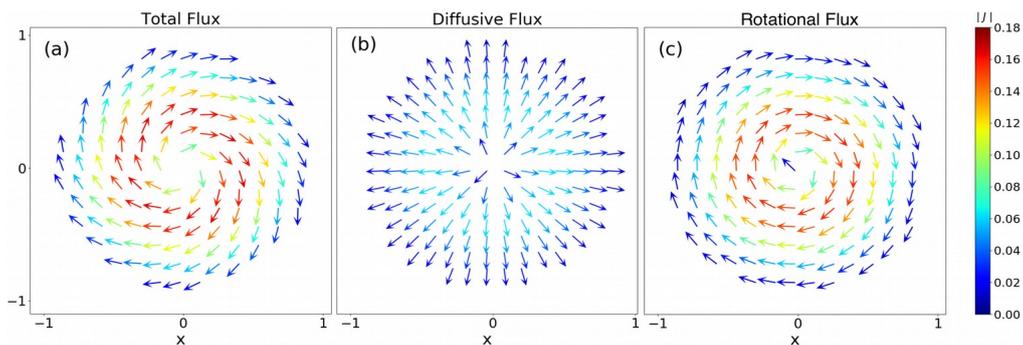
<sup>1</sup>*Leibniz-Institut für Polymerforschung Dresden, Institut Theorie der Polymere,  
01069 Dresden, Germany*

<sup>2</sup>*Institut für Theoretische Physik II: Weiche Materie, Heinrich-Heine-Universität  
Düsseldorf, Düsseldorf, 40225, Germany*

Presenting author's e-mail: [abdoli@ipfdd.de](mailto:abdoli@ipfdd.de)

The characteristic property of an odd-diffusive system is a diffusion tensor which can be decomposed into a symmetric part and an antisymmetric part [1, 2]. Odd-diffusive behavior emerges naturally in systems with broken time-reversal and parity symmetry, for instance charged Brownian particles and chiral active particles [2-4]. For this reason, the probability flux gets a certain handedness. Odd-diffusivity results in steady-state fluxes when subjected to anisotropic driving [3]. Using these fluxes we propose a Brownian magneto-gyrotator as a microengine of which the key properties can be externally tuned [4]. Moreover, the heat current in the magneto-gyrotator is governed by momenta correlations and thus requires explicit knowledge of the particle's mass even in the overdamped regime.

**Keywords:** Odd-Diffusivity, Chirality, Lorentz Force



**Figure 1.** Total probability flux in (a) flows along (b) and perpendicular to (c) density gradients.

### References

- [1] I. Abdoli, H.-D. Vuijk, J.-U. Sommer, J.-M. Brader, A. Sharma, *Physical Review E*, 2020 101, 012120.
- [2] C. Hargus, J.-M. Epstein, and K.-K. Mandadapu, *Physical Review Letters*, 2021, 127, 178001.
- [3] I. Abdoli, J.-U. Sommer, H. Löwen, A. Sharma, To be published in *Europhysics Letters*.
- [4] I. Abdoli, R. Wittmann, J.-M. Brader, J.-U. Sommer, H. Löwen, A. Sharma, arXiv:2110.05284.

# Measuring 3D rotation of colloidal particles from 2D images

Vincent Niggel<sup>1</sup>, Maximilian R. Bailey<sup>1</sup>, Carolina van Baalen<sup>1</sup>, and Lucio Isa<sup>1</sup>

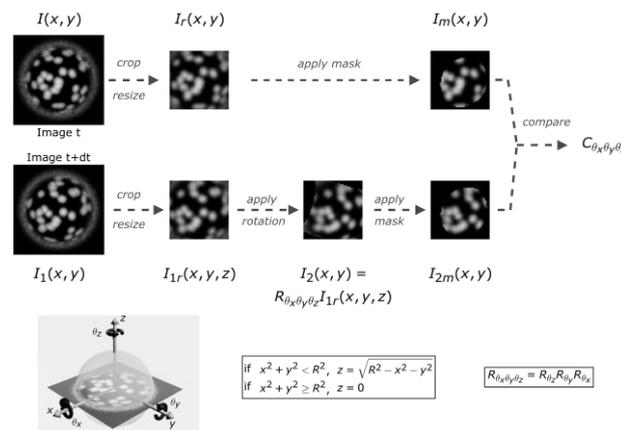
<sup>1</sup>Departement of Materials, ETH Zürich, Switzerland

Presenting author's e-mail: [vincent.niggel@mat.ethz.ch](mailto:vincent.niggel@mat.ethz.ch)

While tracking the displacement of colloidal particles has become a routine task, measuring their rotation is much less frequent. However, accessing the rotational dynamics of colloidal particles is highly interesting in dense suspensions [1]. Characterizing rotation is also important under shear, where a full description of the relative motion between particles can offer insights on contact forces. In order to track rotation, particles must be optically anisotropic [2]. One recent method uses particles decorated with fluorescent asperities to measure 3D rotation via the tracking of individual asperities over time [3]. However, this method requires the acquisition of z-stacks of images, which limits its time resolution. This aspect is particularly critical for tracking under flow, where high frame rates are required.

We instead propose an approach where 3D rotation can be tracked from 2D image sequences, speeding up image acquisition. Our idea can be seen as an adaptation of a 2D rotation/registration algorithm, in which a reference image is compared to the rotated image of a second one. In the 3D case, we create different prospective images corresponding to 3D rotations of a first image and compare them to the subsequent frame (see Figure 1). Even if this approach is restricted to particles with a displacement within the imaging plane, it enables faster acquisition with a simpler setup. We demonstrate examples of tracking the rotation of particles in a channel at different flow rates, the rotation of passive particles confined at a fluid interface and the rotation of active particles swimming on a glass slide.

**Keywords:** Colloids, 3D rotation, microscopy



**Figure 1.** Concept of the 3D rotation/registration method. The images are first cropped and resized. A mask is applied to the reference image  $I_r$ , and the next image  $I_{1r}$  is subjected to a transform to create a hypothetical image  $I_2$  corresponding to a given rotation. We then apply the same mask and compare both images. The rotation that maximizes the correlation  $C$  corresponds to the real rotation.

## References

- [1] L. C. Hsiao, I. Saha-Dalal, R. G. Larson and M. J. Salomon, *Soft Matter*, 2017, 13, 9229-9236.
- [2] [3] T. Yanagishima, Y. Liu, H. Tanaka and R. P. A. Dullens, *Physical Review X*, 2021, 11, 021056.
- [3] B. Ilhan, J. J. Schoppink, F. Mugele and M. H. G. Duits, *Journal of Colloid and Interface Science*, 2020, 576, 322-329.

# Anomalous rotational diffusion of non-spherical particles in viscoelastic fluids

Sergio Martín-Martín <sup>1</sup>, Ángel V. Delgado <sup>1</sup>, Ramos-Tejada, María <sup>2</sup>, Antonio Rubio <sup>1</sup> and María L. Jiménez<sup>1</sup>

<sup>1</sup>Department of Applied Physics, University of Granada, Avda. de Fuente Nueva sn, 18071, Granada, Spain

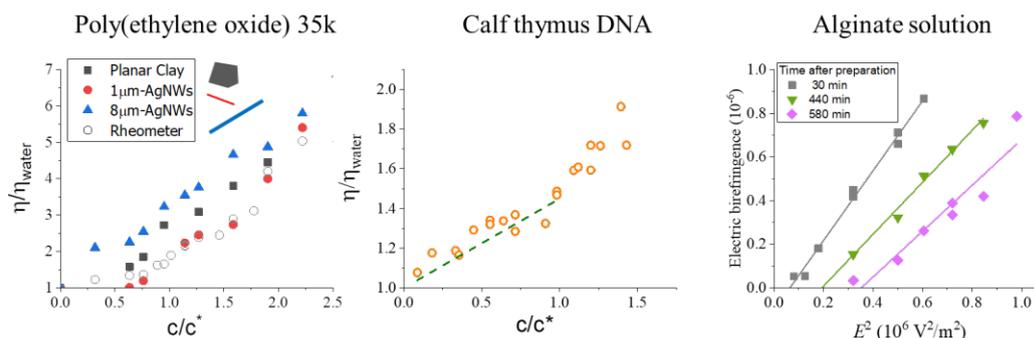
<sup>1</sup>Department of Physics, University of Jaen, Linares 23700, Jaen, Spain

Presenting author's e-mail: [jimenez@ugr.es](mailto:jimenez@ugr.es)

Apart from the well known free diffusion in ideal Newtonian fluids or the total immobilization in a rigid matrix, micro- and nanoparticles exhibit a plethora of behaviors in between these two cases. This is the basis of microrheology [1], devoted to the study of the viscoelastic properties of a complex fluid from the Brownian diffusion of microprobes. However, it is usually found, and it has been extensively studied, that particle diffusion deviates from the Stokes-Einstein predictions, a consequence of the short length scale of diffusion. On the other hand, the much less studied rotational diffusion of nanoparticles can also reveal local properties, out of the reach of conventional rheological techniques.

In this work we focus on the rotational diffusion (through electric birefringence experiments) of non-spherical particles of different sizes and geometries, and in three kinds of polymers: Newtonian poly(ethylene oxide) (PEO), calf thymus DNA (CT-DNA), and alginate solution capable of forming gel networks. In the first and second cases we find a purely diffusive behavior, although an anomalous rotational diffusion coefficient is obtained in some cases. We analyze the effect of particle size, geometry and the particle-polymer interaction on this anomalous diffusion. In the case of (gelating) sodium alginate solutions, we measure at different positions from the bottom of the cell (where an unavoidable deposit of CaCO<sub>3</sub> microparticles, the source of cross-linking Ca<sup>2+</sup> ions, is present) revealing local non-homogeneities in the kinetics of the gel formation. This process has an interesting consequence on birefringence response: Kerr's law fails to be fulfilled, appearing a "yield" applied electric field below which the electric torque that tends to align the particles is not large enough to deform the crosslinked surrounding medium. This yield field correlates with the elastic moduli of the solution.

**Keywords:** Nanowires, polymer, microrheology, electro-orientation, rotational diffusion



**Figure 1.** Some results obtained from electric birefringence techniques: electro-oriented particles produce birefringence. After switching off the electric field, rotational randomization can be measured.

**Acknowledgements:** Financial support by Junta de Andalucía and FEDER funds (Grant No. B-FQM-141-UGR18) and Ministerio de Ciencia, Innovación y Universidades, Spain (PGC2018-098770-B-I00) is gratefully acknowledged.

## References

[1] T.A. Waigh, Rep. Prog. Phys., 2016, 79, 074601.

## Magnetic gold nanoparticles under double external stimulus: magnetic field and laser irradiation

*Guillermo Iglesias Salto, M. Lázaro Callejón, P. Lupiañez Escobar and AV. Delgado*  
NanoMag Laboratory. Department of Applied Physics  
Edificio I+D Josefina Castro, Av. de Madrid, 28.  
(18012). University of Granada, Spain

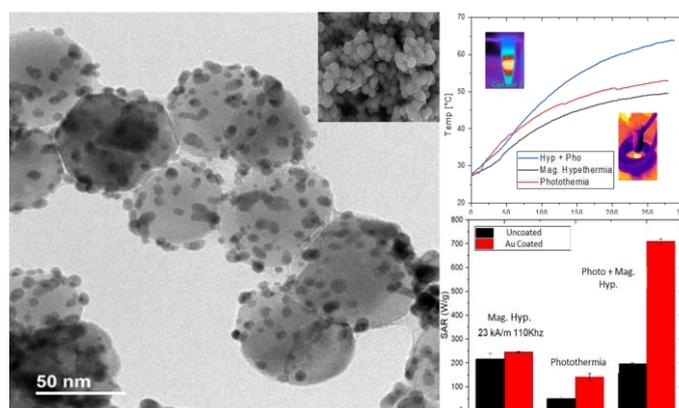
Presenting author's e-mail: [iglesias@ugr.es](mailto:iglesias@ugr.es)

Magnetic nanoparticles (MNPs) have become a very useful tool in the field of biomedicine with great prospects for the future. This is mainly due to their magnetic properties, which allow them to be targeted to a specific area of the body by magnetic fields, and to be used to encapsulate and release drugs in the development of chemotherapeutic systems in the fight against cancer [1]. The innovative properties of both surface and drug-carrying MNPs, as well as the possibility of generating localised heat through external stimuli such as alternating magnetic field (magnetic hyperthermia) and laser irradiation (photothermia techniques), make them a highly innovative system.

In magnetic hyperthermia, if MNPs suspended in an aqueous medium are exposed to an alternating magnetic field with frequencies of the order of 100-200 kHz and amplitudes of about 20 kA/m, it is possible to increase their temperature [2]. In photothermia, on the other hand, the temperature increased is associated with the absorption of electromagnetic radiation due to near-infrared laser irradiation [3]. Both stimuli can be used individually or together to increase their response.

In this work, spherical magnetite nanoparticles have been developed for application in the field of photothermia and magnetic hyperthermia. They have been functionalised by coating the MNPs with a biocompatible polymer. They were then coated with gold to improve the optical properties (Fig. 1). As a main result of the research, an increase in heating by both magnetic hyperthermia and photothermia has been observed, which is enhanced when both stimuli are applied simultaneously compared to uncoated nanoparticles.

**Keywords:** External Magnetic Field, Nanoparticles, Photothermia, Magnetic Hyperthermia



**Figure 1.** Au coating spherical magnetite nanoparticles. Magnetic hyperthermia and Photothermia response.

**Acknowledgements:** The research has been funded by the Junta de Andalucía (Programa Operativo FEDER 2014-2020, A1-FQM-341-UGR-18, C-FQM-497-UGR18,P20\_00346)

### References

- [1] Ian.Y et al., Chemistry of Materials, 2009, 673-681
- [2] G. Iglesias et al., Polymers,2018, 10(3), 269
- [3] Y. Jabalera et al. ,Pharmaceutics, 2021, 13, 625

## Drying Drops of Colloidal Suspensions

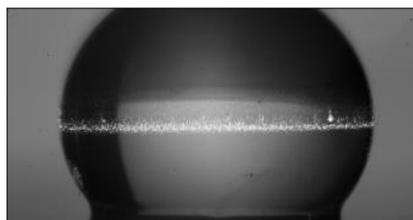
Matteo Milani<sup>1</sup>, Luca Cipelletti<sup>1,2</sup>, and Laurence Ramos<sup>1</sup>

<sup>1</sup>Laboratoire Charles Coulomb (L2C),  
Université Montpellier, CNRS, Montpellier, France  
<sup>2</sup>Institut Universitaire de France (IUF), Paris, France

Presenting author's e-mail: [matteo.milani@umontpellier.fr](mailto:matteo.milani@umontpellier.fr)

Evaporating drops of colloidal suspensions are relevant for a wide variety of processes, including spray drying and surface patterning [1]. Furthermore, evaporating drops of nanoparticle suspensions on superhydrophobic surfaces are used to produce anisotropic supraparticles in applications like catalysis, photonics, or sensing [2]. In these processes, it is important to characterize the spatial distribution of the species confined in the drop during evaporation and to understand which physical processes govern the fate of the drop. Current time- and space-resolved experimental characterizations are scarce and most works aiming at predicting whether a drop of colloidal suspension will evaporate isotropically or buckle are based on assumptions that could not be directly tested so far [3]. Thanks to a unique multispeckle light scattering set-up we probe the microscopic dynamics of charge-stabilized nanoparticles confined in an evaporating drop, with space and time resolution. We show that, depending on evaporation speed, quantified by a Peclet number  $Pe$  comparing evaporation and diffusion, the nanoparticles may remain homogeneously distributed or accumulate at the periphery of the drop, forming a dense shell. We measure the time evolution of the shell's thickness and particle concentration, finding that the particle concentration in the shell increases with time and  $Pe$ , reaching random close-packing only for the largest  $Pe$  investigated. For  $Pe > 10$ , the drop becomes unstable. Measurements of the microscopic dynamics of the nanoparticles in the shell show that the instability sets in when the dynamics imposed by the macroscopic strain rate of the drop become faster than the spontaneous slow dynamics of the dense suspension, demonstrating that viscoelasticity plays a key role in determining the ultimate fate of an evaporating drop of a colloidal suspension.

**Keywords:** drying, drops, colloidal suspensions, light scattering



**Figure 1.** Image of a drop of nanoparticle suspension. The drop diameter is 4 mm. A laser beam propagating along a drop diameter forms a characteristic speckle image, whose time evolution allows for measuring the suspension dynamics.

### References

- [1] F. Iskandar et al., *Journal of Colloid and Interface Science*, Control of the morphology of nanostructured particles prepared by the spray drying of a nanoparticle sol, 2003, 265, 296
- [2] S. Wooh et al, *Advanced Materials*, Synthesis of mesoporous supraparticles on superamphiphobic surfaces, 2015,27, 7338
- [3] N. Tsapis et al., *Physical review letters* 2005, Onset of buckling in drying droplets of colloidal suspensions,94, 018302

## Drying of responsive microgels

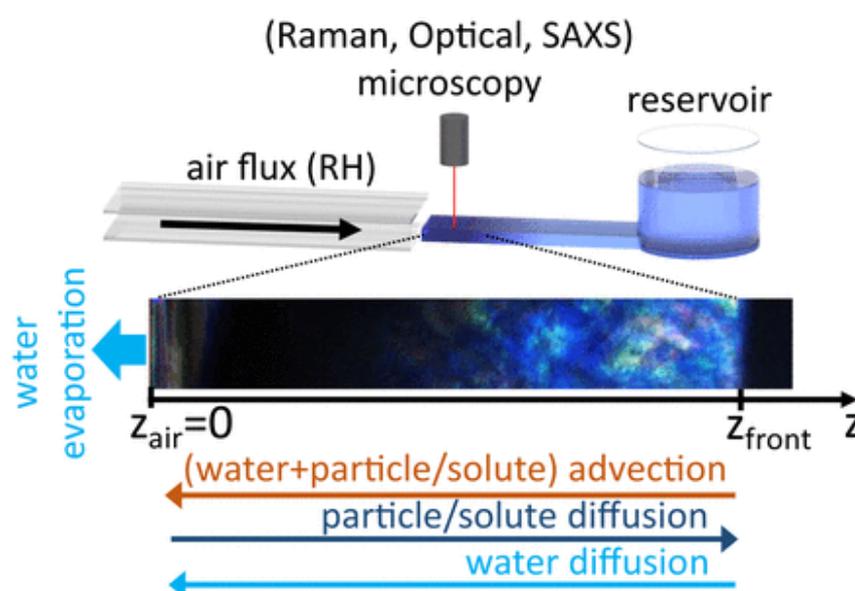
Nabanita Hazra<sup>1</sup>, Kevin Roger<sup>2</sup> and Jérôme J. Crassous<sup>1</sup>

<sup>1</sup> RWTH Aachen University, Institute of Physical Chemistry, Aachen, Germany  
<sup>2</sup> Laboratoire de Génie Chimique, Université de Toulouse, CNRS, Institut National Polytechnique de Toulouse, Université Paul Sabatier, France

Presenting author's e-mail: [crassous@pc.rwth-aachen.de](mailto:crassous@pc.rwth-aachen.de)

At higher volume fractions, depending on their degree of crosslinking, soft microgels may interpenetrate, deform and facet with direct consequences on their collective properties. We discuss how the interplay of molecular and colloidal scales controls drying of microgel dispersions. This is achieved by monitoring the drying at the end of a capillary exposed to a controlled humidity with constant particle feeding ensures by its connection to a reservoir. Hereby, the water evaporation and diffusion set a flow driving the particles at the drying front where they build up crystals. Whether or not the particles are interpenetrable is characterized by the difference of scaling law in the time evolution of the drying front [1]. We evidence an original drying behavior intermediate between colloidal and solution drying, in which a diffusional scaling is observed together with a weak dependence on the air relative humidity. Mapping composition and structuration gradients using Raman spectroscopy and small-angle scattering techniques, we show that this behavior stems from the ability of microgels to both interpenetrate and compact. We further present the influence of the microgel degree of crosslinking down to so-called ultralow crosslinked microgels (ULC) and temperature on the drying process. The described mechanism will be at play in a large diversity of complex colloidal systems and is pivotal for the mastering of drying processes.

**Keywords:** microgels, drying, direct imaging, Raman, scattering



**Figure 1.** Schematic view of the millifluidic setup, which consists of a rectangular capillary connected on one end to a reservoir containing the microgel dispersion and exposed on its other end to an air flux of controlled RH.

### References

[1] K. Roger and J. J. Crassous, Proc. Nat. Acad. Sci., 2021, 118, e2105530118.

## Two Types of Liquid-Liquid Phase Separation Induced by Centrifugation

Helmut Cölfen<sup>1</sup>, Rose Rosenberg<sup>1</sup>, Dirk Haffke<sup>1</sup>, Simon Stemplinger<sup>2,3</sup>, Thomas Zemb<sup>3</sup>,  
Dominik Horinek<sup>2</sup>

<sup>1</sup>Physical Chemistry, University of Konstanz, Universitätsstraße 10, Box 714  
78457 Konstanz, Germany

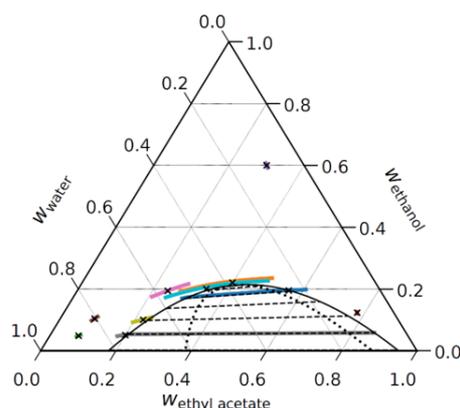
<sup>2</sup>Institute of Physical and Theoretical Chemistry, University of Regensburg,  
Universitätsstraße 31, 93053 Regensburg, Germany

<sup>3</sup>Institute for Separation Chemistry ICSM U Montpellier/CEA/CNRS/ENSCM,  
Marcoule, France

Presenting author's e-mail: [dominik.horinek@ur.de](mailto:dominik.horinek@ur.de)

Water-ethyl acetate-ethanol is a widely used extractant system. We show that two different types of phase separation can be induced upon centrifugation in this ternary system, where ethanol is a co-solvent of water and ethyl acetate: centrifuge-induced criticality and centrifuge-induced emulsification. The expected composition profiles of samples after centrifugation can be represented by bent lines in a ternary phase diagram when gravitational energy is added to the free energy of mixing. The experimental equilibrium composition profiles behave qualitatively as expected and can be predicted using a phenomenological theory of mixing. The concentration gradients are small except near the critical point. These findings open new possibilities of centrifugal separation. These schemes are accessible even at relatively low centrifugation speed for molecules that float and sediment with apparent molar masses several hundred times larger than the molecular mass.

**Keywords:** Separation, Solubilization, Emulsification



**Figure 1.** Theoretically predicted phase diagram and theoretical predictions for the composition profiles in a real centrifugation cell. The densest, water rich compositions appear on the left and bottom of the curves.

### References

- [1] S. Stemplinger, S. Prevost, T. Zemb, D. Horinek, J.-F. Dufreche J. Phys. Chem. B, 2021, 125, 12054.  
[2] T. Zemb, R. Rosenberg, S. Marcelja, D. Haffke, J.-F. Dufreche, W. Kunz, D. Horinek, H. Cölfen, Phys. Chem. Chem. Phys., 2021, 23, 8261.

# Tunable Payload Release from Antibubbles Using Low-Intensity Ultrasound

*Nicolas Moreno-Gomez*<sup>1,2</sup>, *Athanasios G. Athanassiadis*<sup>1</sup>, *Albert T. Poortinga*<sup>3</sup> and *Peer Fischer*<sup>4,5</sup>

<sup>1</sup>Max Planck Institute for Intelligent Systems, Stuttgart, Germany

<sup>2</sup>Institute of Physical Chemistry, University of Stuttgart, Stuttgart, Germany

<sup>3</sup>Polymer Technology, Eindhoven University of Technology, Eindhoven, the Netherlands

<sup>4</sup>Institute for Molecular Systems Engineering, Heidelberg University, Heidelberg, Germany

<sup>5</sup>Max Planck Institute for Medical Research, Heidelberg, Germany

Presenting author's e-mail: [moreno@is.mpg.de](mailto:moreno@is.mpg.de)

Ultrasound-responsive colloids can play an important role in the realization of smart materials. They can be spatially manipulated, used for payload transport, and to initiate chemical processes[1]. However, currently there is no system versatile enough to carry high amounts of a given payload that can be released in a controlled manner using low intensity ultrasound. In this work, we present the use of antibubbles as a novel ultrasound responsive system that can transport and release a payload in a controlled manner. Antibubbles consist of droplets surrounded by a gas shell, and are highly responsive to ultrasound [2]. Here we describe how to tailor the acoustic response of antibubbles by modifying their size and the composition of the external surface during fabrication. Briefly, calcein loaded antibubbles were obtained after freeze-drying water-in-oil-in-water emulsions stabilized with fumed silica. We find that for different types of antibubbles, the required acoustic pressure to release the loaded calcein is low and only on the order of kPa. Additionally, the different fumed silica composition also modifies the release profile between a single event and a step-wise behavior. Finally, we use our results to demonstrate how antibubbles can be embedded into complex media for novel applications, such as imaging ultrasound-fields produced by acoustic holograms [3]. We anticipate that antibubbles can be use as components for ultrasound responsive smart materials owing to the simplicity to load them during fabrication, their high carrying capacity, their exceptional stability, the ability to manipulate them using ultrasound and burst them using low acoustic pressures.

**Keywords:** Ultrasound, Antibubbles, Microbubbles, Acoustic Holograms, Smart Material

**Acknowledgements:** This work is in part supported by the European Research Council under the ERC Advanced Grant Agreement HOLOMAN (No. 788296).

## References

- [1] A.G Athanassiadis, Z. Ma, N. Moreno-Gomez, K. Melde, E. Choi, R. Goyal, and P. Fischer, *Chemical Reviews*, 2021, 122, 5, 5165–5208
- [2] S. Kotopoulos, C. Lame, R. Haugse, S. Snipstad, E. Murvold, T. Jouleh , S. Berg, R. Hansen, M. Popa, E. Mc Cormack, O. Gilja, A. Poortinga, *Ultrasonics Sonochemistry*, 2022, 85, 105986.
- [3] K. Melde, A. Mark, T. Qiu, and P. Fischer, *Nature*, 2016, 537, 518-522.

# Contactless measurement of surface tension on single droplet using acoustic levitation and machine learning

Smaragda-Maria Argyri<sup>1</sup>, Nicolas Paillet<sup>1</sup>, Lars Evenäs<sup>1</sup>, Romain Bordes<sup>1</sup>

<sup>1</sup>Chalmers University of Technology, Department of Chemistry and Chemical Engineering, SE-412 96 Göteborg, Sweden

Presenting author's email: [bordes@chalmers.se](mailto:bordes@chalmers.se)

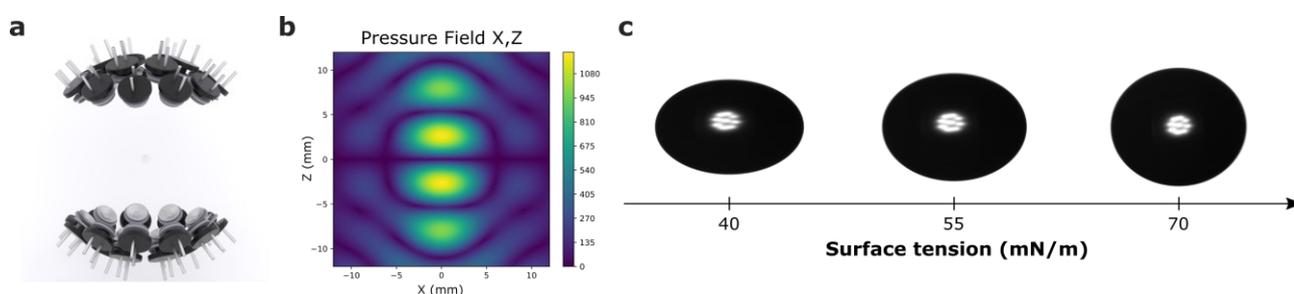
Acoustic levitation enables contact-free manipulation of samples in the micro-liter regime, without the surface-associated shortcomings, such as contamination or other surface-induced effects. It also allows a controlled and quantifiable deformation of the droplet, which gives the possibility to indirectly measure surface tension of liquids. Using a levitator based on Langevin horn, Apfel *et al.* [1] managed to measure surface tension of aqueous surfactant solutions. Even though the method worked, the poor stability of the levitator led to difficulties in conducting reliable measurements. Yet, it had the advantage of a relatively straightforward description of the acoustic force field, which allows a theoretical description of the deformation of the droplet.

Recently, a new generation of more stable levitators has been developed by Marzo *et al.* [2], based on multisource ultrasonic arrays. However, in contrast to Langevin horns, the acoustic field of the new generation of acoustic levitators is more complex and challenging to describe. As a result, the previously established droplet deformation models do not apply, and surface tension cannot be measured.

In this study, we have built a highly stable and compact multi-source levitator and monitored the droplet deformation via a high-speed camera under varying acoustic pressure. Taking advantage of the large amount of data that can be generated, we followed a data-driven approach and developed a neural network able to process the droplet contour and predict the surface tension of surfactant solutions.

With this approach, the surface tension of a single droplet with a volume below 10  $\mu\text{L}$  could be determined, in real-time, with an average mean absolute error below 0.9 mN/m. Furthermore, the methodology allows for the possibility of measuring critical micelle concentration using continuous measurement on a single evaporating droplet of surfactant solution.

**Keywords:** Acoustic levitation, surface tension, machine learning



**Figure 1.** (a) Acoustic levitator (model), (b) pressure field, (c) levitated droplet of different surface tension.

**Acknowledgements:** The authors would like to thank the Swedish Foundation for Strategic Research (SSF) and the Swedish Research Council (VR) for financial support.

## References

- [1] T. Yuren, R. G. Holt, R. E. Apfel, *Review of scientific instruments*, 1995, 66, 3349.  
[2] A. Marzo, B. Adrian, B. W. Drinkwater, *Review of Scientific Instruments*, 2017, 88, 085105.

# Non-linear rheology and rheo-combined methods applied on colloidal systems

*Klein Christopher O.<sup>1</sup>, Radebe Nonkululeko<sup>1</sup>, Wilhelm Manfred<sup>1</sup> and Vlassopoulos Dimitris<sup>2</sup>*

<sup>1</sup>*Polymeric materials, ITCP, KIT, 76131 Karlsruhe Germany*

<sup>2</sup>*Polymer group, IESL, FORTH, 70013, Heraklion, Greece*

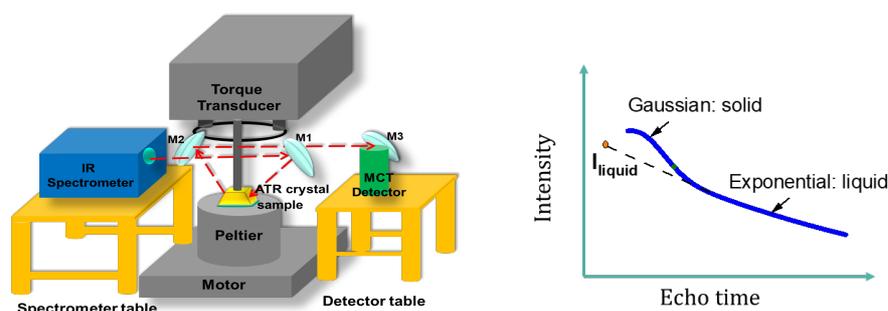
Presenting author's e-mail: [christopher.klein@kit.edu](mailto:christopher.klein@kit.edu)

Rheology is a widely used technique for analyzing the mechanical behavior of colloidal systems and systems with large interfacial contributions, like e.g., lattices and foams. Non-linear rheology is increasingly used as it tests the non-equilibrium behavior of such materials, as in contrast to the linear rheology. This non-equilibrium information allows deeper insight into the structure property relationship of these materials, and many different non-linear rheological techniques, e.g., LAOS [1], startup shear flow, are be used.

For a further understanding of the structure property relationship, acquiring information of the molecular level is desirable. Such information can be collected by spectroscopical methods, e.g., TD-NMR, FT-IR or Dielectric spectroscopy. These spectroscopic methods can supply information of proton mobility, chemical reaction monitoring or molecular dynamics. When rheology and the molecular information is in-situ and simultaneously acquired, correlating the molecular information with the mechanical response can be achieved.

In this presentation different combined methods of rheology and spectroscopy (TD-NMR FT-IR) will be introduced, see figure 1(left). Furthermore, the simultaneously acquired and correlated information will be presented, see figure 1(right), showing the potential benefit of such rheo-combined techniques.

**Keywords:** non-linear rheology, combined methods, molecular information



**Figure 1.** Schematic setup of Rheo-FTIR combination (left), example of TD-NMR data(right).

**Acknowledgements:** The author would like to thank EUSMI grant E210700578 for financial support.

## References

[1] K. Hyun, C.O. Klein, M. Wilhelm, K.S. Cho, J.G. Nam, K.H. Ahn, S.J. Lee, R.H. Ewoldt, and G.H. McKinley, Prog. Polym. Sci. A Review on Nonlinear Oscillatory Shear tests: Analysis and Application of Large Amplitude Oscillatory shear (LAOS), 2011, 36, 1697.

[2] N. W. Radebe, C. Fengler, C. O. Klein, R. Figuli and M. Wilhelm, J Rheology Rheo-IR: A combined setup for correlating chemical changes via FTIR spectroscopy and rheological properties in a strain-controlled rheometer, 2021, 65, 681.

Tuesday 6th September 2022

**Theory and Multi-scale Modeling of Colloids and Interfaces**

## Icosahedral quasicrystals made of patchy particles

*E. G. Noya*<sup>1</sup>, *C. K. Wong*<sup>2</sup>, *P. Llombart*<sup>1</sup>, and *J. P.K. Doye*<sup>2</sup>

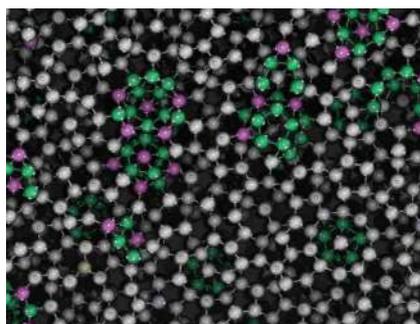
<sup>1</sup>*Instituto de Química-Física Rocasolano, Consejo Superior de Investigaciones Científicas, Calle Serrano 119, Madrid 28006, Spain*

<sup>2</sup>*Department of Physical and Theoretical Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom*

Presenting author's e-mail: [eva.noya@iqfr.csic.es](mailto:eva.noya@iqfr.csic.es)

Icosahedral quasicrystals (IQC) are materials that display long-range order but are not periodic in any direction of space. IQC were the first experimentally discovered quasicrystals in the groundbreaking work of Shechtman *et al.* [1]. Since then, many icosahedral quasicrystals were found in many metallic alloys [2], but, so far, they have not been ever observed in any other type of materials. By contrast, axial quasicrystals have been identified in several soft-matter systems [3,4]. In this talk we will show that, building in our previous work [5,6], model patchy colloids can be designed to assemble into icosahedral quasicrystals. These model systems might be experimentally realized using DNA origami particles [7]. Our rational design strategy leads to model systems that robustly assemble in simulations into target IQC through directional bonding [8]. The key design feature is the geometry of the particles that favors the propagation of an icosahedral network of bonds, even when many particles are not fully bonded.

**Keywords:** quasicrystals, molecular simulation, colloids



**Figure 1.** Icosahedral quasicrystal made of patchy particles.

**Acknowledgements:** E.G.N. acknowledges financial support from the Agencia Estatal de Investigación Grant Number PID2020-115722GB-C21.

### References

- [1] D. Shechtman, I. Blech, D. Gratias, J. W. Cahn, *Phys. Rev. Lett.*, 1984, 53, 1951.
- [2] H. Takakura, C.P. Gómez, A. Yamamoto, M.D. Boissieu, A.P. Tsai, *Nat. Mater.*, 2007, 6, 58.
- [3] X. Zeng, *et al.*, *Nature*, 2004, 428, 157.
- [4] T. Dotera, *Isr. J. Chem.*, 2011, 51, 1197.
- [5] D. Tracey, E. G. Noya, J. P. K. Doye, *J. Chem. Phys.*, 2020, 151, 224506.
- [6] D. Tracey, E. G. Noya, J. P. K. Doye, *J. Chem. Phys.*, 2021, 154, 194505.
- [7] Y. Tian, *et al.*, *Nat. Mater.*, 2020, 19, 789.
- [8] E. G. Noya, C. K. Wong, P. Llombart, J. P. K. Doye, *Nature*, 2021, 596, 367.

# Colloidal monolayers: bridging the gap between two and three spatial dimensions

*Alvaro Domínguez*

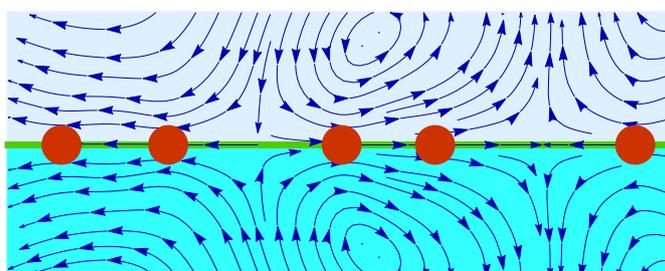
*Universidad de Sevilla, Spain*

Presenting author's e-mail: [dominguez@us.es](mailto:dominguez@us.es)

It is well established that, unlike for a three-dimensional fluid, particle interactions prevent the hydrodynamic transport coefficients from being defined for a two-dimensional fluid due to the notorious "long-time tail" feature of the velocity autocorrelation.

A colloidal monolayer formed at a fluid interface builds a bridge between these two limiting cases, and it provides insight on the transition from three down to two spatial dimensions: the positions of the colloidal particles are constrained to a plane and the colloid thus resembles a two-dimensional fluid. But the exchange of particle momentum takes place in three-dimensional space because it is mediated by the ambient fluid in the form of hydrodynamic interactions.

Here we study the behavior of the colloidal diffusivity, which is the only hydrodynamic transport coefficient for the two-dimensional colloidal fluid. The starting point is the Smoluchowski equation, i.e., the Fokker-Planck equation for the colloidal particles in the overdamped regime with due account of the hydrodynamic interactions. We then show that the diffusivity exhibits an intermediate behavior between purely two-dimensional and fully three-dimensional fluid: on the one hand, Fick's law, which pertains to *collective diffusion*, breaks down altogether [1-3], as confirmed experimentally [4]. On the other hand, the coefficient of *self-diffusion* (or single-particle diffusion) is finite [5], but the transitional nature of the monolayer shows up in a non-analytic dependence on the colloidal packing fraction [6], at odds with the case of a fully three-dimensional colloid.



*Side view of a colloidal monolayer formed at the interface between two fluids, and sketch of the three-dimensional flows responsible for the hydrodynamic interactions.*

**Keywords:** monolayer, diffusion, hydrodynamic interactions, dimensional dependence

## References

- [1] J. Bleibel, A. Domínguez, F. Günther, J. Harting, M. Oettel, *Soft Matter*, 2014, 10, 2945.
- [2] S. Panzuela, R. P. Peláez, R. Delgado-Buscalioni, *Physical Review E*, 2017, 95, 012602.
- [3] J. Bleibel, A. Domínguez, M. Oettel, *Physical Review E*, 2017, 95, 032604.
- [4] B. Lin, B. Cui, X. Xu, R. Zangi, H. Diamant, S. A. Rice, *Physical Review E*, 2014, 89, 022303.
- [5] R. Peláez, F. Balboa Usabiaga, S. Panzuela, Q. Xiao, R. Delgado-Buscalioni, A. Donev, *Journal of Statistical Mechanics: Theory and Experiment*, 2018, 063207.
- [6] A. Domínguez, 2022, unpublished.

## Does the Gibbs Phase Rule apply to the Phase Behaviour of Colloid-Polymer Mixtures?

*Remco Tuinier*<sup>1</sup>

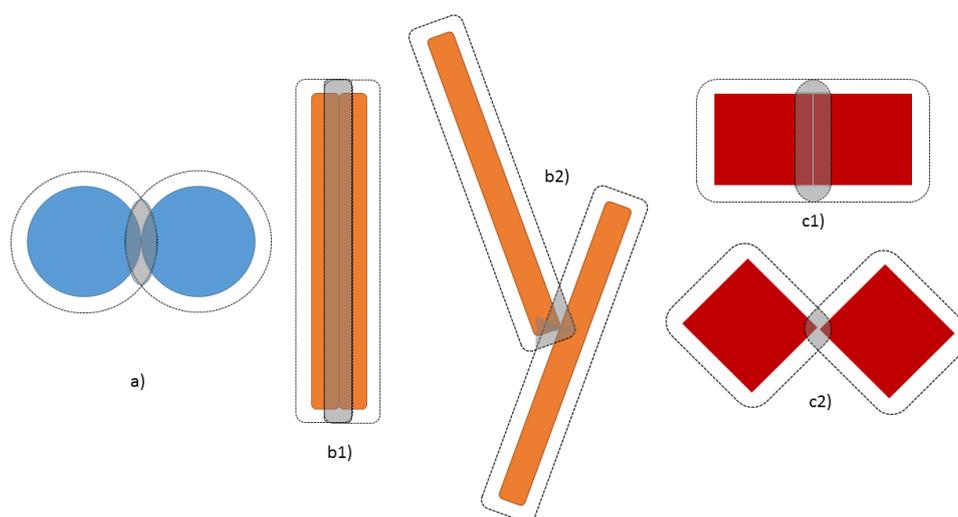
<sup>1</sup> *Laboratory of Physical Chemistry, Department of Chemical Engineering and Chemistry & Institute for Complex Molecular Systems, Eindhoven University of Technology,*

*P.O. Box 513, 5600 MB Eindhoven, Netherlands*

*Presenting author's e-mail: [r.tuinier@tue.nl](mailto:r.tuinier@tue.nl)*

The stability of colloidal dispersions can be controlled by adding non-adsorbing polymers [1]. The origin of this interaction was first explained successfully almost 70 years ago [2]. Often the depletion interaction is used as the tool to induce a controlled, tuneable attraction between colloidal particles [3]. While monodisperse hard spheres only exhibit a fluid–solid phase transition, anisotropic hard particles such as rods, cubes, discs or boards exhibit various phase states. Ordering of such anisotropic particles increases the free volume entropy by reducing the excluded volume between them [4]. In this talk I will demonstrate that mixtures of either platelets, cube-like or rod-like colloids plus added depletants (see **Fig. 1**) exhibit a strikingly rich multi-phase behaviour involving even four- and five-phase equilibria. It is discussed whether the Gibbs phase rule still applies for colloid-polymer mixtures. A modified Gibbs phase rule is proposed which explains a five-phase equilibrium in rod-polymer mixtures [5].

**Keywords:** phase behaviour, colloids, depletion interaction, Gibbs phase rule, rods, platelets



**Figure 1.** Excluded volume between a) spheres, b) rods and c) cubes. For anisotropic particles the overlap volume of depletion zones depends on the orientations of the particles.

### References

- [1] H.N.W. Lekkerkerker, R. Tuinier, ‘Colloids and the Depletion Interaction’, Springer, 2011.
- [2] S. Asakura, F. Oosawa, On interaction between two bodies immersed in a solution of macromolecules. *J. Chem. Phys.* 22 (1954) 1255–1256.
- [3] W.C.K. Poon, Colloids as big atoms, *Science* 304 (2004) 830.
- [4] G. van Anders, D. Klotsa, N.K. Ahmed, M. Engel, S. Glotzer, Understanding shape entropy through local dense packing. *PNAS* 111 (2014) E4812–E4821.
- [5] V.F.D. Peters, M. Vis, Á. García González, H.H. Wensink, R. Tuinier, Defying the Gibbs Phase Rule: Evidence for an Entropy-Driven Quintuple Point in Colloid-Polymer Mixtures, *Phys. Rev. Lett.*, 125 (2020) 127803.

# Modelling colloidal adsorption in bio-oils: effect of molecular chemistry, surface geometry and hydration

*Maisa Vuorte<sup>1,2</sup> and Maria Sammalkorpi<sup>1,2</sup>*

*<sup>1</sup>Aalto University, Finland; <sup>2</sup>Academy of Finland Centre of Excellence in Life-Inspired Hybrid Materials (LIBER), Aalto University, Finland.*

Presenting author's e-mail: [maisa.vuorte@aalto.fi](mailto:maisa.vuorte@aalto.fi)

In common bio-oils, the naturally present surfactant-like components self-assemble to various colloidal assemblies and may adsorb at interfaces. For example, reverse micellar aggregates often form. The formation, shape and size of the formed aggregates and their adsorption response are sensitive to e.g., surfactant chemistry, concentration, temperature, as well as the presence of co-surfactants, water, and other additives in the oil. Importantly, small polar additives, such as water, increase the size of these assemblies. Although the responses are qualitatively understood in chemical engineering processes, microscopic guiding of surfactant adsorption in apolar solvent environments remains elusive. We have employed computational approaches at molecular, coarse-grained and thermodynamic level to gain fundamental understanding on surfactant aggregation and adsorption in apolar solvents.

Here, we summarize our findings on self-assembly and adsorption of surfactant aggregation and colloidal species at solid – liquid interfaces in bio-oils via a diverse array of computational methods: atomistic classical Molecular Dynamics (MD), coarse-grained Dissipative Particle Dynamics (DPD), and equilibrium state thermodynamics modelling. The combined approach allows accessing aggregation and adsorption phenomena at different length and time scales; we discern the effect of individual molecular features and hydration on adsorption strength and aggregation propensity but also report the effect of these on larger scale adsorption vs aggregation equilibrium. The computational findings are compared against experimental adsorption data of corresponding bio-oil surfactant systems. Methodologically, we raise attention to molecular level modelling challenges that include the low charge screening by the apolar solvent, the high solvent viscosity, and modelling time scale limitations, and propose and demonstrate how modelling approaches can be used with higher accuracy in these complex apolar systems. Overall, the work presents a critical multiscale computational modelling overview to the challenges associated with modelling self-assembly in apolar environments with sensitive self-assembly and adsorption equilibria.

**Keywords:** Reverse micelles, adsorption, aggregation, bio-oils

**Acknowledgements:** Academy of Finland Centers of Excellence Programme (2022-29, LIBER) project No. 346111. Fortum and Neste Foundation, Finland. Computational resources by CSC IT Centre for Science, Finland.

## References

- [1] M. Vuorte, S. Vierros, S. Kuitunen, and M. Sammalkorpi, Adsorption of impurities in vegetable oil: a molecular modelling study. *J. Colloid Interface Sci.*, 2020, 571(1), 55-65. <https://doi.org/10.1016/j.jcis.2020.03.012>
- [2] M. Vuorte, S. Kuitunen, and M. Sammalkorpi, Physisorption of bio oil nitrogen compounds onto montmorillonite. *Phys. Chem. Chem. Phys.*, 2021, 23, 21840. <https://doi.org/10.1039/D1CP01880A>
- [3] M. Vuorte, S. Kuitunen, P. R. Van Tassel, M. Sammalkorpi, Equilibrium state model for adsorption and aggregation in apolar solvent, submitted, 2022.

## Yielding of capillary suspensions

Sebastian Bindgen <sup>1</sup>, Rudolf Weeber <sup>2</sup>, George Rempfer <sup>2</sup>, Christian Holm <sup>2</sup>, and Erin Koos <sup>1</sup>

<sup>1</sup>Institute for Computational Physics, University of Stuttgart, Stuttgart, Germany

<sup>2</sup>Department of Chemical Engineering, KU Leuven, Leuven, Belgium

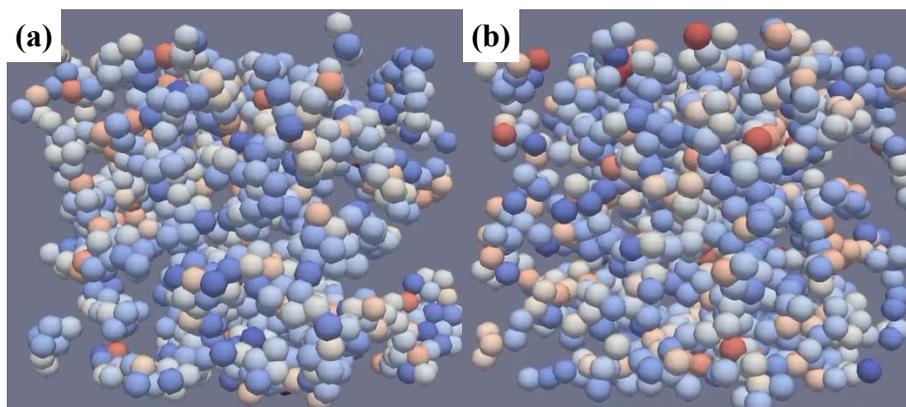
Presenting author's e-mail: [erin.koos@kuleuven.be](mailto:erin.koos@kuleuven.be)

Capillary suspensions [1] are a soft matter system that offer an attractive processing route to adjust the bulk properties of suspensions. They consist of particles and two immiscible liquid phases where the particles are connected via liquid bridges to form a sample spanning network. Previous in-vitro experiments have shown that multiple configurations are possible depending on the physico-chemical properties of the constitutive components [2]. Apart from preliminary results in continuous shear flow [3], a description of the yielding mechanism, however, has not yet been established.

In our study, we describe changes with increasing oscillatory amplitude using the MD simulation package Espresso together with Lees-Edwards boundary conditions [3]. In order to model the yielding behavior of networks formed by capillary forces, we first preform a particle network based on attractive forces computed via a toroidal bridge model in static conditions. As forces act on particle surfaces rather than the center of particles, our model allows us to capture rigid body dynamics to include contact line pinning. The bulk fluid is modeled using the lattice Boltzmann technique.

We show that the linear regime of capillary suspensions ends far below deformations that introduce bond breaking whereas the yield point is mostly controlled by the network collapse. This collapse behavior is dominated by the amount of fluid present in the capillary bridges connecting particles. Bond reformation during shearing further influences the dynamic properties of capillary suspensions. These results have clear implications for industrial processes and networks with other attractive interactions.

**Keywords:** Yielding, Particle networks, Capillary force, Molecular dynamics simulations



**Figure 1.** Two example networks generated using (a) a conservative force field with unbonded particles and (b) rigid body dynamics with explicit bonds

### References

- [1] E. Koos, and N. Willenbacher, *Science*, 2011, 331(6019), 897-900.
- [2] S. Bindgen, et al., *Soft Matter*, 2020, 16(36), 8380-8393.
- [3] S. Bindgen, et al., *Physics of Fluids*, 2021, 33(8), 083615.

# Polyelectrolyte-nanoparticle mutual charge regulation and its influence on their complexation

Morten Stornes <sup>1</sup>, Glenn Kampesveen <sup>1</sup>, Pablo M. Blanco <sup>2</sup>, and Rita S. Dias <sup>1</sup>

<sup>1</sup>Dept. Physics, NTNU–Norwegian Univ. of Science and Technology, Trondheim, Norway

<sup>2</sup>Dept. of Physical and Macromolecular Chemistry, Faculty of Sciences, Charles University, Prague, Czech Republic

Presenting author's e-mail: [rita.dias@ntnu.no](mailto:rita.dias@ntnu.no)

Systems comprising of nanoparticles and oppositely charged polyelectrolytes have a large technological interest, being major components in formulations used in pharmaceutical, food, cosmetics, detergents, and paint industries. The stability of colloidal suspensions and the interaction of its constituents are important issues in formulations, and a large effort has been made to understand how the properties of each individual component affect the overall characteristics of the formulations. Of special interest are weak, or annealed, polyelectrolytes. Contrary to strong (quenched) polyelectrolytes, the ionization of annealed polyelectrolytes is pH dependent. This allows for fine-tuning of the properties of the polyelectrolyte and the resulting complexes they form with other macroions. In addition, annealed polyelectrolytes exhibit charge mobility, where protons are mobile along the chain, giving rise to non-uniform charge profiles [1, 2].

The complexation between a charged nanoparticle and an oppositely charged linear polyelectrolyte is studied using coarse-grained Semi-Grand Canonical Monte Carlo simulations. This is done for systems where one or both of the macromolecules are titratable, *i.e.* they have a pH-dependent charge [3]. The presence of charge fluctuation was found to have a significant impact on the ionization of both macromolecules, the conformational properties of the adsorbed polyelectrolyte and the charge of the resulting complex. When both macromolecules are titratable, we find that the impact is larger when the absolute difference in the pKa values of the nanoparticle and polyelectrolyte increases. The results were found to be in good agreement with previous experimental observations, providing a fundamental basis to rationalize these experiments.

**Keywords:** Monte Carlo simulations, pH effects, pKa, colloidal stability

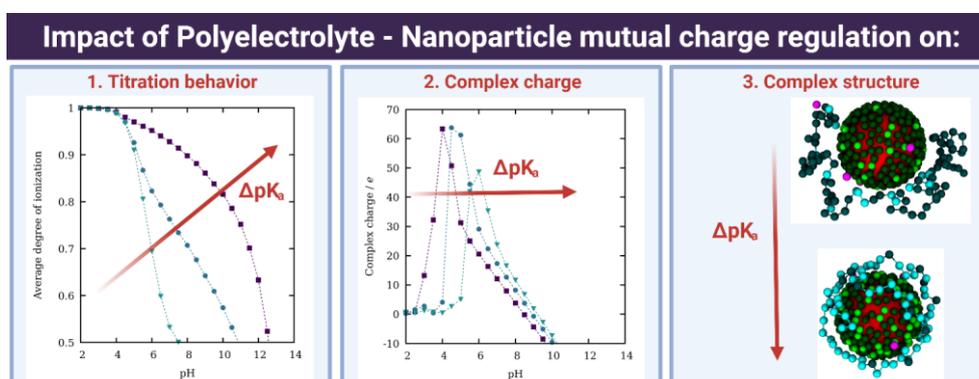


Figure 1. Graphical abstract (created using Biorender.com)

## References

- [1] D. K. Srivastava, S. Wang; K.L. Peterson, Biochemistry, 2007, 36, 6359.
- [2] M. Ullner, B. Jönsson, B. Söderberg and C. Peterson, J. Chem. Phys., 1996, 104, 3048.
- [3] M. Stornes, P.M. Blanco, R.S. Dias Colloids Surf. A 628 (2021) 127258.

# Multi-scale modeling of rates and transport in colloidal nanoreactors

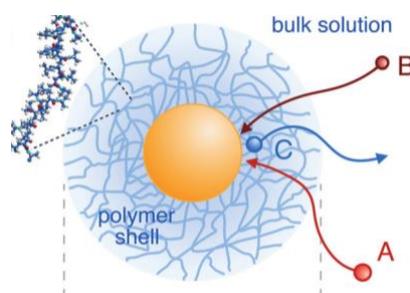
Joachim Dzubiella

*Institute of Physics, University of Freiburg, Germany*

Presenting author's e-mail: [joachim.dzubiella@physik.uni-freiburg.de](mailto:joachim.dzubiella@physik.uni-freiburg.de)

Colloidal nanoreactors with permeable shells made from thermosensitive polymer networks have the ability to shelter and control catalyzed chemical reactions for various applications. Key to function is the permeability of the polymer network (hydrogel) for the selective transport of the molecular penetrants, here the reactants and products. The permeability of polymer membranes is in general a central property in the design of soft functional materials where functional solutes such as drugs, toxins, reactants, etc. have to be adsorbed, transported, and delivered. However, the permeation of dense and hydrated polymer membranes is a complex molecular-level phenomenon, and our understanding of the underlying physicochemical principles is still very limited. Here, I present our recent modeling efforts using coarse-grained as well as atomistic computer simulations in combination with the linear-response solution-diffusion model to understand and quantify the permeability of dense polymer (networks), and how it modifies the reaction rates in colloidal nanoreactors. Our work reveals some universal physical principles, such as strong solute partitioning-diffusion cancellation effects for a wide parameter regime, as well as significant 'chemical' effects (such as solute polarity and shape) which all contribute to the control of permeability. In particular, for charged (ionic) systems the large and fractal water-polymer interface inside the network plays a decisive role. The gained insights enable us to formulate semi-empirical rules and scaling laws to potentially describe and extrapolate the permeability also for other polymer/solute systems.

**Keywords:** stimuli-responsive colloidal nanoreactors, polymer membranes, permeability, simulations, diffusion-influenced rate theory



**Figure 1.** Stimuli-responsive colloidal Nanoreactor for bimolecular ( $A+B \rightarrow C$ ) reactions [1].

## References

[1] M. Kanduc, W. K. Kim, R. Roa, and J. Dzubiella, *Mol. Syst. Des. Eng.*, 2020, 5, 602.

## An explicit multi-scale evaluation of the Gibbs energy of transfer of electrolytes in liquid-liquid extraction

Asmae el Maangar,<sup>1</sup> Mario Spadina,<sup>2</sup> Sandrine Dourdain,<sup>1</sup> Stéphane Pellet-Rostaing,<sup>1</sup> Jean-Francois Dufreche<sup>1</sup>, Stjepan Marcelja<sup>3</sup>, and Thomas Zemb<sup>1</sup>

<sup>1</sup> Marcoule Institute for Separation Chemistry (ICSM), F-30207 Bagnols sur Cèze, France

<sup>2</sup> Faculty of Health sciences, University of Ljubjana -Slovenia

<sup>3</sup> RSPS, Australian National University, Canberra (ACT) Australia

Presenting author e-mail: [Thomas.zemb@icsm.fr](mailto:Thomas.zemb@icsm.fr)

In his last talk at ECIS in Rom (2016), Johannes Lyklema was stressing the importance of entropic terms in the free energy differences involved in any multi-scale transformation of colloidal solutions[1]. Introducing a multi-scale analysis in the estimation of electrolyte transfer between a water phase and a reverse microemulsion phase has allowed for the first time to give a quantitative estimation of the heavily used in practice but previously not understood “extractant synergism” [2]. The standard theory of liquid-liquid restricted to supramolecular scale took into account only competing “complexation” in stoichiometric aggregates, allowing the usage of parametrized mass-action laws. However, the “ienaic” approach takes also into account larger scale terms, such as surfactant film bending energy [3], Gibbs energy of aggregate formation as measured by monomer concentration [4], as well as entropy of mixing in ternary systems [5]. Liquid-liquid extraction relies on equilibrium in a liquid-liquid miscibility gap or in a Winsor II equilibrium. Astonishingly, the distribution coefficient varies linearly over four orders of magnitude, and with a linear variation over four orders of magnitude depending on the distance from the critical point of the relevant tie-line in the phase diagram. We will show in this talk how the multi-scale ienaic decomposition of the free energy of transfer combining molecular forces to short-range complexation [6], allows to understand this strong influence of the formulation of an extractant in hydrometallurgy.

**Keywords:** microemulsions, phase diagram, molecular forces, molecular film bending energy, entropy of complex fluids, long-range interactions

### References:

- [1] L Deschênes and J Lyklema “Entropy studies in interface science: an ageless tool” COCIS 2019, 44, 220
- [2] M Špadina, K. Bohinc, T Zemb and JF Dufrière, “ Solvent extraction is driven by entropy” ACS nano, 2019 13 , 13745
- [3] JF Dufrière and T Zemb, “Bending: from thin interfaces to molecular films in microemulsions” COCIS , 2020 ,49, 133
- [4] O Pecheur, D Guillaumont, S Dourdain, L Berthon, R Turgis, C Fillaux, G Arrachart & F Testard “Uranium Extraction by a Bifunctional Amido-Phosphonic Acid: Coordination Structure and Aggregation” Solvent Extraction and Ion Exchange, 2016 34, 3
- [5] S. Marcelja, Entropy of level-cut random Gaussian structures at different volume fractions, Phys. Rev. 2017, 96, 042147
- [6] M Špadina, JF Dufrière, S Pellet-Rostaing, S Marčelja, T Zemb, “ Molecular Forces in Liquid–Liquid Extraction Langmuir 2021, 37, 10637

## Multiscale Modelling of the adsorption of pheromone molecules at water-air interface

Ludovic Jami <sup>1,2</sup>, Thomas Zemb <sup>1</sup>, Jérôme Casas <sup>2</sup>, Jean-François Dufrêche <sup>1</sup>

<sup>1</sup>ICSM. Univ. Montpellier. CEA. CNRS. ENSCM. Marcoule. France.

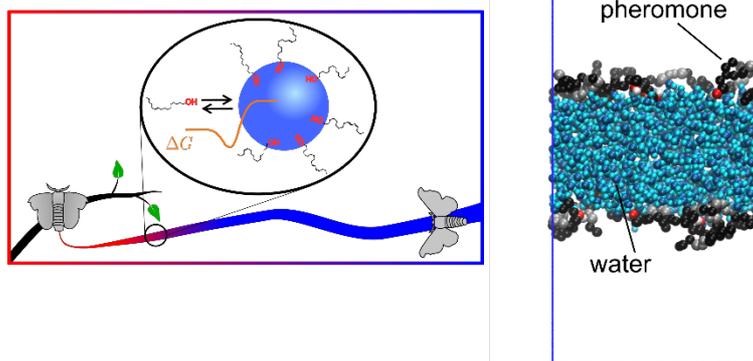
<sup>2</sup>Institut de Recherche sur la Biologie de l'Insecte, Université François Rabelais, 37000 Tours, France.

Presenting author e-mail: [jean-francois.dufreche@icsm.fr](mailto:jean-francois.dufreche@icsm.fr)

Chemical communication is ubiquitous in insects and plants life, but complete understanding of the paths taken by chemicals to explain the performance of these systems is not achieved. Critical gaps exist in the understanding of the physico-chemistry of these chemicals for their transport in the near-ground atmosphere. We proposed that some of them form films on aerosol surface and get transported as clusters [1]. Therefore, aerosols could carry chemical signals over long distances.

The kinetic of this adsorption process is sufficiently fast to occur during the atmospheric transport of the pheromones [1]. To assess this mechanism, identification of molecular candidates and model interface leading to high enough adsorption Gibbs energy is necessary. In this talk, we will present molecular dynamics simulations that enable to compare the film formation of an iconic pheromone (bombykol) and three of its derivatives with adsorption free energy between 5 to 11 k<sub>B</sub>T (13 to 26 KJ/mol) on pure water. These results help us to gain insights in the processes that play a role in pheromonal communication of insects and illustrates the importance of physico-chemistry of interfaces in environmental science.

**Keywords:** Adsorption; aerosols; Langmuir film; molecular dynamics; transport phenomena; pheromones; chemical ecology.



**Figure 1.** The adsorption on aqueous aerosol surface of pheromones emitted by insects is studied by molecular dynamics.

### References

- [1] Ludovic Jami, Thomas Zemb, Jérôme Casas, and Jean-François Dufrêche. ACS central science, 2020, 6(9):1628–1638
- [1] Ludovic Jami, Thomas Zemb, Jérôme Casas, and Jean-François Dufrêche. *submitted*

# Fickian non-Gaussian diffusion in the presence of static and dynamic heterogeneity

*Raffaele Pastore*<sup>1</sup>, *Antonio Ciarlo*<sup>2</sup>, *Francesco Rusciano*<sup>1</sup>, *Giuseppe Pesce*<sup>2</sup>, *Antonio Sasso*<sup>2</sup> and *Francesco Greco*<sup>1</sup>

<sup>1</sup> *Department of Chemical, Materials and Production Engineering, University of Naples Federico II, P.le Tecchio 80, 80125 Naples, Italy*

<sup>2</sup> *Department of Physics E. Pancini, University of Naples Federico II, Via Cintia, 80126 Naples, Italy*

Presenting author's e-mail: [raffaele.pastore@unina.it](mailto:raffaele.pastore@unina.it)

In 2009, ground-breaking experiments on colloidal tracers in biological fluids revealed the existence of an intriguing type of diffusion that is distinct from both standard Brownian motion and anomalous diffusion, being at the same time Fickian and non-Gaussian [1]. Since then, such a Fickian yet non-Gaussian Diffusion (FnGD) has been observed in a variety of soft materials, including colloidal, polymeric and active systems. While FnGD still remains a major open issue in Soft Matter, its appearance is generically associated to some static and/or dynamical heterogeneity of the environment.

In this talk, I will describe recent advances by our group [2-4] drawing on two classes of model-systems, where tracers move in the presence of static and dynamic heterogeneities, respectively.

I will start from experiments [2, 3] on quasi-2d suspensions of colloidal tracers under the action of a static and spatially random optical force field (speckle pattern). This system is found to be an optimal experimental model of FnGD, where the strength and duration of this phenomenon can be finely tuned by changing the optical power.

Next, I will turn to glass-forming liquids, the epitome of dynamic heterogeneity. Experiments on colloidal systems and simulations of molecular liquids reveal that FnGD becomes dramatic on approaching the glass transition and seems to be characterized by a set of universal scaling laws [4].

I will discuss the features and precursors of FnGD in these two classes of model-systems, highlighting differences and similarities. Most notably, FnGD is closely tangled with an earlier subdiffusion in both cases, suggesting the possibility of a quite universal connection between the two regimes.

Finally, I will discuss how the present results can shed new light on previous experimental observations and represent a benchmark for future studies of FnGD in other systems.

**Keywords:** Heterogeneous diffusion, Colloidal suspensions, Glass-forming liquids, Speckle patterns

## References

- [1] B. Wang, J. Kuo, S. C. Bae, and S. Granick, *Nature Materials*, 2012, 11, 481 (2012).
- [2] R. Pastore, A. Ciarlo, G. Pesce, F. Greco, and A. Sasso, *Phys. Rev. Lett.* 2021, 126, 158003
- [3] R. Pastore, A. Ciarlo, G. Pesce, A. Sasso and F. Greco, *Soft Matter* 2022, 18, 351
- [4] F. Rusciano, R. Pastore and F. Greco, *Phys. Rev. Lett.* 2022, in press.

# Changes in the form factor and size distribution of nanogels in crowded environment

*Tom Höfken<sup>1</sup>, Christian Strauch<sup>1</sup>, Stefanie Schneider<sup>1</sup>, and Andrea Scotti<sup>1</sup>*

<sup>1</sup>Institute of Physical Chemistry, RWTH Aachen University, 52056 Aachen Germany

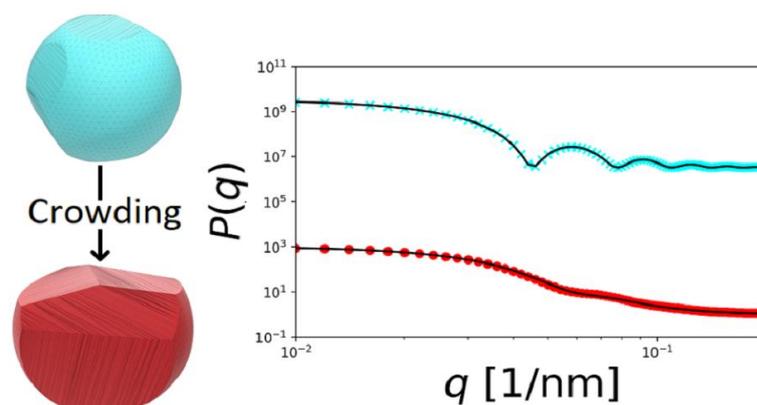
<sup>2</sup>Affiliation Two

Presenting author's e-mail: [hoefken@pc.rwth-aachen.de](mailto:hoefken@pc.rwth-aachen.de)

Particle size disparities suppress crystallization. However, soft deformable nanogels can change the size of the larger particles in suspension and crystallize even at high initial size-polydispersity. Using neutron scattering with contrast variation, the response of individual nanogels in crowded environments was probed and an increase of the parameter describing size-polydispersity is found and often interpreted as deformation.

Here, computer simulations are used to generate deformed nanogels and the corresponding form factor. The data are fitted with the spherical model used to analyze scattering data. The fits show the same qualitative increase of the parameter related to the size-polydispersity with increasing particle deformation. Starting from the simulated deformed spheres, we also reproduce experimental scattering data. A further analysis of the particle shows that the size disparities between particles do not increase significantly. In contrast, their shapes strongly vary from one nanogel to the other.

**Keywords:** nanogels, deformable particles, scattering, simulation



**Figure 1.** The average form factor of strongly faceted nanogels shows broader and less pronounced minima. This trend is very similar to the effect a higher size-polydispersity has on the form factor.

## References

[1] T. Höfken, C. Strauch, S. Schneider and A. Scotti, Nano Letters 2022, 22 (6), 2412-2418.

## Bottom-Up Coarse-Grained Modelling of DNA minicircles

*Terpsichori S. Alexiou<sup>1</sup>, Christos N. Likos<sup>1</sup>*

<sup>1</sup>*University of Vienna*

Presenting author's e-mail: [alexiou.terpsichori@univie.ac.at](mailto:alexiou.terpsichori@univie.ac.at)

In the crowded intracellular milieu, DNA molecules frequently assume circular molecular conformations, ranging from simple, topologically unlinked configurations (even exhibiting supercoiling or knots) to structurally complex, topologically interlinked configurations such as the kinetoplast DNA (kDNA). Comprising a gigantic network composed of thousands of circular DNA molecules that are topologically linked into a chain mail-like network, the kinetoplast poses a considerable computational modelling challenge that requires a coarse-grained (CG) level of description suitable to address the relevant range of length scales in a computationally efficient manner.

The objective of the work presented here is to systematically derive a bottom up, coarse-grained model for the accurate description of the conformation and dynamic behavior of the individual minicircle constituents comprising a 2D kinetoplast network. Starting from an atomistic level resolution description of DNA minicircles (finer scale), a reduced description at a base-pair and nucleotide level resolution (coarser scale) is attained by employing a three bead per nucleotide coarse graining structural mapping. The ensuing effective interactions between the coarse-grained structural beads, including bonded, angle and non-bonded interactions between DNA beads, between charged mobile ions, as well as between ions and DNA are fully accounted for, and the respective effective interaction potentials are obtained in a systematic and rigorous bottom-up fashion using the Iterative Boltzmann Inversion method.

The resulting set of effective interaction potentials are subsequently employed to investigate the equilibrium behavior of DNA minicircles in unlinked and linked states and are compared against the findings of previous experimental and atomistic simulation studies,<sup>1</sup> as well as against other proposed coarse-grained models.

**Keywords:** DNA minicircles, effective interactions

### References

- [1] J. Lukeš, D. L. Guilbride, A. Zíková, *et al.*, *Eukaryotic Cell*, 2002, 1, 495.
- [2] T.S. Alexiou, P.V. Alatas, D.G. Tsalikis, and V.G. Mavrantzas, *Macromolecules*, 2020, 53, 5903.

# Clustering and Dynamics in quasi-two-dimensional Dispersions of Proteins with competing Interactions

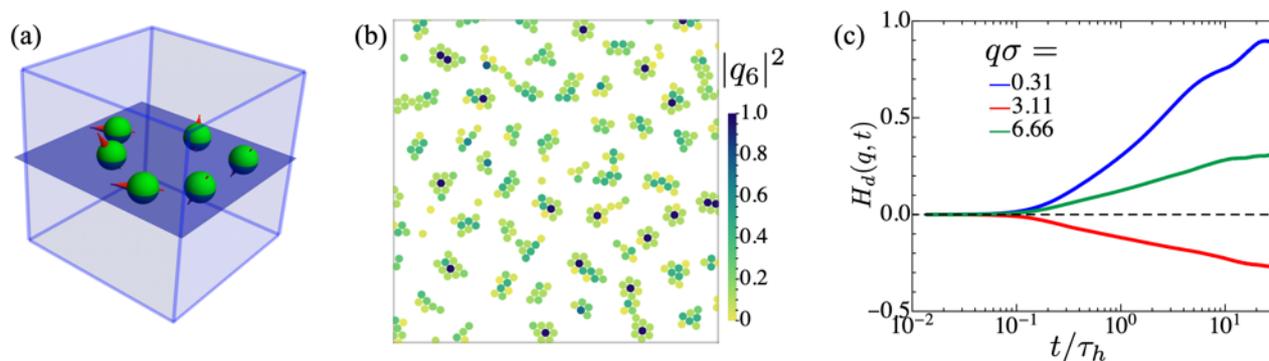
Zihan Tan <sup>1</sup>, Jan K. G. Dhont <sup>1</sup>, and Gerhard Nägele <sup>1</sup>

<sup>1</sup>Institute of Biological Information Processing, IBI-4  
Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

Presenting author's e-mail: [g.naegle@fz-juelich.de](mailto:g.naegle@fz-juelich.de)

Dispersions of globular proteins or colloids with competing short-range attractive (SA) and long-range repulsive (LR) interactions exhibit a rich phase behavior with a variety of different cluster phases. While three-dimensional SALR dispersions have been intensely studied also regarding their cluster dynamics [1], little is known about the structure and dynamics of quasi-two-dimensional (Q2D) dispersions. The SALR particles in a Q2D dispersion form a planar monolayer inside the bulk fluid, with their centres confined to in-plane Brownian motion. The interplay of Q2D motion, SALR direct interactions and solvent-mediated hydrodynamic interactions (HIs) give rise to peculiar effects such as anomalously enhanced collective diffusion. Using Langevin dynamics simulations, we have determined the generalized phase diagram, and cluster shape and size distributions of a generic Q2D model dispersion of SALR particles [2]. The particles in the monolayer are described as Brownian spheres interacting via short-range attractive generalized Lennard-Jones and long-range repulsive screened Coulomb potential contributions. These interactions apply, e.g., to protein solutions under low-salinity conditions. Additionally, in an elaborate multiparticle collision dynamics (MPC) simulation study, we explored hydrodynamic and direct interaction effects on the Q2D translational and rotational particles diffusion [2]. The MPC study covers a broad range of correlation times, from very short times where the particle dynamics is non-instantaneously affected by sound propagation and transversal momentum diffusion in the solvent, to long times where HIs are fully developed. We analyzed the concentration dependence of collective diffusion at different wavenumbers, in conjunction with mean-squared displacements and real-space van Hove functions characterizing self- and collective diffusion, and non-Gaussian dynamics. To reveal the development of inter-particles HIs by multiple scattering of sound and vorticity diffusion, we examined velocity self- and cross-correlations in conjunction with associated time-dependent hydrodynamic functions.

**Keywords:** quasi-two-dimensional, SALR protein systems



**Figure:** (a) Q2D layer of model proteins (sketch). (b) Simulation snapshot of Q2D cluster-fluid phase system. (c) Time-dependent distinct hydrodynamic function at different wavenumbers  $q$  as indicated.

## References

- [1] S. Das, J. Riest, R. Winkler, G. Gompper, J.K.G. Dhont and G. Nägele, *Soft Matter*, 2018, **14**, 92.  
[2] Z. Tan, J.K.G. Dhont and G. Nägele, two papers in preparation, 2022.

# Analysis of the ice surface structure after binding of an antifreeze protein and its correlation with the Gibbs-Thomson equation

*Gerhäuser Julian<sup>1</sup>, Gaukel Volker<sup>1</sup>*

<sup>1</sup>Karlsruhe Institute of Technology, Institute of Process Engineering in Life Sciences, Chair of Food Process Engineering, Karlsruhe, Germany

Presenting author's e-mail: [julian.gerhaeuser@kit.edu](mailto:julian.gerhaeuser@kit.edu)

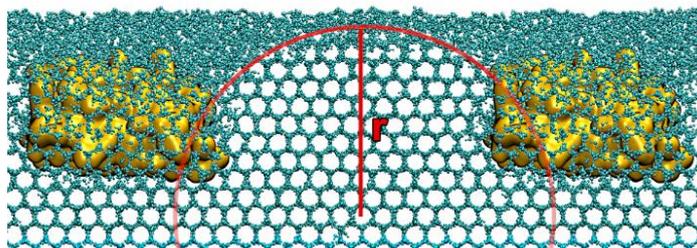
Antifreeze proteins (AFP) are able to adsorb to the ice crystal surface and to modulate the ice crystal growth and the recrystallization process due to the Gibbs-Thomson effect. The adsorption of AFP leads to the formation of a curved ice surface and it is generally believed that there is a critical ice crystal radius between the proteins on the ice surface, which determines the maximum thermal hysteresis. In this work, molecular dynamics simulations were performed to analyze the resulting structure of the ice crystal surface after adsorption of an AFP (*spruce budworm* AFP [1]) and to determine the location of the critical radius.

In contrast to earlier assumptions from literature, we were able to show that the critical radius is not directly between the adsorbed proteins. Furthermore, we have shown that the minimum temperature at which the system does not freeze is in very good agreement with the value calculated with the Gibbs-Thomson equation at the critical radius, provided that dynamic system conditions are taken into account. This proves that the Gibbs-Thomson effect is the basis of ice crystal growth inhibition and that MD simulations are useful for predicting melting point depression by AFP [2]. The knowledge gained in this study will also be applied to other molecules and systems in the future.

**Keywords:** antifreeze protein, Gibbs-Thomson equation, molecular dynamics simulation

## Gibbs-Thomson Eq.

$$T_m(x) = T_m^\infty - \frac{M * \sigma * T_m^\infty}{\rho * \Delta H_f} * \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$$



**Figure 1.** Curvature between the antifreeze proteins and Gibbs-Thomson equation. [2]

## References

[1] Graether SP, Kuiper MJ, Gagné SM, Walker VK, Jia Z, Sykes BD, Davies PL. Betahelical structure and ice-binding properties of a hyperactive antifreeze protein from an insect. *Nature*. 2000 Jul 20;406(6793):325-8. doi: 10.1038/35018610.

[2] Gerhäuser J, Gaukel V. Detailed Analysis of the Ice Surface after Binding of an Insect Antifreeze Protein and Correlation with the Gibbs-Thomson Equation. *Langmuir*. 2021 Sep 29. doi: 10.1021/acs.langmuir.1c01620.

## Monitoring freezing at surfactant-stabilized hexadecane/water interface by molecular dynamics

*Sonya Tsibranska*<sup>1</sup>, *Stoyan Iliev*<sup>2</sup>, *Anela Ivanova*<sup>2</sup>, *Slavka Tcholakova*<sup>1</sup>, and *Nikolai Denkov*<sup>1</sup>

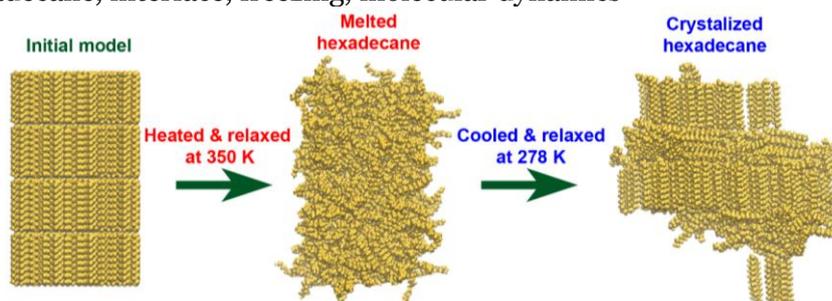
<sup>1</sup>*Department of Chemical and Pharmaceutical Engineering, Faculty of Chemistry and Pharmacy, Sofia University, 1 J. Bourchier Ave., 1164 Sofia, Bulgaria*

<sup>2</sup>*Department of Physical Chemistry, Faculty of Chemistry and Pharmacy, Sofia University, 1 J. Bourchier Ave., 1164 Sofia, Bulgaria*

Presenting author's e-mail: [st@lcpe.uni-sofia.bg](mailto:st@lcpe.uni-sofia.bg)

We have recently discovered that micrometer drops exhibit a spectacular series of shape transformations upon cooling [1]. Shapes such as spheres, icosahedra, prisms, and even fibers or drops bursting into nanoparticles are witnessed [2]. The proposed mechanism of this unusual phenomenon is that the shapes are caused by freezing layers of long-chain surfactants at the drop surfaces which act as a 2D template for ordering of alkane molecules into thin surface multilayers [3]. Experimental investigation of drops dynamics shows: (1) the alkane multilayers resemble “intermediate rotator phases” [4] and (2) all phenomena depend strongly on the interfacial curvature. The factors governing these two events at the molecular level still need to be understood. In this study, we performed molecular dynamics simulations of surfactant-stabilized hexadecane-water interfacial models upon cooling by gradually lowering the temperature of the system to monitor the freezing of the molecules and the formation of a multilayer alkane rotator phase. We studied flat and cylindrical models to investigate the role of the interface curvature. We checked the effect of cooling rate and starting temperature on the crystallization behavior. We tracked and analyzed the thermodynamic parameters and changes in the intermolecular orientation and structure to quantify the phase state of all studied systems.

**Keywords:** hexadecane, interface, freezing, molecular dynamics



**Figure 1.** Illustration of the molecular dynamics procedure developed to study the initial stages of freezing of hexadecane-containing systems; representative structures in liquid and frozen state are shown.

**Acknowledgements:** The work was funded by the Bulgarian Ministry of Education and Science, under the National Research Program “VIHREN”, project ROTA-Active (no. KP-06-DV-4/16.12.2019). Computational time was provided by the HPC facilities CSCS and ARIS.

### References

- [1] N. Denkov, S. Tcholakova, I. Lesov, D. Cholakova, and S.K. Smoukov, *Nature*, 2015, 528, 392.
- [2] S. Tcholakova, Z. Valkova, D. Cholakova, Z. Vinarov, I. Lesov, N. Denkov, and S.K. Smoukov, *Nat. Commun.*, 2017, 8, 1.
- [3] P. A. Haas, R. E. Goldstein, S. K. Smoukov, D. Cholakova, and N. Denkov, *Phys. Rev. Lett.*, 2019, 118, 088001.
- [4] D. Cholakova and N. Denkov, *Adv. Colloid Interface Sci.*, 2019, 269, 7.

## Like-charge attraction at the nanoscale: ground-state correlations and water destructuring

*Ivan Palaia*<sup>1</sup>, *Abhay Goyal*<sup>2</sup>,  
*Emanuela Del Gado*<sup>2</sup>, *Ladislav Šamaj*<sup>3</sup>, and *Emmanuel Trizac*<sup>4</sup>

<sup>1</sup> *Institute of Science and Technology Austria, Klosterneuburg, Austria*

<sup>2</sup> *Department of Physics, Georgetown University, Washington DC, USA*

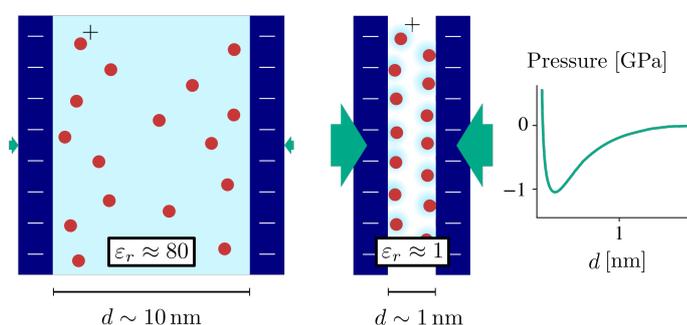
<sup>3</sup> *Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovakia*

<sup>4</sup> *LPTMS, Université Paris-Saclay and CNRS, Orsay, France*

Presenting author's e-mail: [ivan.palaia@ist.ac.at](mailto:ivan.palaia@ist.ac.at)

Like-charge attraction is a central effect in charged soft matter, ruling DNA condensation and self-assembly of lipid bilayers or polyelectrolytes. It is essential to understand cohesion forces at the nanoscale in materials such as clays and cement. The fact that similarly charged objects may attract is counter-intuitive, but many fundamental works have identified in it the signature of ionic correlations. A number of exact requirements have been obtained so far, yet no reliable equation of state (pressure versus distance) is known to fulfil these constraints. This hampers the construction of coarse-grained models and leads to much empiricism in bridging the nano- with the macroscale.

In our work [1] we fill this gap, showing that zero-temperature physics, oblivious of fluctuations, is surprisingly relevant even at finite temperature. Our ground-state approach allows to write down a simple equation of state that fulfills known exact requirements and nicely describes like-charge attraction, as confirmed by Monte Carlo simulations. We then look at real systems under nanometric confinement, where the continuum model of water, the so-called bulk primitive model, fails. A comparison to molecular simulations shows that the destructuring of water molecules under confinement is accurately described by a primitive model *in vacuum*, with drastically lowered permittivity. The resulting pressures are orders of magnitude stronger than what predicted by the commonly used bulk primitive model (Fig. 1). Our equation of state, at low permittivity, explains attraction between like-charged platelets in cement and clays, providing an analytical understanding of the cohesion forces therein. Using it as an effective potential paves the way to a physically sound upscaling of cohesion forces.



**Figure 1.** Water destructuring upon confinement is responsible for huge cohesion forces, even in presence of monovalent counterions, as seen in simulations and predicted by our analytical theory.

**Keywords:** electrostatics, ionic correlations, like-charge attraction, cohesion forces, cement, clays

### References

[1] I. Palaia et al., J. Phys. Chem. B, 2022, [10.1021/acs.jpcc.2c00028](https://doi.org/10.1021/acs.jpcc.2c00028), [arXiv:2203.10524](https://arxiv.org/abs/2203.10524)

## **Confinement vs Rigidity and its Influence on the Structure Development of Semi-Dense and Dense Suspensions**

*Erika I Barcelos<sup>1,2</sup>, Shaghayegh Khani<sup>1</sup>, Arman Boromand<sup>3</sup>, Felliipe C. Oliveira<sup>5</sup>, M. Naccache<sup>2</sup>, J. Maia<sup>1</sup>*

<sup>1</sup> *Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH, USA*

<sup>2</sup> *Department of Mechanical Engineering, Pontífica Universidade Católica do Rio de Janeiro, Rio de Janeiro Brazil*

<sup>3</sup> *Department of Mechanical Engineering and Materials Science, Yale University, New Haven, CT, USA* <sup>5</sup> *COPPE, Department of Chemical Engineering, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil*

Presenting author's e-mail: [jmm272@case.edu](mailto:jmm272@case.edu)

Suspensions have been extensively studied over the past decades and continue to be the focus of many works. A particular application in which suspensions have been increasingly explored is in confined systems. Although some attempts have been made at addressing confinement in suspensions, a systematic study evolving the combined effects of confinement, flow rate and particle rigidity in concentrated suspensions is still lacking. In this work, Core-Modified Dissipative Particle Dynamics is employed to model semi-dense and dense suspensions under confinement. The walls as well as the solvent are represented as traditional DPD particles which interact center-to-center by soft potentials. Colloidal particles, on the other hand, are modelled as Core-Modified particles, having a rigid core and a soft shell and the interactions are driven by a semi-hard potential. Colloidal particles interactions take place by means of a core force, responsible to tune the rigidity, and a lubrication force, representative of the short-range hydrodynamic interactions. Since the interactions between wall and the particles are soft, penetration may occur, which is undesirable, so a Machine Learning model was used to determine the interaction parameters that minimize wall penetration by the solve and colloidal particles. The effect of flow rate, confinement and particle rigidity were systematically studied in semi-dense and dense suspensions in a pressure driven flow. Rigid particle suspensions are more viscous and have a slower motion compared to the soft ones. Different microstructures and particles arrangement were observed depending on the values of the parameters adopted, with confinement being the most important factor driving particle migration and optimal confinement value existing for the formation of a percolating network, which is a necessary condition for discontinuous shear-thickening.

## Bronze-Mean Hexagonal Quasicrystals

Tomonari Dotera <sup>1</sup>, Joichiro Nakakura <sup>1</sup>, Shin-ichi Bekku <sup>1</sup>, Jun-ichi Matsuzawa <sup>2</sup>,  
and Primož Ziherl <sup>3,4</sup>

<sup>1</sup>Kindai University, Osaka, Japan

<sup>2</sup>Nara Women's University, Nara, Japan

<sup>3</sup>Faculty of Mathematics and Physics, University of Ljubljana, Ljubljana, Slovenia

<sup>4</sup>Jožef Stefan Institute, Ljubljana, Slovenia

Presenting author's e-mail: [primoz.ziherl@fmf.uni-lj.si](mailto:primoz.ziherl@fmf.uni-lj.si)

The most striking feature of conventional quasicrystals is their non-traditional symmetry characterized by icosahedral, dodecagonal, decagonal or octagonal axes. The symmetry and the aperiodicity of these materials stem from an irrational ratio of two or more length scales controlling their structure, the best-known examples being the Penrose and the Ammann–Beenker tiling as two-dimensional models related to the golden and the silver mean, respectively. Surprisingly, no other metallic-mean tilings have been discovered so far. We propose a self-similar bronze-mean hexagonal pattern [1], and we use numerical simulations to demonstrate that a disordered variant of this quasicrystal can be materialized in colloidal particles with a core–shell architecture. Moreover, by varying the geometry of the pattern we generate a sequence of structures, which provide an alternative interpretation of quasicrystalline approximants observed in some metal–silicon alloys. We also propose generalizations of the bronze-mean tiling that consist of increasingly larger periodic domains, which can be viewed as aperiodic approximants of a periodic crystal [2]. Consisting of small and large triangles and rectangles, these tilings are based on the metallic means of multiples of 3, have a 6-fold rotational symmetry. Together with the non-metallic-mean three-tile hexagonal tilings, they provide a comprehensive theoretical framework for the complex structures seen, e.g., in some binary nanoparticles, oxide films, and intermetallic alloys. We also discuss other quasicrystalline patterns with allowed rotational symmetries.

**Keywords:** quasicrystals, bronze mean, core-shell particles, approximants

### References

[1] T. Dotera, S. Bekku and P. Ziherl, *Nat. Mater.*, 2017, 16, 987.

[2] J. Nakakura, P. Ziherl, J. Matsuzawa and T. Dotera, *Nat. Commun.*, 2019, 10, 4235.

Wednesday 7th September 2022

**Chinese-European Symposium**

# Supramolecular Polymerization at Interfaces

*Xi Zhang*

*Department of Chemistry, Tsinghua University, Beijing, China*

Presenting author's e-mail: [xi@mail.tsinghua.edu.cn](mailto:xi@mail.tsinghua.edu.cn)

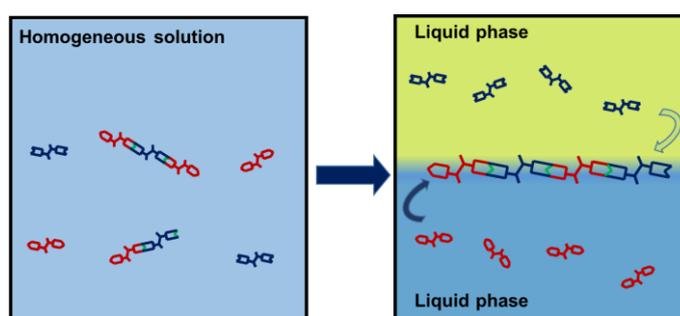
Supramolecular polymers, originating from the interplay between polymer science and supramolecular chemistry, have attracted increasing interest in scientific and industrial communities. Supramolecular polymerization normally takes place spontaneously by self-assembly in solutions. By the marriage of supramolecular polymerization and interfacial polymerization, supramolecular polymerization can be transferred from homogeneous solutions to interfaces.

We have employed oil-soluble supramonomers and water-soluble covalent monomers to implement supramolecular interfacial polymerization, which allows for the production of supramolecular polymers in a controlled manner. Compared with solution polymerization, supramolecular polymerization at interfaces has exhibited a variety of advantages, such as easy operation and separation, feasibility for immiscible monomers, and producing supramolecular polymers with well-defined structures.

In addition to macroscopic liquid-liquid interfaces, we have also established supramolecular emulsion interfacial polymerization at the microscopic interfaces. Compared with a homogeneous solution, the liquid-liquid interface offers a confined reaction region, where monomers tend to react with growing polymer chains rather than starting new chains, thus allowing for the direct preparation of supramolecular polymeric films and nanospheres with higher molecular weights.

It is anticipated that supramolecular polymerization at interfaces will enrich the methodology of controllable supramolecular polymerization and facilitate the construction of supramolecular polymeric materials with diverse architectures and tailor-made functions.

**Keywords:** supramolecular polymers, interfaces, supramonomer



**Figure 1.** Supramolecular polymerization from homogeneous solutions to liquid-liquid interfaces.

## References

- [1] B. Qin, J.-F. Xu, X. Zhang, *Langmuir*, 2022, 38, 4157.
- [2] B. Qin, S. Zhang, Q. Song, Z. Huang, J.-F. Xu, X. Zhang, *Angew. Chem. Int. Ed.*, 2017, 56, 7639.
- [3] B. Qin, S. Zhang, Z. Huang, J.-F. Xu, X. Zhang, *Macromolecules*, 2018, 51, 1620.
- [4] S. Zhang, B. Qin, Z. Huang, J.-F. Xu, X. Zhang, *ACS Macro Lett.*, 2019, 8, 177.
- [5] Y. Liu, Y. Yu, J. Gao, Z. Wang, X. Zhang, *Angew. Chem. Int. Ed.*, 2010, 49, 6576.
- [6] P. Sun, B. Qin, J.-F. Xu, X. Zhang, *Prog. Polym. Sci.*, 2022, 124, 101486.

# Counterion Effect on the Water Wettability of Polycationic Surfaces

*Dayang Wang*

*State Key Lab of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun, China*

Presenting author's e-mail: [wangdayang@jlu.edu.cn](mailto:wangdayang@jlu.edu.cn)

This talk will present an overview of our recent studies of how the surface hydrophilicity of polyelectrolyte multilayer films, obtained via LbL assembly is correlated with the molecular nature and structures of their outmost surfaces.<sup>[1-3]</sup> Here the focus is laid particularly on the effect of the nature of surface counterions on the water wettability of the polycationic surfaces of polydiallyldimethylammonium (PDADMA).<sup>[3]</sup> The counterions of the PDADMA coatings were systematically altered by incubation in aqueous solutions of different electrolytes. Oil de-wetting on the resulting polycationic surfaces upon water action exhibited a surprisingly straightforward connection with the sign of Jones-Dole viscosity B-coefficient ( $B\eta$ ) of surface counter-anions<sup>[4]</sup>. The anions with negative  $B\eta$  make the PDADMA coatings reasonably adhering to oil in water, whereas those with positive  $B\eta$  render the PDADMA coatings strikingly self-cleaning upon immersion into or flushing with water. This specific ion effect on oil de-wetting upon water action enabled us to direct and confine the oil flow on the PDADMA surfaces according to the  $B\eta$  sign of surface counterions selectively patterned on designated regions. Thanks to their excellent self-cleaning function arising from surface counter-anions with positive  $B\eta$ , the PDADMA coating enabled conventional meshes to effectively separate or skim oil from water without need of prior water wetting on the dry surfaces.

**Keywords:** Wetting, Hydration, Self-cleaning, Anions, Polyelectrolyte

## References

- [1] X. Liu, C. Leng, Y. Li, K. He, L. Brown, Z. Chen, J. Cho, D. Wang, *Angew. Chem. Int. Ed.* 2015, 54, 4851.
- [2] S. Huang, D. Wang, *Angew. Chem. Int. Ed.* 2017, 56, 9053.
- [3] Q. Tao, S. Huang, Y. Li, X.-F. Chu, X. Lu, D. Wang, *Angew. Chem. Int. Ed.* 2020, 59, 14466.
- [4] H. D. B. Jeakins, Y. Marcus, *Chem. Rev.* 1995, 95, 2695.

## Multi-dimensional manipulation of Solid/Liquid interaction

Xu Deng

*Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu, China*

Presenting author's e-mail: [dengxu@uestc.edu.cn](mailto:dengxu@uestc.edu.cn)

Solid/Liquid interaction play important role in many research and application fields. In this presentation, we will introduce a radically new strategy that resolves the bottleneck through the creation of an unexplored gradient in surface charge density (SCD) [1]. By leveraging on a facile droplet printing on superamphiphobic surfaces as well as the fundamental understanding of the mechanisms underpinning the creation of the preferential SCD, we demonstrate the self-propulsion of droplets with a record-high velocity over an ultra-long distance without the need for additional energy input. We envision that our work enriches and extends our capability in the manipulation of droplet transport and would find numerous potential applications otherwise impossible. We will also show that robust superhydrophobicity can be realized by structuring surfaces at two different length scales, with a nanostructure design to provide water repellency and a microstructure design to provide durability. The microstructure is an interconnected surface frame containing ‘pockets’ that house highly water-repellent and mechanically fragile nanostructures. This surface frame acts as ‘armour’, preventing the removal of the nanostructures by abrasants that are larger than the frame size [2]. We apply this strategy to various substrates—including silicon, ceramic, metal and transparent glass—and show that the water repellency of the resulting superhydrophobic surfaces is preserved even after abrasion by sandpaper and by a sharp steel blade. This design strategy could also guide the development of other materials that need to retain effective self-cleaning, anti-fouling or heat-transfer abilities in harsh operating environments.

**Keywords:** Solid-liquid interface, Wetting, droplet

### References

- [1] QQ. Sun, ZK. Wang, HJ. Butt and X. Deng *et al.*, *Nature Materials*, 2019, 18, 936.
- [2] DH. Wang, R. Ras and X. Deng *et al.*, *Nature*, 2020, 582, 55.
- [3] JN. Song and X. Deng *et al.*, *Advanced Materials*, 2021, 33, 2007154.
- [4] WL. Zhang and X. Deng *et al.*, *Chemical Society Reviews*, 2021, 50, 4031.

# PeptoMicelles in Cancer Immune Therapy

Matthias Barz

*Leiden Academic Center for Drug Research, Leiden University, Leiden,  
Netherlands*  
*Department of Dermatology, University Medical Center of the Johannes  
Gutenberg University Mainz, Mainz, Germany*

Presenting author's e-mail: [m.barz@lacdr.leidenuniv.nl](mailto:m.barz@lacdr.leidenuniv.nl)

The enormous potential of polymeric nanomedicines arises from the possibility to combine desirable material properties with compartmentalized functionalities in one distinct nanoparticle,<sup>[1]</sup> to encapsulate and deliver drugs and limit their side of action to diseased tissues. While a vaccination against cancer aims for systemic immunity against cancer specific antigens, the abolishment of immune tolerance should ideally occur locally to avoid systemic adverse effects.<sup>[2]</sup>

In this talk, we present 2 approaches for the local abolishment of immune suppression to enable the body own immune system to fight existing tumors. One way tumor cells and related tolerogenic immune cell use to dampen or completely silence immune responses against solid tumors is the use of cyclic adenosine monophosphate (cAMP). In elevated concentrations this secondary messenger generates an immune suppressive environment supporting tumor progression. To break this cycle, we use PeptoMicelles<sup>[3,4]</sup> containing an adenosine cyclase inhibitor, which block the enzyme producing cAMP. When these micelles are locally applied to existing tumor by peritumoral injection, a sustained drug release was observed, which induced the reduction of cAMP levels locally without detectable adverse effects and lead to pronounced reduction of tumor growth. In combination with selective, non-therapeutic regulatory T cell depletion, PeptoMicelles achieve a complete remission of established B16-F10-OVA tumors.<sup>[5]</sup>

In the second approach we use iron oxide nanoparticle loaded PeptoMicelles to target tolerogenic macrophages to restore a tumor suppressive M1 phenotype. When applied to primary murine and human macrophages, these nanoparticles display preferential uptake, sustained intracellular iron release, and induce a strong inflammatory response. This response is also demonstrated in vivo when nanoparticles are intratracheally administered to wild-type C57Bl/6N mice. Most importantly, the controlled release concept to deliver iron oxide in redox-responsive CCPMs induces significantly stronger macrophage activation than any other iron source at identical iron levels (e.g., Feraheme), directing to a new class of immune therapeutics.<sup>[6]</sup> Both approaches underline the potential of PeptoMicelles in immune therapies.

## References

- [1] Blanco E, Shen H, Ferrari M. *Nature Biotechnol.* **2015**, 33, 941-951.
- [2] Sun Q, Barz M et al. *Chem. Soc. Rev.* **2019**, 48 (1), 351-381.
- [3] Klinker K, Barz M. *Macromol. Rapid. Commun.* **2015**, 36 (22), 1943-1957.
- [4] Klinker K et al. *Angew. Chem. Int. Ed.* **2017**, 56 (32), 9608-9613.
- [5] Johan K et al. *Nature Commun.* **2021**, 12 (1), 1-9.
- [6] Bauer TA et al. *Adv. Healthcare Mat.* **2021**, 10 (19), 2100385.

## Acknowledgments

We acknowledge support by the German Research Council (Deutsche Forschungsgemeinschaft) SFB 1066-3, the Max Planck Graduate Center with the Johannes Gutenberg-Universität Mainz (MPGC) and the HaVo Foundation.

# Basic Study on Colloid Dispersed Systems Stimulates Chemical Industrialization

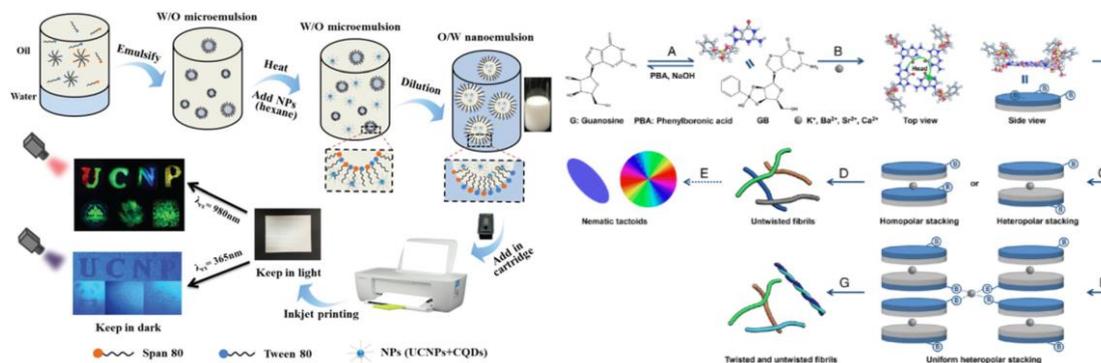
*Jingcheng Hao*<sup>1</sup>

<sup>1</sup>Key Laboratory of Colloid and Interface Chemistry of the Ministry of Education, Shandong University, Jinan, Shandong 250100, China.

Presenting author's e-mail: [jhao@sdu.edu.cn](mailto:jhao@sdu.edu.cn)

The micelles have been investigated for more than one hundred years since discovered by McBain,[1] colloidal dispersion systems have always been the focus of applied basic research, and new research directions appear constantly, such as soft matter and self-assembly cutting-edge research. This is because the colloidal dispersion systems to the basic research of traction, such as the preparation of basic chemicals, surfactant purification, colloid electrolyte, as well as drug delivery and nanomaterial synthesis with important applications in a broad range of areas. [2,3] In many applications of colloidal dispersion systems, the application of aggregates and surface/interface assembly, such as micelles, vesicles, emulsions, gels and other contents in the surfactant solution, have drawn the development technology and green utilization of bulk basic chemicals, and extracted the key scientific issues. In this report, the application of basic research results of our group in recent years is taken as a typical case, and the relevant basic research results, such as the preparation and performance of emulsion gel materials, thermotropic liquid crystal phase transformation, and the industrialization and application of traction surfactant-based materials are summarized.

**Keywords:** stealth, poly(ethylene glycol), drug delivery, colloidal nanoparticles



**Fig. 1.** Fluorescent anti-counterfeiting inks and applying to inkjet printing dual-mode fluorescence patterns (Left), Self-assembly of guanosine derivative at different scale levels (Right).

## References

- [1] J. W. McBain, et al. Colloids and their viscosity, *Trans. Faraday Soc.* 1913, 9, 99-101.
- [2] J. Hao, et al. Metal ions confinement defines the architecture of G-quartet, G-quadruplex fibrils and their assembly into nematic tactoids, *Proc. Natl. Acad. Sci. USA* 2020, 117, 9832-9839.
- [3] J. Hao, et al. Photovoltaic energy conversion and storage of micro-supercapacitors based on emulsion self-assembly of upconverting nanoparticles, *ACS Central Sci.* 2021, 7, 1611-1621.

# Structural Water and Crown Ether: New Functional Supramolecular Assemblies

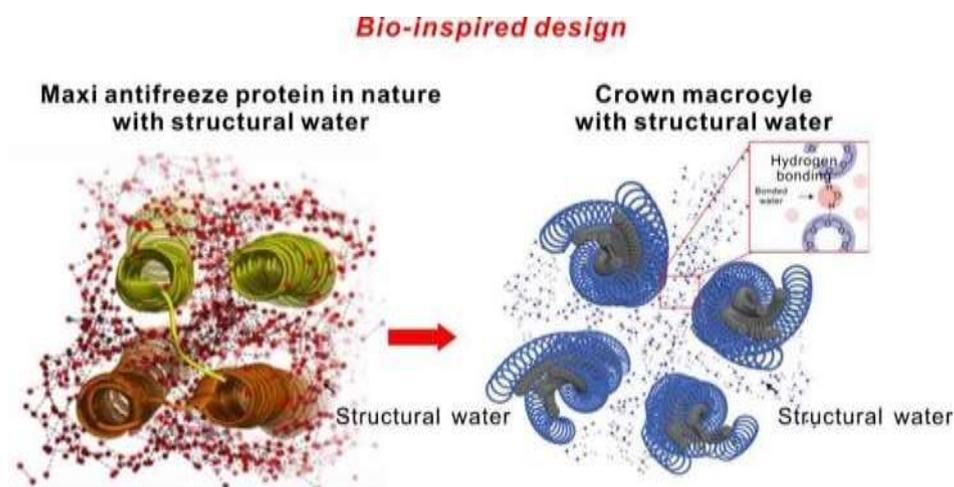
*Qi Zhenhui*

*Northwestern Polytechnical University, Xi'an, China*

*Presenting author's e-mail: [qi@nwpu.edu.cn](mailto:qi@nwpu.edu.cn)*

The inspiration derives from the concept of structural water in nature that water molecules are bound inside hydrophobic pockets and help to stabilize protein structures. However, water has rarely been found a similar role in material science. By introducing crown ether into aqueous medium, the crown-water interaction triggered the supramolecular polymerization which exhibits strong adhesion to surfaces, and can be reused many times without losing its performance. Considering the unique feature of water, this discovery revealed the unprecedented role of structural water and crown ether in material science, including the novel anti-icing performance.

**Keywords:** Structural Water, Crown Ether, Supramolecular Polymerization, Anti-icing



**Figure 1.** The hydrogen networks for water molecules for design bio-inspired materials.

## References

- [1] S. Dong, J. Leng, Y. Feng, M. Liu, C. J. Stackhouse, A. Schonhals, L. Chiappisi, L. Gao, W. Chen, J. Shang, L. Jin, Z. Qi and C. A. Schalley, *Sci Adv*, 2017, 3, eaa00900.  
 [2] T. Pan, J. Li, B. Li, Q. Xu, Z. Cui, J. Shang, Y. Ge and Z. Qi, *J Phys Chem Lett*, 2021, 12, 7418.

Wednesday 7th September 2022

**Design and Synthesis of Colloidal Systems and Nanoparticles**

# Functional Microgels with Non-Covalent Crosslinks: Towards Soft Adaptive Colloidal Systems

Sehyeong Jung <sup>1,2</sup>, Susanne Braun <sup>1,2</sup>, Andrij Pich <sup>1,2</sup>

<sup>1</sup> DWI, Leibniz Institute for Interactive Materials e.V., Aachen, Germany

<sup>2</sup> Functional and Interactive Polymers, Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany

Presenting author's e-mail: [pich@dwil.rwth-aachen.de](mailto:pich@dwil.rwth-aachen.de)

Biological tissues are frequently composed of macromolecular and low-molecular components, containing covalent and non-covalent crosslinks, and are assembled in a modular way exhibiting different hierarchy levels.<sup>1</sup> Such hydrogel-like materials often exhibit hysteresis effects and non-linearity of their properties, which is essential to functions like adaptability and time-programming. At present, the performance of synthetic hydrogel materials is not on par with these advanced biological hydrogels.

This contribution will focus on chemical design of stimuli-responsive microgels exhibiting non-covalent dynamic crosslinks based on host-guest complexes, ionic bonds or hydrogen bonds.<sup>2-9</sup> The development of new synthesis methods that allow controlled integration of supramolecular functionalities into microgels opens new ways to generate functional polymer materials and systems with unique functions like stimuli-responsiveness, re-shaping, and triggered disassembly.

Stimuli-responsive aqueous microgels containing degradable crosslinks based on the supramolecular host-guest complexes between  $\beta$ -cyclodextrin and cholesterol or ferrocene were synthesized.<sup>2,3</sup>

Microgels functionalized with zwitterionic units contain two types of crosslinks: -covalent and ionic.<sup>4,5,6</sup> Monodisperse colloidal stable microgels with a high amount (> 30 mol-%) of zwitterionic groups were synthesized using W/O miniemulsion approach. High contents of zwitterionic groups in microgels led to the formation of dynamic reversible ionic crosslinks along with permanent covalent crosslinks generated by bisacrylamide. Obtained microgels exhibit temperature-triggered swelling/deswelling behavior and co-existence of UCST- and LCST-type transitions in aqueous solutions.

A new synthesis method to obtain aqueous supramolecular temperature-responsive microgels using tannic acid as multifunctional physical cross-linker was developed recently.<sup>7,8</sup> The precipitation polymerization of *N*-vinylcaprolactam in the presence of tannic acid leads to the formation of well-defined stimuli-responsive microgels cross-linked by hydrogen bonds. We demonstrate that obtained microgels exhibit reversible temperature-triggered swelling/deswelling and undergo pH-triggered degradation and re-shaping in aqueous solutions.

Microgels equipped with non-covalent crosslinks exhibit unique properties like on-demand degradation, controlled release of ions and small molecules and mechanical re-enforcement.<sup>9</sup>

**Keywords:** Microgels, Supramolecular Bonds, Soft Materials

## References

- [1] R. Eelkema, A. Pich, *Adv. Mater.* **2019**, 1906012.
- [2] D. Schmitz, A. Pich, *Polymer Chemistry* **2016**, 7, 5687.
- [3] S.-H. Jung, S. Schneider, F. Plamper, A. Pich, *Macromolecules* **2020**, 53, 1043-1053.
- [4] R. Schröder, W. Richtering, I. Potemkin, A. Pich, *Macromolecules* **2018**, 51, 17, 6707-6716.
- [5] P. Saha, M. Kather, S. Banerjee, N. Singha, A. Pich, *Eur. Polym. Journal* **2019**, 118, 195-204.
- [6] P. Saha, M. Santi, M. Frenken, A. Palanisamy, R. Ganguly, N. Singha, A. Pich, *ACS Macro Letters* **2020**, 9, 895-901.
- [7] C. Molano, A. Pich, *Macromolecular Rapid Communications* **2018**, 39, 1700808.
- [8] S. Jung, S. Bulut, L. P. B. Guerzoni, L. De Laporte, A. Pich, *J Colloid Interf Sci*, **2022**, 617, 409-421.
- [9] E. Izak-Nau, S. Braun, A. Pich, R. Göstl, *Advanced Science*, **2022**, 2104004.

# Chitosan-based hydrogels: Influence of crosslinking strategy on rheological properties

*Fabien Dutertre<sup>1</sup>, Nelmary Roas Escalona<sup>1</sup>, Thierry Delair<sup>1</sup> and Frédéric Becquart<sup>1</sup>*

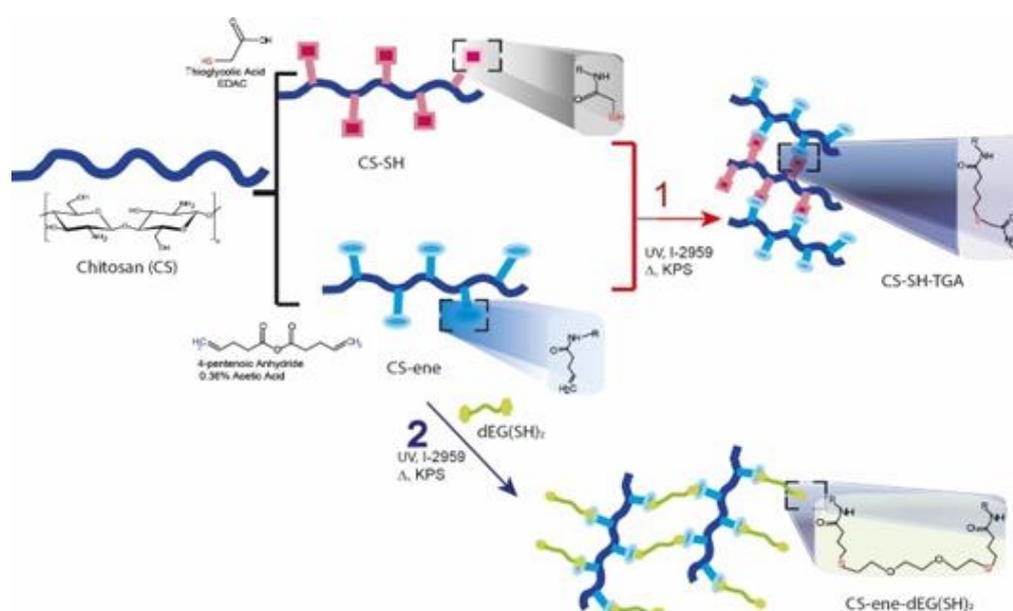
<sup>1</sup>Univ Lyon, CNRS, Ingénierie des Matériaux Polymères, Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, France

Presenting author's e-mail: [fabien.dutertre@univ-st-etienne.fr](mailto:fabien.dutertre@univ-st-etienne.fr)

The thiol-ene click chemistry is a versatile methodology widely used to form bio-hydrogel by crosslinking polysaccharides. In this opportunity, chitosan-based macrogels were prepared through thiol-ene reactions. First, the chitosan (CS) was functionalized with a vinyl group (CS-ene) or thiol groups (CS-SH). Then, two crosslinking strategies (photochemically and thermochemically activated) were compared: (1) CS-ene with CS-SH and (2) CS-ene cross-linked with di(ethylene glycol)-bis(thiol) (dEG-(SH)<sub>2</sub>).

The first strategy, where the crosslinking reaction occurs between two functionalized macromolecules and intra-chains crosslinking reactions are avoided (“no loop”), leads to the formation of weak gels. In this case, rheology displays a critical gel point ( $G' \approx G'' \approx \omega^{0.5}$ ) and the cross-linking density estimated by NMR slightly depends on the substitution degree of pentenoate-modified CS. The second strategy, where the functionalized chitosan (CS-ene) is crosslinked by reaction with a small di-thiol molecule (dEG-(SH)<sub>2</sub>), provided stronger gels with a faster diffusion of the dEG-(SH)<sub>2</sub> during the network formation, which strengthen the gel modulus. The last strategy is the most efficient methodology for the macrogel synthesis, despite that the “loop” formation cannot be fully avoided. Finally, both methodologies were transposed at the microscale through inverse emulsion to attempt to synthesize chitosan-based microgel.

**Keywords:** Thiol-ene, Chitosan, Hydrogel/Microgel, Rheology



**Figure 1.** : Scheme of chitosan functionalization by-thioglycolic acid (CS-SH) and pentenoic anhydride (CS-ene); and thiol-ene reaction with strategy 1 (CS-ene and CS-SH) and strategy 2 (CS-ene and dEG(SH)<sub>2</sub>).

# Synthesis of biocompatible microporous dextran-based microgels via microfluidics

*Selin Bulut<sup>1</sup>, Se-Hyeong Jung<sup>1,2</sup>, Susanne Braun<sup>1,2</sup> and Andrij Pich<sup>1,2</sup>*

<sup>1</sup> *Functional and Interactive Polymers, Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen, Germany*

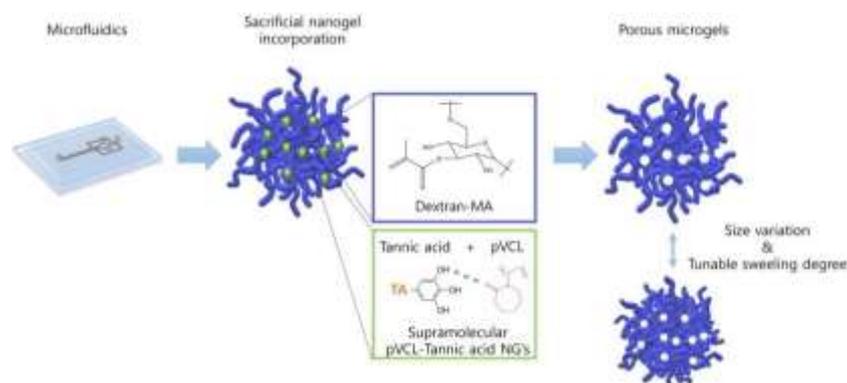
<sup>2</sup> *DWI-Leibniz Institute for Interactive Materials e.V., Aachen, Germany*

Presenting author's e-mail: [bulut@dwil.rwth-aachen.de](mailto:bulut@dwil.rwth-aachen.de)

For tissue-engineering scaffold utility, porous structures are often crucial for sufficient nutrient support, cell, and tissue penetration, where pores of sizes between 50 nm – 300 µm are preferred. Common fabrication techniques include the freeze-drying method, where water inside the gels forms ice crystals at temperatures below 0 °C. Through lyophilization, the ice crystals are turned directly into vapor, and cavities are left. The downside of this method is that pore size and geometry are difficult to control, and especially large pores are more difficult to achieve.

The aim of the present work is to design microporous polysaccharide microgels with controllable pore size using colloidal templating and droplet-based microfluidics for the potential application as tissue-engineering scaffolds. Dextran methacrylate (DexMA) has already been studied as a possible matrix for soft tissue engineering and will therefore be used as a photochemically cross-linkable pre-polymer. A series of DexMA microgels with a size range of 100-150 µm and a pore size of 690 nm were synthesized. The pores were formed through supramolecular monodisperse poly(N-vinylcaprolactam) (pVCL) microgels cross-linked with tannic acid (TA), which are used as a sacrificial colloidal template to generate well-defined pores inside the Dex-MA microgel. These sacrificial microgels can be easily degraded by changing the pH to alkaline conditions leaving cavities of the same size inside the Dex-MA microgel.[1,2] Most importantly, the microgels fundamental characteristics, such as the swelling degree, are altered by the introduction of pores. The tunability of softness, swelling degree and the pore size are beneficial to achieve a porous and tunable bio-based polymeric matrix allowing for enhanced infiltration of cells. Therefore, facilitating migration across the microgel assembly without the need to degrade the microgels first.

**Keywords:** Bio-based materials, Porous microgels, Polysaccharides, Microfluidics



**Figure 1.** Generation of bio-based porous microgels by a sacrificial colloidal template method via microfluidics

## References

- [1] S.-H. Jung, S. Bulut, L.P.B. Busca Guerzoni, D. Günther, S. Braun, L. De Laporte, A. Pich, J. Colloid Interface Sci., 2022, 617, 409–421.
- [2] C.M. López, A. Pich, Macromol. Rapid Commun., 2018, 39, 1700808.

# Encapsulation of neuroactive drugs in desolvated serum album nanoparticles

*Viktória Varga*<sup>1</sup>, *Alexandra N. Kovács*<sup>1</sup>, *Keristina Wagdi Kamil Amin*<sup>1</sup>  
and *Edit Csapó*<sup>1,2</sup>

<sup>1</sup> *Interdisciplinary Excellence Center, Department of Physical Chemistry and Materials Science, University of Szeged, Hungary*

<sup>2</sup> *MTA-SZTE Lendület “Momentum” Noble Metal Nanostructures Research Group, University of Szeged, Hungary*

Presenting author's e-mail: [vhornok@chem.u-szeged.hu](mailto:vhornok@chem.u-szeged.hu)

The application of drug delivery systems (DDS) to free drugs is advantageous for several reasons. With the application of nanoparticles (NPs), poorly soluble drugs can be solubilized, protected by the carrier and their degradation is prevented thus their half-life can be appropriately adjusted, moreover the release of their properties can be sustained or tuned according to the proposed application. Among the different types of carrier systems, the serum albumins, mainly the bovine- (BSA) and human serum albumin (HSA) are often applied in today's research.

The encapsulation of neuroprotective kynurenic acid (KYNA) and its analogue of more hydrophilic nature (SzR72) among other drugs is examined. The encapsulation possibilities of these drugs in serum albumin NPs prepared via desolvation method under various preparation conditions such as protein concentration, protein-to-drug ratio, pH, ionic strength, type and amount of desolvation agent and cross linker concentration are discussed. The encapsulation was only successful if the drugs were added to the pre-prepared BSA NPs via adsorption route and the efficiency increased (from 14.0 % to 72.4 % for KYNA) when the pH decreased from 7.4 to 4.0 resulting in a drug loading of 20.7 % due to the electrostatic interaction between the oppositely charged functional groups. Along with the drug encapsulation properties, the structural change of the protein is also presented verified by fluorescence quenching measurements and circular dichroism spectroscopy (CD) suggesting the drug insertion in the hydrophobic pockets of the protein [2]. The observed sustained release of the drugs from the carriers suggests partly different mechanism for the two molecules, Fickian diffusion-controlled for the KYNA and both diffusion and Case-II transport for the SzR72, respectively. The blood-brain barrier (BBB) permeability of the drug-containing NPs were studied through parallel artificial membrane permeability assay (PAMPA) measuring the passive diffusion through an artificial hexadecane membrane.

**Keywords:** serum albumin nanoparticles, kynurenic acid, desolvation

**Acknowledgements:** Project no. TKP2021-EGA-32 has been implemented with the support provided by the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021-EGA funding scheme. This paper was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences.

## References

- [1] V. Hornok, *Polymers*, 2021, 13, 3759.  
[2] V. Hornok, Á. Juhász, G. Paragi, A.N. Kovács and E. Csapó, *Journal of Molecular Liquids*, 2020, 313, 112869.

## Fluorescence and sensor properties of colloidal europium based metal organic framework nanoparticles

*Linda Rozenberga<sup>1</sup>, William Skinner<sup>1</sup>, David G. Lancaster<sup>1</sup>, Witold M. Bloch<sup>2</sup>, Anton Blencowe<sup>3</sup>, M. Krasowska<sup>1</sup>, David A. Beattie<sup>1</sup>*

<sup>1</sup> *Future Industries Institute, University of South Australia, Australia.*

<sup>2</sup> *Department of Chemistry and Physics, University of Adelaide, Australia.*

<sup>3</sup> *Applied Chemistry and Translational Biomaterials Group, UniSA Clinical and Health Science, University of South Australia, Australia.*

Presenting author's e-mail: [linda.rozenberga@mymail.unisa.edu.au](mailto:linda.rozenberga@mymail.unisa.edu.au)

Iron is one of the most important elements in metabolic processes, and is extensively distributed in environmental and biological materials, however precise measurement of iron concentration in solutions, particularly the ferric ion ( $\text{Fe}^{3+}$ ), is still challenging. Fluorescent sensors have the potential to provide fast, selective and accurate detection of difficult to measure analytes. Lanthanide based Metal–Organic Frameworks (MOFs), in which organic ligands connect to lanthanide metal ions to produce periodic polymeric structures, are a particularly promising class of fluorescent sensors. Fluorescent colloidal MOF nanoparticle sensors are a fast growing field, with MOFs capable of sensing not only cations, but also anions, small molecules, nitroaromatics, gasses, pH, and temperature.<sup>1</sup> Their potential applications include wastewater treatment and mineral processing, and they can also be applied to biological systems and medicine. In this work, the structure and fluorescence properties of a previously reported ratiometric europium based MOF<sup>2</sup> was investigated with a focus on its  $\text{Fe}^{3+}$  sensing in acidic media for application in mineral processing. The study resulted in new information on the true MOF structure, its  $\text{Fe}^{3+}$  sensing mechanism, and the sensing selectivity of the MOF. The results highlight the unique properties of lanthanide based MOFs, but also highlight the difficulties of assessing novel colloidal, ratiometric ion sensors. Finally, the limitations of colloidal nanoparticle sensor systems are addressed through encapsulation of the MOF in a polymer matrix.

**Keywords:** Fluorescence sensor,  $\text{Fe}^{3+}$  sensor, pH sensor, Metal-organic framework, colloidal nanoparticles

### References

- [1] Zhao, S. N., Wang, G., Poelman, D. & Van Der Voort, P. *Materials* (Basel), 2018, 11, 1.  
[2] Xu, H. et al. *J. Solid State Chem.*, 2018, 258, 441.

## Synthesis of high molecular weight water-soluble polymers as low-viscosity latex particles in salty media

Rory J. McBride<sup>1</sup>, John F. Miller<sup>2</sup>, Adam Blanz<sup>3</sup>, Hans-Joachim Hähnle<sup>3</sup>, and Steven P. Armes<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Sheffield, Sheffield, UK

<sup>2</sup>Enlighten Scientific, Hillsborough, NC, USA

<sup>3</sup>BASF SE, Ludwigshafen, Germany

Presenting author's e-mail: [rmcbride1@sheffield.ac.uk](mailto:rmcbride1@sheffield.ac.uk)

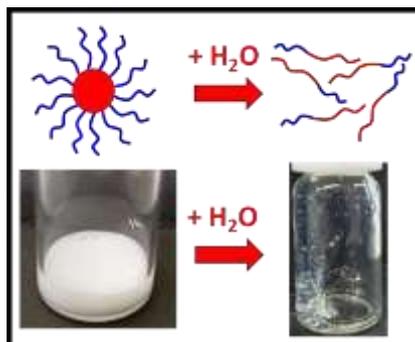
We report the synthesis of sterically-stabilized diblock copolymer particles at 20% w/w solids via RAFT aqueous dispersion polymerization of *N,N'*-dimethylacrylamide (DMAC) in highly salty media (2.0 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). This is achieved by selecting a well-known zwitterionic water-soluble polymer, poly(2-(methacryloyloxy)ethyl phosphorylcholine) (PMPC), to act as the salt-tolerant soluble precursor block. A relatively high degree of polymerization (DP) can be targeted for the salt-insoluble block, which produces a turbid free-flowing dispersion by a steric stabilization mechanism.

<sup>1</sup>H NMR spectroscopy studies indicate that relatively high DMAC conversions (>99%) can be achieved within a few hours at 30 °C. Aqueous GPC analysis indicates high blocking efficiencies and unimodal molecular weight distributions, although dispersities increase monotonically as higher degrees of polymerization (DPs) are targeted for the PDMAC block.

Particle characterization techniques include dynamic light scattering (DLS) and electrophoretic light scattering (ELS) using a state-of-the-art instrument that is capable of accurate measurements in concentrated salt solution. <sup>1</sup>H NMR spectroscopy studies confirm that subsequent dilution using deionized water lowers the background salt concentration and hence causes *in situ* molecular dissolution of the salt-intolerant PDMAC chains, which leads to a substantial thickening effect and the formation of transparent gels.

Thus this new PISA formulation enables high molecular weight water-soluble polymers to be prepared in a highly convenient, low-viscosity latex-like form. In principle, such aqueous PISA formulations are highly attractive: there are various commercial applications for high molecular weight water-soluble polymers while the negative aspects of using a RAFT agent (i.e. its cost, color and malodor) are minimized when targeting such high DPs.

**Keywords:** RAFT, PISA, polymer, latex, viscosity, thickening



**Figure 1.** Schematic cartoon and corresponding digital images to illustrate the sterically-stabilized diblock copolymer particles obtained after RAFT aqueous dispersion polymerization of DMAC in the presence of 2.0 M ammonium sulfate. Addition of sufficient water to the initial aqueous dispersion lowers the salt concentration and results in molecular dissolution of these particles, with the concomitant formation of a highly viscous transparent aqueous solution.

**Wednesday 7th September 2022**

**Active and Bioinspired Colloidal Systems**

## Separation by Complexation

*Saskia Lindhoud<sup>1</sup>, Jéré van Lente<sup>1</sup>*

<sup>1</sup>*Department of Molecules and Materials, University of Twente, the Netherlands*

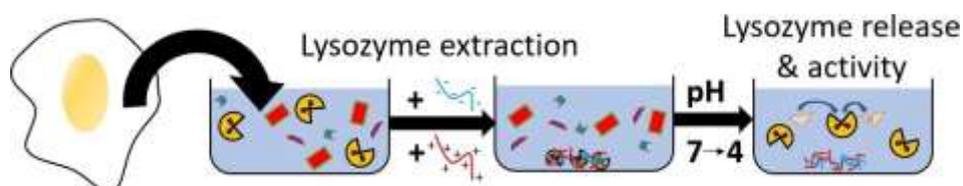
Presenting author's e-mail: [s.lindhoud@utwente.nl](mailto:s.lindhoud@utwente.nl)

Cellular processes are extremely efficient and the most complex reactions occur in the blink of an eye. This efficiency can be only be achieved by good spatiotemporal organisation, that can be obtained by compartmentalisation of the right components in structures called organelles. In the traditional view these organelles are surrounded by a phospholipid membrane. However, it appears that the cellular fluids are highly organized. It consists of dynamic droplet-like condensates, referred to as membraneless organelles. A hypothesis is that these droplet-like structures ensure spatiotemporal control of components. Our work is inspired by this spatiotemporal organisation of components, if we can mimic this in the lab we can use to develop aqueous extraction media.

Many cellular condensates consist of cationic intrinsically disordered proteins and RNA and strongly resemble polyelectrolyte complexes. In our group we therefore use polyelectrolyte complexes as model systems for the cellular condensates and study the partitioning of molecules [1] and proteins [2, 3] between the dilute aqueous phase and the dense condensate.

Previous research has demonstrated that protein uptake strongly depends on the polyelectrolyte complex composition.[2] This suggests that polyelectrolyte complexes can be used to selectively extract proteins from a multi-protein mixture. With this in mind, we studied the uptake and release of the protein lysozyme using different polyelectrolyte complexes and release procedures. Complexes of poly(allylamine hydrochloride) and poly(acrylic acid) had the best uptake and release properties. These were used for selective extraction of lysozyme from a hen-egg white protein matrix. The (back)-extracted lysozyme retained its enzymatic activity, showing the capability of polyelectrolyte complexes to function as extraction media for proteins.[3]

**Keywords:** polyelectrolyte complexes, complex coacervates, membraneless organelles, extraction



**Figure 1.** lysozyme from egg-white, extracted by polyelectrolyte complexation remains catalytically active

### References

- [1] van Lente J, Pazos Urrea M, Brouwer T, Schuur B, Lindhoud S. Complex coacervates as extraction media. *Green Chemistry* 2021; 23:5812-5824.
- [2] van Lente JJ, Claessens MMAE, Lindhoud S. Charge-Based Separation of Proteins Using Polyelectrolyte Complexes as Models for Membraneless Organelles. *Biomacromolecules* 2019; 20:3696-3703.
- [3] van Lente, J. J. & Lindhoud, S. Extraction of Lysozyme from Chicken Albumen Using Polyelectrolyte Complexes. *Small* 18, 2105147, 2022.

## In-situ Magnetic Microrheology of Airway Mucus

Gerald Fuller<sup>1</sup>, Maggie Braunreuther<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, Stanford University, Stanford, California

Presenting author's e-mail: [gjf@stanford.edu](mailto:gjf@stanford.edu)

Mucus that lines the lungs acts as the primary defense against inhaled foreign particles and infectious agents by trapping these invaders and preventing them from penetrating the cell layer below. Effective mucus clearance, and thus removal of the trapped invaders, is vital for healthy airway function. Cystic Fibrosis (CF) is a genetic disease that is characterized by hindered ion transport in airway epithelial cells. As a result, the mucus secreted by these cells becomes dehydrated, forming thick stratified layers. This change in mucus material properties can severely impair mucus clearance, leading to airway obstruction, chronic infection, and inflammatory lung damage. It is well established that CF mucus exhibits viscosities orders of magnitude greater than those of healthy mucus. However, thus far it has not been feasible to measure mucus properties on live cells as it is produced by the epithelial cell layer, neglecting the relationship between the physiological environment and mucus rheology. A new instrument, the “Magnetic Live Cell Rheometer”, recently developed by the Fuller group has been adapted to examine mucus rheology *in situ* via magnetic microrheology. Human airway epithelial cells (HAECs) are grown in 2D air-liquid interface (ALI) cultures, mimicking the airway surface environment. During rheological experiments, we maintain cells at ALI and use micron scale magnetic wires (microwires) to probe the properties of the mucus as a function of distance from the cell layer. We apply and remove a magnetic force and track microwire displacement to determine the compliance and viscosity of healthy and diseased mucus on the respective HAEC cultures. We then test existing mucoactive drugs designed to reduce the elasticity and viscosity of the mucus layer to establish correlation with clinical response assess the impact of genetic variants. With this method, we demonstrate the ability to study mucus rheology in a physiologically relevant environment, examine phenotypic differences in mucus rheology, and rapidly test drugs on mucociliary mechanics.

**Keywords:** mucus, bronchial epithelial cells

## Active soft colloids for the transduction of bio-chemical information

*Lukas Zeininger*

*Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces,  
Potsdam, Germany*

*Presenting author's e-mail: [lukas.zeininger@mpikg.mpg.de](mailto:lukas.zeininger@mpikg.mpg.de)*

Dynamic complex emulsions formed from two or more immiscible fluids offer a unique platform for the generation of new triggerable materials. In designing our methods, we make use of solvent combinations that are immiscible at room temperature but exhibit a lower (LCST) or upper critical solution temperature (UCST). Emulsification of the mixture below LCST or above UCST enables a simple one-step fabrication of complex multicomponent emulsions as well as structured soft-matter particles in highly uniform morphologies.

The morphology of these dynamic complex colloids is exclusively controlled by the interfacial tension balance and thus, droplet geometries can be controllably altered after emulsification. We have shown that the complex droplet morphologies are sensitive to a variety of external stimuli such as the presence of specific analytes, small pH changes, light or high energy irradiation, and the presence of an electric or magnetic field and therefore provide a new active element for novel and existing applications of emulsions including biomimicry, the fabrication of optical metamaterials, and chemical and biological sensing platforms.

Here, we will demonstrate that the introduction of permanent asymmetry to the internal droplet geometry and composition, combined with the ability to reversibly adjust the internal droplet morphology, opens a path towards a continuous and reversible modulation of the directional chemotactic response of moving droplet systems. While isotropic single-phase emulsion droplets display an exclusively unidirectional motion towards lowering their interfacial tension, Janus emulsion droplets comprised of two hemispherically aligned phase-separated fluids can reversibly and controllably move up or down an oncoming chemical gradient and their velocity can be predictively fine-tuned.

Combined with the dynamic morphological reconfigurability of Janus droplets, we obtain a highly adaptive material system that can autonomously regulate its response to marginal changes in the chemical environment. This has implications for the design of smart and adaptive soft microswimmers that can self-regulate their response towards or away a certain chemoattractant or –repellent e.g. by chemotactically responding to a bacterium.

**Keywords:** droplets, complex emulsions, active soft matter, microswimmers, chemotaxis, biosensors

## Drop self-shaping, self-bursting and swimming: simple non-living system which enlivens upon temperature variations

*Diana Cholakova, Slavka Tcholakova and Nikolai Denkov*

*Department of Chemical and Pharmaceutical Engineering,  
Faculty of Chemistry and Pharmacy, Sofia University, Sofia, Bulgaria*

Presenting author's e-mail: [dc@lcpe.uni-sofia.bg](mailto:dc@lcpe.uni-sofia.bg)

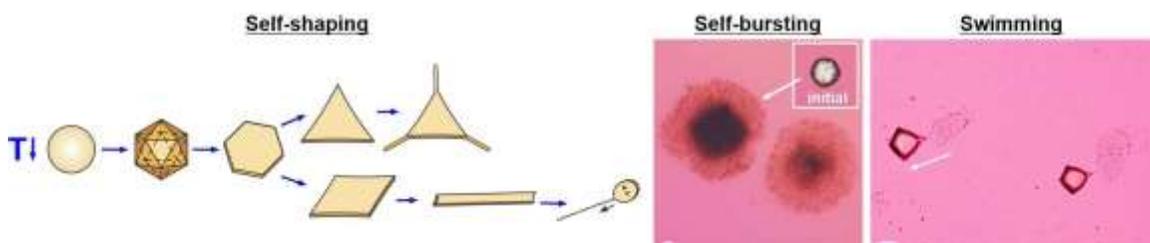
Emulsion drops usually have spherical shape which minimizes their interfacial area at positive interfacial tension. We discovered a versatile method to spontaneously break symmetry and transform oily drops into particles with complex shapes, incl. hexagonal, tetragonal and triangular platelets, rods, fibers and even swimmers [1,2]. This method includes slow cooling of oil-in-water emulsion droplets, which may be prepared from wide range of lipids, incl. alkanes, alkenes, alcohols, triglycerides, alkylmetacrylates and their mixtures, stabilized by long-chain surfactants.

The drop self-shaping mechanism relies on formation of intermediate (rotator) phases next to the drop surface which have the mechanical strength to counteract the capillary pressure of the liquid oil remaining inside the drop interior. These phases form at temperatures close to the lipid melting point. Such plastic phases are widely spread in nature and several technologies, as they possess intrinsic properties which may ensure self-healing, super-hydrophobicity and lubrication [3]. The drops may also evolve into microswimmers which harvest energy from the temperature variations of the disperse system and self-propel on cooling, pushed by rapidly growing elastic tails. These swimmers are observed to swim for several minutes and can be recharged upon heating [2].

We discovered also that temperature variations around the lipid melting temperature may induce spontaneous drop fragmentation without any input of mechanical energy [4,5]. 20 to 50 nm nanoparticles were produced from initial coarse emulsions (sizes up to 50-100  $\mu\text{m}$ ) by several consecutive cooling-heating cycles only, without using any homogenization device [4].

These new approaches can be of high interest for cosmetic, food, pharma and chemical industries. The presentation will make an overview of our current understanding of these fascinating and unexpected phenomena.

**Keywords:** emulsion, rotator phase, phase transition, spontaneous emulsification, swimmer



**Figure 1.** Schematic illustration of main shapes obtained upon drop cooling. Microscopy pictures of self-bursting and swimming. Scale bars = 20  $\mu\text{m}$ .

**Acknowledgements:** Current work is supported by the Bulgarian Ministry of Education and Science, under the National Research Program "VIHREN", project ROTA-Active (no. KP-06-DV-4/2019).

### References

- [1] N. Denkov, S. Tcholakova, I. Lesov, D. Cholakova and S. Smoukov, *Nature*, 2015, 528, 392.
- [2] D. Cholakova et al., *Nature Physics*, 2021, 17, 1050.
- [3] D. Cholakova and N. Denkov, *Adv. Colloid Interface Sci.*, 2019, 269, 7.
- [4] D. Cholakova et al., *ACS Nano*, 2020, 14, 8594.
- [5] S. Tcholakova et al., *Nature Communications*, 2017, 8, 15012.

# Viscoelastic patchy particle architectures as models for living matter

*H.J. Jonas<sup>1</sup>, P. Schall<sup>2</sup>, and P.G. Bolhuis<sup>1</sup>*

<sup>1</sup> *van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands*

<sup>2</sup> *Institute of Physics, University of Amsterdam, Amsterdam, The Netherlands*

Presenting author's e-mail: [h.j.jonas@uva.nl](mailto:h.j.jonas@uva.nl)

Structural architectures in living cells, such as the cytoskeleton in muscle or plant tissue, are both viscoelastic and active, i.e. undergo continuous injection of energy, leading to remarkable collective non-equilibrium properties. The simulation of active systems is relatively straight forward, but the thermodynamics, kinetics and statistical mechanics of such systems are far from understood. Understanding such phenomena remains one of the grand challenges of modern statistical physics. We use patchy particles as a model system for exploring complex architectures that exhibit viscoelastic properties [1]. Patchy particles are micron-sized colloidal particles dressed with hydrophobic patches that are able to form controllable directed bonds using critical Casimir interactions [2]. Their size makes them directly observable with e.g. confocal microscopy, while having similar statistics as atoms and molecules. Their ability to make directed bonds enables self-assembled molecular or bio-inspired network-like structures [3,4]. Next, we push these self-assembled patchy particle architectures out-of-equilibrium by active Brownian particles and investigating their response. For small chainlike structures, we show that activity leads to enhanced breakage, i.e. that the time scales and the mechanisms involved are very different from equilibrium, and depends strongly on the orientation of the active force. Finally, we increase the complexity of the structures to networks and investigate the collective viscoelastic responses and structural properties affected by the active forces. Our findings clearly show how self-assembled patchy particle structures can act as a model system to study viscoelastic out-of-equilibrium materials with properties akin to living matter.

**Keywords:** out-of-equilibrium viscoelasticity, patchy particles, simulation

## References

- [1] S.G. Stuij, H.J. Jonas, Z. Gong, S. Sacanna, T.E. Kodger, P.G. Bolhuis, and P. Schall, *Soft Matter*, 2021, 17, 8291.
- [2] H.J. Jonas, S.G. Stuij, P. Schall, P.G. Bolhuis, *Journal of Chemical Physics*, 2021, 155, 034902.
- [3] S.G. Stuij, J. Rouwhorst, H. J. Jonas, N. Ruffino, Z. Gong, S. Sacanna, P.G. Bolhuis, and P. Schall, *Physical Review Letters*, 2021, 127, 108001.
- [4] P. J.M. Swinkels, S. G. Stuij, Z. Gong, H.J. Jonas, N. Ruffino, B. van der Linden, P. G. Bolhuis, S. Sacanna, S. Woutersen, and P. Schall, *Nature Communications*, 2021, 12, 2810.

## Hydration responsive strain-induced self-rolling of mesostructured bio-inspired mineral sheets

Viktoria Gruen <sup>1</sup>, Jonas Schwan <sup>1</sup>, Sabine Rosenfeldt <sup>2</sup>, and Anna S. Schenk <sup>1</sup>

<sup>1</sup>Colloidal Systems, University of Bayreuth, Bayreuth, Germany

<sup>2</sup>Physical Chemistry I, University of Bayreuth, Bayreuth, Germany

Presenting author's e-mail: [anna.schenk@uni-bayreuth.de](mailto:anna.schenk@uni-bayreuth.de)

Directional passive motion based on reversible strain-induced self-folding of chemically or structurally heterogeneous two-dimensional bilayer, multilayer or gradient systems is a common phenomenon in Nature, especially in the plant kingdom. Different responsivities of the sub-layers to external stimuli such as drying/swelling cycles characteristically lead to non-uniform deformation along the surface normal direction and the associated mechanical stress is eventually released by a bending motion (Figure 1, left).

We here explore the translation of this design principle into functional inorganic materials, as reports on self-folding in geological and synthetic have remained conspicuously scarce due to the high bending strain which needs to be accommodated by these brittle materials to introduce curvature. Specifically, we use a bio-inspired mineralization approach for the room-temperature deposition of cobalt hydroxide carbonate from aqueous solution mediated by structure-directing polyelectrolytes. Two-dimensional sheets of the inorganic material are obtained *via* electrodeposition on electrode surfaces as well as by diffusion-based liquid phase precipitation at the air/solution interface or on substrates.

Remarkably, when deposited in the presence of the metal-coordinating, amine-functionalized polymer polyethyleneimine, interface-derived mineral films undergo substantial drying-induced coiling, such that spiralling morphologies are formed (Figure 1, centre). The extremely low polymer content occluded within the mineral structure suggests that even a very minor amount of macromolecules seems to exert a strong effect on the uniformity of the mesostructure in the deposited inorganic films (Figure 1, right). [1] Additionally, hydration-driven passive motion based on reversible folding/unfolding can be achieved by intentionally incorporating poly(acrylic acid) with a strong capacity for water absorption into an active (hydration-responsive) mineral film deposited on a passive layer of gold. In view of potential applications, self-supported cobalt hydroxide carbonate spirals with mesoscale channels are pseudomorphically converted into porous cobalt(II,III) oxide, a functional material with applications in various technological fields, e.g. as an electrocatalyst in clean energy conversion systems.



**Figure 1.** Strain-induced self-rolling in biogenic seed pods (left) and interface-derived cobalt hydroxide carbonate films (centre). Schematic illustrating the principle of polymer-mediated deposition of mineral films at the air/solution interface. Domains with different mesostructures lead to a non-uniform response to drying resulting in curling (right)

**Keywords:** self-rolling, mesostructures, bio-inspired mineralization, interfacial deposition

### References

[1] V. Gruen, N. Helfricht, S. Rosenfeldt and A. S. Schenk, *Chemical Communications*, 2021, 57, 7244

**Wednesday 7th September 2022**

**Composite Materials and Nanostructures**

## Diffusion in a realistic simulated model for the stratum corneum

*Peter D Olmsted<sup>1</sup>, Oleh Tovkach<sup>1</sup>, Gustavo S Luengo<sup>2</sup>, Fabien Leonforte<sup>2</sup>, Sebastian Gregoire<sup>2</sup>, Ann Detroyer<sup>2</sup>*

<sup>1</sup> *Department of Physics and Institute for Soft Matter Synthesis & Metrology, Georgetown University, Washington DC USA*

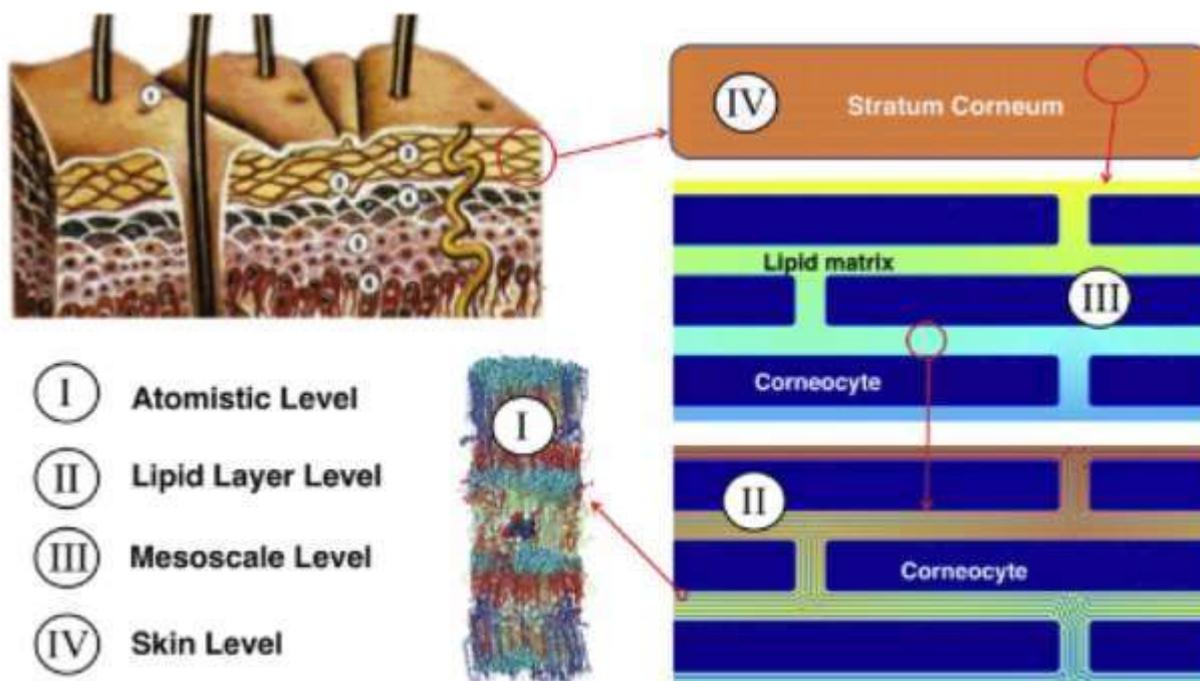
<sup>2</sup> *L'Oreal Research and Innovation, Aulnay-sous-Bois, Paris, France*

Presenting author's e-mail: [pdo7@georgetown.edu](mailto:pdo7@georgetown.edu)

The outermost layer of mammalian skin, called the stratum corneum (SC), constitutes a self-healing barrier against moisture loss and ingress of foreign substances. The SC comprises flat "bricks" (50-100 micron wide and 1 micron thick corneocytes largely filled with keratins) held together by a "mortar" of 6-10 layers of lipids (100 nm thick). The corneocytes are hydrophilic, while the lipid matrix is hydrophobic. The ability and way of a chemical to pass the SC is a key point for risk assessment and development of cosmetics.

Here we propose a realistic simulation model with which to study transport through the SC. We explicitly calculate the layered structure between corneocytes and endow it with the local anisotropy in mobility such that diffusion across layers differs from diffusion within layers. By investigating steady-state transport in the SC our results suggest that the crossover between transcellular and extracellular localization during transport is set by an interplay between (1) the relative hydrophobicity (or lipophilicity) of a species; (2) the anisotropy of diffusion within in the lipid matrix; (3) the difference in mobilities within the lipid matrix and the corneocytes; (4) the aspect ratio of the corneocytes and the thickness of the lipid "mortar".

**Keywords:** lipid layers, stratum corneum, diffusion, multiscale modeling, nanostructured media



**Figure 1.** Levels of coarse-graining for studying diffusion in the Stratum Corneum.

# Templated Colloidal Growth of Semiconductors Toward Heterostructured Nanomaterials

*Eric H. Hill*<sup>1,2</sup>, *Junying Liu*<sup>1</sup>, *Sanjay Jatav*<sup>1</sup>, *Marcel Herber*<sup>1</sup>

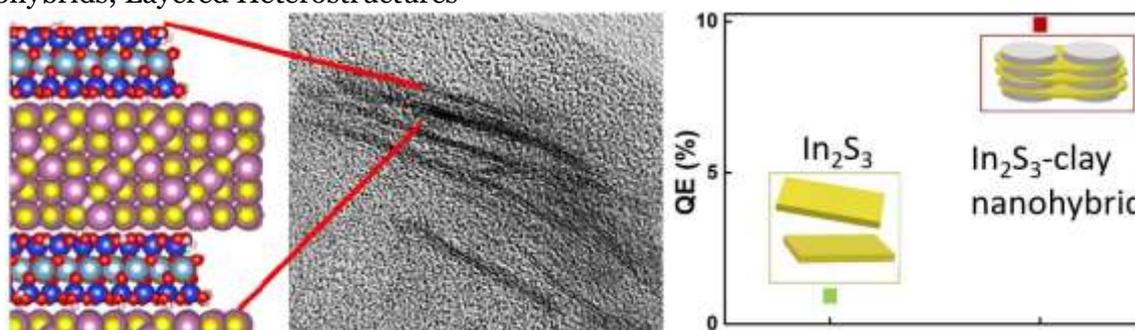
<sup>1</sup> *University of Hamburg, Institute of Physical Chemistry, Hamburg, Germany*

<sup>2</sup> *The Hamburg Center for Ultrafast Imaging Hamburg, Germany*

Presenting author's e-mail: [eric.hill@chemie.uni-hamburg.de](mailto:eric.hill@chemie.uni-hamburg.de)

Thickness and anisotropy of nanoscale materials has been shown to strongly influence photophysical properties. While different exfoliation strategies for 2D materials have been proposed in this direction, many cause damage or chemical modifications, and control over size and aggregation can be problematic. In this talk, methods for templating the synthesis of semiconductors using colloidal particles that are anisotropic in both shape and surface charge is presented as a means to achieve 1D and 2D nanomaterial hybrids. Initial progress in colloidal growth of ultrathin layers of semiconducting materials such as MoS<sub>2</sub>[1], In<sub>2</sub>S<sub>3</sub>, [2], ZnIn<sub>2</sub>S<sub>4</sub> [3], and BiOI [4] in the modified interlayer space. These nanohybrids show promising enhancements in catalytic and photophysical properties, and provide routes to engineer the growth of specific crystalline facets, which can also enhance the uniformity of the internal electric field perpendicular to the basal surface in certain materials [4]. In addition to providing increased aqueous dispersibility, the resulting thin growth of semiconductors and the isolation of these 2D layers from one another via the template allows improved photophysical and optoelectronic properties. The improved quantum efficiency and interfacial charge transfer, and reduced recombination of photogenerated charge carriers will lead to improved applications in aqueous-phase photocatalysis. Current directions include the use of robust clay-like MXene templates for 2D growth and nanotubular templates for 1D growth toward unique nanohybrid photocatalysts.

**Keywords:** Templated Synthesis; Layered Silicate Clays; 2D Materials; Ultrathin Semiconductors; Nanohybrids; Layered Heterostructures



**Figure 1.** An example of templating growth of 2D In<sub>2</sub>S<sub>3</sub> with surfactant-pillared layered silicate clays. [2]

## References

- [1] Jatav, S., Furlan, K. P., Liu, J., Hill, E. H. ACS Appl. Mater. Int. 2020, 12(17), 19813.
- [2] Liu, J., Jatav, S. and Hill, E.H., Chem. Mat. 2020, 32(23), 10015.
- [3] Liu, J., Jatav, S., Herber, M. and Hill, E.H., Langmuir 2021, 37(15), 4727.
- [4] Liu, J., Jatav, S., Wessel, P. and Hill, E.H., J. Phys. Chem. C 10.1021/acs.jpcc.1c10853.

## Design of soft homocomposite silicone gels for 3D printed architectures with magneto-capillary reconfiguration

*Lilian B. Okello<sup>1</sup>, Sangchul Roh<sup>1</sup>, Orlin D. Velev<sup>1</sup>*

<sup>1</sup>*North Carolina State University, Raleigh, NC, USA.*

*Presenting author's email: [lbokello@ncsu.edu](mailto:lbokello@ncsu.edu)*

We will discuss the colloidal design of silicone-based pastes used for 3D printing by pressure-extrusion. These inks are fabricated by synthesizing silicone microbeads from polydimethylsiloxane (PDMS), then adding small volumes of uncured liquid PDMS precursor to the cured microbeads to induce capillary-mediated gelation into a thixotropic paste. The microbeads can be functionalized by embedding magnetic nanoparticles during their synthesis. Capillary pastes fabricated with these active microbeads can be shaped into three dimensional structures by a 3D printer. The result is a new class of novel and smart elastomeric architectures that undergo complex reconfiguration in magnetic fields. These Homocomposite Thixotropic Capillary Pastes (HTCPs) consist of a colloidal suspension of silicone microbeads in water and liquid uncured silicone precursor [1, 2]. The ferromagnetic nanoparticles inside the microbeads do not compromise their final mechanical stability. The cured magnetoactive soft actuators are strong, yet soft and extensible, an essential property for applications such as soft robotics. We investigate the ink's elastic moduli that result in maximum extensibility without breaking. We show how optimal magnetic material loading results in active structures with maximum actuation distance when an external magnetic field is applied. The volume of polymer precursor used for capillary bridging and polymer crosslink density can be optimized to fabricate soft 3D printed active structures that can withstand many cycles of extension, expansion and contraction when actuated by external magnetic fields. This HTCP 3D printing method has made possible the fabrication of soft architectures with different actuation modes, such as isotropic/anisotropic contraction and multiple shape changes [3]. The material is ultrasoft and biocompatible, hence suitable for biomedical applications such as fabricating bioscaffolds. The cyclic actuation of these objects can be modulated to mimic the pumping mechanism seen in heart and lung muscles, while the moduli can be tuned to match that of live organ tissues.

**Key words:** Colloidal, gels, 3D printing, magneto-capillary, reconfigurable.

### References

- [1] S. Roh, D. P. Parekh, B. Bharti, S. D. Stoyanov and O. D. Velev, *Adv. Mater.*, 2017, 29, 1701554.
- [2] S. Roh and O. D. Velev, *A/ChE J.*, 2018, 64, 3558-3564.
- [3] S. Roh, L. B. Okello, N. Golbasi, J. P. Hankwitz, J. A.-C. Liu, J. B. Tracy and O. D. Velev, *Adv. Mater. Technol.*, 2019, 1800528.

# Metallic NanoParticle-on-Mirror: Multiple-Band Light Harvesting and Efficient Photocurrent Generation under Visible Light Irradiation

*Alexander B. Tesler,<sup>1</sup> Takumi Sannomiya,<sup>2</sup> Seyed sina Hejazi,<sup>1</sup> Reza Mohammadi,<sup>3</sup> Nicolas Vogel,<sup>3</sup> Marco Altomare,<sup>4</sup> and Patrik Schmuki<sup>1, 5, 6</sup>*

<sup>1</sup> Department of Materials Science and Engineering, Institute for Surface Science and Corrosion WW4-LKO, University of Erlangen-Nuremberg, Erlangen, Germany

<sup>2</sup> Department of Materials Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan

<sup>3</sup> Department of Chemical and Biological Engineering, Institute of Particle Technology, University of Erlangen-Nuremberg, Erlangen, Germany

<sup>4</sup> Photocatalytic Synthesis Group, Faculty of Science and Technology, MESA+ Institute for Nanotechnology, University of Twente, AE Enschede, The Netherlands

<sup>5</sup> Chemistry Department, Faculty of Sciences, King Abdul-Aziz University, Jeddah, Saudi Arabia.

<sup>6</sup> Regional Centre of Advanced Technologies and Materials, Palacky University, Olomouc, Czech Republic

Presenting author's e-mail: [ab.tesler@gmail.com](mailto:ab.tesler@gmail.com)

A hybrid photoanode concept for photoelectrochemical (PEC) water splitting based on metal nanoparticles (Au, Ag, Cu) deposited on a Ti mirror (NPOM) to photosensitize an intermediate TiO<sub>2</sub> layer to induce the harvesting of light with sub-bandgap photon energies is presented. The generation of hot electron-hole pairs in metallic nanostructures can occur either by intraband excitation, i.e., plasmon electrons, or by the interband transition of the d-band electrons to the unoccupied conduction band states. Our results demonstrate that the underlying Ti mirror significantly amplifies the PEC activity of such NPOM systems in the visible spectral range. We show that the PEC enhancement in the visible spectral range is not limited to the intraband excitations but is affected mainly by the light trapping pathway within the TiO<sub>2</sub> layer, i.e. due to a favorable interplay between thin-film interference cavity modes with both intraband and interband excitations. Among tested metals, Cu and Ag NPs demonstrate a ~3-fold higher enhancement factor than that of Au NPs, while in both former cases the nature of the excited electrons is different. The experimentally determined internal quantum efficiency demonstrates alternating behavior with wavelength showing higher efficiencies at short wavelengths, which is attributed to the reduced Schottky barrier of the NPOMs at constructive interference maxima.

**Keywords:** titanium dioxide, metallic nanoparticles, Fabry-Pérot interference, photoelectrochemistry, water splitting

# Fabrication of electrospun organic-inorganic fibrous nanocomposites starting from highly stable colloidal solutions

*Theodora Krasia-Christoforou*

*University of Cyprus, Department of Mechanical and Manufacturing Engineering,  
Nicosia, Cyprus*

*Presenting author's e-mail: [krasia@ucy.ac.cy](mailto:krasia@ucy.ac.cy)*

Electrospinning is considered to be one of the most powerful and versatile fabrication methods used in the production of fibers with diameters in the nano- and micrometer size range. This technique - which has already entered the industrial sector - enables the production of polymer, ceramic, and organic-inorganic polymer-based nanocomposite fibers [1].

Starting from highly stable colloidal nanohybrids, organic-inorganic (nano)fibrous nanocomposites can be fabricated by electrospinning under ambient conditions. Such materials are highly attractive in biomedical, environmental, optoelectronic, sensing, catalytic and energy-related applications, owned to their unique properties including high surface to volume ratios, high porosity, and multifunctionality, deriving from the combination of the organic and inorganic counterparts.

In this presentation selected examples on the fabrication of electrospun organic-inorganic fibrous nanocomposites obtained by electrospinning, starting from highly stable colloidal solutions will be presented and discussed. These include Fe<sub>3</sub>O<sub>4</sub> NP-containing electrospun microfibers and microrods with applicability in biomedicine [2], water remediation [3], and sensing [4], Pd-, Au- and Cu<sub>2</sub>O NP-containing electrospun fibrous mats employed as heterogeneous catalytic supports in organic synthesis [5, 6], and light-emitting fabrics [7].

**Keywords:** electrospinning, nanocomposite fibers, colloidal nanohybrids

## References

- [1] I. Savva, T. Krasia-Christoforou, (Eds. S. Thomas, K. Ghosal, E. Kny), *Electrospinning – Basic Research to Commercialization*, 2018, “Encroachment of Traditional Electrospinning”, Royal Society of Chemistry, U.K.
- [2] M. Nikolaou, K. Avraam, A. Kolokithas-Ntoukas, A. Bakandritsos, F. Lizal, O. Misik, M. Maly, J. Jedelsky, I. Savva, F. Balanean, T. Krasia-Christoforou, *Materials Science and Engineering C*, 2021, 126, 112117.
- [3] I. Savva, O. Marinica, C. A. Papatryfonos, L. Vekas, T. Krasia-Christoforou, *RSC Advances*, 2015, 5, 16484.
- [4] A. Petropoulou, S. Kralj, X. Karagiorgis, I. Savva, E. Loizides, M. Panagi, T. Krasia-christoforou, C. Riziotis, *Scientific Reports*, 2020, 10, Article no. 367, 1.
- [5] I. Savva, A. Kalogirou, A. Chatzinicolaou, P. Papaphilippou, A. Pantelidou, E. Vasile, Eu. Vasile, P. A. Koutentis, T. Krasia-Christoforou, *RSC Advances*, 2014, 4, 44911.
- [6] I. Savva, A. S. Kalogirou, M. Achilleos, E. Vasile, P. A. Koutentis, T. Krasia-Christoforou, *Molecules*, 2016, 21, 1218.
- [7] P. G. Papagiorgis, A. Manoli, A. Alexiou, P. Karacosta, X. Karagiorgis, G. Papaparaskeva, M. Bernasconi, M. I. Bodnarchuk, M. V. Kovalenko, T. Krasia-Christoforou, G. Itskos, *Frontiers in Chemistry*, 2019, 7, 87.

## Colloidal Sol-Gel Route for the synthesis of mixed actinide oxide

*Diane Rébiscoul<sup>1</sup>, Zijie Lu<sup>1</sup>, Xavier Le Goff<sup>1</sup>, Joseph Lautru<sup>1</sup>, Thomas Zemb<sup>1</sup>*

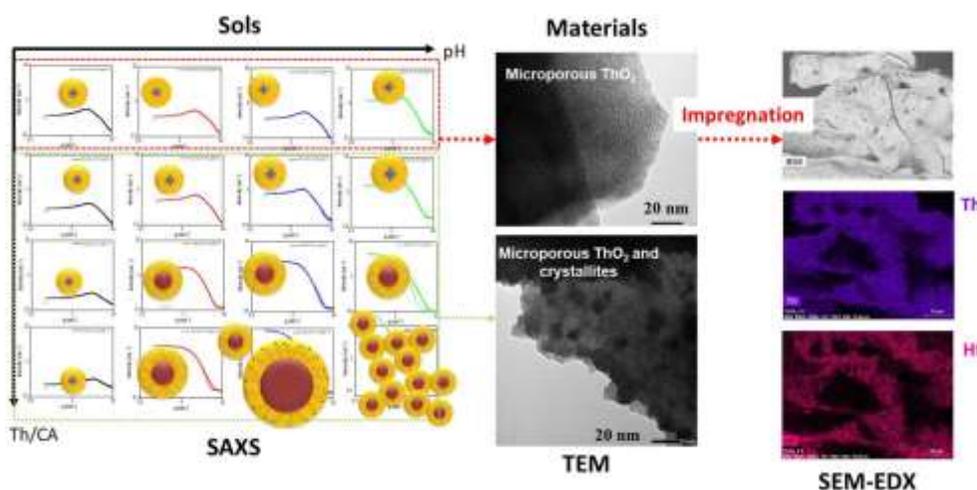
<sup>1</sup> *Institut de Chimie Séparative de Marcoule, CEA, Bagnols-sur-Cèze, France*

Presenting author's e-mail: [diane.rebiscoul@cea.fr](mailto:diane.rebiscoul@cea.fr)

The identification of new colloidal sol-gel routes for the preparation actinide oxides having a homogenous and accessible porosity that can easily be impregnated by any concentrated actinide solution open new perspectives for the preparation of homogenous nuclear fuel for minor actinide transmutation. This homogeneity allows to avoid “hot spot” formation due to local accumulation of more fissile elements. In addition, this safer technology relying on colloidal synthesis and formulation of complex fluids used as templating colloids open new perspectives for the reuse of nuclear waste solutions as new fuel.

Here, we report the preparation of microporous ThO<sub>2</sub> materials by a colloidal sol-gel route [1]. Using a thorium salt with a complexing agent at a controlled pH, we were able to pilot the condensation of thorium hydroxo species forming colloids of tuned nanometric size and thus the sol stability. After a freeze-drying process used to concentrate colloids and a thermal treatment allowing the complexing agent removal, a loose packing of ThO<sub>2</sub> nanoparticles with an ordered distribution of interparticular porosity and a fraction of nanometric crystallites which for the size depends on the initial colloid size were obtained. The sols and the final materials were characterized by Small Angle X-ray Scattering (SAXS) to determine the colloid sizes and the final structure of the materials that was also confirmed by Transmission Electron Microscopy. The SAXS characterization of these highly absorbing materials have required a new evaluation of the contribution of the reflectivity and the scattering on the same cross-section scale in order to correctly determine the specific surface area, the porosity and the mean pore size of microsized powder grains.

**Keywords:** actinides, colloidal sol-gel, nuclear fuel, SAXS



**Figure 1.** Illustration of the method used to characterize the interactions of grafted organosilane having a diglycolamide headgroup for the understanding of REE extraction.

### References

[1] under patenting process.

**Thursday 8th September 2022**

**Chinese-European Symposium**

# Lowering ice and gas hydrate adhesion

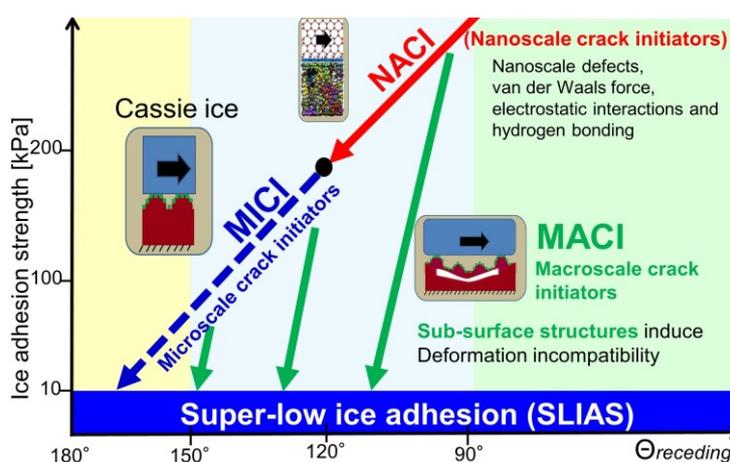
*Jianying He*<sup>1</sup>

<sup>1</sup> *Norwegian University of Science and Technology Trondheim, Norway*

Presenting author's e-mail: [jianying.he@ntnu.no](mailto:jianying.he@ntnu.no)

Preventing the formation and accretion of ice on exposed surfaces is of great importance for Arctic operation, renewable energy, electrical transmission cables in air and shipping. While studies on suppressing ice nucleation by surface structuring and local confinement are highly desired, a realistic roadmap to icephobicity for many practical applications is perhaps to live with ice, but with the lowest possible ice adhesion. From the viewpoint of fracture mechanics, the key to lower ice adhesion is to maximize the ice-substrate interface-crack driving forces at multiple length scales. Herein, we propose a novel macro-crack initiator mechanism in addition to the nano-crack and micro-crack initiator mechanisms, and demonstrate a new strategy to design super-low ice adhesion surfaces to fatally weaken ice-substrate interface. The results show that PDMS thin films with 1 mm inner holes in two layers approach an ice adhesion strength of 5.7 kPa. The introduction of sub-structures into PDMS thin films promotes macro-crack initiators, and is able to reduce ice adhesion strength by ~50% compared with that of PDMS thin films without sub-structures, regardless of layer thickness, curing temperature, weight ratio and the size of inner hole. The ice adhesion can be even lowered to around 1 kPa with porous sponge layer. The design concept has also been applied to gas hydrate and achieved hydrate adhesion strength down to ~3 kPa. Therefore, rationalizing the three crack-initiator mechanisms and their interactions at multi-length scales may provide an effective strategy towards designing icephobic and hydrate-phobic surfaces.

**Keywords:** Interface crack, ice adhesion, gas hydrate adhesion



**Figure 1.** Multiscale crack-initiator mechanisms at the interface.

**Acknowledgements:** The Research Council of Norway is acknowledged for the support to project SLICE (No. 250990), AIM (No. 255507), Dandra (No. 302348) and NorFab (No.295864).

## References

- [1] Z. He et al, *Soft Matter*, 2018, 14, 4846.
- [2] Y. Zhuo et al, *Chemical Engineering Journal*, 2021, 405, 127088.
- [3] F. Wang et al, *Chemical Engineering Journal*, 2022, 437, 135274.

## Lipid assembly morphological changes induced by changes of the solution conditions.

Meifang Fu<sup>1,2</sup>, Qi Li<sup>1,2</sup>, Bingbing Sun<sup>1,2</sup>, Yang Yang<sup>3</sup>, Luru Dai<sup>3</sup>, Tommy Nylander<sup>4</sup>, and Junbai Li<sup>1,2</sup>

<sup>1</sup>Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Lab of Colloid, Interface and Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China

<sup>2</sup>University of Chinese Academy of Sciences, Beijing, China

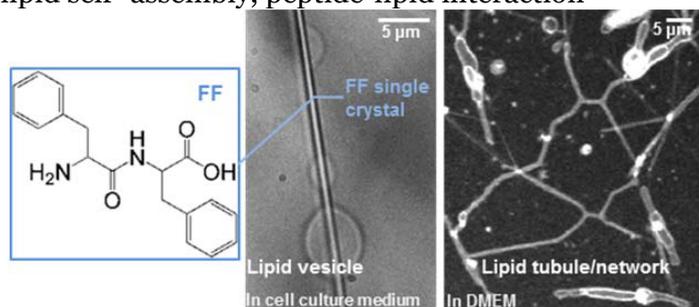
<sup>3</sup>CAS Key Laboratory for Biomedical Effects of Nanomaterials and Nanosafety, National Center for Nanoscience and Technology, Beijing, China

<sup>4</sup>Division of Physical Chemistry, Department of Chemistry, Lund University, Lund, Sweden

Presenting author's e-mail: [Tommy.Nylander@fkem1.lu.se](mailto:Tommy.Nylander@fkem1.lu.se)

Lipid assembly into different morphologies, where the assembly structure and morphology is not only determined by the lipid composition but also by the external conditions as well as the interaction with peptides. We will discuss several aspects of this and in particular the dynamic nature of the process. Liposomes composed of phospholipids can be deformed into vesicles, tubular structures, or networks that depend on buffer conditions. An interesting observation is that the disassembly of supramolecular dipeptide, i.e. diphenylalanine (FF), single crystals induces the deformation and translocation of liposomes at a physiological condition [1]. Membrane tubules can be formed through different processes leading to the construction of membrane tubulus. This dynamic behaviour involving lipids and peptides are likely to be important for processes in living cells, where e.g. tubule translocation is an important factor to construct the ER morphology. We will discuss how external conditions can participate in the deformation of liposomes.

**Keywords:** vesicles, lipid self-assembly, peptide-lipid interaction



**Figure 1.** Disassembly of diphenylalanine (FF) single crystals deformed supported membranes into vesicles in cell culture medium, and tubular structures and ER-like networks in (Dulbecco's Modified Eagle Medium) DMEM.

**Acknowledgements:** The financial support from the National Natural Science Foundation of China (Project Nos. 21433010, 21320102004, and 21673056) and National Basic Research Program of China (973 program, 2013CB932802) as well as Joint China-Sweden Mobility programme (Swedish Foundation for International Cooperation in Research and Higher Education, CH2017-7159) is acknowledged.

### References

[1] M. Fu, Q. Li, B. Sun, Y. Yang, L. Dai, T. Nylander, J. Li. Disassembly of dipeptide single crystals can transform the lipid membrane into a network. *ACS Nano*, 2017, 11, 7349–7354, doi: 10.1021/acsnano.7b03468

# An efficient multiparticle collision dynamics approach to membrane protein diffusion

*Zihan Tan*<sup>1</sup>, *Vania Calandrini*<sup>2</sup>, *Kai Qi*<sup>3,4</sup>, *Jan K. G. Dhont*<sup>1</sup>, *Roland G. Winkler*<sup>5</sup>, and *Gerhard Nägele*<sup>1</sup>

<sup>1</sup> IBI-4, Forschungszentrum Jülich, Jülich, Germany

<sup>2</sup> IAS-5, Forschungszentrum Jülich GmbH, Jülich, Germany

<sup>3</sup> CECAM, EPFL, 1015 Lausanne, Switzerland

<sup>4</sup> 2020 X-Lab, Chinese Academy of Sciences, Shanghai, China

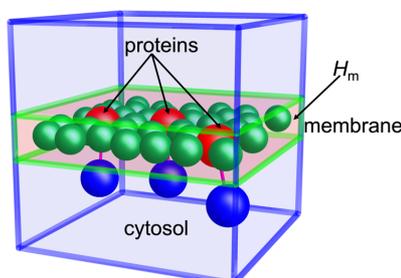
<sup>5</sup> IBI-5, Forschungszentrum Jülich GmbH, Jülich, Germany

Presenting author's e-mail: [z.tan@fz-juelich.de](mailto:z.tan@fz-juelich.de)

The lateral diffusion of proteins inside or near a lipid membrane is important in biological information processes such as post-synaptic signal transduction mediated by diffusing proteins, and the oligomerization of receptor proteins. Owing to the crowded cellular environment, spatio-temporal correlations of membrane proteins are strongly affected by direct and many-body hydrodynamic interactions (DIs and HIs) whose theoretical description is challenging.

We have developed a multiparticle collision dynamics (MPC) mesoscale protein-membrane-cytosol simulation model which allows to investigate efficiently the dynamics of membrane proteins with time-resolved HIs accounted for. In this model, the membrane and cellular fluids are summarily described as layered immiscible fluids of different viscosities separated by planar interfaces. In salient tests of the MPC model, we show that the simulated flow profile for imposed shear, and the time-dependent shear stresses, are in excellent agreement with our accompanying continuum hydrodynamics results for a composite fluid model [1]. The wave-vector dependent velocity auto-correlation functions in the bulk regions of the fluid layers decay exponentially and agree with those of a single-phase isotropic MPC fluid. In another test, we analyze the enhanced lateral self-diffusion of a membrane-embedded globular proteins as function of its interfacial distance, for large membrane-cytosol viscosity ratios. We also present simulation results for the mean-squared displacements of interacting, dumbbell-shaped receptor proteins diffusing alongside the membrane, showcasing hereby the computational efficiency of the model for studying protein diffusion over extended time scales. To summarily account for membrane viscoelasticity in the simulations, a monolayer of interacting small Brownian beads is embedded into the membrane fluid layer [2].

**Keywords:** membrane protein diffusion, hydrodynamics



**Figure 1.** Sketch of the mesoscale membrane-protein-cytosol model. Proteins are modeled as two-beads dumbbells with a membrane (red) and cytosol (blue) part. Viscoelasticity of the membrane (thickness:  $H_m$ ) is accounted for by a monolayer of (green) beads.

## Reference:

- [1] Z. Tan, V. Calandrini, J. K. G. Dhont, G. Nägele and R. G. Winkler, *Soft Matter*, **17**, 7978 (2021)  
 [2] Z. Tan, J. S. Hernandez-Fragoso, V. Calandrini, K. Qi, J. K. G. Dhont, R. G. Winkler, G. Nägele, *work in progress* (2022)

# Durable Liquid-repellent Poly(dimethylsiloxane) Coating with Anti-fouling and Anti-icing Performances

*Jie Liu*<sup>1</sup>

<sup>1</sup>Key Laboratory of Green Printing, Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing China

Presenting author's e-mail: [liujie123@iccas.ac.cn](mailto:liujie123@iccas.ac.cn)

A rapid removal of liquid droplets from surfaces is of great concern in practical applications and fundamental research such as water harvesting [1], heat transfer [2, 3], liquid manipulation [4], and so on. However, it remains a challenge to have a fast, easy, and universal preparation method for coatings that are long-term stable, robust, and environmentally friendly. Here, a one-step grafting-from approach is reported for poly(dimethylsiloxane) (PDMS) brushes on surfaces through spontaneous polymerization of dichlorodimethylsilane fulfilling all these requirements [5]. Drops of a variety of liquids slide off at tilt angles below 5°. The strong covalent attachment of the PDMS brush to the substrate makes them mechanically robust and UV-tolerant. Their resistance to high temperatures and to droplet sliding erosion, combined with the low film thickness ( $\approx 8$  nm) makes them ideal candidates to solve the long-term degradation issues of coatings for heat-transfer surfaces. The autophobic performance provides possibilities to apply PDMS brush coatings to liquid containers, which avoids loss of products due to incomplete emptying and reduces waste of water and solvents for subsequent cleaning. In addition, the thin nanocoating exhibits excellent anti-icing performance.

**Keywords:** poly(dimethylsiloxane), coating, anti-fouling, anti-icing

**Acknowledgements:** The author would like to express his gratitude to Prof. Hans-Jürgen Butt and Prof. Jianjun Wang for their fruitful suggestions.

## References

- [1] K.-C. Park, P. Kim, A. Grinthal, N. He, D. Fox, J. C. Weaver, J. Aizenberg, *Nature* 2016, 531, 78.
- [2] H. J. Cho, D. J. Preston, Y. Zhu, E. N. Wang, *Nat. Rev. Mater.* 2016, 2, 16092.
- [3] S. Daniel, M. K. Chaudhury, J. C. Chen, *Science* 2001, 291, 633.
- [4] X. Wang, Z. Wang, L. Heng, L. Jiang, *Adv. Funct. Mater.* 2019, 30, 1902686.
- [5] J. Liu, Y. Sun, X. Zhou, X. Li, M. Kappl, W. Steffen, H.-J. Butt, *Adv. Mater.* 2021, 33, 2100237.

## Bumpy colloids: synthesis and their applications

Yang Lan

*Centre for Nature-Inspired Engineering, Department of Chemical Engineering,  
University College London, United Kingdom*

Presenting author's e-mail: [yang.lan@ucl.ac.uk](mailto:yang.lan@ucl.ac.uk)

Bumpy colloids refer to colloidal particles with patches raised above the surfaces. Here, the synthesis and applications of two types of bumpy colloids, raspberry-like colloids and Janus particles, are presented.

**Raspberry-like colloids.** The one-step preparation of polymeric raspberry-like colloids, which behave almost like hard spheres, is demonstrated [1]. In aqueous solutions, such prepared raspberry-like colloids show unexpected stability over large variations of salt concentrations without addition of stabilisers. Derjaguin–Landau–Verwey–Overbeek (DLVO) calculations is performed to illustrate the relationship between the unusual colloidal stability and particle morphology. Further, the stability of raspberry-like colloids is applied to prepare superspheres and thin films with hexagonally close-packed structures.

**Janus particles.** A homologous series of amphiphilic Janus particles with shifting Janus boundaries and tunable chemical properties are synthesised via seeded emulsion polymerisation [2]. The effect of the relative size of the hydrophilic domain to the total particle (configuration) and chemical nature of Janus particles on their emulsification properties are systematically investigated. The concept of the Janus structure parameter (JSP) is introduced to describe the configuration of Janus particles. The emulsification results show that the configuration of Janus particles has a limited effect on the emulsion type when the contrast in the water affinity of the two domains is weak. In contrast, the configurations of Janus particles determine the emulsion type when there is a significant difference in water affinity between the two regions of Janus particles.

**Keywords:** bumpy colloids, raspberry-like colloids, Janus particles, colloidal stability, emulsification, self-assembly.

### References

- [1] Y. Lan, O. A. Scherman and E. Eiser, *et al.*, Nature Communications, 2018, 9, 3614.  
[2] Y. Lan, K. J. Stebe and D. Lee, *et al.*, Industrial & Engineering Chemistry Research, 2019, 58, 20961.

# Tunable mobility of bubble surface and inward flow in ethanol-NaCl aqueous solution

*Xurui Zhang*<sup>1</sup>, *Rogerio Manica*<sup>2</sup>, *Qingxia Liu*<sup>2</sup>, and *Zhenghe Xu*<sup>2,3</sup>

<sup>1</sup>*State Key Laboratory for Strength and Vibration of Mechanical Structures, School of Aerospace Engineering, Xi'an Jiaotong University, Xi'an, China*

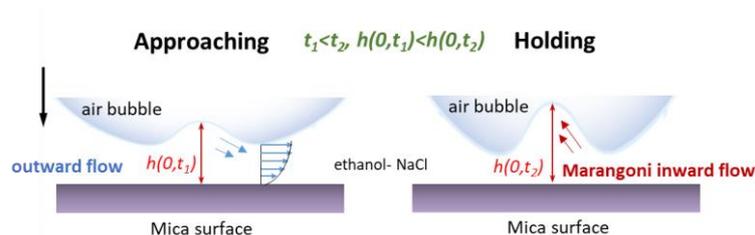
<sup>2</sup>*Department of Chemical and Materials Engineering, University of Alberta, Alberta Canada*

<sup>3</sup>*Department of Materials Science and Engineering, Southern University of Science and Technology, Shenzhen China*

Presenting author's e-mail: [xurui\\_zhang@xjtu.edu.cn](mailto:xurui_zhang@xjtu.edu.cn)

The mobility of bubble surfaces in aqueous solutions can be hindered by even trace amount of contaminants at the air-liquid interface. In this study, the mobility of the bubble surface was characterized by measuring dynamic interactions between a millimeter-size air bubble and a flat mica surface in ethanol-NaCl aqueous solutions using the newly developed dynamic force apparatus and quantified by the Stokes-Reynolds-Young-Laplace model [1]. For a given bubble approach velocity, the hydrodynamic boundary condition at the air-liquid interface deviated from a tangentially immobile boundary at a critical ethanol concentration and converged gradually to fully mobile boundary with further increasing the ethanol concentration. Increasing the bubble approach velocity was found to reduce the critical ethanol concentration that was needed to change the mobility of the bubble surface. The mobile air-liquid interface resulted in a concentration gradient of ethanol between the film and the bulk solution, which led to the observation of inward Marangoni flow during the thin liquid film drainage process [2]. These results provide a mechanism for the inhibition of bubble coalescence and bubble–solid attachment in alcohol aqueous solutions in many engineering processes, such as flotation.

**Keywords:** mobility of bubble surface, inward flow, ethanol-NaCl aqueous solution



**Figure 1.** Schematic illustration of the mobile bubble surface and inward flow in ethanol-NaCl solution.

## References

- [1] Zhang, X.; Manica, R.; Tang, Y.; Liu, Q.; Xu, Z. Bubbles with tunable mobility of surfaces in ethanol-NaCl aqueous solutions. *J. Colloid Interface Sci.* 2019, 556, 345.
- [2] Zhang, X.; Manica, R.; Liu, Q.; Xu, Z. Inward Flow of Intervening Liquid Films Driven by the Marangoni Effect during Bubble–Solid Collisions in Ethyl Alcohol–NaCl Aqueous Solutions. *Langmuir* 2021, 37, 4121.

**Thursday 8th September 2022**

**Colloids at Interfaces, Membranes and Biointerfaces,  
Emulsions and Foams**

## Separating Chemicals in Nanostructured, Fluid-Bicontinuous Gels

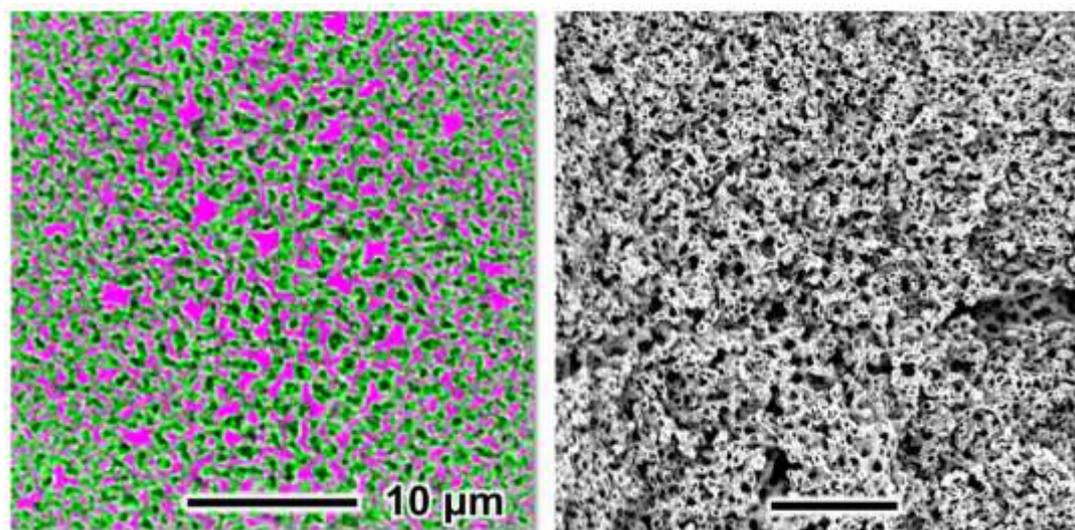
Mohd A. Khan <sup>1</sup>, Alessio J. Sprockel <sup>1</sup>, Katherine A. Macmillan <sup>1</sup>, Meyer T. Alting <sup>1</sup>,  
Shankar P. Kharal <sup>2</sup>, Stephen Boakye-Ansah <sup>2</sup>, Martin F. Haase <sup>1</sup>

<sup>1</sup>Utrecht University, Van't Hoff Lab, Debye Institute for Nanomaterials Science, The Netherlands

<sup>2</sup>Rowan University, Department of Chemical Engineering, USA

Presenting author's e-mail: [m.f.haase@uu.nl](mailto:m.f.haase@uu.nl)

Fluid-bicontinuous gels, also known as bijels, are unique materials that allow two distinct fluids to interact through a percolating, rigid scaffold [1, 2]. Current limitations for their use are the large fluid-channel sizes ( $>5 \mu\text{m}$ ), restricting the fluid–fluid interaction surface-area, and the inability to flow liquids through bijels. In this work a scalable synthesis route of nanoparticle stabilized bijels with channels sizes below 500 nm and specific surface areas of  $2 \text{ m}^2 \text{ cm}^{-3}$  is introduced [3]. Moreover, it is demonstrated that liquids can be pumped through the bijel via electroosmosis. The fast liquid flow facilitates the use of bijels for molecular separations in continuous-flow liquid–liquid extraction. Combining the high surface areas with liquid flow enhances the potentials of bijels as highly permeable porous materials with possible uses as microreaction media, fuel-cell components, and separation membranes.



**Figure 1.** The nightmare of each plumber is a large network of entangled and branched pipes. Here, this assembly is realized for pipes with diameters of a few hundred nanometers. Water is pumped through the network and solute molecules are exchanged between adjacent pipes. This liquid-liquid extraction process demonstrates the potentials for continuous flow molecular separations, important for a sustainable chemical industry.

### References

- [1] Stratford, Kevin, et al. "Colloidal jamming at interfaces: A route to fluid-bicontinuous gels." *Science* 309.5744 (2005): 2198-2201.
- [2] Herzig, Eva M., et al. "Bicontinuous emulsions stabilized solely by colloidal particles." *Nature materials* 6.12 (2007): 966-971.
- [3] Khan, Mohd A., et al. "Nanostructured, Fluid Bicontinuous Gels for Continuous Flow Liquid-Liquid Extraction." *Advanced Materials* (2022): 2109547.

## Bicontinuous soft solids with a gradient in channel size

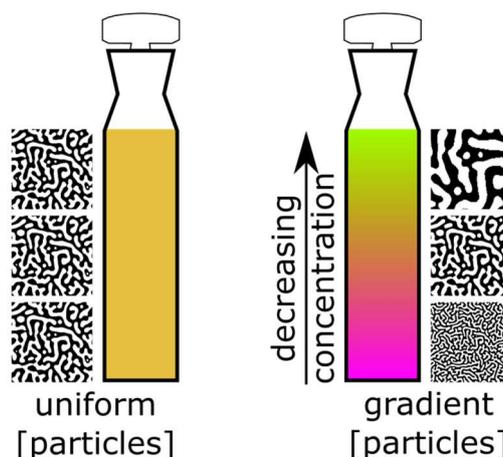
David J. French<sup>1</sup>, Andrew B. Schofield<sup>1</sup>, and Job H. J. Thijssen<sup>1</sup>

<sup>1</sup>SUPA School of Physics and Astronomy, The University of Edinburgh, Edinburgh, UK

Presenting author's e-mail: [j.h.j.thijssen@ed.ac.uk](mailto:j.h.j.thijssen@ed.ac.uk)

We present examples of bicontinuous interfacially jammed emulsion gels ("bijels") with a designed gradient in the channel size along the sample [1]. These samples are created by quenching binary fluids which have a gradient in particle concentration along the sample, since the channel size is determined by the local particle concentration. A gradient in local particle concentration is achieved using a 'layered cocktail' approach i.e. a two-stage loading process, with different particle volume fractions in each stage. Confocal microscopy and image analysis were used to quantitatively measure the channel size of the bijels. Bijels with a gradient in channel size of up to 2.8%/mm have been created. Such tailored soft materials could act as templates for energy materials optimised for both high ionic transport rates (high power) and high interfacial area (high energy density), potentially making them useful in novel energy applications.

**Keywords:** bijels, emulsions, Pickering



**Figure 1.** Bicontinuous Pickering emulsions with a gradient in channel size, designed with energy storage applications in mind, are fabricated through spinodal decomposition following a temperature quench in samples with a gradient in colloidal particle concentration; the gradient in particle concentration is achieved via a 'layered cocktail' approach. Transmission measurements, confocal microscopy and image analysis confirm a significant gradient in channel size.

**Acknowledgements:** the Engineering and Physical Sciences Research Council (EPSRC, UK) for funding via Grant EP/PO07821/1 and P. S. Clegg for useful initial discussions.

### References

[1] D. J. French, A. B. Schofield and J. H. J. Thijssen, *Advanced Materials Interfaces*, 2022, 9, 2102307.

## Rheological characterization of aqueous two-phase emulgels

Chandra Shekhar<sup>1</sup>, Sai Geetha Marapureddy<sup>1</sup>, Vishwajeet Mehandia<sup>1</sup> and Manigandan Sabapathy<sup>1</sup>

<sup>1</sup>Indian Institute of Technology Ropar, Punjab, India

Presenting author's e-mail: [2018chz002@iitrpr.ac.in](mailto:2018chz002@iitrpr.ac.in)

Water-in-water (w/w) pickering emulsion represents the classic example of an aqueous two-phase system (ATPS) stabilized by colloidal particles. To prepare the emulsion of this kind, we employ two different aqueous polymer solutions (PEO & Dextran), emulsification of which would phase separate into two immiscible phases beyond particular concentrations [1]. We demonstrate the novel yet straightforward synthesis methodology to produce emulsion-filled gels or emul-gels stabilized by silica nano-particles. Further, we performed the rheological characterization of these particle-stabilized gels by tuning the concentrations of polymers and nano-particles, in addition to the molecular weight of the polymer used in the aqueous phase. We observed a distinct sol-gel transition in a particular experimental regime through several repeated experimental studies. The time evolution of shear-induced structures reveals that the viscoelastic properties of these emulsion gels have direct correspondence with several parameters such as storage time, molecular weight, and polymer compositions. Besides, the emul-gels prepared by us displayed excellent storage stability of up to 60 days. As the method involves using an aqueous-based template route for synthesis, the proposed study finds several applications in various fields such as tissue engineering, wound dressing, drug delivery, and soft robotics. We believe our work would provide good insight into the physics of emul-gels having reasonable control over size, shape, appearance, and shelf-life.

**Keywords:** Aqueous two-phase system (ATPS), emulgels, water-in-water (w/w) Pickering emulsion, rheology

### References

[1] S. Chandra, K. Abhimanyu, M. Vishwajeet, D. Venkateshwar Rao and S. Manigandan, *Langmuir*, 2021, 37(23), 7055-7066.

# Understanding the early growth of gold films to provide thin impermeable metal films onto emulsions

*Cheng Cheng<sup>1</sup>, James P. Hitchcock<sup>1</sup>, Thomas A. Hughes<sup>2</sup> and Olivier J. Cayre<sup>1</sup>*

<sup>1</sup> School of Chemical and Process Engineering, University of Leeds, UK

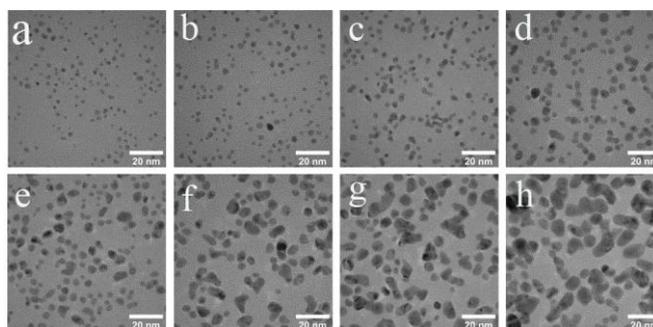
<sup>2</sup> School of Medicine, University of Leeds, UK

Presenting author's e-mail: [pmcc@leeds.ac.uk](mailto:pmcc@leeds.ac.uk)

Despite many colloidal/particulate drug carriers having been developed, only very few have resulted in applied systems, partly due to the low doses still possible with these carriers, partly due to their high levels of drug leaching in biological conditions. Noble metals are potential alternatives to organic microcapsule shells to achieve permanent encapsulation of small molecules and thus to allow encapsulation of higher concentrations. Indeed, recent report has demonstrated the use of gold shell microcapsules to fully retain drugs [1]. In this study, metal-shell microcapsules have been produced by electroless deposition of gold film on emulsion droplets containing the encapsulated drugs. However, smaller capsules (~100nm) are required for systemic delivery [2]. To retain a sufficient core volume for such nanoscale capsule systems, impermeable metal shells of ~20nm or less are needed, which so far has proven challenging. Thus, studying the early stages of the growth mechanism of gold films onto droplet surfaces or onto model surfaces will allow a better understanding of how to achieve such thin impermeable metal films.

In this work, we use 2-5nm platinum nanoparticles (Pt-NPs) to stabilise nanoscale Pickering emulsions. Such emulsions can be used as templates for preparing metal-shell capsules. Particularly, we demonstrate emulsion size control by adjusting the oil volume fraction. We also use TEM grids onto which Pt-NPs films of controlled density are deposited as models to study the early stages of gold growth from these surfaces. Careful characterization of the phenomena occurring in these early stages (Figure 1) reveals the influence of coating time on the growth rate of the gold film, both locally and across the whole surface. Evidence of Ostwald ripening during the growth process is also demonstrated and key aspects to growing thin impermeable films are identified. Specifically, we focus on the influence of density and interparticle distance of Pt-NPs.

**Keywords:** Platinum nanoparticles-stabilised Pickering emulsion, Metal film growth mechanism, Electroless deposition



**Figure 1.** Example of the growth of a gold film over time on a model solid substrate, where the electroless deposition of gold from the bulk occurs onto the surface of Pt-NPs (a) acting as nucleation points. The growth times are (b) 2s, (c) 5s, (d) 10s, (e) 30s, (f) 60s, (g) 90s and (h) 120s.

## References

- [1] J. Hitchcock, A.L. White, N. Hondow, T.A. Hughes, H. Dupont, S. Biggs and O.J. Cayre, *Journal of Colloid and Interface Science*, 567 (2020) 171-180.  
[2] Y. Matsumura and H. Maeda, *Cancer Research*, 46 (1986) 6387-6392.

## Diffusion across particle-laden interfaces in Pickering emulsions

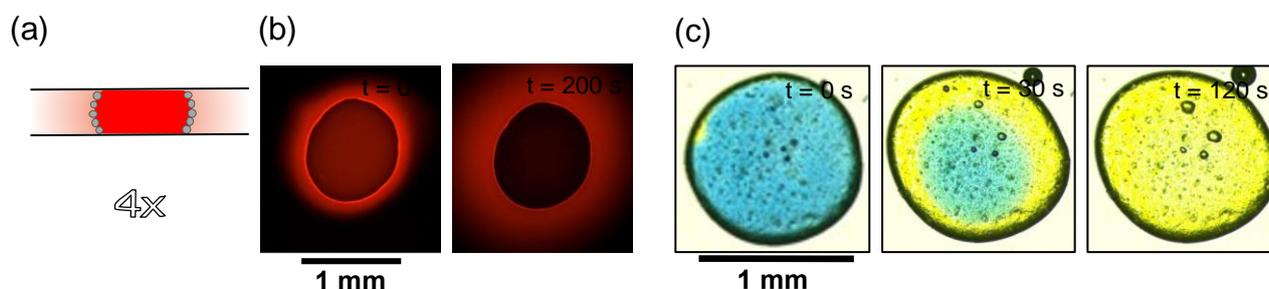
*Yanyan Liu, Mingjun Xu, Aza Alawi, Luis Portela, Ruud van Ommen and Valeria Garbin*

*Department of Chemical Engineering, Delft University of Technology, The Netherlands*

Presenting author's e-mail: [Y.Liu-19@tudelft.nl](mailto:Y.Liu-19@tudelft.nl)

Emulsions stabilized by nanoparticles at the interfaces of the droplets (Pickering emulsions) exhibit remarkable stability, and have many applications in advanced materials, food and pharma. After the pioneering demonstration of Pickering emulsions for chemical reactions, research in this new application area has been rapidly expanding. Yet, this novel technique is still optimized by trial and error, primarily because of a lack of understanding of diffusion in multi-phase systems with particles at interfaces. To address this gap, we developed an experimental approach for in-situ, real-time visualization and quantification of concentration fields in Pickering droplets in a Hele-Shaw geometry [Figure 1(a)], to investigate the effect of a layer of colloidal particles on diffusive transport across interfaces in model multi-component systems. We used a fluorescent dye to map the spatio-temporal evolution of the concentration field during diffusion from the droplet to the outer phase [Figure 1 (b)]. An acid-base neutralization, where the acid transfers from the outer phase to the droplet across the particle-laden interface, enables us to monitor via color-changing pH indicator the interplay of diffusion across the particle-laden interface and reaction [Figure 1 (c)]. The concentration profiles and diffusion time-scales are compared with measurements for bare droplets to dissect the effect of the particles on diffusion across the interface. Guided by a continuum model and numerical simulations, we established the effects of sizes and surface coverages of the nanoparticles on diffusive transport across a liquid-liquid interface. These insights will ultimately contribute to control the performance in Pickering emulsions for sustainable chemical reactions.

**Keywords:** particle-laden interface, Pickering emulsion, diffusion



**Figure 1.** (a) Pickering droplet in Hele-Shaw geometry. (b) Visualizing diffusion of fluorescent dye across particle-laden interface. (c) Visualizing reaction in Pickering droplet using color-changing pH indicator.

## No silver bullet: compositional ripening in water-in-oil systems

*Raj Tadi<sup>1</sup>, Tom Curwen<sup>2</sup>, Beth Green<sup>2</sup>, Paul Clegg<sup>1</sup>*

<sup>1</sup>*School of Physics & Astronomy, University of Edinburgh, UK*

<sup>2</sup>*Mondelez International, Reading Science Centre, UK*

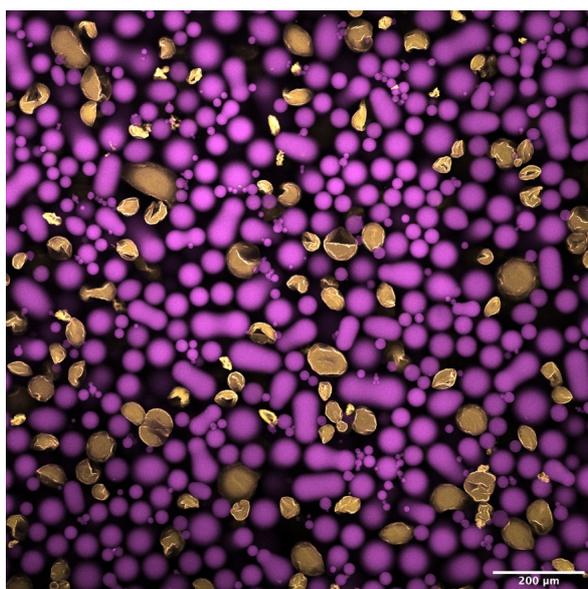
*Presenting author's e-mail: [raj.tadi@ed.ac.uk](mailto:raj.tadi@ed.ac.uk)*

One approach to achieve low calorie foods is to substitute regions of high calorie content with water droplets. Such water-in-oil emulsion systems are naturally unstable due to coalescence and Ostwald ripening. These effects can be reduced, for example, via an interfacial layer of solid particles. In complex food systems consisting of multiple species of dispersed phases, compositional ripening may also occur in which the water undergoes mass transfer to regions filled with other less soluble species.

Here we present a model system to study compositional ripening for water-in-oil particle stabilised (Pickering) emulsions. Water-in-dodecane emulsions stabilised by PMMA particles were prepared and combined with similar emulsions that included sugar in the water. Overtime the pure water droplets appear to crumple (Figure 1. yellow droplets) due to the loss of water; in extreme cases they eventually 'explode'. Simultaneously, the sugar-filled droplets (Figure 1. purple droplets) slowly coalesce.

Evidently, our interfacial coating of particles is unable to suppress this effect. Using particle tracking, quantitative analysis of the individual droplets shows a decrease in the concentration of the sugar solution results in a reduction in the rate of change of water droplet size. Observations of droplet 'explosions' indicate that the driving force is vastly stronger than that of Ostwald ripening. Forthcoming experiments will show further explorations to the system including modifying the continuous phase and the liquid-liquid interface.

**Keywords:** compositional ripening, pickering, emulsions, mass transfer



*Figure 1: Confocal still illustrating the mass migration from pure water droplets (yellow) to sugar droplets (purple).*

## Theory of Shape-Shifting Droplets

*Pierre A. Haas*<sup>1,2,3</sup>, *Diana Cholakova*<sup>4</sup>, *Nikolai Denkov*<sup>4</sup>, *Raymond E. Goldstein*<sup>5</sup>,  
and *Stoyan K. Smoukov*<sup>6</sup>

<sup>1</sup> *Max Planck Institute for the Physics of Complex Systems, Dresden, Germany*

<sup>2</sup> *Max Planck Institute of Molecular Cell Biology and Genetics, Dresden, Germany*

<sup>3</sup> *Center for Systems Biology Dresden, Dresden, Germany*

<sup>4</sup> *Department of Chemical and Pharmaceutical Engineering, Faculty of Chemistry and Pharmacy, University of Sofia, Sofia, Bulgaria*

<sup>5</sup> *Department of Applied Mathematics and Theoretical Physics, University of Cambridge Cambridge, United Kingdom*

<sup>6</sup> *School of Engineering and Materials Science, Queen Mary University of London, London, United Kingdom*

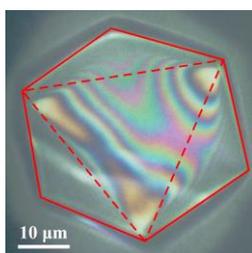
Presenting author's e-mail: [haas@pks.mpg.de](mailto:haas@pks.mpg.de)

Oil emulsion droplets in aqueous surfactant solution flatten, on slow cooling, into a remarkable host of polygonal shapes with straight edges and sharp corners [1], but the physical and chemical mechanisms driving these beautiful deformations remained debated for quite some time.

In this talk, I will show theoretically how the simplest geometric competition between a phase transition to a rotator phase near the droplet interface [1] and surface tension in planar polygons explains the observed sequence of polygonal shapes [2]. I will then explain how this phase transition mechanism extends to reproduce the complex dynamics of the initial stages of the evolution of these “shape-shifting” droplets, during which an icosahedral droplet flattens into a hexagonal platelet (Fig. 1) via an intermediate, octahedral stage [3].

Finally, I will show how a physically very different elastic mechanism of these “shape-shifting” phenomena is mathematically equivalent to this phase-transition mechanism [4]. Together with the differences of experimental systems, this suggests that these systems are physically different realisations of general “shape-shifting” mechanism based on the interplay of positive surface tension and negative edge tension in faceted droplets [4]. Can other instances of it be found experimentally?

**Keywords:** Emulsion droplets, Phase Transitions, Rotator Phases, Morphogenesis



**Figure 1.** Reflected-light microscopy image of a hexagonal oil emulsion droplet; surface outline highlighted in red. (Image credit: D. Cholakova)

### References

- [1] N. Denkov, S. Tcholakova, I. Lesov, D. Cholakova, and S. K. Smoukov, Self-shaping of oil droplets via the formation of intermediate rotator phases upon cooling, *Nature*, 2015, 528, 392.
- [2] P. A. Haas, R. E. Goldstein, S. K. Smoukov, D. Cholakova, and N. Denkov, Theory of Shape-Shifting Droplets, *Phys. Rev. Lett.*, 2017, 118, 088001.
- [3] P. A. Haas, D. Cholakova, N. Denkov, R. E. Goldstein, and S. K. Smoukov, Shape-shifting polyhedral droplets, *Phys. Rev. Res.*, 2019, 1, 023017.
- [4] P. A. Haas, R. E. Goldstein, D. Cholakova, N. Denkov, and S. K. Smoukov, Comment on “Faceting and Flattening of Emulsion Droplets: A Mechanical Model”, *Phys. Rev. Lett.*, 2021, 259801.

# Droplet dynamics and emulsion ageing in microgravity by DWS experiments onboard the International Space Station

*Luigi Cristofolini<sup>1,2</sup>, Davide Orsi<sup>1</sup>, Valentina Lorusso<sup>1</sup>, Marco Vaccari<sup>1</sup>, Francesca*

*Ravera<sup>2</sup>, Eva Santini<sup>2</sup>, Robert McMillin<sup>3</sup>, James Ferri<sup>3</sup>, Angeliki Chondrou<sup>4</sup>, Margarithis Kostoglou<sup>4</sup>, Thodoris Karapantsios<sup>4</sup>, Libero Liggieri<sup>2</sup>*

*<sup>1</sup> University of Parma, Italy; <sup>2</sup> CNR-ICMATE Genova, Italy;*

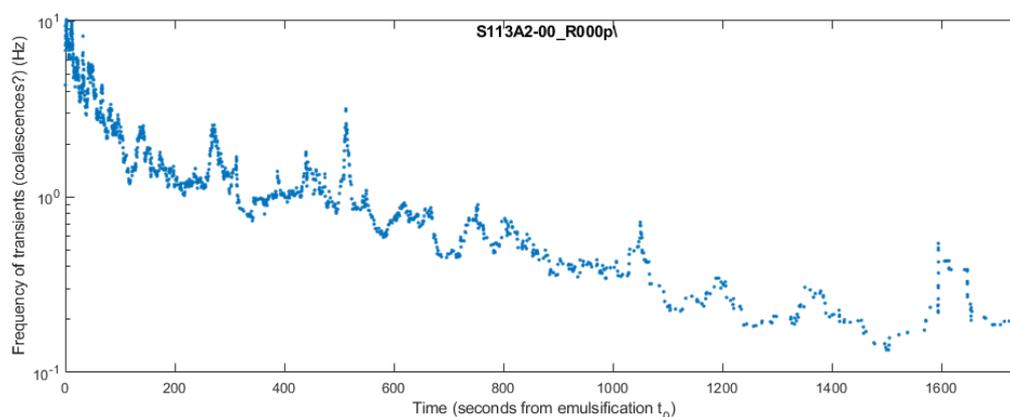
*<sup>3</sup> Virginia Commonwealth University, USA; <sup>4</sup> Aristotile University Thessaloniki, Greece*

*Presenting author's e-mail: [luigi.cristofolini@unipr.it](mailto:luigi.cristofolini@unipr.it)*

We report here on the first results of experiments currently being carried out onboard the International Space Station, using the ESA facility Soft Matter Dynamics (SMD) [1] to investigate drop dynamics and emulsion ageing in microgravity by Diffusing Wave Spectroscopy (DWS) [2,3]. To the best of our knowledge, this is the first time that such an investigation is undertaken: weight-less condition allows to investigate the intrinsic drop dynamics, and the processes influencing emulsions stability (e.g., drop aggregation, drop coalescence, Ostwald ripening) which are normally convoluted with the predominant gravity-induced dynamics of drop creaming/sedimentation and affected by the resulting drop-crowding effects and the enhanced coalescence rate.

We focus on marginally stable oil-in-water emulsions stabilized by minimal amounts of non-ionic surfactant (e.g. C12E021). After a careful preparatory calibration campaign [4] we employ DWS and related techniques as powerful optical diagnostics to investigate dynamics in dense emulsions. Our preliminary results indicate strong resemblances with the important results obtained by DWS on foam coarsening [2,3], notwithstanding the significant difference of the persistence of diffusion-like dynamics for emulsions droplets. By combining data from different detection channels, we extract information on drop size and its evolution with age, obtained independently from diffusion coefficient and from optical transport length, and on drop-coalescence events (see figure below), hallmarked by transients in the time-resolved DWS correlation function.

**Keywords:** emulsions; diffusing wave spectroscopy; droplet dynamics; coalescence; microgravity.



**Figure 1.** Frequency of transients in the dynamics of a marginally stable oil-in-water emulsion in microgravity

**Acknowledgements:** European Space Agency, MAP project “Emulsion Dynamics and Droplet Interface - EDDI” (ESA Contract n. 4000128643/19). Nikko-Chemical, Japan for surfactants

## References

- [1] P. Born et al., Review of Scientific Instruments, 2021, 92, 124503.
- [2] D.A. Weitz et al., Dynamic Light Scattering: Method Some Appl., Clarendon Press, 1993.
- [3] R. Hohler et al., Current Opinion in Colloid & Interface Science, 2014, 19, 242-252.
- [4] V. Lorusso et al., Advances in Colloid and Interface Science, 2021, 288, 102341.

# Uptake kinetics of spontaneously emulsified microdroplets at an air interface

Léa Delance <sup>1,2</sup>, Charlotte Veillon <sup>1,2</sup>, Nicolas Passade-Boupat <sup>2,3</sup>, Emilie Verneuil <sup>1,2</sup>, François Lequeux <sup>1,2</sup> and Laurence Talini <sup>4</sup>

<sup>1</sup> CNRS, SIMM, ESPCI Paris, PSL Research University, Sorbonne Université, Paris, France

<sup>2</sup> Laboratoire PIC, ESPCI, Paris, Bâtiment CHEMSTARTUP, Lacq, France

<sup>3</sup> Total S.A., Lacq, France

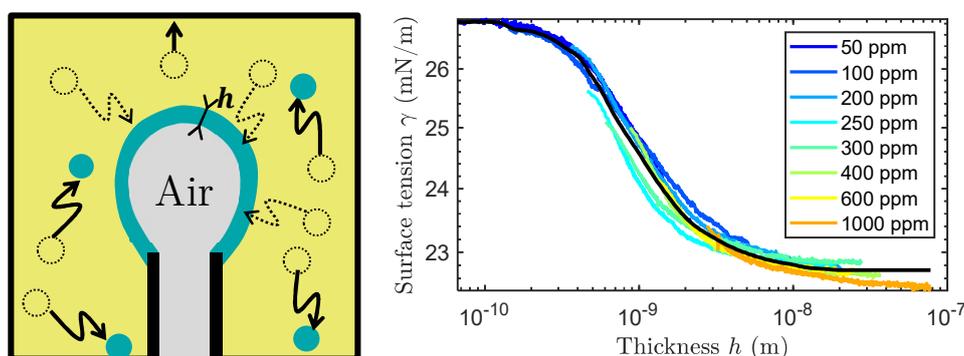
<sup>4</sup> CNRS, SVI, Saint-Gobain, Aubervilliers, France

Presenting author's e-mail: [lea.delance@espci.fr](mailto:lea.delance@espci.fr)

Foamed emulsions are encountered in various situations: antifoaming additives, injection of fluid for oil extraction or in the food industry. The presence of microdroplets in a foaming solution allows one to tune the properties of the foam, since either a stabilizing or a destabilizing effect is expected, depending for instance on the oil fraction in the liquid [1-2]. The interactions between microdroplets and air also play a major role in the stability of such systems. In the case of oil-in-water emulsions, they are often modified by adding surfactants. Here, we focus on oil-in-oil emulsions without surfactants, which are commonly used as lubricants and exhibit surface properties that are different from the ones of aqueous solutions.

Using a ternary mixture of oils including Polydimethylsiloxane (PDMS), we obtain an emulsion of PDMS-rich microdroplets resulting from a spontaneous emulsification. We show that the microdroplets coalesce without delay due to Brownian motion. Then, we use surface tension measurements to probe the behavior of the emulsion at an air interface. We suggest two mechanisms by which microdroplets are uptaken by the air interface, creating a thin layer of PDMS at the surface of a rising bubble (see figure) and we provide a model for the growth of this layer. Within this framework, we find that the experimental data collapse onto a master curve, which gives the surface energy of the thin film of PDMS as a function of its thickness  $h$  (see figure) and allows a description at very small scales of the uptake of droplets at an interface.

**Keywords:** emulsion, air, coalescence, surface tension



**Figure 1.** Left: schematic representation of droplets uptake at the air-liquid interface. Right: surface tension of a PDMS thin film as a function of its thickness  $h$  for different PDMS fractions (ppm). The black line is a guide for the eye.

## References

- [1] M. Schneider, Z. Zou, D. Langevin and A. Salonen, *Soft Matter*, 2017, 13, 4132-4141.  
[2] R. Mensire and E. Lorenceau, *Advances in Colloid and Interface Science*, 2017, 247, 465-476.

# Self-positioning of colloids and fluorophores on interfacially-frozen alkane-in-water liquid spheres

Alexander V. Butenko<sup>1</sup> and Eli Sloutskin<sup>1</sup>

<sup>1</sup>Physics Dept., Institute of Nanotechnology & Advanced Materials, Bar-Ilan Univ., Israel

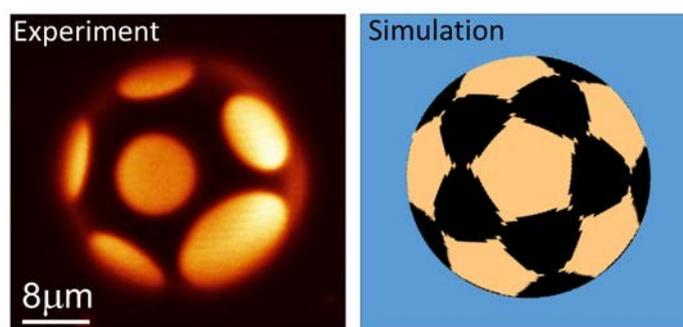
Presenting author's e-mail: [eli.sloutskin@biu.ac.il](mailto:eli.sloutskin@biu.ac.il)

Surfaces of classical spherical liquid droplets are isotropic, promoting random distribution of surface-adsorbed colloidal particles and molecules. While self-focusing of surface adsorbant concentration at particular locations of droplets' interfaces is necessary for precise positioning of surface-attached ligands and for local initiation of chemical reactions, such self-focusing has never been previously realized.

I will present the first observation of a counterintuitive temperature-controlled self-assembly of well-defined and highly ordered self-focused concentration patterns of surface-adsorbed fluorescent molecules and colloidal particles on the surfaces of surfactant-stabilized spherical alkane-in-water liquid emulsion droplets. These patterns are induced by precisely self-positioned, topology-dictated, structural defects in a crystalline interfacial monolayer, which covers these droplets' surfaces over a wide temperature range[1-2]. Similar phenomena are detected for a wide range of cationic, anionic, and non-ionic alkyl tail-bearing surfactants, for a wide range of colloid sizes and surface properties[3], and for many different fluorescent molecules[3].

We visualized the defects' positions, mapped the stress fields within the molecularly thin surface crystal, and elucidated the fundamental physical mechanism, which drives the formation of these patterns. This mechanism is very general and may play an important role in many different fields of physics, material science, biology, and nanotechnology. The observed phenomena provide deep insight into the fundamentals of curved surfaces' crystallization, enable precise positioning of functional ligands on droplets for their self-assembly into higher-hierarchy structures, and may play a significant role in vital protein positioning on cell membranes and morphogenesis.

**Keywords:** emulsions, interfacial freezing, faceted liquid droplets



**Figure 1.** Self-assembled fluorescent pattern on the surface of a liquid spherical oil-in-water emulsion droplet. The experimental icosahedrally-symmetric pattern (left panel) is correctly reproduced by the theory (right panel).

## References

- [1] S. R. Liber, O. Marin, A. V. Butenko, R. Ron, L. Shool, A. Salomon, M. Deutsch and E. Sloutskin, *J. Am. Chem. Soc.*, 2020, 142, 8672.
- [2] O. Marin, M. Tkachev, E. Sloutskin, and M. Deutsch, *Curr. Opin. Colloid Interface Sci.*, 2020, 49, 107.
- [3] S. R. Liber, A. V. Butenko, M. Caspi, S. Guttman, M. Schultz, A. B. Schofield, M. Deutsch, E. Sloutskin, *Langmuir*, 2019, 35, 13053; S. Das et al. (under review, 2022).

# ‘Hydrophobic’ cellulose microgels: the influence of particle size on water-in-oil emulsion stability

*Katherine Lefroy*<sup>1</sup>, *Brent Murray*<sup>1</sup>, *Michael Ries*<sup>2</sup> and *Thomas Curwen*<sup>3</sup>

<sup>1</sup>*University of Leeds, School of Food Science and Nutrition, Leeds, UK*

<sup>2</sup>*University of Leeds, School of Physics and Astronomy, Leeds, UK*

<sup>3</sup>*Mondelēz International, Reading Science Centre, Reading, UK*

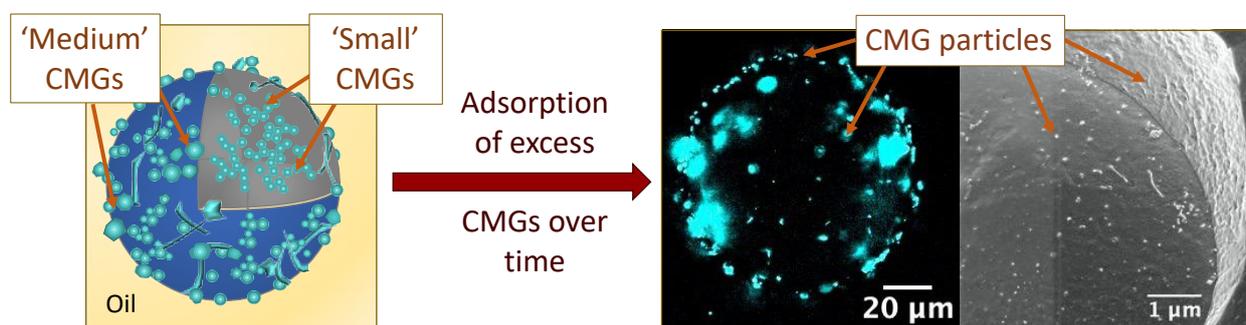
Presenting author’s e-mail: [fskl@leeds.ac.uk](mailto:fskl@leeds.ac.uk)

Colloids are used extensively in foods as thickening, stabilizing and gelling agents. Nonetheless, the design of new colloids for food products is a challenge due to restrictions on ingredients, influenced by legislation and consumer preferences. Nowadays, the emphasis on ‘clean-label’ additives has led to demand for reformulation of many existing products which contain ‘unnatural’ ingredients. As a result, there has been a huge increase in the development of more sustainable food colloids derived from natural, readily available plant materials and functionalized with minimal processing.

Amongst one of the most explored biopolymers is cellulose, an insoluble dietary fiber. Until recently, chemically unmodified cellulose has only been considered for water-based systems, since it contains glucose units with 4 hydroxy groups and appears molecularly to be hydrophilic. However, hydrophobic regions are also present between the glucopyranose rings which could potentially be exposed and/or enhanced through physical modification, making native cellulose more suitable for oil-based systems. We previously demonstrated this phenomenon by producing ‘oily’ cellulose microgels (CMGs), via a dissolution-coagulation method using an ionic liquid.[1] These ‘hydrophobic’ CMGs showed promising capabilities for stabilizing water-in-oil (W/O) emulsions.

More recently, we have carried out detailed characterization of the CMGs and employed different methods to tune particle size. In this work, we show that whilst ‘smaller’ CMGs adsorb more rapidly to the interface and form smaller water droplets, ‘larger’ CMGs provide a steric barrier and give greater emulsion stability. When two types of CMG produced via different methods are used, excess microgel in the oil-phase can adsorb over time and increase interfacial coverage, producing highly stable emulsions which showed no signs of significant sedimentation for at least 3 months. Thus, our system has great potential to be used in food products, as well as finding application in personal care and biomedical fields.

**Keywords:** Cellulose; microgel; emulsion; ionic liquid



**Figure 1.** Schematic to show thick interfacial CMG layers in W/O emulsions, as evidenced by confocal microscopy (left, cellulose stained by Calcofluor White) and scanning electron microscopy (right)

**Acknowledgements:** We gratefully acknowledge the Engineering and Physical Sciences Research Council (EPSRC) funded Centre for Doctoral Training in Soft Matter and Functional Interfaces (SOFI) and Mondelēz International (Reading, UK), for financial support.

## References

[1] K. S. Lefroy, B. S. Murray, M. E. Ries and T. D. Curwen, *Food Hydrocolloids*, 2021, **113**, 106408.

## Probing surfactant dynamics through interfacial surface tension using millifluidic elongational flow

*Julian Wailliez<sup>1</sup>, Marc Leonetti<sup>2</sup>, Gang Chen<sup>2</sup>, Marc Jaeger<sup>2</sup>, Anniina Salonen<sup>1</sup> and Emmanuelle Rio<sup>1</sup>*

<sup>1</sup> CNRS / Laboratoire de Physique des Solides, Université Paris-Saclay Orsay, France

<sup>2</sup> CNRS / Laboratoire Mécanique, Modélisation & Procédés Propres, Centrale - Marseille Marseille, France

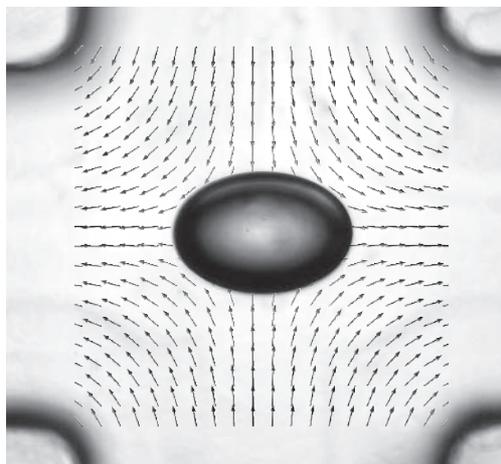
Presenting author's e-mail: [julian.wailliez@universite-paris-saclay.fr](mailto:julian.wailliez@universite-paris-saclay.fr)

Surface-active materials which adsorb onto interfaces such as surfactants, polymers, proteins or particles can confer mechanical properties to the interfaces [1], which are useful to stabilize emulsions, foams or bubbles against coarsening and/or coalescence.

Hereby, we propose to explore the influence of these mechanical properties on the deformation of a droplet in an extensional flow. Theoretical models [2,3,4] predict that this deformation can be larger in presence of surface viscoelasticity. Using a home-made millifluidic device, we create a controlled elongational flow allowing to attain large strains and high strain rates on the droplet surface. And we measure the deformation of water droplets in oil continuous phase for various surfactants.

Our first results allow to identify systems in which the influence of surface viscoelasticity is important and to link our observations with Marangoni elasticity and dilatational and shear viscosities, opening the route to a non-invasive method to measure these quantities at high shear rates.

**Keywords :** Interfacial Rheometry, Surfactants, Elongational Flow



**Figure 1.** Elongated droplet of surfactant solution in silicon oil.

### References

- [1] Nick Jaensson and Jan Vermant, *Current Opinion in Colloid & Interface Science*, 2018, 38, 136-150.
- [2] Raymond W. Flumerfelt, *Journal of Colloid and Interface Science*, 1980, 76, 330-349
- [3] Y. T. Hu and A. Lips, *Phys. Rev. Lett.*, 2003, 91, 044501
- [4] Charles D. Eggleton and Kathleen J. Stebe, *Journal of Colloid and Interface Science*, 1998, 208, 68-80

**Thursday 8th September 2022**

**Colloids in Biomaterials and Biomedical Applications**

# Peptide Decorated Silica Nanoparticles as Phosphate Binders for the Treatment of Hyperphosphatemia

Roza Truberman<sup>1</sup>, Matthew V. Tirrell<sup>2</sup>, and Moshe Gottlieb<sup>1</sup>

<sup>1</sup>Chemical Engineering Department, Ben Gurion University of the Negev, Beer Sheva, Israel

<sup>2</sup>Pritzker School of Molecular Engineering, University of Chicago, Chicago, Illinois, United States

Presenting author's e-mail: [mosheg@bgu.ac.il](mailto:mosheg@bgu.ac.il)

Hyperphosphatemia is a disorder characterized by abnormally high serum phosphate levels. It can result from increased phosphate intake, decreased phosphate excretion, or conditions that shifts intracellular phosphate to extracellular space. Hyperphosphatemia is a major concern because of its association with cardiovascular morbidity and mortality among chronic kidney disease and dialysis patients. Furthermore, increased levels of serum phosphate have been associated with rewired cell signaling pathways, impaired bone mineralization, infertility, arteriosclerosis, and accelerated aging [1-3].

Due to the shortcomings in existing phosphate binding (PhB) remedies there is a need to develop a non-systemic PhB active in the physiological gastric and intestine pH values. To achieve this goal, silica nanoparticles (NP) decorated with phosphate-binding hexapeptides (SiO<sub>2</sub>-CysHex) were synthesized, characterized, and tested for their ability to capture phosphate in simulants of gastrointestinal (GI) fluids. It was determined that the CysHex peptides were successfully attached to the silica NP surface at a surface concentration of approximately 0.5 peptide molecules per nm<sup>2</sup> of silica surface area. Phosphate binding to the SiO<sub>2</sub>-CysHex PhB evaluated by means of a colorimetric technique, showed the highest phosphate binding in all three GI tract fluid simulants at the physiologically relevant range of pH values. The amount of phosphate captured varied between 1.3 to 2.6 mg phosphate/gr PhB in the different simulants. The phosphate binding ability of the peptide based PhB was found to be comparable to the clinically used lanthanum carbonate PhB but lower than that of Sevelamer- another frequently used medication.

**Keywords:** Phosphate binding peptide, silica nanoparticles, hyperphosphatemia, surface functionalization

**Acknowledgements:** This research was supported by Grant No. 2015292 from the United States-Israel Binational Science Foundation (BSF).

- References**
- [1] Kuroki, M. *Nature* **2018**, 553 (7689), 409–410. <https://doi.org/10.1038/d41586-017-09032-4>
  - [2] Alexander, R.; Debiec, N.; Razzaque, M. S.; He, P. *IUBMB Life* **2021**, 23 (September), 1–8. <https://doi.org/10.1002/iub.2561>
  - [3] Lederer, E. Hyperphosphatemia <https://emedicine.medscape.com/article/241185>

## Microbubble Agents for Biomedical Applications: Soft Nano/Micromechanics at the Interface

Adeel S Shafi <sup>1</sup>, Jake McClements <sup>1</sup>, Tom S, Glen <sup>2</sup>, Norbert Radacsi <sup>1</sup>, Carmel M. Moran <sup>3</sup>,  
Vasileios Koutsos <sup>1</sup>

<sup>1</sup>*Institute for Materials and Processes, School of Engineering, The University of Edinburgh, Edinburgh United Kingdom*

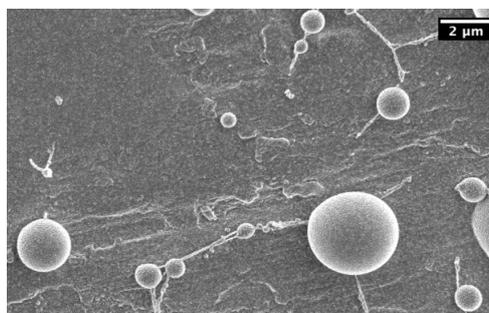
<sup>2</sup>*School of Physics and Astronomy, Institute for Condensed Matter and Complex Systems, The University of Edinburgh, Edinburgh United Kingdom*

<sup>3</sup>*Centre for Cardiovascular Science, Queen's Medical Research Institute, The University of Edinburgh, Edinburgh, United Kingdom*

Presenting author's e-mail: [vasileios.koutsos@ed.ac.uk](mailto:vasileios.koutsos@ed.ac.uk)

Stable, haemodynamically inert, hollow, micrometre-size spheres, composed of a shell (usually phospholipid-based which encapsulates an inert gas) are used as ultrasound contrast agents and are normally referred to as microbubbles (MBs). They are smaller than the smallest blood vessel of a human body to allow improved visualization of the vascular bed and differentiate vascular patterns of tumours non-invasively. Such nano-shelled microstructures can be used as carriers for drug/gene delivery, which is a topic of much current interest in biomedical research. Furthermore, with appropriate surface modification such MBs can acquire targeting capability for certain cell types (e.g. cancerous cells). Their nanomechanical properties are extremely important since they have to be stable for considerable time until they rupture/degrade under specific conditions in order to release their load in the right place and at the right time. Moreover, materials at the nanoscale (such as thin-shell structures) may behave differently to those on the macroscale, so predicting their mechanical properties presents a challenge. We have conducted a systematic study of phospholipid-shelled MBs in their natural hydrated state employing tapping-mode atomic force microscopy (AFM, state-of-the-art quantitative imaging (QI-mode AFM, and focused-ion-beam (FIB) cryo-scanning electron microscopy (cryo-SEM). Combining these techniques, we show unequivocally and for the first time that the thin phospholipid shell of the MBs is ca. 6.5 nm and corresponds to a trilayer. We discuss in detail the structure of the shell, including the polyethylene glycol (PEG) layer that surrounds the phospholipid shell. Furthermore, using the measured value of the shell thickness we revisit the MB nanomechanics (based on AFM force-distance curves showing which mechanical theories predict more accurately their mechanical properties [1]).

**Keywords:** Microbubbles, Phospholipids, Ultrasound, AFM, cryo-SEM, Nanomechanics, Nanoshells



**Figure 1.** A cryo-SEM image showing a range of microbubbles.

### References

[1] A. S. Shafi, J. McClements, I. Albaijan, R. H. Abou-Saleh, C. Moran, V. Koutsos. *Colloids and Surfaces B: Biointerfaces* 2019, 181, 506-515

## Charge effects on stability and self-assembly of antibodies in solutions – a colloid approach

Polimeni Marco <sup>1</sup>, Gulotta Alessandro <sup>1</sup>, Zaccarelli Emanuela <sup>2</sup>, Stradner, Anna <sup>1,3</sup>, and Schurtenberger Peter <sup>1,3</sup>

<sup>1</sup>Physical Chemistry, Lund University, Lund, Sweden

<sup>2</sup> CNR-ISC and Department of Physics, Sapienza University of Rome, Roma, Italy <sup>3</sup>Lund Institute of advanced Neutron and X-ray Science, Lund University, Lund, Sweden

Presenting author's e-mail: [peter.schurtenberger@fkem1.lu.se](mailto:peter.schurtenberger@fkem1.lu.se)

Monoclonal antibodies (mAbs) have moved into the focus of pharmaceutical industry as a major platform for potential drug candidates. However, successful mAb applications that allow for facile home administration require stable and low viscosity high concentration formulations, which are often difficult to achieve. mAbs are prone to exhibit reversible self-association at high concentrations that result in enhanced viscosity. This creates the need for an advanced predictive understanding of the stability and viscosity of concentrated protein solutions. Here we investigate the link between self-assembly and viscosity in concentrated solutions of monoclonal antibodies using a soft condensed matter approach that combines different experimental techniques, primarily scattering methods and microrheological experiments, with theory and simulations based on colloid models. We in particular focus on the importance of electrostatic interactions in controlling self-assembly, and provide a theoretical and experimental framework for a quantitative assessment of antibody charge, interactions, self-assembly and flow properties.

The complexity of the system, formed by anisotropic and flexible large molecules that interact through a number of different intermolecular forces, makes a theoretical treatment capable of providing a quantitative link between the molecular structure and the various structural and dynamic quantities obtained in experiments a real challenge. We discuss different coarse graining strategies that allow us to incorporate crucial molecular information into colloid-like models that are then amenable to computer simulations as well as numerical and analytical calculations. We present comparisons between experimental data and theoretical predictions for different antibodies that form either stable low viscosity concentrated solutions or are prone to self-assemble into transient clusters that result in strongly increased viscosity values.

**Keywords:** monoclonal antibodies, self-assembly, protein-protein interactions, high concentration formulations

# Morphological Control in Multifunctional Iron Oxide: Gold Nanoparticles for Theranostics

*Javier Reguera*

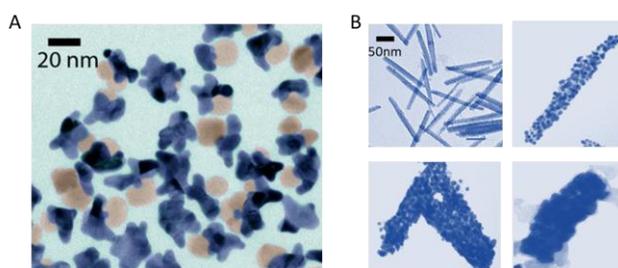
*BCMaterials, Basque Center on Materials, Applications and Nanostructures, Leioa, Spain*

Presenting author's e-mail: [javier.reguera@bcmaterials.net](mailto:javier.reguera@bcmaterials.net)

Nanomaterials applied to diagnosis and therapy in precision and personalized medicine have undergone a burst of development in the last years. As their application evolves, it is ever clearer the necessity of more sophisticated and multifunctional nanomaterials to accomplish a more integrated theranostics (therapy & diagnosis) approach. Among the different nanomaterials available, iron oxide (magnetic) and gold (plasmonic) are prominent examples. Both nanomaterials can be used as drug delivery carriers, contrast agents, and enablers of therapeutic treatments like hyperthermia. Their combined use in single multi-component nanoparticles harnesses the versatility provided by the combination of properties of each nanomaterial while offering synergistic and complementary features.

Here, we have synthesized two novel types of gold : iron oxide multicomponent nanoparticles with two different configurations: Janus nanostars, and core-shell nanorods (with tunable relative dimensions). Their properties have been characterized for use in theranostic applications, including magnetothermia and photothermia,[1,2] sensing,[3] and as contrasts agents in multimodal imaging.[4] Both morphologies have shown an outstanding versatility to be used in theranostics, but with marked differences which opens a whole new range of possibilities to overcome the new nanobiomedical challenges.

**Keywords:** Janus, core-shell, magneto-plasmonic, theranostics.



**Figure 1.** Two configurations of multicomponent gold: iron oxide nanoparticles. A) TEM image of Janus nanostars (iron oxide sphere and a gold nanostar). B) TEM images of core-shell nanorods (iron oxide nanorod and gold shell) at different states of the shell growth.

**Acknowledgements:** Spanish State Research Agency (AEI), project PID2019-106099RB-C43/AEI/10.13039/501100011033

## References

- [1] M. Rincón-Iglesias, I. Rodrigo, L. B. Berganza, E. S. A. Serea, F. Plazaola, S. Lanceros-Méndez, E. Lizundia and J. Reguera, *ACS Appl. Mater. Interfaces*, 2022, **14**, 7130–7140.
- [2] A. Espinosa, J. Reguera, A. Curcio, Á. Muñoz-Noval, C. Kuttner, A. Van de Walle, L. M. Liz-Marzán and C. Wilhelm, *Small*, 2020, **16**, 1904960.
- [3] L. Litti, S. Trivini, D. Ferraro and J. Reguera, *ACS Appl. Mater. Interfaces*, 2021, **13**, 34752–34761.
- [4] J. Reguera, D. de Aberasturi, M. Henriksen-Lacey, J. Langer, A. Espinosa, B. Szczupak, C. Wilhelm and L. M. Liz-Marzán, *Nanoscale*, 2017, **9**, 9467–9480.

## Thin films of PNIPAM microgels for biocompatible nuclear track detectors in radiobiology

*Valentina Nigro*<sup>1</sup>, *Elena Buratti*<sup>2</sup>, *Enrico Nichelatti*<sup>3</sup>, *Massimo Piccinini*<sup>1</sup>, *Maria Aurora Vincenti*<sup>1</sup>, *Barbara Ruzicka*<sup>2</sup> and *Rosa Maria Montereali*<sup>1</sup>

<sup>1</sup>*ENEA C.R. Frascati, Fusion and Technologies for Nuclear Safety and Security Department, Frascati, Rome, Italy*

<sup>2</sup>*Institute for Complex Systems, National Research Council (CNR-ISC), Sapienza University of Rome, Rome, Italy*

<sup>3</sup>*ENEA C.R. Casaccia, Fusion and Technologies for Nuclear Safety and Security Department, Rome, Italy*

Presenting author's e-mail: [valentina.nigro@enea.it](mailto:valentina.nigro@enea.it)

Stimuli-responsive thin films have attracted great interest in recent years since they can be employed as smart materials for fabrication of sensors and bio-interfaces or for their integration in technological devices with applications in different fields.

Poly(N-isopropylacrylamide) (PNIPAM) is one of the most used thermo-responsive polymers for biomedical applications thanks to its lower critical solution temperature (LCST around 32°C, close to human body temperature). It is indeed widely used to fabricate temperature-responsive cell culture surfaces, which allow to modulate cell attachment/detachment with temperature [1]. PNIPAM-based microgels provide an even higher degree of control for complex behaviours answering to the growing demand for innovative solutions to couple technological devices with biological systems [2].

In this framework we propose a new generation of Fluorescent Nuclear Track Detectors (FNTD [3]), based on visible emitting colour centres induced by ionising radiation in lithium fluoride (LiF [4]) and functionalized with thin films of PNIPAM microgels for cell culture, for experiments in radiobiology with proton beams. Radiobiological efficacy in hadron therapy requires a good knowledge of the number of incident ions, of their direction and of the energy released within the cancer cells. These innovative detectors will allow to directly correlate the radiation dose locally provided to the cancer cell with their death response.

We have therefore grown by spin-coating thin films of PNIPAM microgels on glass surfaces to investigate the effects of particle size, particle concentration, deposition rate and film thickness on their optical and morphological properties. By combining UV-Vis-NIR spectroscopy, fluorescence and confocal laser scanning microscopy and atomic force microscopy, we have obtained a good control of the thin film properties allowing for their integration on the surface of the LiF-based detectors.

**Keywords:** microgels, thin films, PNIPAM, radiobiology, radiation detectors, cell culture.

**Acknowledgements:** We acknowledge financial support from Regione Lazio, L.R. 13/2008, Progetto BIOTRACK (Fluorescent Nuclear Track Detectors for Radiobiology N.Prot. AO375-2020-36509).

### References

- [1] I. Sanzari, E. Buratti, R. Huang, C. G. Tusan, F. Dinelli, N. D. Evans, T. Prodromakis and M. Bertoldo, *Scientific Reports*, 2020, 10, 6126.
- [2] V. Nigro, R. Angelini, M. Bertoldo, E. Buratti, S. Franco and B. Ruzicka, *Polymers*, 2021, 13, 1353.
- [3] P. Bilski, B. Marczewska, W. Gieszczyk, M. Kłosowski, T. Nowak and M. Naruszewicz, *Radiation Protection Dosimetry*, 2018, 178, 3.
- [4] R.M. Montereali, E. Nichelatti, M. Piccinini, V. Nigro and M.A. Vincenti, *ECS Journal of Solid State Science and Tehnology*, 2021, 10, 116001.

# Pre-programmed rod-shaped microgels to create multi-directional Anisogels for 3D tissue engineering

*Dominik L. Braunmiller*<sup>1</sup>, *Susan Babu*,<sup>2,3</sup> *David B. Gehlen*,<sup>2</sup> *Maximilian Seuß*,<sup>2</sup> *Tamás Haraszti*,<sup>2,3</sup> *Andreas Falkenstein*,<sup>1</sup> *Julian Eigen*,<sup>1</sup> *Laura De Laporte* <sup>2,3</sup> and *Jérôme J. Crassous*<sup>1</sup>

<sup>1</sup> RWTH Aachen University, Institut für Physikalische Chemie, Aachen, Germany

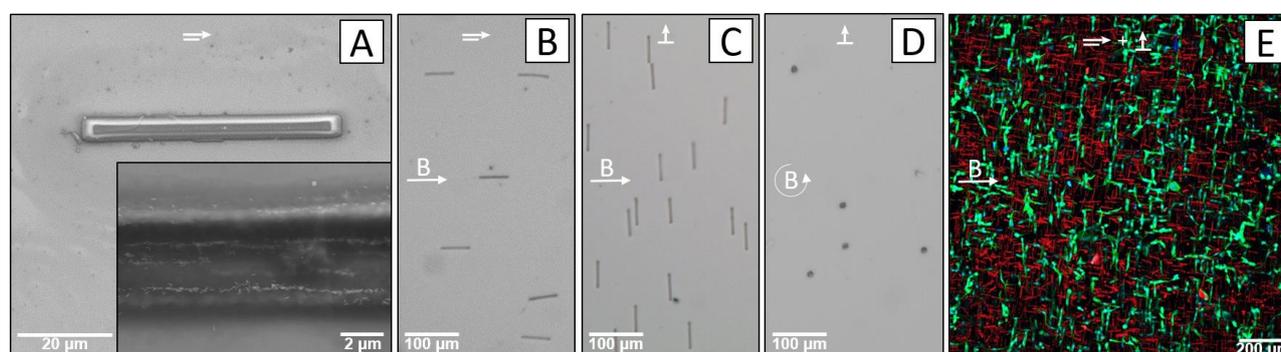
<sup>2</sup> DWI Leibniz-Institut für Interaktive Materialien, Aachen, Germany

<sup>3</sup> RWTH Aachen University, Institut für Technische und Makromolekulare Chemie, Aachen, Germany

Presenting author's e-mail: [braunmiller@pc.rwth-aachen.de](mailto:braunmiller@pc.rwth-aachen.de)

Microscale anisotropic building blocks have been receiving increasing attention in respect to their use as model systems to study complex phase diagrams, dynamics and self-assembly processes and for their biomedical applications. Tissue engineering is one of them, where rod-like magnetic microgels loaded with superparamagnetic iron oxide nanoparticles (SPIONs) were found to direct cell growth when aligned under a homogeneous magnetic field [1]. We are currently aiming at controlling the magnetic orientation and actuation of such microgels using maghemite spindles as anisotropic magnetic fillers instead of SPIONS [2]. Polyethyleneglycol based rod-shaped microgels were produced using particle replication in non-wetting templates (PRINT). The maghemite spindles were pre-aligned and self-assembled into dipolar chains during the microgel synthesis as evidenced by the examination of the resulting composite microgels through scanning electron microscopy (SEM) (Figure 1A). This procedure allows us to pre-program the orientation of the composite microgels parallel or perpendicular to the applied magnetic field as shown in Fig. 1B,C. The actuation of these systems by an external rotating magnetic field further offers the possibility to dynamically align the microgel rods with an orthogonal magnetic moment in the third dimension (Figure 1D). When embedded in Anisogels for cell culture, cell growth can be directed in the orientation of the pre-programmed microgel rods. Depending on the pre-alignment of the nanoparticles inside, different orientations are possible, e.g. parallel and perpendicular (Figure 1E).

**Keywords:** anisotropic magnetic microgels, composite materials, Anisogel, tissue engineering



**Figure 1.** (A) SEM image of incorporated maghemite nanoparticles inside a rod-like microgel. (B,C) Bright field micrographs of the composite microgel alignment parallel and perpendicular to the applied magnetic field. (D) Vertical alignment of the composite microgels with an orthogonal magnetic moment under rotating field (70 mT, 10 rpm). (E) Mouse fibroblast cells (green) growing along parallel and perpendicularly aligned rod-shaped microgels (red).

## References

- [1] J.C. Rose, M. Cámara-Torres, K. Rahimi, J. Köhler; M. Möller; L. De Laporte, *Nano Letters*, 2017, 17, 3782.  
[2] V. Malik, A. Pal, O. Pravaz, J.J. Crassous, S. Granville, B. Grobety, A.M. Hirt, H. Dietsch, P. Schurtenberger, *Nanoscale*, 2017, 9, 14405.

## Nanodispersions as effective vehicles for drug delivery

Aristotelis Xenakis

*Institute of Chemical Biology, National Hellenic Research Foundation  
Athens, Greece*

Presenting author's e-mail: [arisx@eie.gr](mailto:arisx@eie.gr)

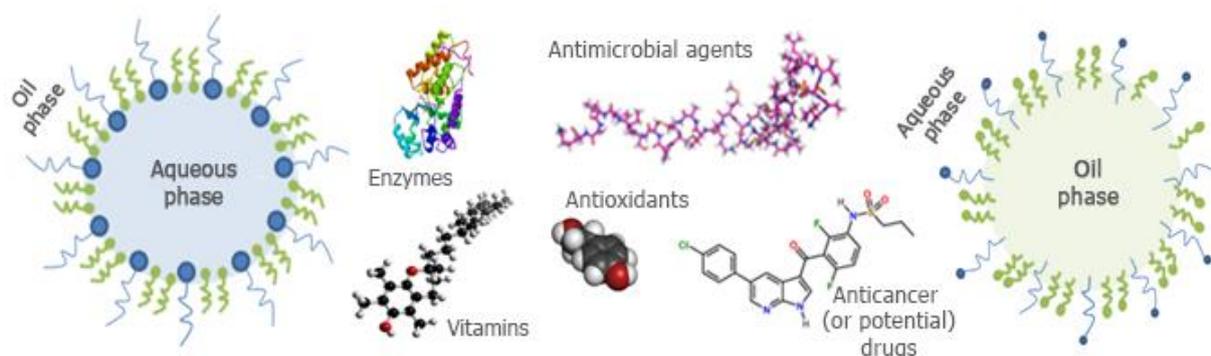
Soft colloidal nanodispersions are used in pharmaceutical applications due to their significant advantages including enhanced drug solubilization, ease of preparation and enhanced absorption.

In the present study various biocompatible W/O and O/W microemulsions and nanoemulsions were developed with the use of "GRAS" ingredients in order to encapsulate, protect and controlled release different bioactives.

The idea is to offer effective means of solubilizing, protecting from the environment and finally carry and release to a specific target of various active substances.

A variety of nanocarriers have been developed with high or low energy techniques, involving biocompatible and biodegradable surfactants, oils of natural origin as well as biopolymers. The nanocarriers are physiochemically characterized with advanced techniques, *in vitro* evaluated via cytotoxicity using specific cell lines and additionally evaluated towards their ability to release the encapsulated bioactive compounds.

**Keywords:** microemulsions; nanoemulsions; bioactives;



**Figure 1.** Soft nanodispersions for encapsulation of bioactives.

### References

- [1] G. Vaz et al. *Pharmaceutics*, (2022) 14, 194
- [2] I. Theochari, et al. *J.Mol.Liquids* (2021) 334, 116021
- [3] E. Mitsou et al. *Colloids and Surfaces B. Biointerfaces*. (2020) 190, 110974

# Nanostructures for X-ray Photodynamic Therapy characterized by direct detection of singlet oxygen during Radiotherapy

*Davide Orsi*<sup>1</sup>, *Marco Vaccari*<sup>1</sup>, *Andrea Baraldi*<sup>1</sup>, *Giovanna Benecchi*<sup>2</sup>, and *Luigi Cristofolini*<sup>1</sup>

<sup>1</sup> *Università di Parma, Dip. di Scienze Matematiche, Fisiche e Informatiche, Parma, Italy*

<sup>2</sup> *Servizio di Radiologia, Azienda Ospedaliera di Parma, Parma, Italy*

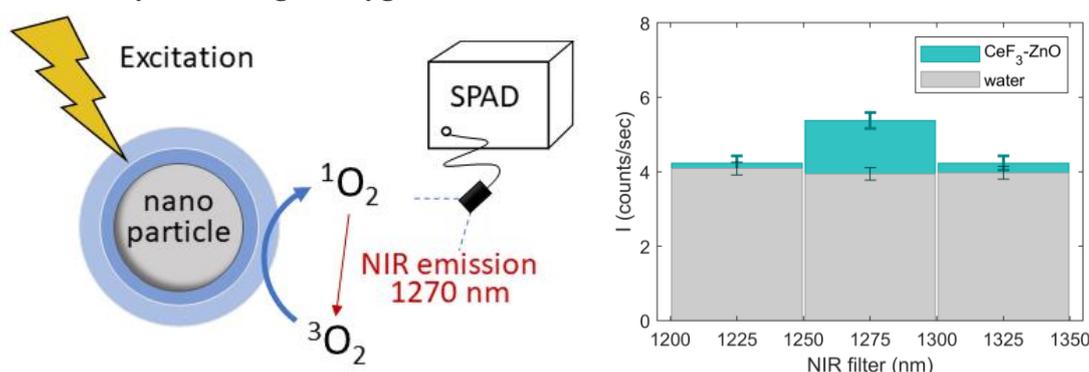
Presenting author e-mail: [davide.orsi@unipr.it](mailto:davide.orsi@unipr.it)

X-ray Photodynamic Therapy (XPDT) is a nanostructure-based approach to extend standard PDT to the treatment of tumors in deep tissues, where NIR or visible light cannot reach. XPDT uses nanostructures capable of generating Reactive Oxygen Species (ROS) and singlet oxygen (<sup>1</sup>O<sub>2</sub>) under Radiotherapy (RT) irradiation [1]. The resulting oxidative stress alters the metabolism of cancer cells, reducing their viability and thus enhancing the efficacy of RT.

A XPDT nanostructure combine scintillating nanostructures and photosensitizers [2,3]. The scintillating part is excited by X-ray photons and by the cascade of secondary particles produced within the tissue; it excites in cascade the photosensitizers, which in turn generate ROS and <sup>1</sup>O<sub>2</sub>. A bottleneck in the characterization of XPDT nanostructures is the reliable detection of generated <sup>1</sup>O<sub>2</sub>.

A possible solution to this problem is provided by direct detection of <sup>1</sup>O<sub>2</sub> by measuring its feeble fluorescence emission at 1270nm. The performances of an XPDT nanostructure combining scintillating CeF<sub>3</sub> and photoactive ZnO [2,4] were measured under irradiation from a 6MV RT accelerator, using a portable NIR fluorimeter based on a modern InGaAs SPAD detector coupled to a custom-made integrating sphere (Fig. 1) [5]. This novel experimental approach determined quantitatively the amount of generated <sup>1</sup>O<sub>2</sub> per unit RT dose and unit nanostructure concentration, paving the way towards tests on cell cultures and animal model.

**Keywords:** X-ray PDT, Singlet Oxygen, Nanomedicine



**Figure 1.** left) Direct detection of singlet oxygen generated by an XPDT nanostructure using NIR fluorimetry. right) <sup>1</sup>O<sub>2</sub> NIR fluorescence signal measured in presence of CeF<sub>3</sub>-ZnO XPDT nanostructures irradiated by 6MeV photons (cyan) compared to pure water (gray).

**Acknowledgements:** This work was supported by the programme “FIL-Quota Incentivante” of University of Parma, co-sponsored by Fondazione Cariparma.

## References

- 1 W. Fan et al., *Adv. Mater.* 31 1 (2019).
- 2 T. Rimoldi et al., *J. Mater. Sci. Mater. Med.* 27 159 (2016).
- 3 F. Rossi et al., *Sci. Rep.* 5 1 (2015).
- 4 D. Orsi et al., *Nanomedicine.* 13 2311 (2018).
- 5 D. Orsi et al., *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* 265 120357 (2022).

# Engineering of pH-triggered nanoplatfoms based on novel poly(2-methyl-2-oxazoline)-*b*-poly[2-(diisopropylamino)ethyl methacrylate] copolymers with tunable morphologies for biomedical applications

Peter Černocho,<sup>1</sup> Alessandro Jager,<sup>1</sup> Zulfiya Černochoová,<sup>1</sup> Vladimír Sincari,<sup>1</sup> Lindomar J.C. Albuquerque,<sup>2</sup> Rafal Konefal,<sup>1</sup> Ewa Pavlova,<sup>1</sup> Fernando C. Giacomelli,<sup>2</sup> Eliezer Jager<sup>1</sup>

<sup>1</sup> Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic

<sup>2</sup> Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Santo André, Brazil

Presenting author's e-mail: [fernando.giacomelli@ufabc.edu.br](mailto:fernando.giacomelli@ufabc.edu.br)

A two-step synthetic approach *via* the combination of living cationic ring-opening (CROP) and reversible addition-fragmentation chain transfer (RAFT) polymerization techniques was used to produce novel amphiphilic block copolymers based on the water-soluble poly(2-methyl-2-oxazoline) (PMeOx), which holds protein repelling properties, linked to the hydrophilic-hydrophobic pH-responsive block poly[2-(diisopropylamino)ethyl methacrylate] (PDPA). Hydrodynamic flow focusing nanoprecipitation microfluidics (MF) was further employed to manufacture block copolymer self-assemblies. Interestingly, although all the synthesized macromolecules contained higher amounts of the pH-responsive segment, the microfluidic approach allowed the manufacturing of core-shell micelles and polymersomes. The morphology seems to be driven by the overall molecular weight of the block copolymers rather than by the hydrophilic-to-hydrophobic weight ratio. Longer and shorter amphiphilic chains enabled respectively the manufacturing of core-shell assemblies and polymeric vesicles. The use of PMeOx and PDPA blocks confers respectively serum stability and pH-responsive behavior to the nanoparticles in a pH window which is particularly useful for tumor detection and therapy. The self-assembled nanostructures are non-toxic even at fairly high polymer concentrations. All these features therefore can be useful in the design of pH-triggered nanoplatfoms of distinct morphologies towards a variety of biomedical applications, for instance, the load and delivery of hydrophobic and hydrophilic therapeutics.[1]

**Keywords:** poly(2-methyl-2-oxazoline), poly((2-diisopropylamino)ethyl methacrylate), pH-responsiveness, microfluidics, polymersomes, micelles.

**Acknowledgements:** The authors gratefully acknowledge Grant Agency of the Czech Republic, GAČR (grant 20-15479J) and FAPESP (grant 2019/06634-8) for financial support. L.J.C.A. acknowledges FAPESP (grants 2016/23844-8 and 2017/11261-0). A. J. and E.J. acknowledge the financial support from the Czech Science Foundation (grant no. #20-13946Y for A. J. and grant no. #20-15077Y for E. J.).

## References

[1] Černocho, P.; Jäger, A.; Černochoová, Z.; Sincari, V.; Albuquerque, L.J.C.; Konefal R.; Pavlova, E.; Giacomelli, F.C.; Jäger E. *Polym. Chem.*, 2021, 12, 2868.

# Nanotherapeutics for cardiac pathologies: from NP development to their biological behaviour comprehension

*Beatrice Lucia Bona*<sup>1</sup>, *Pagiatakis Christina*<sup>2</sup>, *Cindy Cardenas Rincon*<sup>2</sup>, *Prescillia Marie Lagarrigue*<sup>1</sup>, *Roberto Papait*<sup>2</sup>, *Roberto Rusconi*<sup>2</sup>, *Francesco Cellesti*<sup>1</sup>, *Pierangelo Metrangolo*<sup>1</sup> and *Francesca Baldelli Bombelli*<sup>1</sup>

<sup>1</sup>*Departement of Chemistry, Materials and Chemical Engineering “Giulio Natta”, Politecnico di Milano, Milano, Italia*

<sup>2</sup>*IRCCS Humanitas Research Hospital, Rozzano, Italia*

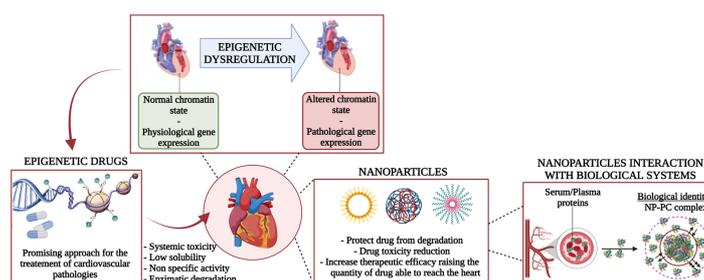
Presenting author's e-mail: [beatrice.lucia.bona@polimi.it](mailto:beatrice.lucia.bona@polimi.it)

Because of the emerging role of epigenetic dysregulation in heart failure, epigenetic drugs have recently been proposed as a promising approach for the cure of cardiovascular diseases [1]. The development of systems able to encapsulate these drugs and specifically deliver them to the site of interest is essential to reduce drugs toxicity and increase their therapeutic efficacy.

At the same time, characterizing nanoparticles (NPs) protein corona (PC) in dependence of the nano-system physicochemical properties and dynamic blood stream environment is essential to understand NP *in vitro* and *in vivo* behaviour [2-3].

Here we aim at developing fluorinated theranostic NPs for the delivery of new epigenetic drugs in the treatment of cardiac pathologies, by exploiting the role of fluorine in <sup>19</sup>F-MRI application and increasing drug encapsulation efficiency [4]. We produced drug loaded fluorinated PCL-PEG NPs, showing promising therapeutic effects *in vitro* on HL-1 cell line (murine cardiomyocytes). Moreover, we developed a method to study NPs behaviour and biological identity, in physiological blood flow conditions, using a microfluidic system. This method allows efficient isolation and characterization of the NP PC, unravelling the role shear stress and confinement display in the NP-protein interaction.

**Keywords:** protein corona, microfluidic, drug delivery



**Figure 1.** Representation of the role of epigenetic in cardiovascular disease, nanoparticles for drug delivery and their interaction with proteins.

**Acknowledgements:** The NewMed project ID: 1175999 (funded by Regione Lombardia POR FESR 2014 2020) is thanked for funding.

## References

- [1] C.Pagiatakis, E. Musolino, R. Gornati, *Aging Clin Exp Res.*, 2021, 33(4), 737-745.
- [2] D. Di Silvio, N. Rigby, B. Bajka, A. Mayes, et al., *Nanoscale*, 2015, 28, 11980–11990.
- [3] M. N. Vu, H. G. Kelly, A. K. Wheatley, *Small*, 2020, 16, 2002861.
- [4] G. Neri, G. Mion, A. Pizzi, *Chem. Eur. J.*, 2020, 26, 10057–10063.

## XMaNs - Universal Lipid Nanoparticles for Nucleic Acid Delivery

*Pavel Švec<sup>1</sup>, Lenka Loukotová<sup>1</sup>, Václav Vaněk<sup>1</sup>, Anastasiia Priss<sup>1</sup>, Audrey Diederichs<sup>1</sup>, Klára Grantz Šašková<sup>1</sup>, Petr Cígler<sup>1</sup>*

*<sup>1</sup>Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic Prague, Czech Republic*

Presenting author's e-mail: [pavel.svec@uochb.cas.cz](mailto:pavel.svec@uochb.cas.cz)

Lipid nanoparticles (LNPs) are currently the most advanced nonviral nucleic acid delivery system and have attracted great interest in the field of vaccine development and gene delivery [1]. LNPs generally consist of: 1 a cationic lipid which is essential for the entrapment of negatively charged nucleic acid; 2 cholesterol which has an impact on membrane fluidity or lipid packing (e.g., 1,2-dioleoyl-sn-glycero-3-phosphoethanolamine); 3 helper lipid which facilitates membrane fusion and thus improves transfection efficacy; and 4 PEGylated lipid which decreases the protein adsorption and protects LNPs from the immune system [2-3].

We have described ionizable adamantane-based lipidoids named XMaNs as an exceptionally universal system for nucleic acid delivery. XMaN6 lipidoid delivers: 1 siRNA into human primary hepatocytes and cell lines that are hard-to-transfect; 2 mRNA into mouse liver; 3 plasmid DNA; and 4 2',3'-cGAMP into cells [4].

Here, we screened a series of proprietary ionizable and biodegradable XMaN lipidoids for mRNA delivery in a mouse model when administered intravenously and evaluated their tolerability, immunogenicity, and protein expression.

**Keywords:** lipid nanoparticles; mRNA; siRNA; nucleic acid delivery

### References

- [1] X. Hou, R. Langer, Y. Dong, *Nat. Rev. Mater.*, 2021, 6, 1078-1094.
- [2] J. A. Kulkarni, D. Witzigmann, J. Leung, Y. Y. C. Tam, P. R. Cullis, *Nanoscale*, 2019, 11, 21733.
- [3] Y. Weng, C. Li, T. Yang, B. Hu, M. Zhang, S. Guo, H. Xiao, X. J. Liang, Y. Huang, *Biotechnol. Adv.*, 2020, 40, 107534.
- [4] Z. Hejdankova, V. Vanek, F. Sedlak, J. Prochazka, A. Diederichs, S. Kereiche, B. Novotna, M. Budesinsky, G. Birkus, K. Grantz Šašková, P. Cígler, *Adv. Funct. Mater.*, 2021, 31, 2101391.

## Unusual gold nanoparticle-antibody interactions

Helena Mateos<sup>1</sup>, Antonia Mallardi<sup>2</sup>, Esther Serrano-Pertierra<sup>3</sup>, Maria Carmen Blanco-López<sup>3</sup>, Margherita Izzi<sup>1</sup>, Nicola Cioffi<sup>1</sup>, and Gerardo Palazzo<sup>1</sup>

<sup>1</sup> Dipartimento di Chimica and CSGI, Università di Bari, Bari, Italy

<sup>2</sup> CNR-IPCF, National Research Council (CNR), Bari, Italy

<sup>3</sup> Dep. de Química Física y Analítica, Universidad de Oviedo, Oviedo, Spain

Presenting author's e-mail: [gerardo.palazzo@uniba.it](mailto:gerardo.palazzo@uniba.it)

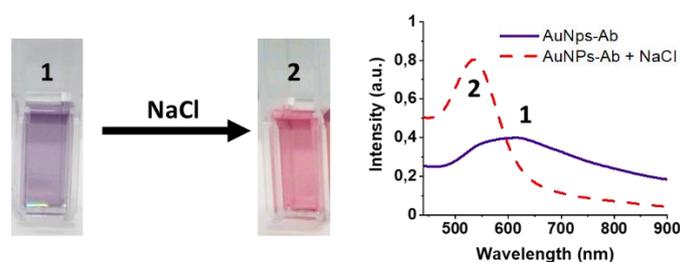
The unique properties of gold nanoparticles (AuNPs) hold great promise for novel diagnostic tools. The correct conjugation of antibodies to nanoparticles is fundamental to many of these techniques. One of the most common routes for antibody-nanoparticle conjugation is based on the spontaneous formation of a protein corona on the AuNPs surface. To check for the correct conjugation, antibody-nanoparticles (Ab-NPs) solutions are loaded with NaCl. If AuNPs coagulation occurs more protein should be added to completely stabilize the system and form a complete protein corona.

Ab-NPs conjugates are actively used for the sensitive detection of extracellular vesicles (EVs) biomarkers. EVs are small membrane vesicles secreted by cells and their variation in type and quantity in body fluids can be used for the early diagnose and treatment of various pathologies. In the case of neurodegenerative diseases, the quantification of EVs of neural origin present in the blood provides a minimally invasive way to probe the health of brain tissue. With this purpose, neural cell adhesion molecule L1 (L1CAM) has been proposed as suitable marker of neural EVs.

Accordingly, we have embarked on the bioconjugation of AuNPs with anti-L1CAM antibodies to obtain low-cost lateral flow immunoassay (LFIA) for neural EVs. Strikingly, the outcome of the bioconjugation was other than expected since high enough concentrations of antibody provoke the formation of large AuNP aggregates, which resuspend in the form of monomeric or dimeric AuNPs after the addition of high NaCl concentrations. This is confirmed by the change in color from blue to pink (see figure). We have investigated in detail the phenomenon using a combination of UV-vis absorption, dynamic light scattering, colloidal stability analysis and transmission electron microscopy techniques.

The formation of bioconjugates containing two AuNPs increases the sensitivity of a LFIA test and therefore can be potentially exploited to improve the assay

**Keywords:** Immunoassay, colloidal stability, protein corona, DLS, TEM, zeta-potential



**Figure 1.** Effect of the addition of NaCl to a mixture of AuNPs-antiL1CAM..

**Acknowledgements:** POR PUGLIA FESR-FSE 2014/2020 Research for Innovation (REFIN)-Codice Pratica: 7BDC8679 is acknowledged for financial support.

# Depletion interaction mediated micronization of proteins

Jiankang Song<sup>1</sup> and Remco Tuinier<sup>1</sup>

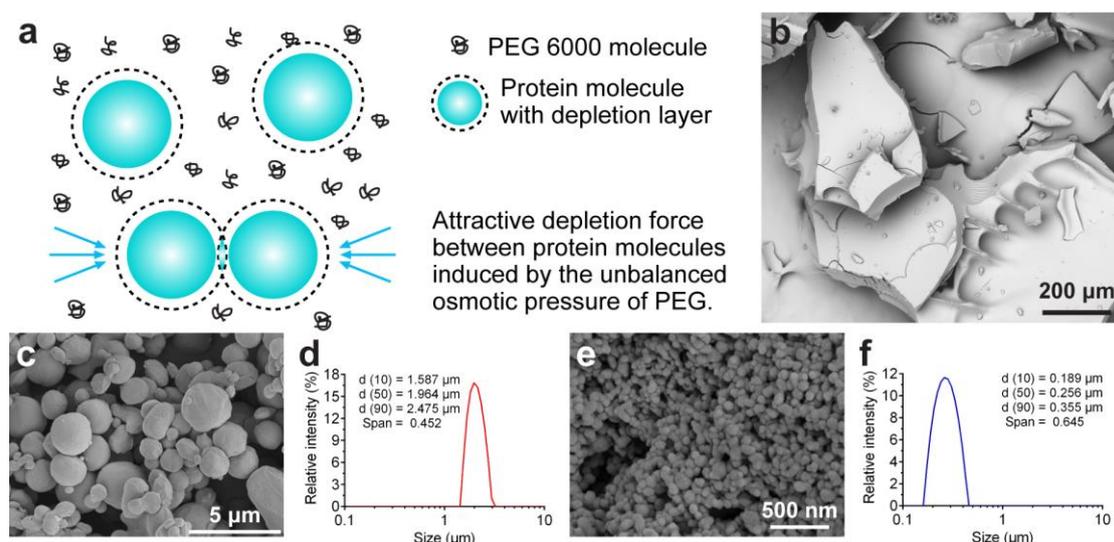
<sup>1</sup> Laboratory of Physical Chemistry, Department of Chemical Engineering and Chemistry & Institute for Complex Molecular Systems, Eindhoven University of Technology, Eindhoven, Netherlands

Presenting author's e-mail: [j.song@tue.nl](mailto:j.song@tue.nl)

Biopharmaceutical drugs including recombinant therapeutic proteins have transformed the pharmaceutical industry with a growing contribution to modern health science. These therapeutic proteins have high specificity and potency compared to small molecular drugs [1]. However, frequent administrations are required to achieve therapeutic effects due to the short *in vivo* half-lives of proteins, which results into patient inconvenience and poor compliance [2]. Therefore, long-acting delivery systems including polymeric microparticles and implantable devices need to be developed. To improve proteins' conformational stability, loading efficiency and dispersion inside a polymeric matrix, controlled micronization of protein drugs is required. Here we report a method to prepare such protein microstructures using depletion forces.

Globular bovine serum albumin (BSA, horseradish peroxidase (HRP) and lysozyme were used as model proteins to make microstructures. A benign method by co-lyophilization of these proteins with poly(ethylene glycol) (PEG) was used to achieve the protein micronization. This micronization process is based on the depletion of PEG6000 polymers near the surfaces of the globular proteins (Figure 1a. Concentration initiated by freezing water induces phase separation, followed by the arrest of the demixing system. The size of the micronized proteins is related to the dominant length scales during demixing and can be fine-tuned by adjusting the freezing temperature of the protein-PEG6000 solutions (Figure 1, c-f. This method is suitable for model proteins with various molar masses and different protein surface charges.

**Keywords:** protein micronization, depletion interaction, drug delivery



**Figure 1.** Schematic illustration of depletion interactions (a); Scanning electron micrograph of pristine bovine serum albumin (BSA) material (b); Scanning electron micrograph (c and e) and the size and size distribution (d and f) of micronized BSA with PEG-BSA solution frozen at -20 °C (c and d) and with liquid nitrogen (e and f), respectively.

**Acknowledgements:** The authors acknowledge the financial support of DSM Biomedical.

## References

- [1] S. Mitragotri, P.A. Burke and R. Langer, *Nature Reviews Drug Discovery*, 2014, 13, 655-672.
- [2] Y. Zheng and J.K. Pokorski, *WIREs Nanomedicine and Nanobiotechnology*, 2021, 13, e1712.

## A novel approach for the determination of number concentration of liposomes by Laser Transmission Spectroscopy.

*Simona Sennato<sup>1,2</sup>, Angelo Sarra<sup>1,3</sup>, Cecilia Bombelli<sup>4</sup>, Enrica Donati<sup>4</sup>, Paolo Postorino<sup>2</sup> and Federico Bordi<sup>1,2</sup>*

<sup>1</sup>*Institute for Complex Systems ISC-CNR c/o Sapienza University of Rome, Italy.*

<sup>2</sup>*Physics Department, Sapienza University of Rome, Italy*

<sup>3</sup>*Microscopy Centre, University of L'Aquila, L'Aquila (Aq Italy (present affiliation*

<sup>4</sup>*Institute for Biological Systems ISB-CNR, Rome, Italy.*

Presenting author's e-mail: [simona.sennato@cnr.it](mailto:simona.sennato@cnr.it)

Size and absolute number of liposomal nanocarriers are crucial determinants for their physiological behavior and of paramount importance for quality assurance. Currently there are no validated experimental methods for determining the particle number-concentration of formulations, since theoretical calculation methods rely on several assumptions and other empirical counting methods suffer of different limitations.

To overcome these limitations, we are developing a Laser Transmission Spectroscopy (LTS) apparatus [1] that allows to determine the size distribution of the particles in a colloidal suspensions in terms of their absolute concentration. I will show how LTS can be used as a unique and powerful tool for studying liposomes suspensions where the true number of particles is relevant for drug delivery [2]. SoyPC:Cholesterol liposomes are used as test to validate data analysis by comparison with HPLC determination of lipid mass and to define the LTS sensitivity and detection range for vesicles. Then novel lipid formulations based on mixtures of zwitterionic HSPC and anionic DPPG lipids, loading the antitubercular drug isoniazid, have been studied by a new approach which has never been used for the investigation of a nanocarrier. For the first time in this ambit, LTS have been used to determine the liposome geometrical size and their number concentration, that allows evaluating the real volumetric drug entrapment capability of the nanocarrier, to be compared with the drug encapsulated in the vesicles, determined by UV spectroscopy [2].

I will highlight the importance of considering unilamellar liposomes as a suspension of colloids, whose geometrical size and volume fraction impact their efficacy as nanocarriers. The proposed method is conceptually simple, since it relies on Mie scattering theory and hence simply on the a-priori knowledge of the carrier form factor, and it can be extended to colloids with different shape and structure or nature, as to biogenic vesicles (exosomes).

**Keywords:** number concentration, liposomes, Laser Transmission Spectroscopy

**Acknowledgements:** Research project on antitubercular liposomal carriers was funded by Phospholipid Research Center (Grant no. FBO-2017-051/1-1).

### References

- [1] Sarra, Angelo, et al. "IEEE Transactions on Biomedical Circuits and Systems 2021, 15, 177  
[2] Sciolla, F., Truzzolillo, D, ... Sarra, A ...and Sennato, S. Coll Surf B, 2021, 208, 112054

# Factors Determining the Interactions of Drugs Used to Treat Chronic Obstructive Pulmonary Disease with Model Lung Surfactants.

*Dorota Matyszewska<sup>1</sup>, Philippe Fontaine<sup>2</sup>*

<sup>1</sup>*Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Warsaw, Poland*

<sup>2</sup>*Synchrotron Soleil, L'Orme des Merisiers, Saint Aubin, France*

Presenting author's e-mail: [dorota.matyszewska@chem.uw.edu.pl](mailto:dorota.matyszewska@chem.uw.edu.pl)

Langmuir technique allows one to form phospholipid monolayers at the air-water interface, which can be used as simple models of cell membranes to investigate the interactions of drugs and other biologically important species. We have recently employed this methodology to systematically study the effect of anthracyclines on simple models of healthy and cancer cell membranes and shown that apart from electrostatic interactions between the drug and polar head of the lipid, the lipophilicity of anthracyclines is the most important factor [1-4]. This feature was also determining the interactions between the model lipid rafts and statins, cholesterol-lowering drugs [5].

We have also investigated the effect of statins on the model pulmonary surfactants, since these drugs may be potentially employed in the treatment of chronic obstructive pulmonary disease (COPD). The increasing lipophilicity of selected statins such as e.g. rosuvastatin and simvastatin allows for a more efficient penetration of DPPC and DPPG monolayers, which constitute the main components of pulmonary surfactant [6]. On the contrary, in the case of anticholinergic drugs (e.g. ipratropium bromide) traditionally used for the treatment of COPD, the electrostatic interactions between positively charged drug and negatively charged DPPG played the most important role. The increasing fluidity of the monolayer composed of DOPG reflecting the changes taking place in the pulmonary surfactant composition of COPD patients increased the interactions with anticholinergic drugs. The possibility of effective drug penetration of model pulmonary surfactant was also verified by multiple compression-expansion cycles, which mimic the breathing mechanism. The changes in the membrane morphology, imposed by the incorporation of statins and anticholinergic drugs were also followed by Brewster angle microscopy, which proved the fluidization of the model lung surfactant layers. Grazing incidence X-ray diffraction (GIXD) studies demonstrated the differences in the 2D organization of monolayers of pulmonary surfactant components upon contact with the drugs.

**Keywords:** model membranes, Langmuir technique, lung surfactant, antivirals, pulmonary diseases

**Acknowledgements:** This work was partially financially supported by the "Excellence Initiative – Research University (2020-2026)" (New Ideas in Priority Research Area I).

## References

- [1] D. Matyszewska, BBA Biomembranes, 2020, 1862, 183104.
- [2] D. Matyszewska, A. Jocek, J. Molec. Liquids, 2021, 323, 114633
- [3] D. Matyszewska, E. Nazaruk, R.A. Campbell, J. Colloid Interf. Sci. 2021, 581, 403–416.
- [4]. M. Zaborowska, D. Dziubak, P. Fontaine, D. Matyszewska, Colloids and Surfaces B, 211 (2022) 112297
- [5] M. Zaborowska, D. Dziubak, D. Matyszewska, R. Bilewicz, Electrochimica Acta 2021, 386, 138514.
- [6] Ch. Autilio, J. Perez-Gil, Arch Dis Child Fetal Neonatal Ed., 2019, 104, 443–451.

## Polymeric-based nanocarriers for the treatment of the central nervous system disorders

*Marta Szczęch<sup>1</sup>, Magdalena Prochner<sup>2</sup>, Monika Leśkiewicz<sup>2</sup>, Natalia Łopuszyńska<sup>3</sup>, Krzysztof Jasiński<sup>3</sup>, Władysław P. Węglarz<sup>3</sup>, Władysław Lasoń<sup>2</sup>, Piotr Warszyński<sup>1</sup>, and Krzysztof Szczepanowicz<sup>1</sup>*

<sup>1</sup>*Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland*

<sup>2</sup>*Maj Institute of Pharmacology, Polish Academy of Sciences, Krakow, Poland*

<sup>3</sup>*Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Krakow, Poland*

Presenting author's e-mail: [marta.szczech@ikifp.edu.pl](mailto:marta.szczech@ikifp.edu.pl)

Neurodegenerative disorders are among the most lethal diseases of our civilization. Nowadays, the issue is even superior due to the soaring mortality rates correlated with concerns of a rapidly aging of our population. Therefore, modern medicine faces a significant challenge in finding efficient treatment for such diseases as Alzheimer's and Parkinson's, multiple sclerosis, or stroke-related brain damage.

One of the critical limitations in treating such complex conditions is an inefficient delivery of neuroprotective substances through the blood-brain barrier (BBB). Most promising neuroprotectants are poorly water-soluble or even in-soluble substances, which make them challenging to deliver. Their poor bioavailability in biological fluids, toxicity, low therapeutic concentration, non-targeted delivery, and undesirable side effects result in the low therapeutic effectiveness of neurodegenerative disorders treatment. Therefore, novel and effective drug delivery systems to the central nervous system (CNS) are strongly desired.

Herein, we present a novel methodology for preparing multifunctional nanocarriers of neuroprotective substances based on polymeric nanoparticles (PNPs), dedicated to the CNS therapies. The neuroprotectants-loaded PNPs were prepared from nanoemulsion template methods, i.e., the spontaneous emulsification solvent evaporation method [1]. The PNPs were composed of poly(caprolactone) (PCL) with the encapsulated active neuroprotective agents (Edaravone, Ebselen, or Carnosic acid). Such drug-containing PNPs were further modified/functionalized for theranostics using the layer-by-layer approach by creating multifunctional polyelectrolytes shells composed of poly-L-glutamic acid (PGA) and poly L-lysine (PLL) or Gadolinium-labeled poly L-lysine (PLL-Gd), and PEGylated-PGA. Such prepared core@shell structures were characterized by size, size distribution, zeta potential, and imaged by MRI. Biocompatibility and neuroprotective action of received drug-loaded PNPs were evaluated using cell viability and toxicity assays in the SH-SY5Y human neuroblastoma cell line.

**Keywords:** polymeric nanoparticles, neuroprotectants, drug delivery systems, layer-by-layer, central nervous system disorders

**Acknowledgements:** The research leading to these results was supported by the Polish National Science Centre, grant GRIEG 2019/3/4/H/ST5/00578

### References

[1] M. Szczęch and K. Szczepanowicz, *Nanomaterials* 2020, Vol. 10, Page 496, vol. 10, no. 3, p. 496

## Small angle X-ray scattering (SAXS) to explore blood proteins interactions with polymers

*Merzougui Charaf Eddine<sup>1</sup>, Pierre Roblin<sup>1</sup>, Pierre Aimar<sup>1</sup>, Christel Causserand<sup>1</sup> and Patrice Bacchin<sup>1</sup>*

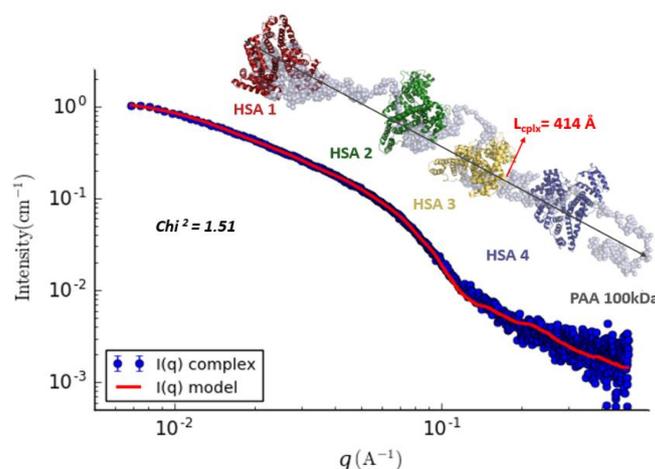
<sup>1</sup> *Laboratoire de Génie Chimique, Université de Toulouse, CNRS, UPS, Toulouse, France*

Presenting author's e-mail: [charafmerzougui@gmail.com](mailto:charafmerzougui@gmail.com)

Proteins interaction with polymeric materials are key phenomena to understand and control responses of body fluids and tissues towards medical devices. In some cases, these interactions can be unwanted for example to avoid plasmatic coagulation due to thrombocytes adhesion and activation. In other instances, they could be wanted to enhance a specific affinity for example to catch and activate platelets in order to extract PDGF proteins (Platelets Derived Growth Factors) using membranes. For this purpose, the surface chemical properties of membranes are often modified by coating or grafting functional groups such as polyacrylic acid (PAA) to create a specific affinity with some proteins at the interface. It is then important to appraise the interactions between PAA and blood components as such human serum albumin (HSA). For a PAA1.8kDa, previous studies report the formation of 1HSA-1PAA complexes using Isothermal titration calorimetry (ITC).

In the present work, we study interactions between HSA and larger PAA (100kDa) for various physicochemical conditions using Small Angle X-ray Scattering (SAXS) combined to chromatography. The SAXS spectra analysis reveals the adsorption of HSA molecules on PAA chains. The investigation of ionic strength-pH combined effect shows that HSA-PAA binding takes place only at pH 5 and low ionic strength (0.15M). Otherwise, for higher pH and salts concentration (0.75M) the HSA-PAA complex tends to dissociate completely showing the reversibility of the complexation [1]. The assessment of HSA/PAA molar ratio influence on the complex size (radius of gyration and Porod volume) evinces that 4 HSA molecules would bind to each PAA100kDa chain. This stoichiometry is supported by an all atom SAXS model calculated using BUNCH program and found to fit well the complex scattering data [1]. This model allows to portray the complex as a pearl-necklace assembly with 4 HSA on the 100 kDa PAA chain.

**Keywords:** HSA, PAA, interaction, Complexation, SAXS



**Figure 1.** Superimposition of SAXS scattering data (dotted thick blue circle) of the HSA-PAA complex and those of the all atom compatible model calculated with the program Bunch (red line).

### References

[1] C. Merzougui, P. Roblin, P. Aimar, A. Venault, Y. Chang, C. Causserand, P. Bacchin. *Soft Matter*, 2020, 16, 9964–9974.

## Synergistic Therapy of Breast Cancer by NIR-Responsive Nanostructured Lipid Carriers Containing Gold Nanorods

*Nihal Aydoğan<sup>1</sup>, Cigdemnaz Ersoz<sup>1</sup>, Gokce Dicle Kalaycioglu<sup>1</sup>, Ayse Kevser Ozden<sup>2</sup>*

*<sup>1</sup>Hacettepe University, Chemical Engineering Department, Ankara, Turkey*

*<sup>2</sup>Lokman Hekim University, Faculty of Medicine, Ankara, Turkey*

*Presenting author's e-mail: [anihal@hacettepe.edu.tr](mailto:anihal@hacettepe.edu.tr)*

Despite various technical advances in cancer treatment, chemotherapy is still a good option, but it is more promising when combined with photothermal therapy for resistant breast cancer cells [1]. Therefore, this study presents the smart-drug-delivery system, designed for dual chemo/photothermal therapy. Type-III nanostructured lipid carriers (NLCs) used as drug delivery systems were preferred because of their advantages, such as high drug loading capacity, high stability, and biocompatibility. Doxorubicin (DOX) was used as a chemotherapeutic agent as in the form of ion-pair with oleic acid which was also the liquid lipid used in the formation of NLCs. Verapamil (VERA, that is a chemosensitizer as well as an agent can help to overcome the multiple drug resistance developed during the chemotherapy, was used as a second drug. In vitro release studies reveals that only 20% of the DOX-OA and 50% of the VERA were released within first two hours. Only 38% of DOX-OA can be released within 48 h. Gold nanorods (AuNRs, used as a photothermal therapy agent, were also encapsulated into the NLCs (25-165 µg/ml NLC dispersion. Atomic force microscopy (AFM and TEM results reveal that the size of these smart systems loaded with dual drugs and inorganic nanoparticles as ~320 nm. DOX-OA and VERA releases were examined in vitro by triggering the release of the drug with NIR (808 nm laser irradiation. Thus, a state-of-art drug delivery system was designed to release active pharmaceutical ingredients (APIs) at higher concentrations in the desired region and provided both chemo/photothermal therapy. The resultant effects were investigated using the MDA-MB-231 cell line. In the light of these results, it is thought that this functionalized, smart, and state-of-art drug delivery system will have a vital role in the synergistic treatment of breast cancer where chemotherapy and photothermal therapy are simultaneously applied.

**Keywords:** Nanostructured lipid carriers, synergistic therapy, doxorubicin, verapamil, breast cancer, photothermal therapy

### References

[1] R. Agabeigi, S. H. Rasta, M. Rahmati-Yamchi, R. Salehi and E. Alizadeh, *Nanoscale Res. Lett.*, 2020, 15, 62.

**Thursday 8th September 2022**

**Composite Materials and Nanostructures**

# Thermal transport in self-assembled materials: From high anisotropy to high temperatures

Markus Retsch<sup>1</sup>

<sup>1</sup>Physical Chemistry I, Department of Chemistry, University of Bayreuth,  
Bayreuth, Germany

Presenting author's e-mail: markus.retsche@uni-bayreuth.de

Thermal transport can be significantly influenced by the presence of nano- and mesostructures and the interfaces that exist in such materials. This structuring can be employed to realize super-insulation properties as well as efficient heat spreading. Consequently, nanoscale thermal transport has attracted a lot of research interest for the past 20 years.[1]

Colloidal materials represent an ideal platform to access well-defined devices structured on hierarchical length scales. Colloidal superstructures, which can be amorphous or crystalline, cover size ranges from a few nanometers up to micrometers and beyond. Additionally, one can quickly implement different kinds of materials and fabricate heterostructured composites and hybrid materials.

In this contribution, I will focus on two extreme cases of thermal transport derived from colloiddally self-assembled materials. The first example will cover extremely anisotropic thermal conductors based on 1D crystalline Bragg stacks.[2] Spray-coating of nematic dispersions of 1 nm thick clay dispersions with a distinct amount of water-soluble polymers leads to strictly hard-soft alternating layers. The ratio between in-plane and cross-plane thermal conductivity reaches up to 38 in such fully dielectric materials.[3] Based on a complete mechanical tensor analysis, we can also assess the influence of the nanostructure on the phonon mean free path in such systems.

The second example comprises an isotropic, thermally insulating material based on colloidal ensembles of hollow silica nanoparticles. The combination of low density, disorder, and interparticle constriction results in ultralow thermal conductivities at room temperature.[4] When using such particle packings at high temperatures, the thermal insulation is compromised by an increasing amount of thermal radiation. Laser flash analysis allowed us to directly measure the temperature-dependent transition from purely conducting to radiative transport mechanisms. Combined with a detailed optical and theoretical characterization of the colloidal assembly structures, we work out the relevance of their mid-infrared optical properties.[5]

**Keywords:** nanoscale thermal transport; colloidal superstructures; anisotropy; radiative transport

**Acknowledgements:** The cooperation with Prof. Breu, Prof. Fytas, Prof. Ikkala, and PD Dr. Biehs on the diverse projects presented here is highly appreciated.

## References

- [1] Cahill, D. G.; Braun, P. V.; Chen, G.; Clarke, D. R.; Fan, S.; Goodson, K. E.; Keblinski, P.; King, W. P.; Mahan, G. D.; Majumdar, A.; Maris, H. J.; Phillpot, S. R.; Pop, E.; Shi, L., *Appl. Phys. Rev.* 2014, 1 (1), 011305.
- [2] Dörres, T.; Bartkiewicz, M.; Herrmann, K.; Schöttle, M.; Wagner, D.; Wang, Z.; Ikkala, O.; Retsch, M.; Fytas, G.; Breu, J., *ACS Appl. Nano Mater.* 2022, 5 (3), 4119-4129.
- [3] Wang, Z.; Rolle, K.; Schilling, T.; Hummel, P.; Philipp, A.; Kopera, B. A. F.; Lechner, A. M.; Retsch, M.; Breu, J.; Fytas, G., *Angew. Chem. Int. Ed.* 2020, 59 (3), 1286-1294.
- [4] Ruckdeschel, P.; Philipp, A.; Retsch, M., *Adv. Funct. Mater.* 2017, 27 (38), 1702256.
- [5] Neuhöfer, A. M.; Herrmann, K.; Lebeda, F.; Lauster, T.; Kathmann, C.; Biehs, S.-A.; Retsch, M., *Adv. Funct. Mater.* 2021, 32, 2108370

# Bio-Inspired Phenolic Polymers in Composite Materials: From the Nanostructure to the Multifunctionality

*Gerardino D'Errico*<sup>1,2</sup>

<sup>1</sup>Department of Chemical Sciences, University of Naples Federico II, Naples, Italy

<sup>2</sup>CSGI, Unit of Naples, Italy

Presenting author's e-mail: [gerardino.derrico@unina.it](mailto:gerardino.derrico@unina.it)

With their distinctive carbogenic diversity and the tunable redox behaviour, natural polyphenolic polymers (*e.g.*, melanins, lignins, tannins) provide a unique reservoir of versatile, bioaccessible, biocompatible and biodegradable compounds endowed with a plethora of functions, including a striking antioxidant and radical scavenging activity and ion chelating ability [1]. In addition, bio-inspired phenolic polymers can be purposely designed and synthesized from selected polyphenol monomers which can be obtained from natural sources (*e.g.*, by-products of food processing) thus constituting an outstanding example of industrial waste valorization [2].

The practical exploitation of these substances requires a solid background of experimental observations and a reliable conceptual framework of structure–property–activity relationships [3].

In this contribution we investigate the electronic structure, mesoscopic organization and antioxidant activity of various polyphenolic polymers biocatalytically produced from natural monomers or extracted from agri-food byproducts. In all cases a black/dark brown and insoluble pigment is obtained, presenting broad-band UV/Vis absorption and a distinct electron paramagnetic resonance (EPR) signal, due to free radicals associated with non-localized  $\pi$  system, stabilized by resonance in the polyaromatic centers. A further stabilizing contribution arises from stacking, indicating that polyphenolic biopolymers properties critically depend on their supramolecular structure and interaction with other (macro)molecules, and can be optimized by the rational design of the chemical formulations in which they are included.

In this direction, we demonstrate that polyphenolic polymers are effective multifunctional components of: i.) polymer blends with synthetic as well as natural polymers, including proteins and polysaccharides; ii.) lipid/surfactant nanostructures formed by surfactants and lipids for delivery purposes.

**Keywords:** polyphenols, antioxidants, functional materials, drug delivery, electron paramagnetic resonance, nanostructure

## References

- [1] F. Moccia, G. D'Errico, et al. *Antioxidants*, 2020, 9, 438.
- [2] L. Panzella, G. D'Errico, et al. *Chem. Commun.*, 2018, 54, 9426.
- [3] M.L. Alfieri, G. D'Errico, et al. *J. Colloid Interface Sci.*, 2022, 606, 1779.

# Preparation of structured biomimetic composite materials through magnetic control of sol-gel phase transitions

*Marco Lattuada<sup>1</sup>, and Joelle Medinger<sup>1</sup>*

<sup>1</sup>*University of Fribourg, Department of Chemistry, Fribourg, Switzerland*

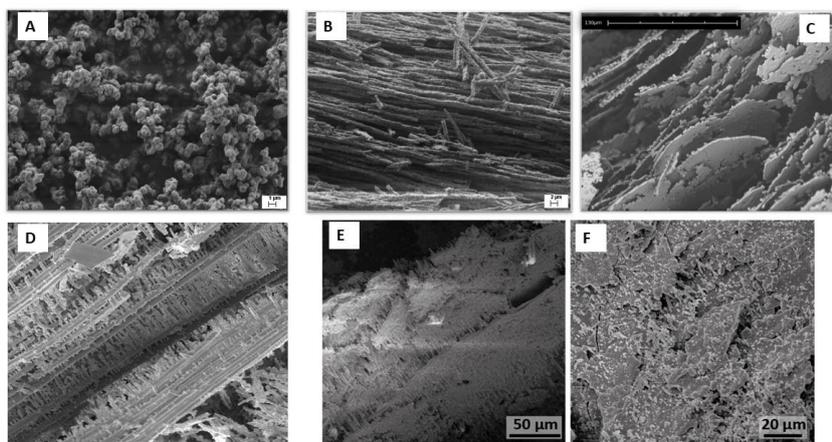
Presenting author's e-mail: [marco.lattuada@unifr.ch](mailto:marco.lattuada@unifr.ch)

Nanocomposites are an important class of materials, with unique properties resulting from the unique combination of the matrix and the dispersed phase. Here we present a new strategy for the preparation of bioinspired composite materials, by using magnetic colloids to control the structure of a silica gel phase by magnetically manipulate the sol-gel phase transition. The gel phase has then be used as a skeleton for the preparation of a polymer-inorganic hybrid material. Magnetic colloids were added to the silica sol precursor solution, and a magnetic field was applied during the sol-gel transition.

A static field led to a fiber-like structure, with silica fibers aligned in the direction of a field. Conversely, when exposed to a rotating magnetic field, magnetic colloids organized in layers parallel to the plane of rotation of the field and template the growing silica phase, resulting in a layered anisotropic silica, reminiscent of the inorganic structure of nacre. The final nanocomposite materials have been created by filling the porous structure with a monomer, leading to an elastomer upon polymerization. Compression tests of the structured composite show that their mechanical properties far exceed those of non-structured composite materials with an identical chemical composition.

Furthermore, more complex silica structures have been obtained by first creating a structured silica gel, and then impregnating it with a second sol solution containing magnetic colloids, and applying a magnetic field in a different direction. In this case, silica gels with a fiber structure connected by perpendicular rods connecting them, or layered silica gels with rods perpendicular to the layer and connecting them were obtained, eventually leading to even stronger composite materials, with defined anisotropy and with a complex architecture could be prepared. Some of these architecture are shown in the Figure below.

**Keywords:** Magnetic colloids, Composite materials, Sol-gel phase transition, Bioinspired materials, magnetically-induced self-assembly



SEM images of the microstructure of various silica gels A)no magnetic field applied; B) Static magnetic field applied; C) rotating magnetic field applied; D) Double sol-gel with magnetic field applied in two orthogonal directions; E) und; F) Double sol-gel with first a rotating magnetic field and then a static orthogonal field applied

## References

[1] J. Medinger, M. Nedyalkova, M. Furlan, T. Lüthi, J. Hofmann, A. Neels, M. Lattuada, *ACS Applied Materials & Interfaces*, **13**, 8040-48052 (2021)

# Conformations and Dynamics of Polymer Chains in Cis and Trans Polybutadiene/Silica Nanocomposites through Atomistic Simulations

*Anastassia Rissanou<sup>1,2,3</sup>, Alireza F. Behbahani<sup>1</sup>, and Vagelis Harmandaris<sup>1,2,3</sup>*

<sup>1</sup>*Institute of Applied and Computational Mathematics, Foundation for Research and Technology Hellas, Heraklion, Greece*

<sup>2</sup>*Department of Mathematics and Applied Mathematics, University of Crete, Heraklion, Greece*

<sup>3</sup>*Computation-Based Science and Technology Research Center, The Cyprus Institute, Nicosia, Cyprus*

Presenting author's e-mail: [rissanou@iesl.forth.gr](mailto:rissanou@iesl.forth.gr)

The conformations and the dynamics of poly-(butadiene) chains, of various molecular weights, in PB/silica nanocomposites are studied through long-time atomistic molecular dynamics simulations at  $T = 413$  K, well above  $T_g$ . The effect of the stereochemistry of PB chains is addressed by simulation of cis-1,4-PB/silica and trans-1,4-PB/silica nanocomposites. The model systems contain 30wt % silica nanoparticles of diameter  $\approx 4$  nm. The nanocomposites are characterized through analyzing (i) interfacial packing and the dimensions of the PB chains; (ii) statistics of the train, bridge, loop, and tail conformations of adsorbed chains and the coupling between segmental orientational dynamics and chain conformations; and (iii) the orientational and translational dynamics of the polymer chains and the desorption kinetics of chains and segments. The dimensions of PB chains, excluding a small fraction of chains that wrap around the NP, are not affected. The segmental and terminal dynamics of PB chains are slower in the nanocomposites than in the respective bulk melts. Moreover, the dynamics of PB chains in the nanocomposites is very heterogeneous and a coupling between the dynamics and the conformation of PB chains is observed: the adsorbed segments (trains) and the chains that have a higher number of contacts to the NPs are more decelerated. The self-diffusion coefficients,  $D$ , of PB chains in the nanocomposites are also reduced compared to the respective bulk systems. A clear crossover from the unentangled (Rouse-like) to the entangled (reptation-like) regime is observed based on the calculation of the segmental mean-square displacement and  $D$  as a function of the chain length. The deceleration of dynamics in the nanocomposites, in both Rouse and reptation-like regimes, is discussed in terms of a higher effective monomeric friction coefficient. Finally, the correlation times for the desorption of segments and chains are much larger than the segmental and end-to-end-vector correlation times, respectively.

**Keywords:** polymer nanocomposites; Atomistic Molecular Simulations

**Acknowledgements:** The work was supported by computational time granted from the Greek Research & Technology Network (GRNET) in the National HPC facility--ARIS under project named POLCOMP-TIRE. This work is supported by the Goodyear Tire and Rubber Company.

## References

- [1] A. F. Behbahani, A. Rissanou, G. Kritikos, M. Doxastakis, C. Burkhart, P. Polinska, V. Harmandaris, *Macromolecules*, 2020, 53, 6173
- [2] G. Maurel, F. Goujon, B. Schnell, P. Malfreyt, *J. Phys. Chem. C*, 2015, 119, 4817.

## **Dispersion mechanism of organogly in a polymer nanocomposite studied by in-extruder rheo-optical characterization**

*Loïc Hilliou, Paulo F. Teixeira and José A. Covas*

*Institute for Polymers and Composites, University of Minho, Guimarães, Portugal*

Presenting author's e-mail: [loic@dep.uminho.pt](mailto:loic@dep.uminho.pt)

The dispersion mechanisms in a clay-based polymer nanocomposite (CPNC) during twin screw extrusion are studied by in-situ rheo-optical techniques [1]. The pertinence of such experimental set-up for the study of structure-rheological properties relationships in polymer nanocomposites will first be introduced. Results from clay dispersion in a polydimethylsiloxane (PDMS) matrix obtained with the in-line rheo-optical extrusion set-up are then presented. Local heating in the first part of the extruder allows testing the concepts proposed for clay dispersion mechanism in polymer matrices [2]. The comparison of clay particle sizes measured in line with models for the kinetics of particle dispersion indicates that larger stresses promote the break-up of clay particles, whereas smaller stresses favor the erosion of the clay tactoids. Thus, different levels of clay dispersion are generated, which do not simply relate to a progressively better PDMS intercalation and higher clay exfoliation as stress is increased. Reducing the PDMS viscosity in the first mixing zone of the extruder facilitates dispersion at lower screw speeds, but a complex interplay between stresses and residence times at larger screw speeds is observed. More importantly, the results underline that the use of larger stresses is inefficient per se in dispersing clay if sufficient time is not given for PDMS to intercalate the clay galleries and thus facilitate tactoid disruption or erosion

### **References:**

- [1] Teixeira, P.F.; Covas, J.A.; Hilliou, L. In-Line Rheo-Optical Investigation of the Dispersion of Organoclay in a Polymer Matrix during Twin-Screw Compounding. *Polymers* 2021, 13, 2128. <https://doi.org/10.3390/polym13132128>.
- [2] Bousmina, M. Study of intercalation and exfoliation processes in polymer nanocomposites. *Macromolecules* 2006, 39, 4259–4263.

### **Acknowledgements:**

Funded financial support by the Fundação para a Ciência e Tecnologia (FCT) under the framework of Strategic Funding grants UIDB/05256/2020 and UIDP/05256/2020 is also acknowledged.

## Compression-enhanced thermal conductivity of carbon loaded polymer composites

Avia Ohayon-Lavi<sup>1</sup>, Matat Buzaglo<sup>1</sup>, Shani Ligati<sup>1</sup>, Sivan Peretz-Damari<sup>1</sup>, Gal Shachar<sup>1</sup>, Noam Pinsk<sup>1</sup>, Michael Riskin<sup>3</sup>, Yotam Schatzberg<sup>3</sup>, Isaschar Genish<sup>3</sup> and OrenRegev<sup>1,2</sup>

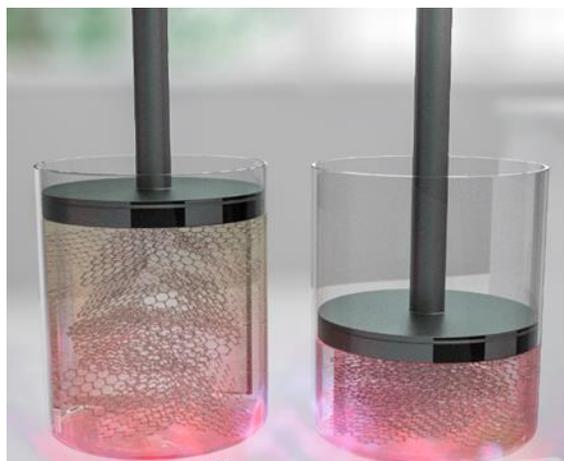
<sup>1</sup>Department of Chemical Engineering and <sup>2</sup>Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva, Israel

<sup>3</sup>R&D Inst., Engineering and Development Center, Israel Aerospace Industry, Israel

Presenting author's e-mail: [oregev@bgu.ac.il](mailto:oregev@bgu.ac.il)

The miniaturization, integration and compatibilization of electronic devices dictate the need for efficient thermal management to prevent heat accumulation, which may reduce the operation speed and shorten their lifetime. Addressing this challenge requires the development of novel polymer-based composite materials with enhanced thermal conductivity. Here, we report a compression-based (25-250 bars) approach for the preparation of polymer composites loaded with carbon-based hybrid fillers [1], i.e., graphene nanoplatelets and graphite flakes. The carbon-based fillers contribute significantly to the thermal conductivity of the composite while boron nitride nanoparticles provide the desirable inhibition of the electrical conductivity to avoid short circuits. An optimal thermal conductivity of 27.5 W/m K is obtained, for the compressed system (measured under atmospheric pressure for epoxy polymer loaded with 30 wt% graphene nanoplatelets and 40 wt% graphite flakes compared to 0.2 W/m K of the neat thermoset polymer [2].

**Keywords:** thermal conductivity, composite, graphene



**Figure 1.** Schematics demonstrating a compressed effect on the thermal conductivity of composites.

### References

- [1] G. Shachar-Michaely et al. Carbon, 2001, 176, 339.
- [2] A. Ohayon-Lavi et al. Carbon 2020, 163, 333.

**Thursday 8th September 2022**

**Self-Assembly and Supramolecular Structures**

# Cellulose nanocrystals in simple and not-so-simple flows

Roland Kádár

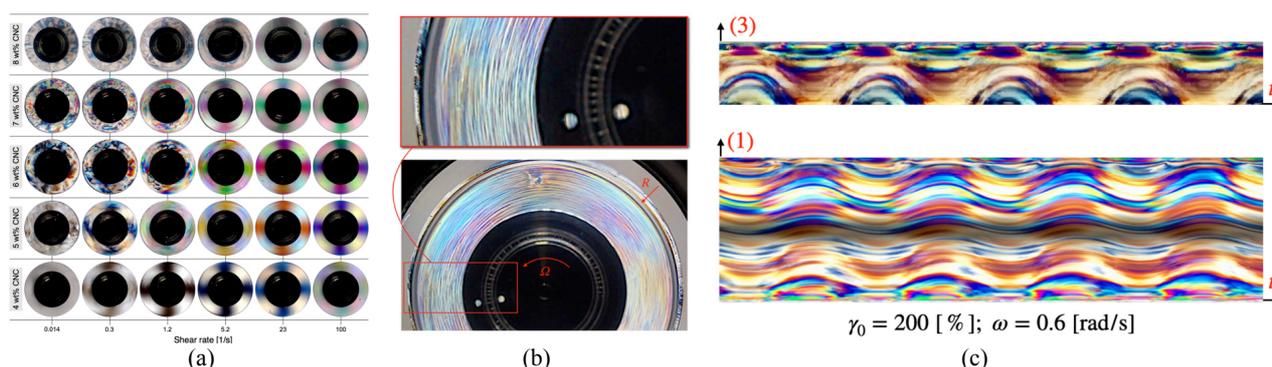
Chalmers University of Technology, 412 96 Gothenburg, Sweden

Wallenberg Wood Science Centre (WWSC), 412 96 Gothenburg, Sweden

Presenting author's e-mail: [roland.kadar@chalmers.se](mailto:roland.kadar@chalmers.se)

Cellulose nanocrystals (CNCs) are 1D nanoparticles and part of the rodlike family of lyotropic materials. CNCs self-assemble and can be flow-assembled into liquid crystalline orders in a water suspension. The orders range from nano- to macroscale with contributions of individual crystals, their micron clusters, and macroscopic assemblies influencing their rheological properties and flow behavior. The resulting hierarchies are optically active materials that exhibit iridescence, reflectance, and light transmission. This has inspired a number of applications in the fields of optics and electronics. Although these assemblies have the potential for future-renewable materials, details about structures on different hierarchical levels that span from the nano- to the macroscale are still not unraveled [1]. Elucidating their flow behavior is an ideal study case for combined rheo-optical methods, as they have the potential to relate bulk-averaged rheological properties to microstructural dynamics [1]. Here we will present an overview from our work on CNCs suspensions in flow and how rheo-PLI (polarized light imaging) can reveal surprising findings from resolving flow-induced orientation to the onset elastically-driven instabilities in the form of radially-periodic birefringence patterns in steady shear flow [2,3]. Under nonlinear deformations in oscillatory shear, we show that shear stress nonlinearities are sensitive to percolation and phase behavior, effectively distinguishing isotropic, biphasic and liquid crystalline phases [4]. The exact nonlinear signatures depends strongly on whether the preparation methods yield coarse or fine microstructures. Furthermore, nonlinearities directly from PLI can be related within a similar analysis framework to shear stress nonlinearities.

**Keywords:** cellulose nanocrystals; rheo – polarized light imaging; nonlinear oscillatory shear



**Figure 1.** Examples of using rheo-optical experimental setups for (a) resolving flow-induced orientation, (b) identification of elastically driven instabilities and (c) space-time orthogonal decomposition of birefringence patterns that can be related to shear stress nonlinearities.

## References

- [1] R. Kádár, S. Spirk, T. Nypelö, ACS Nano, 2021, 15, 5, 7931
- [2] R. Kádár, M. Fazilati, T. Nypelö, Cellulose, 2019, 27(4), 2003–2014
- [3] M. Fazilati, S. Ingelsten, S. Wojno, T. Nypelö, R. Kádár, J Rheol, 2021, 65(5), 1035–1052.
- [4] S. Wojno, M. Fazilati, T. Nypelö, G. Westman, R. Kádár, Cellulose, 2022, 29, 3655–3673

# From wet spinning to 3D printing of carbohydrate supramolecular hydrogels

*Andriamiseza Faniry<sup>1</sup>, Coudret Christophe<sup>1</sup>, Fitremann Juliette<sup>1</sup>*

<sup>1</sup> IMRCP, CNRS-Université de Toulouse, Université Paul Sabatier, Toulouse, France

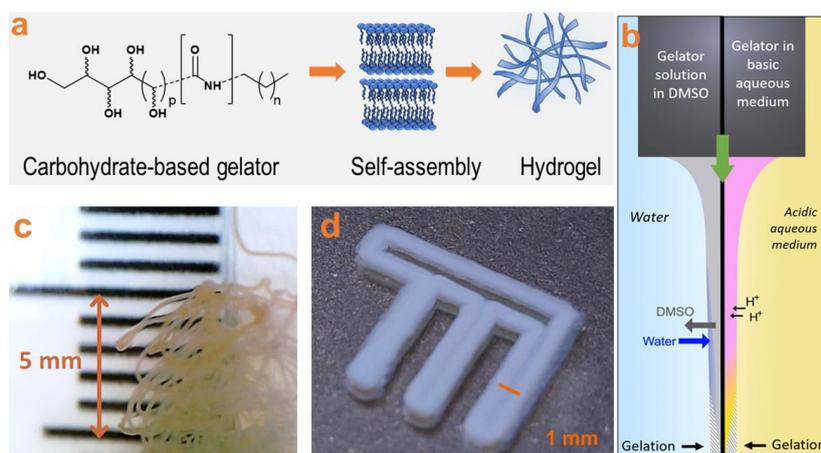
Presenting author's e-mail: faniry-meva.andriamiseza@univ-tlse3.fr

Small amphiphile molecules with a carbohydrate polyol polar head, a fatty chain, and amide linkers self-assemble in supramolecular fibers leading to the formation of soft hydrogels. These non-polymer hydrogels are biocompatible and have been successfully used for the 3D cell culture of human neural [1] or mesenchymal [3] stem cells. However, because of the mechanical fragility of the assembly, they cannot be directly injected and cannot be used in conventional 3D printing.

To allow the extrusion of these gels we have developed a wet spinning method in which a filament of gel is formed in situ during the injection. Two different approaches have been used to trigger the gelation. The first approach requires the solvation of the gelator in a good solvent and injecting the solution into a bath of water. The very fast self-assembly of the molecules in contact with water leads to a quick setting of the gel [2]. To avoid the use of organic solvent, we have developed a second approach in which the gelator is dissolved in a strongly basic aqueous solution. The injection of this solution in an acidic aqueous solution also triggers the gelation in gel filaments. The onset of the gelation and pH changes have been monitored along the jet.

A 3D printing method has been developed based on the principle of the wet spinning method. This new method allows the 3D printing of these fragile hydrogels, allowing designing scaffolds with precise and more complex architectures [2-3]. By alternating soluble and non-soluble hydrogels of this family of gelators, more complex architectures with channels have been built. Both methods, wet spinning and 3D printing have been generalized to other supramolecular low molecular weight hydrogels.

**Keywords:** Molecular gel, LMWG, Self-assembly



**Figure 1.** a) Structure of gelators and mechanism of self-assembly b) Principle of the wet spinning method c) Filament of gel obtained by wet spinning d) Result of the novel 3D printing method

## References

- [1] A. Chalard, L. Vaysse, P. Joseph, L. Malaquin, S. Souleille, B. Lonetti, J.-C. Sol, I. Loubinoux, J. Fitremann, *ACS Appl. Mater. Interfaces* 2018, 10, 17004–17017.  
 [2] C.C. Piras, A.G. Kay, P.G. Genever, J. Fitremann, D.K. Smith, *Chem. Sci.* 2022, 13, 1972–1981.  
 [3] F. Andriamiseza, D. Bordignon, B. Payré, L. Vaysse, J. Fitremann, *Journal of Colloid and Interface Science* 2022, 617, 156.

# Self-Assembled Nano-Objects for Solar Energy Conversion: Photocatalysis and Switchability in Aqueous Solution

*Franziska Gröhn<sup>1</sup>, Anja Krieger<sup>1</sup>, Alexander Zika<sup>1</sup>, Mohit Argawal<sup>1,2</sup>, Ralf Schweins<sup>2</sup>*

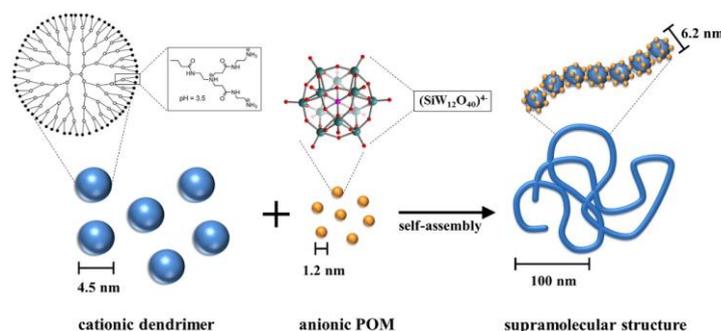
<sup>1</sup> *Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials (ICMM and Bavarian Polymer Institute (BPI, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany*

<sup>2</sup> *Institut Laue-Langevin, Grenoble, France*

Presenting author e-mail: [franziska.groehn@fau.de](mailto:franziska.groehn@fau.de)

With the increasing need for clean and sustainable energy, developing novel strategies to exploit solar energy becomes more and more important. Inspired by the photosynthesis of natural systems it is highly promising to self-assemble building blocks to form functional supramolecular entities. Spontaneous electrostatic self-assembly can lead to the functional interconnection of different molecular and particular components. Supramolecular nano-objects with shapes ranging from spheres and cylinders over vesicles to networks can be built in aqueous solution. In particular, we will present photocatalytically active nano-objects consisting of macroions and oppositely charged species ranging from ionic porphyrins to inorganic nanoclusters. Through the self-assembly, the photocatalytic activity of the active species can be enhanced up to a factor of 20, and a novel selectivity can be achieved.<sup>[1-4]</sup> Currently, we also build multicomponent structures and investigate design principles towards tunable functionality and multifunctionality. With regard to various applications, key to a targeted structure and functionality design is to fundamentally understand structure directing effects. Self-assembly thermodynamics, the interplay of interaction forces and structure-function relationships will be discussed.

**Keywords:** Photocatalysis, Polyelectrolytes, Polymers, Self-Assembly, Stimuli-Responsive



**Figure 1.** Electrostatic Self-Assembly for Photocatalysis <sup>[1]</sup>

## References

- [1] A. Kutz, G. Mariani, R. Schweins, C. Streb, F. Gröhn, *Nanoscale*, 2018, 10, 914.  
 [2] A. Krieger, J.-P. Fuenzalida Werner, G. Mariani, F. Gröhn, *Macromolecules*, 2017, 50, 3464. [3] A. Kutz, W. Alex, F. Gröhn, *Macromol. Rapid Commun.*, 2017, 38, 1600802.  
 [4] A. Krieger, A. Zika, F. Gröhn, *Frontiers in Chemistry*, 2022, 9, 779360.

# Development of cross-linked porous materials for membrane filtration: polymerization of microemulsions using non-polymerizable surfactants

*Chloé Guzelot, Jean-François Lahitte, Martine Meireles, Jean-Christophe Remigy*

*Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France*

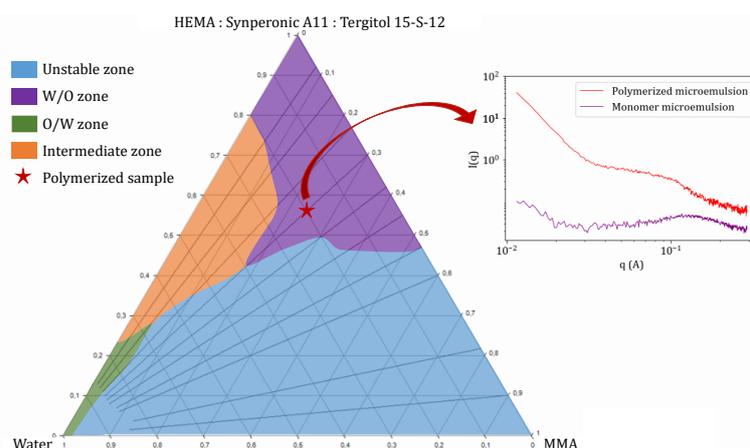
Presenting author's e-mail: [chloe.guzelot@toulouse-inp.fr](mailto:chloe.guzelot@toulouse-inp.fr)

One of the main challenge in improving the efficiency of membrane filtration is to increase the selectivity of the membrane without substantially decreasing its flux and thus its permeability. Interconnected cross-linked networks based on microemulsion templates are of great interest because of their nanoscale pore channels, allowing both high selectivity and limited permeability reduction [1].

Polymerizable surfactants are mostly used as they are supposed to retain the initial monomer microstructure. Yet they need to be synthesized in the laboratory prior to their use, unlike a lot of non-polymerizable surfactants that are commercially available. Using a commercial non-polymerizable surfactant may therefore be more versatile, but its inability to integrate the polymer network may result in a rearrangement of the microstructure during the polymerization process [2].

Our work focused on the synthesis of a nanostructured polyacrylate system based on a microemulsified template using non-ionic, non-polymerizable surfactants. Conductimetric measurements, SAXS and PGSE-NMR have been used to demonstrate the existence of a bicontinuous monomer system. Considering that the microstructure may evolve during the polymerization, cross-linkers associated to a UV-polymerization process have been used to prevent structural reorganization and to retain the bicontinuous network. The resulting polymer has been characterized using SEM, SAXS and ATR-FTIR analyses to assess its porous nanostructure.

**Keywords:** microemulsion, non-polymerizable surfactant, porous polymer, SAXS, ternary diagram



**Figure 1.** Pseudo-ternary phase diagram of the microemulsion system along with the SAXS curves of the monomer and polymerized microemulsion sample.

## References

- [1] F. Galiano, A.S. Schmidt, X. Ye, R. Kumar, R. Mancuso, E. Curcio, B. Gabriele, J. Hoinkis, A. Figoli, *Sep. Purif. Technol.*, 2018, 194, 149–160.  
[2] S. Dos Santos, L. Piculell, O.J. Karlsson, M. Da Graa Miguel, *Soft Matter*, 2011, 7, 1830–1839.

## Self-assembled nanocolloidal resonators for advanced metasurfaces

*Maeva Lafitte<sup>1</sup>, Philippe Barois<sup>1</sup>, Alexandre Baron<sup>1</sup>, Olivier Mondain-Monval<sup>1</sup> and Virginie Ponsinet<sup>1</sup>*

<sup>1</sup> *Univ. Bordeaux, CNRS, Centre de Recherche Paul Pascal, Pessac, France.*

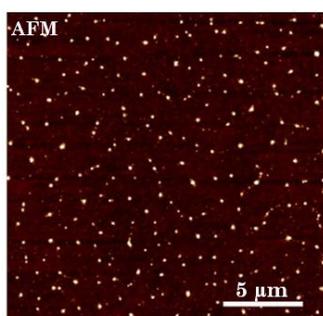
Presenting author's e-mail: [maeva.lafitte@crpp.cnrs.fr](mailto:maeva.lafitte@crpp.cnrs.fr)

The assembly of plasmonic nanoparticles (NPs) into tailored complex colloids can produce desired and original optical resonators, shown to be excellent building blocks for functional metadevices in the visible [1-2-3]. Within this trend, we have produced resonators consisting of clusters of NPs, by adapting an emulsion route [2]. We have also applied this methodology to the fabrication of controlled depositions of the complex colloids on surfaces.

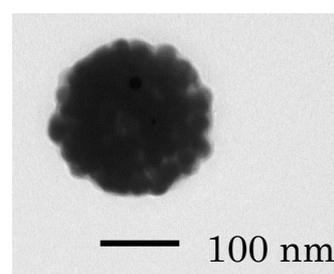
The synthesis technique used to obtain colloidal assemblies of NPs involved the emulsification followed by a controlled ripening of an aqueous suspension of gold or silver nanoparticles (10-20 nm radius) in an oil phase. Deposits of such colloidal particles were also obtained by slowly drying the initial emulsions as liquid films above a flat substrate, resulting in a deposition of dense NP-clusters with a regular surface density (see Fig 1).

The structure of self-assembled clusters was monitored by different techniques, such as electron microscopy (see Fig 2) and small-angle X-ray scattering (SAXS). Measurements using a spectroscopic angle- and polarization- resolved light scattering set-up were also performed. In agreement with modelling and simulations [4-5], they demonstrated that the resonators present a strong magnetic dipolar scattering mode, significantly overlapping spectrally with the electric dipolar mode. As a consequence, the colloids scatter strongly and mostly forward. These optical properties can be tuned by monitoring the clusters inner structure, changing the NPs radius and initial volume fraction, as well as the thickness of the ligands layer on the NPs surfaces.

**Keywords:** self-assembly, nanocolloids, emulsion, metamaterial



**Figure 1.** Atomic force microscopy image (height image in tapping mode) of a surface assembly of gold NPs-clusters.



**Figure 2.** Transmission electron microscopy image of a silver NPs-cluster

### References

- [1] A. Baron, A. Aradian, V. Ponsinet, P. Barois, *Comptes Rendus – Physique*, 2020, 21 (4-5), 443.
- [2] R. Elanchelivan, R. Dezert, S. Castano, A. Bentaleb, E. Nativ-Roth, O. Regev, P. Barois, A. Baron, O. MondainMonval, V. Ponsinet, *Nanoscale*, 2020, 12, 24177.
- [3] L. Lermusiaux, V. Many, P. Barois, V. Ponsinet, S. Ravaine, E. Duguet, M. Tréguer-Delapierre, A. Baron, *Nano Letters*, 2021, 21, 2046.
- [4] C. Rockstuhl, F. Lederer, C. Etrich, T. Pertsch, T. Scharf, *Physical Review Letters*, 2007, 99, 017401.
- [5] R. Dézert, P. Richetti, A. Baron, *Physical Review B*, 2017, 96, 180201.

## Influence of lead driers on oil paints' properties: Correlating supramolecular organization and rheology

*L. Laporte<sup>1</sup>, G. Ducouret<sup>2</sup>, F. Gobeaux<sup>3</sup>, T. Bizien<sup>4</sup>, C. Hotton<sup>5</sup>, L. Michot<sup>5</sup>, L. de Viguerie<sup>1</sup>*

<sup>1</sup> *LAMS, CNRS UMR 8220, Sorbonne Université, , Paris, France*

<sup>2</sup> *Laboratoire SIMM, CNRS UMR 7615, ESPCI Paris, PSL Research University, Paris, France*

<sup>3</sup> *LIONS – NIMBE, CEA/CNRS UMR 3685, CEA Saclay, France*

<sup>4</sup> *Synchrotron SOLEIL, l'Orme des Merisiers, Saint-Aubin, France*

<sup>5</sup> *Laboratoire Phenix, CNRS UMR 8234, Sorbonne Université, Paris, France*

Presenting author's e-mail: [lucie.laporte@sorbonne-universite.fr](mailto:lucie.laporte@sorbonne-universite.fr)

Since the 15<sup>th</sup> century, artistic painters have prepared paint mixtures by adding oil binders to pigments. Oils used in historical paintings are called drying oils: they exhibit natural hardening properties after a long period of exposure to air. To accelerate the oil drying process, historical recipes mention the use of inorganic drying compounds (or “driers”), such as lead oxide (PbO). The driers are ground, added to the oil and the mixture is heated [1]. The subsequent formation of lead soaps in the oil modifies the paints' properties [2].

We aim to characterize these modifications and to relate them to the formulation and organization of paint, at the molecular and supramolecular scale. More specifically, we wish to connect the flow properties of treated oils on a macromolecular scale with their structuring on a supramolecular scale. To do so, we combined rheology to SAXS (Small Angle X-ray Scattering) and carried out RheoSAXS measurements (SWING beamline at Synchrotron SOLEIL). The supramolecular structure of treated oils under shear could be elucidated and linked to the different stages of paint application.

At rest, the SAXS profiles of the treated oils show periodic oscillations, indicating that the lead soaps formed during heating self-organize into a lamellar phase with a characteristic distance of 50 Å. [3]. The more lead soaps the sample contains, the more the lamellar phase contracts, until it reaches a characteristic dimension of 40 Å. The lamellar organization is also modified under shear, depending on the type of shear applied : continuous shear leads to a parallel alignment of the lamellar phases and a to decrease in viscosity. Under oscillatory shear, the lamellae progressively structure themselves into vertically oriented cylindrical objects in the rheometer cell. This change in organization is correlated with the loss of viscoelastic properties at the macroscopic scale.

**Keywords:** RheoSAXS, lead soaps, lamellar phases

### References

- [1] M. Faidutti and C. Versini, *Le Manuscrit de Turquet de Mayerne présenté par M. Faidutti et C. Versini*, 1967, p.18, Audin Imprimeurs. Lyon, France.
- [2] L. De Viguerie *et al.*, *Colloids and Surfaces: A Physicochemical and Engineering Aspects*, 2008, vol. 331, no. 1–2, pp. 119–125.
- [3] F. J. Martínez-Casado *et al.*, *Phys. Chem. Chem. Phys.*, 2017, vol. 19, no. 26, pp. 17009–17018.

# Tuning the properties of multicomponent polysaccharide/peptide self-assembled macroscopic membranes

*Ronit Bitton*

*Department of Chemical Engineering and Ilse Katz Institute for Nanoscale Science and Technology (IKI) Ben-Gurion University of the Negev, Israel.*

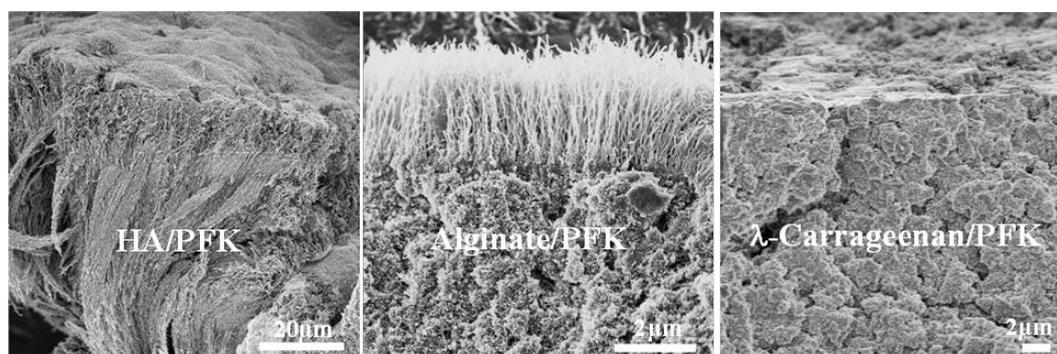
*Presenting author's e-mail: [rbitton@bgu.ac.il](mailto:rbitton@bgu.ac.il)*

Hierarchically organized self-assembled peptides and polyelectrolytes that form macroscopic membranes at liquid-liquid interfaces can serve as a platform for 3D cell culture. However, controlling their structure and mechanical properties is imperative to tailor their characteristics to meet specific requirements. We recently reported on the formation of planar and spherical membranes (sacs) at the interface of a cationic  $\beta$ -sheet peptide PK(FK)<sub>5</sub>P (PFK) aqueous solution and a negatively charged aqueous alginate solution.

Utilizing small-angle X-ray scattering (SAXS) and scanning electron microscopy (SEM), the system was found to form either a fully developed membrane structure with three distinct regions, including characteristic perpendicular fibers (as seen in the figure below), or a non-fully developed contact layer lacking these standing fibers. The morphological differences were found to strongly depend on the peptide age, membrane geometry, and membrane incubation time, which influence both the peptide's intrinsic alignment and the reaction-diffusion process taking place at the interface. A three-stage mechanism was suggested, and critical parameters affecting the membranes development process were identified.

Aiming to expand the versatility of this platform, we formed self-assembled membranes with PFK and other polymers (e.g., HA, l-carrageenan, PSS). Remarkably, membranes made in the same conditions exhibited different morphologies. Here we present the effect of the polymer characteristics on the structure and mechanical properties of PFK/polymer self-assembled membranes and examine the validity of the three-stage mechanism to their formation.

**Keywords:** peptides, polysaccharides, self-assembly, SAXS, SEM



**Figure 1.** SEM of self-assembled membranes made with PFK and different polysaccharides in the same conditions.

## Transition from a Sponge-Like to a Foam-Like Nanostructure in Water-Rich $L_3$ Phases

Philipp Menold<sup>1</sup>, Natalie Preisig<sup>1</sup>, Cosima Stubenrauch<sup>1</sup> and Reinhard Strey<sup>2</sup>

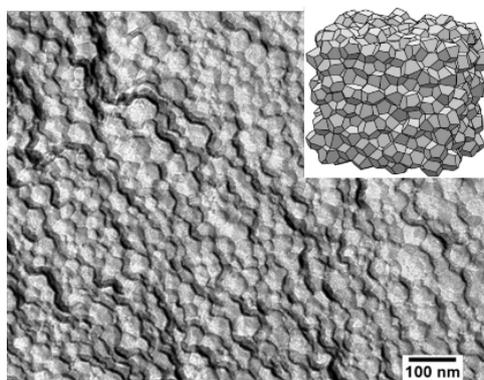
<sup>1</sup>Institute of Physical Chemistry, University of Stuttgart, Germany

<sup>2</sup>Department of Chemistry, University of Cologne, Germany

Presenting author's e-mail: [cosima.stubenrauch@ipc.uni-stuttgart.de](mailto:cosima.stubenrauch@ipc.uni-stuttgart.de)

Early studies [1-3] on water – *n*-alkane – ionic surfactant microemulsions provide first hints for the possible existence of a foam-like nanostructure, i.e. a dense packing of polyhedral nanometer-sized water droplets separated by a thin layer of a continuous oil phase. We chose the system water/NaCl – hexyl methacrylate ( $C_6MA$ ) - dioctyl sulfosuccinate sodium salt (AOT) for two reasons. First, because AOT is a single, pure surfactant known to form inverse structures and, secondly, our ultimate goal is to polymerize the continuous oil ( $C_6MA$ ) phase, i.e. to synthesize genuine nanoporous polymer foams. Inspired by the pioneering work of Skouri et al. [4] we were able to locate an isotropic one-phase channel, the  $L_3$  phase, emanating from the pseudo-binary system water/NaCl - AOT at ambient temperature. In addition, there is an isotropic oil-in-water microemulsion found at high temperatures [5]. Already upon addition of small amounts of oil to the  $L_3$  Phase the conductivities become very low and the viscosities very high [6]. Freeze fracture electron microscopy allows us to actually see the anticipated foam-like nanostructure (see Fig.1). The structure is reminiscent of that of Wolf et al. [8] for a related system with a technical grade nonionic / anionic surfactant mixture. Currently, we are studying the kinetics of the oil ( $C_6MA$ ) polymerisation. Subsequently, the structural transition in the  $L_3$  channel will be investigated by small angle neutron scattering (SANS) and NMR self-diffusion (FTPGSE).

**Keywords:** foam-like nanostructure;  $L_3$  phase; high internal phase microemulsion



**Figure 1:** Freeze fracture electron microscopy (FFEM) image of an oil-continuous microemulsion  $H_2O/NaCl - C_6MA - AOT$  with AOT mass fraction  $\gamma = 0.15$  and  $C_6MA$  mass fraction  $\alpha = 0.04$ . Scale bar = 100 nm [6]. The inset illustrates the polyhedral foam-like structure taken from [7].

### References

- [1] D.F. Evans et al, J. Phys. Chem., 1986, 90, 2817.
- [2] W. Jahn and R. Strey, J. Phys. Chem., 1988, 92, 2294.
- [3] S.H. Chen et al, J. Phys.: Condens. Matter, 1991, 3, F91.
- [4] M. Skouri et al, Colloid Polym Sci, 1991, 269, 929.
- [5] O. Lade, Charakterisierung, Modellierung und Polymerisation von Microemulsion aus Alkylmethacrylaten, 2001, Cuvillier Verlag, Göttingen, Germany.
- [6] P. Menold, R. Strey, N. Preisig and C. Stubenrauch, JCIS, 2021, 601, 133.
- [7] A. M. Kraynik, Advanced Engineering Material, 2006, 8, 9, 900.
- [8] L. Wolf et al, J. Phys. Chem. B, 2011, 115, 11081.

# Modifying Macrocycle Stability and Supramolecular Chemistry in a Deep Eutectic Solvent

*Ilan Shumilin, and Daniel Harries*

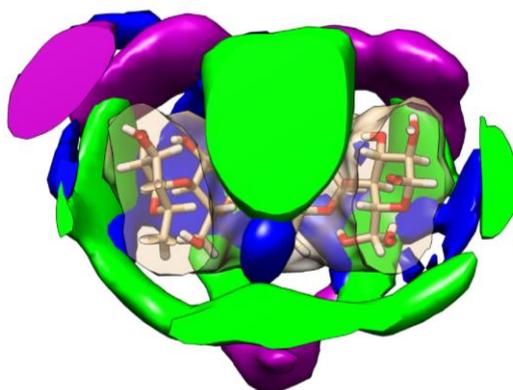
*Institute of Chemistry, The Fritz Haber Research Center, and The Harvey M. Krueger Family Center for Nanoscience and Nanotechnology, The Hebrew University, Jerusalem, Israel*

Presenting author's e-mail: [ilan.shumilin@mail.huji.ac.il](mailto:ilan.shumilin@mail.huji.ac.il)

Deep eutectic solvents (DESs) are unique solvents composed of at least two organic components that are usually solid at room temperature, which upon mixing form a liquid with remarkable solvation capabilities [1,2]. Although DESs and their applications for industrial use have spurred considerable interest, very little is known about their molecular mechanism of solvation.

Here we focus on reline, the DES formed from choline chloride and urea, and resolve the mechanism through which its constituents solubilize  $\beta$ -cyclodextrin, over an order of magnitude more than water [3]. Combining experiments and simulations, we determined that  $\beta$ -cyclodextrin solubility increases by a unique synergism between both urea and choline chloride [4]. We further show that  $\beta$ -cyclodextrin solubility grows remarkably when choline chloride is replaced by other salts, and that the attained solubility is much higher than expected from the summed urea-salt effect. Finally, we show how  $\beta$ -cyclodextrin solvated in reline maintains its supramolecular complexation capability with a guest dye molecule even in the complete absence of water. By resolving how multiple solutes act together to mediate both solubility and supramolecular assembly, we provide guiding principles to design future solvents that are tailored for specific needs.

**Keywords:** Supramolecular chemistry, Solubility enhancement, Deep eutectic solvents.



**Figure 1.** Spatial distribution of urea (green), choline cations (purple), and water (blue) around  $\beta$ -CD extracted from a molecular dynamics simulation of a 50 wt% reline solution.

## References

- [1] E. Smith, A. Abbott and K. Ryder, *Chemical Reviews*, 2014, 114, 11060.
- [2] Y. Dai, J. van Spronsen, G.-J. Witkamp, R. Verpoorte, and Y.H. Choi, *Anal. Chim. Acta*, 2013, 766, 61.
- [3] A. Triolo, F. Lo Celso and O. Russina, *J. Phys. Chem. B*, 2020, 124, 2652.
- [4] I. Shumilin and D. Harries. *The Journal of Chemical Physics*, 2021, 154, 224505.

## Inverse Internally Self-Assembled Particles (ISAsomes)

*Otto Glatter*<sup>1</sup>, *Florian Trummer*<sup>1,2</sup>, *Franz Pirolt*<sup>1</sup>, and *Angela Chemelli*<sup>1</sup>

<sup>1</sup>*Institute of Inorganic Chemistry, Graz University of Technology, Graz, Austria*

<sup>2</sup>*Current address: Institute for Ion Physics and Applied Physics, University of Innsbruck, Innsbruck, Austria*

Presenting author's e-mail: [otto.glatter@tugraz.at](mailto:otto.glatter@tugraz.at)

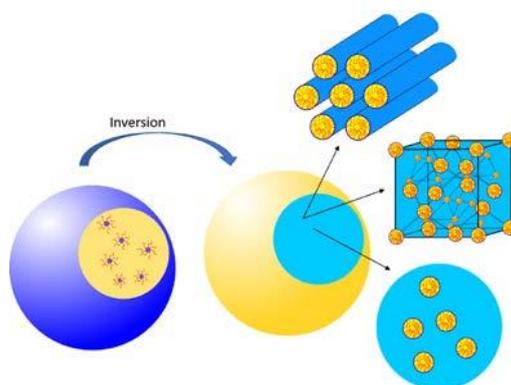
In contrast to their more common counterparts in aqueous solutions like cubosomes and hexosomes [1], inverse ISAsomes (Internally Self-Assembled some/particles) are formulated as kinetically stabilized dispersions of hydrophilic, lyotropic liquid-crystalline (LC) phases in non-polar oils (Fig. 1). In 2018, a first inverse system was achieved by dispersing a hydrophilic LC with hexagonal nanostructure ( $H_1$ -phase) in an alkane – resulting in the first report of inverse hexosomes [2].

This contribution focuses on their formation in bio-compatible oils [3]. We found that it's possible to create inverse hexosomes, inverse micellar cubosomes (Fd3m) and an inverse emulsified microemulsion (EME) in excess squalane with a polyethylene glycol alkyl ether as the primary surfactant forming the LC phase and to stabilize them with hydrophobized silica nanoparticles. Furthermore, an emulsified  $L_1$ -phase and inverse hexosomes were formed in excess triolein with the triblock-copolymer Pluronic® P94 as the primary surfactant. Stabilization was achieved with a molecular stabilizer of type polyethylene glycol (PEG)-dipolyhydroxystearate.

For the inverse hexosomes in triolein, the possibility of a formulation without any additional stabilizer was explored. It was found that a sufficiently strong stabilization effect was created by the primary surfactant alone. Finally, triolein was replaced with olive oil which also led to the successful formation of inverse hexosomes.

As far as we know, there exists no previous contribution about inverse ISAsomes in complex oils like triolein or plant oils and the existence of stabilizer-free (i.e., self-stabilizing) inverse hexosomes has also not been reported until now.

**Keywords:** Inverse Cubosomes, Inverse Hexosomes, ISAsomes



**Figure 1.** Inverse ISAsomes are formulated as kinetically stabilized dispersions of hydrophilic, lyotropic liquid-crystalline (LC) phases in non-polar oils.

### References

- [1] J. Gustaffson, H. Ljusberg-Wahren, M. Almgren and K. Larsson, *Langmuir* 1996, 12, 4611  
 [2] F. Pirolt, O. Glatter, G. Trimmel, *Langmuir* 2018, 34, 8379  
 [3] F. Trummer, O. Glatter and A. Chemelli, *Nanomaterials* **2022**, 12(7), 1133

# Optical tweezer platform for the characterization of pH-triggered colloidal transformations in the oleic acid / water system

Marco Manca<sup>1,2</sup>, Chi Zhang<sup>2</sup>, Frank Scheffold<sup>2</sup>, and Stefan Salentinig<sup>1</sup>

<sup>1</sup> University of Fribourg Chemistry Department, Fribourg, Switzerland

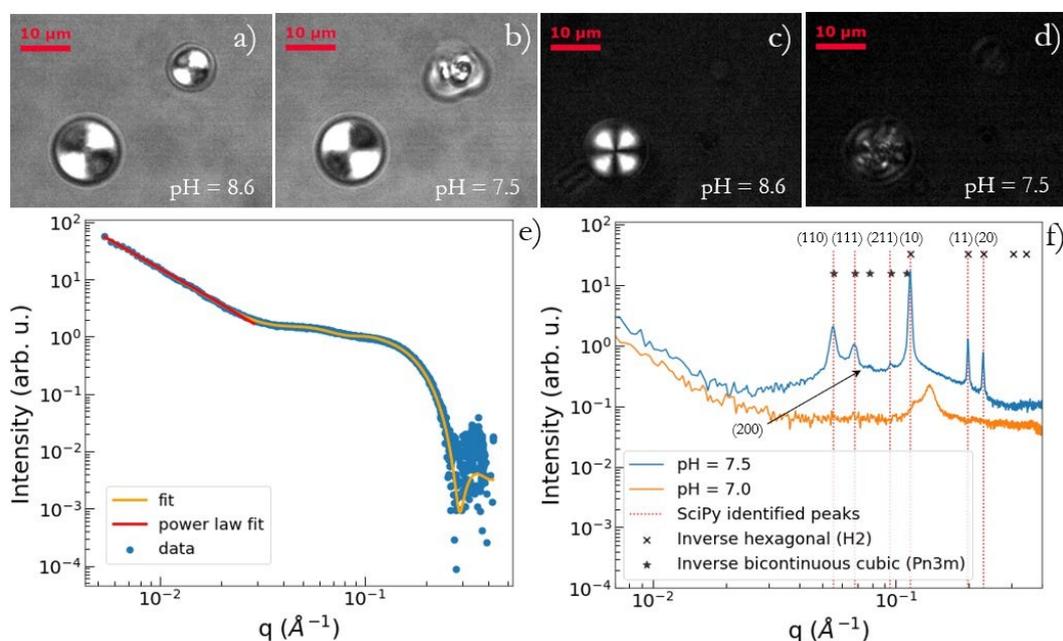
<sup>2</sup> University of Fribourg Physics Department, Fribourg, Switzerland

Presenting author's e-mail: [marco.manca@unifr.ch](mailto:marco.manca@unifr.ch)

The study of soft colloids (e.g. vesicles and emulsions) has become more important thanks to its potential applications in different fields such as food, health, biotechnology or oil recovery.

In this contribution<sup>1</sup>, the micro- and nano-structural transformations of oleic acid (OA) in water colloids are investigated as a function of the pH of the solution. A custom-made multiple trap optical tweezers is built and used in combination with a microfluidic chip to trap and isolate OA droplets. The response of a single particle upon pH change, induced by replacing the solution inside the microfluidic channel, is observed through polarized video microscopy and its micro-structural transformation is recorded. In addition, synchrotron small angle X-ray scattering and numerical data analysis are used to identify the internal nano-structure of the investigated particles. It is found that self-assembled OA vesicles at pH 8.6 transform into internally nano-structured emulsions above pH 6.5 and eventually phase separate in the two oil and water components. The interactions between the different micro- and nano-structured particles at different pH are investigated in order to better understand their stabilization mechanisms and insights into the relationship between the structure and the properties of the emulsions are obtained. This may contribute to a better fundamental understanding for nutrient and drug delivery applications and guide the design of advanced emulsion-based nanostructures.

**Keywords:** optical tweezers, single particle characterization, oleic acid emulsions, SAXS, birefringence, self-assembly



**Figure 1.** Video microscopy transformation of oleic acid vesicles in mixed a) and b) and cross-polarization c) and d). images e) and f) shows SAXS curves of oleic acid in water emulsions at pH 8.6, 7.5 and 7.0.

**Reference:** [1] M. Manca, C. Zhang, F. Scheffold and S. Salentinig, submitted to Small, status April 2022

## Morphological transition in ethoxylated coacervate core micelles

*Júlia B. Sabadini*<sup>1</sup>, *Cristiano Oliveira*<sup>2</sup> and *Watson Loh*<sup>1</sup>

<sup>1</sup> *Institute of Chemistry, University of Campinas, Campinas, SP, Brazil.*

<sup>2</sup> *Institute of Physics, University of São Paul, Brazil.*

Presenting author's e-mail: [j230055@dac.unicamp.br](mailto:j230055@dac.unicamp.br)

Amphiphilicity, size and molecular architecture of copolymer blocks, as well as the composition of the system (e.g., selective solvent) allow macromolecules to self-assemble in different morphologies. Therefore, aggregates varying from spheres to cylinders or vesicles may be formed due to favoring of, respectively, greater to lower curvatures.<sup>1</sup> These structural changes can also be induced by external stimuli, such as the thermal effect over ethoxylated surfactants. Sphere to lower curvature transitions induced by temperature is well characterized for ethoxylated amphiphiles, but less investigated for aggregates obtained by the association of a charge-neutral diblock copolymer and an oppositely charged through electrostatic coacervation.<sup>2</sup> These core-shell aggregates, called complex coacervate core micelle (C<sub>3</sub>M)<sup>3</sup>, consists of a highly hydrated core composed by the charged species surrounded by the shell formed by the neutral and water-soluble block. In the present study, C<sub>3</sub>M<sub>s</sub> were prepared with poly(ethelene oxide)-b-poly(acrylic acid), PEO-b-PAA, containing different PEO chain lengths and poly(diallyldimethylammonium chloride), PDADMAC. Their thermal behavior was investigated using dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS) measurements, whose results suggest that anisotropic and large aggregates could be obtained upon temperature increase. This transition from globular to elongated aggregates was confirmed by cryogenic transmission electron microscopy (Cryo-TEM). Therefore, we demonstrate, for the first time, that the control of morphology of these coacervate micelles containing temperature sensitive blocks is similar to that established for aggregates of ethoxylated surfactants, being controlled by the surfactant or polymer molecular packing and resulting curvature control.

**Keywords:** Coacervate micelles, polyelectrolyte, morphological transition, scattering techniques, cryogenic transmission electron microscopy

**Acknowledgements:** we gratefully acknowledge the Brazilian National Laboratory (LNNano) for the use of cryo-TEM facilities and the financial support from São Paulo Research Foundation (FAPESP) (grant number 2015/25406-5). J.B.S. acknowledges FAPESP for the PhD scholar ship (grant number 2020/11735-5). W. L. also thanks the Brazilian Agency CNPq-senior research grant (grant number 306398/2018-4)

### References:

- (1) Allen, B. P.; Wright, Z. M.; Taylor, H. F.; Oweida, T. J.; Kader-Pinky, S.; Patteson, E. F.; Bucci, K. M.; Cox, C. A.; Senthilvel, A. S.; Yingling, Y. G.; Knight, A. S. Mapping the Morphological Landscape of Oligomeric Di-Block Peptide–Polymer Amphiphiles<sup>\*\*</sup>. *Angew. Chemie Int. Ed.* **2022**, *61* (14), e202115547.
- (2) Wibowo, A.; Osada, K.; Matsuda, H.; Anraku, Y.; Hirose, H.; Kishimura, A.; Kataoka, K. Morphology Control in Water of Polyion Complex Nanoarchitectures of Double-Hydrophilic Charged Block Copolymers through Composition Tuning and Thermal Treatment. *Macromolecules* **2014**, *47* (9), 3086–3092.
- (3) Voets, I. K.; de Keizer, A.; Cohen Stuart, M. A. Complex Coacervate Core Micelles. *Adv. Colloid Interface Sci.* **2009**, *147–148*, 300–318.

**Thursday 8th September 2022**

**Advanced Colloid Science for Applications and Products**

## Advanced structuring technologies at micro- and nanoscale for product functionality control

*Krassimir P. Velikov*<sup>1,2,3</sup>

<sup>1</sup>Unilever Innovation Centre Wageningen, Wageningen, The Netherlands

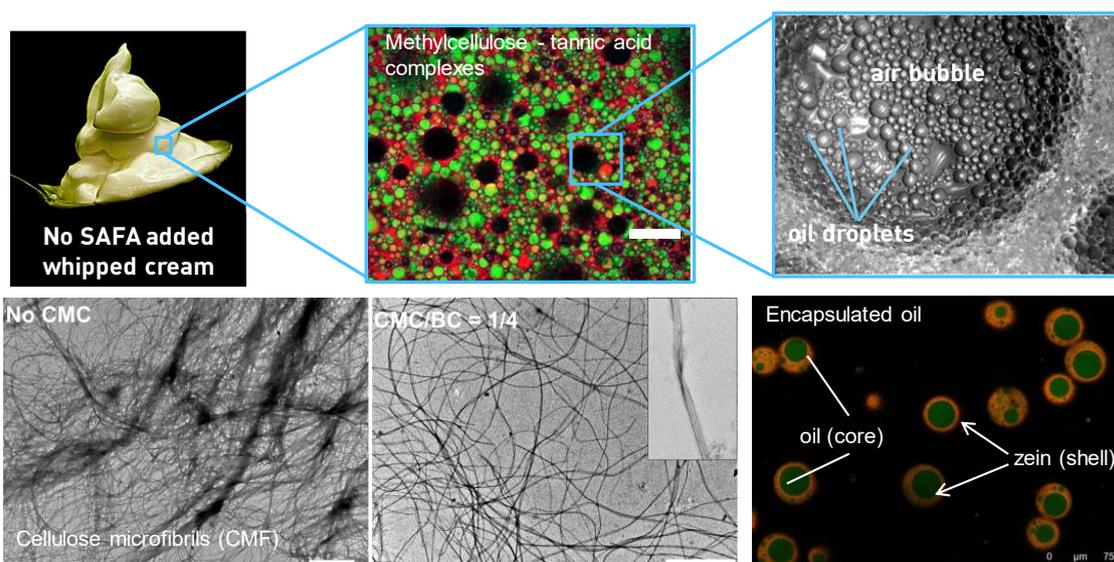
<sup>2</sup>Institute of Physics, University of Amsterdam, Amsterdam, The Netherlands

<sup>3</sup>Soft Condensed Matter, Debye Institute for NanoMaterials Science, Utrecht University, Utrecht, The Netherlands

Presenting author's e-mail: [krassimir.velikov@unilever.com](mailto:krassimir.velikov@unilever.com)

Food industry is driven by strong demand for high quality products with little health concern that contain sustainably sourced natural ingredients. It is however very challenging to build consumer perceived differentiating textures with current ingredients. In addition, the introduction of new ingredients is strongly limited by safety, consumer perception, and regulatory. To address these challenges, we need to achieve better control on the consumer relevant product functionality aspects (i.e. appearance, taste, texture, stability) by optimizing existing structures and ingredient interactions. This could be achieved by alternative and novel uses of the existing materials and their interactions. Another approach is to further unlock the potential of underutilized natural materials (e.g. cellulose microfibrils, insoluble plant proteins). These approaches can be used to build new architectures (e.g. composite materials, hierarchical or hybrid structures). Novel uses of ingredients (e.g. stabilization by particles) or exploring unwanted interactions to create useful structures are other potential approaches. Finally, control of structure breakdown based on known digestion and physiological effect is necessary to assure full utilization of nutrients and micronutrients. In this talk, several examples of such approaches will be discussed. These will include utilization of strong intermolecular interactions, plant cellulose microfibrils, and water insoluble plant proteins.

**Keywords:** fibrils, emulsions, colloids, encapsulation, food, cosmetics



## Utilising inorganic perovskite quantum dots as a 2D high-sensitivity optical heat flux meter

*Yanshen Zhu<sup>1</sup>, Maria Rosaria Vetrano<sup>2</sup> and Erin Koos<sup>1</sup>*

<sup>1</sup>*Soft Matter, Rheology and Technology, Department of Chemical Engineering, KU Leuven, Leuven, Belgium*

<sup>2</sup>*Department of Mechanical Engineering, KU Leuven, Leuven, Belgium*

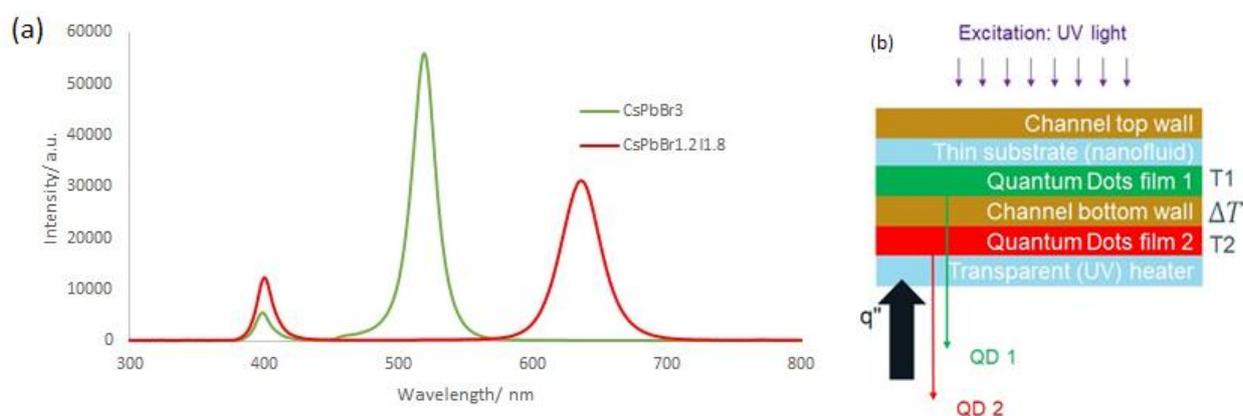
Presenting author e-mail: [yanshen.zhu@kuleuven.be](mailto:yanshen.zhu@kuleuven.be)

Thermal design and heat management is an important aspect in process intensification among many other applications. Since the late 19<sup>th</sup> century[1], various contact and non-contact techniques have been developed to measure the heat flux. Oftentimes, however, there is a trade-off between accuracy and the physical dimension of the device.

Lead halide perovskite quantum dots are well-known for their low lasing threshold, high photoluminescence quantum yields, and easily tuneable luminescent wavelength. The good temperature dependent sensitivity of its photoluminescence intensity makes it a promising candidate to be used as a temperature sensor. [2]

In this study, we have utilised CsPbX<sub>3</sub> perovskite quantum dots as the base of a highly sensitive 2D optical heat flux meter for the room temperature range. Two colours of quantum dots used are synthesised via the supersaturated recrystallisation method at room temperature and dispersed into a PMMA solution. The result dispersions are then cast onto each side of a sample microchannel, which forms two layers of uniform film of about 20 μm. External UV light source and cameras are used to excite the quantum dots and record the photoluminescence. Calibration curves between the quenching behaviour of photoluminescent and increasing temperature are then developed simultaneously for all pixels of both quantum dots films, leading to precise and accurate temperature and heat flux measurement which exceeds the current conventional methods on both spatial and temporal resolution. Sample tests are conducted with the optical heat flux meter to prove the practicality of the proposed design.

**Keywords:** perovskite quantum dots, optical heat flux meter, quantum extinction, sensor design



**Figure 1.** (a) Photoluminescent intensity of CsPbX<sub>3</sub> quantum dots vs Temperature (in °C). The peak at 400 nm is the UV light used to excite the quantum dots. (b) Design sketch of optical heat flux meter

### References

- [1] A.J. Angstrom, Ann. Der Phys. Und Chemie, 1861, 114, 33.  
[2] Han, Q., Wu, W., Liu, W., Yang, Q. and Yang, Y., Journal of Luminescence, 2018, 198, 350-356

## Rheo-SAXS study of lamellar-to-onion structure changes

*P. M. Worsch<sup>1</sup>, Y. Takasaki<sup>2</sup>, Y. Yamagata<sup>2</sup>*

<sup>1</sup>Anton Paar GmbH

<sup>2</sup>Anton Paar Japan

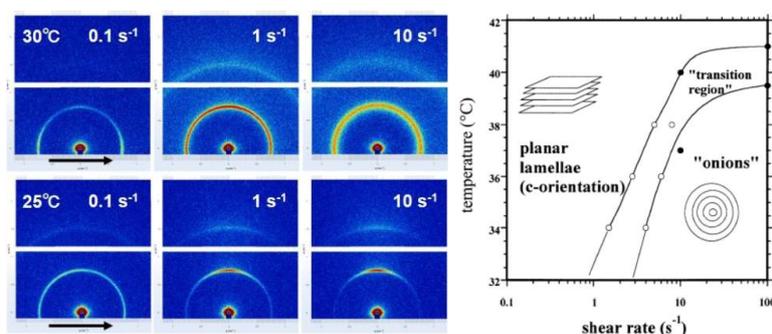
Presenting author's e-mail: [peter.worsch@anton-paar.com](mailto:peter.worsch@anton-paar.com)

Non-ionic surfactants are used as detergents, wetting agents, emulsifiers and solubilizers in cosmetics, personal and health care, textile and other industrial sectors. They do not disassociate into ions in aqueous solution and compared to ionic surfactants, some non-ionic surfactants have several superior properties, e.g. superior cleaning performance, higher solubility, in particular in hard water and also a better chemical stability.

Aqueous non-ionic surfactant systems typically form molecular assemblies and structures at the nanometer level. Small-angle X-ray scattering (SAXS) is the perfect tool for analyzing these structures in solution. In addition, rheology helps to elucidate the flow and deformation of matter under shear as well as the viscosity, and therefore allows relating a material's internal structure to its mechanical properties.

In this study, we show how the unique Rheo-SAXS module of the SAXSpoint 5.0 system was used for a simultaneous characterization of the flow behavior and the structure of the non-ionic surfactant polyoxyethylene alkyl ether (CmEn)-water two-component system. These systems are known to form planar lamellae at no shear or low shear rates, however, at higher shear rates and in dependence of the temperature onion-like structures can evolve. A detailed analysis of the Rheo-SAXS data shows that the number of bilayers and the structural irregularity of the bilayers are strongly affected by temperature and shear rate.

**Keywords:** instrument, rheology, SAXS, surfactant, X-ray



**Figure 1.** 2D scattering patterns of C12E4.2/H<sub>2</sub>O obtained by Rheo-SAXS measuring system. SDD: 1300 mm. Exposure time 5min, number of frames: 6.

**Acknowledgements:** Dr. Y. Takasaki and Dr. Y. Yamagata (Anton Paar Japan) for providing the samples and performing the laboratory Rheo-SAXS measurements and data evaluation.

### References

- [1] M. Ito, Y. Kosaka, Y. Kawabata, T. Kato, Lang-muir, 27, 7400–7409 (2011)
- [2] L. Gentile, et al., J. Phys. Chem. B, 118, 3622–3629 (2014)
- [3] Oliviero C., et al., Dynamic phase diagram and onion formation in the system C<sub>10</sub>E<sub>3</sub>/D<sub>2</sub>O. Colloids Surf. A: Physicochem. Eng. Asp. 228 (2003) 85
- [4] Fritz G., Glatter O., Structure and interaction in dense colloidal systems: evaluation of scattering data by the generalized indirect Fourier transformation method. J. Phys.: Condens. Matter 18 (2006) S2403

# Spatially Resolved Dynamic Light Scattering: characterizing colloids over unprecedented ranges of turbidity and flow

*Rut Besseling, Michiel Hermes, Remy van Tuijn, Carl Schuurmans, Ad Gerich*

*InProcess-LSP, Oss, The Netherlands*

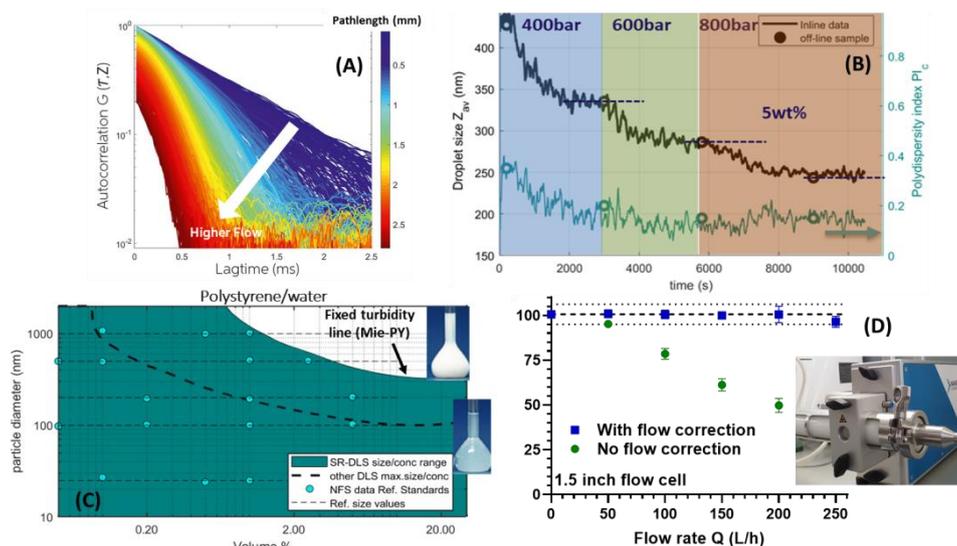
*Presenting author's e-mail: [r.besseling@inprocess-lsp.com](mailto:r.besseling@inprocess-lsp.com)*

The last decades, Dynamic Light Scattering (DLS) techniques have progressed significantly. Many developments have focused on accessing turbid samples or probing colloid dynamics in non-equilibrium cases particularly flow [1]. Yet their applicability has remained limited: for fundamental studies on colloid dynamics, relatively low turbidity systems are often still required, while for highly turbid nanosuspensions in e.g. pharmaceutical industry, current DLS methods still require sample preparation, complicating formulation and process development. Additionally, available DLS methods struggle to provide purely non-invasive measurement in (flowing) sample environments. E.g. in applied, industrial colloid research, this precludes inline realtime measurement during colloid processing, which is highly desired for process understanding, quality and control.

Here we describe advances and applications of Low Coherence, Spatially Resolved Dynamic Light Scattering (SR-DLS) as emerging tool for colloid characterization in largely extended turbidity and flow regimes [2]. Instantaneous depth resolution of backscattered light is achieved using coherence gating via Fourier Domain Low Coherence Interferometry. This technique, supplemented with new analysis methods for Depth-Resolved 'Correlation Matrices' (see Fig 1A), offers fully non-invasive characterization -particularly particle sizing- of nano-suspensions with extremely high turbidity (Fig 1C), and allows both diffusion measurements and velocimetry in non-equilibrium situations including industrial processes (Fig 1B,D).

After describing basic SR-DLS principles, the new physical operational limits regarding sample turbidity and flow are discussed and compared to other DLS methods. Several applications of the new instrumentation will be described, from monitoring of colloid synthesis processes to nano-emulsification and controlled liposome manufacturing, in different sample/process environments. For highly concentrated systems, challenges in converting information on diffusive modes to particle size, particularly the generalized Stokes-Einstein relation, are also discussed.

**Keywords:** DLS, particle sizing, process monitoring



**Figure 1.** (A) Depth Resolved Correlation Matrix of a nanosuspension in laminar flow (B) inline droplet size measurement of a 5 wt% sunflower oil/water emulsion during high pressure homogenization at 8L/hr. (C) Operational range diagram for SR-DLS measurements of Polystyrene colloids (D) Inline particle sizing in flow for 100nm 5wt% silica colloids. Blue (green) data show SR-DLS results with(out) flow correction based on implicit velocimetry analysis.

## References

- [1] J. A. Richards, *et al*, *Soft Matter*, 2021, **17**, 3945; A. B. Leung, *et al*, *Appl. Opt.*, 2006, **45**, 2186.  
[2] R. Besseling *et al*, *Eur. J. Pharm. Sci.*, 2019, **133**, 205.

# Potential Filtration Technique for Microparticles of Equal Size but Different Surface Modifications

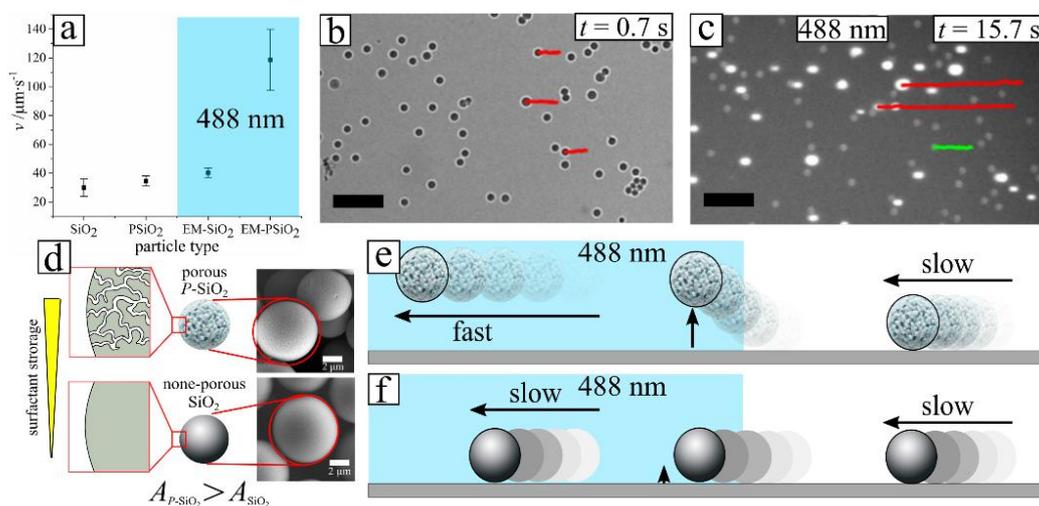
Marek Bekir<sup>1</sup>

<sup>1</sup>Institut für Physik und Astronomie, Potsdam-Golm, Germany

Presenting author's e-mail: [marek.bekir@uni-potsdam.de](mailto:marek.bekir@uni-potsdam.de)

Over the last three decades,[1] filtration over microfluidic devices has been a rapidly growing field of technology for many applications likewise electronic industries, chemical analysis, or diagnostics.[2] Especially for micro sized objects, until now the separation is mainly possible by size. We provide a new promising tool which can separate particles of different surface morphology, but equal size stimulated from light irradiation under specific wavelengths and lamellar liquid flow. For this we use the advances of microfluidic technology with the combination of a photosensitive surfactant, where the passive motion of the particles can be manipulated from light irradiation by stopping or accelerating their motion velocity along the streamline. The latter can be used as a potential tool for separation of non- and porous particles, where the light irradiation with blue light induces a local-light driven diffusioosmosis[3] strong enough to elevate particles up to several micrometer from liquid-glass interface of the microfluidic chamber. In combination of a superimposed fluid flow the elevation leads to a stronger passive motion. We demonstrate that the lift off depends on the size but also on the surface morphology, i.e., non- and porous particles have a different surface area and therefore a different motion velocity.

**Keywords:** surface sensitive filtration, light induced motion



**Figure 1.** (a) Average velocity of mixture of non- ( $\text{SiO}_2$ ) and porous ( $\text{P-SiO}_2$ ) silica microparticles recorded in optical micrograph of (b) transmission mode (TM) and (c) emission mode (EM,  $\lambda = 488\text{ nm}$ ), Trajectory in red for  $\text{P-SiO}_2$  and green for  $\text{SiO}_2$ . (d) Cartoon of surface area,  $A$ , of  $\text{P-SiO}_2$  and  $\text{SiO}_2$  with displayed SEM images. Surfactant storage ability is bigger for  $\text{P-SiO}_2$  which yields under light illumination ( $\lambda = 488\text{ nm}$ ) into different motion velocity of (e)  $\text{P-SiO}_2$  against (f)  $\text{SiO}_2$ .

## References

- [1] N. Convery, N. Gadegaard, *Micro and Nano Engineering*, 2019, 2, 76.
- [2] P. Sajeesh, A. Kumar Sen, *Microfluid Nanofluid*, 2014, 17, 1.
- [3] M. Bekir, A. Sharma, M. Umlandt, N. Lomadze, S. Santer, *Advanced Materials Interfaces*, 2022, 2102395.

# Langmuir-Blodgett and LbL deposition of graphene based conductive semitransparent coatings

*Tamas Szabo*

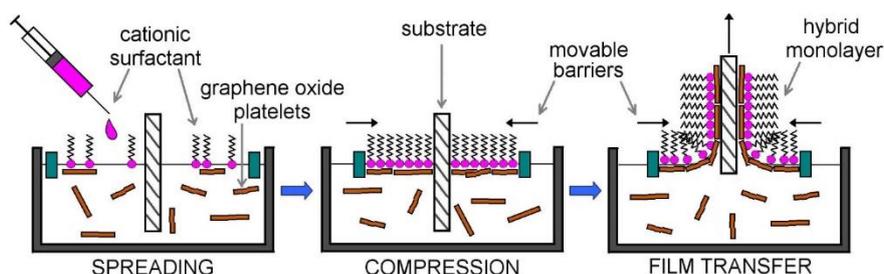
*Department of Physical Chemistry and Materials Science, University of Szeged,  
Hungary*

*Presenting author's e-mail: [sztamas@chem.u-szeged.hu](mailto:sztamas@chem.u-szeged.hu)*

One of the most promising applications of graphene relates to transparent conductive surfaces owing to its optical transparency, chemical stability, high conductivity and flexibility. The economical use of such graphene-based conductive coatings prompts development of techniques for the large-scale production of ultrathin graphene films.

This presentation will demonstrate that the colloid chemical methods of layer-by-layer self-assembly (LbL) and Langmuir-Blodgett (LB) afford uniform graphene films of reproducible thickness, high electric conductivity and transparency. Both methods developed involved the following steps: (i) strong oxidation of graphite to graphite oxide (GO), (ii) delamination of GO to single graphene oxide nanosheets in aqueous dispersion, (iii) deposition of such sheets on a solid substrate (either by LB or LbL), and (iv) transformation of insulating GO films to conductive graphene films by chemical reduction/calcination. For LbL, we have exploited the self-assembly between negatively charged GO sheets with a water-soluble cationic polyelectrolyte [1]. For LB, hybrid monolayers of GO and a cationic surfactant have been assembled at the air/water interface and this insoluble film was transferred to the substrate [2], according to Figure 1. Several deposition conditions were optimized to obtain films of the lowest possible roughness and highest surface coverage. The conductivities of transparency of the reduced assemblies were in the same range to those found by others for graphene-based large-area films [3].

**Keywords:** graphene, ultrathin films, self-assembly, transparent conductors



**Figure 1.** Scheme of the Langmuir-Blodgett deposition of hybrid graphene oxide monolayers.

**Acknowledgements:** The project no. 124851 has been implemented with the support provided from the National Research, Development, and Innovation Fund of Hungary (NKFIH), financed under the FK funding scheme. We also thank the support from the EU Horizon 2020 research and innovation programme and the NKFIH (project No. 2019-2.1.7-ERA-NET-2021-00029) for the Visegrad Group-Japan 2021 Joint programme. Support of the János Bolyai Research Scholarship from the Hungarian Academy of Sciences is also acknowledged.

## References

- [1] T. Szabó, Zs. Péter, E. Illés, L. Janovák and A. Talyzin, *Carbon*, 2017, 111, 350.
- [2] T. Szabó, V. Hornok, R.A. Schoonheydt and I. Dékány, *Carbon*, 2010, 48, 1676.
- [3] L.G. De Arco, Y. Zhang, C.W. Schlenker, K. Ryu et al., *ACS Nano*, 2010, 4, 2865.

# A microstructural investigation of an industrial attractive gel at pressure and temperature

*Andrew Clarke<sup>1</sup>, Elizabeth Jamie<sup>1</sup>,  
Nikolaos A. Burger<sup>2</sup>, Benoît Loppinet<sup>2</sup> and George Petekidis<sup>2</sup>*

<sup>1</sup>*Schlumberger Cambridge Research, UK*

<sup>2</sup>*Institute of Electronic Structure and Laser, Foundation for Research and Technology Hellas (FORTH), GR-70013 Heraklion, Crete, Greece*

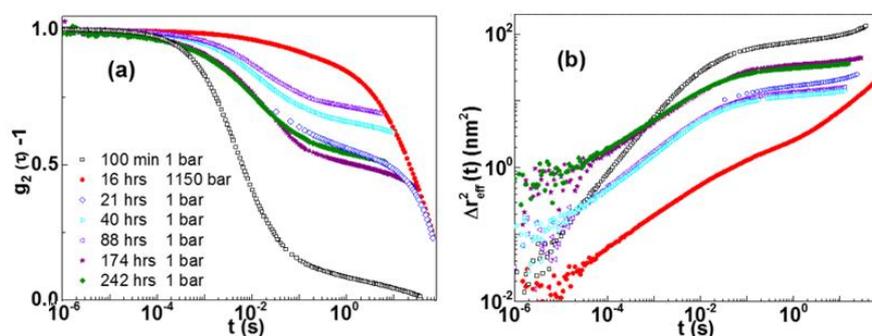
Presenting author's e-mail: [aclarke3@slb.com](mailto:aclarke3@slb.com)

Oil-continuous drilling fluids used in the oil and gas industry are formulated to be pseudoplastic with a relatively weak yield stress. They are complex colloidal systems comprising a brine-in-oil emulsion together with hydrophobically modified clay, surfactants in large excess and low concentrations of polymeric and other additives. These fluids are required to maintain their properties over wide temperature and pressure ranges, i.e. maintain a so-called “flat” rheology. Whereas flow curve information can be measured directly [1], there are few methods that can sensitively study the inherent structure and mechanical properties of the fluids, particularly in their gel state, under the extreme pressure and temperature conditions that a drilling fluid will experience in use [2].

Here we study a model oil-continuous drilling fluid formulation, comprising a colloidal gel network of hydrophobically modified clay particles and trapped emulsion droplets, as a function of both temperature (up to 153°C) and pressure (up to 1330 bar) with Diffusive Wave Spectroscopy (DWS). As a function of temperature, the system undergoes local structural changes reflected in the DWS dynamics which are consistent with macroscopic rheological measurements. On cycling to high pressure, the system exhibits similar structural and dynamic changes but together with a strong hysteresis, i.e. changes observed on increasing pressure are not recovered on removing the pressure.

Although multiple scattering in multicomponent non-ergodic samples does not directly yield self-diffusion probe dynamics, the use of micro-rheological analysis here appears to be in good agreement with direct rheological measurements of the sample linear viscoelasticity at ambient pressure. Thus, DWS microrheology successfully probes irreversible changes in the structure and the mechanical response of the drilling fluid formulation as it transitions a high-pressure cycle.

**Keywords:** gel, colloid, pressure, DWS



**Figure 1.** DWS correlation functions (a) and effective MSD (b) at  $T=25$  °C following high pressure application and release after ~14 hrs at 1150 bars. The time evolution upon return to 1 bar at times indicated in the legend.

**Acknowledgements:** The authors would like to thank EUSMI for supporting this work.

## References

- [1] O.H. Houwen, T. Geehan, Rheology of Oil-Base Muds, SPE Journal, 1986, SPE15416.  
[2] A. Clarke, E. Jamie, N.A. Burger, B.Loppinet, G. Petekidis, Soft Matter, submitted 2022

# Shaping alginate hydrogel and tuning its properties for the design of a tubular bioreactor

Jessica Kui<sup>1</sup>, Arslane Bouamama<sup>1</sup>, Jean Baudry<sup>1</sup> and Nicolas Bremond<sup>1</sup>

<sup>1</sup>Laboratoire Colloïdes et Matériaux Divisés, CBI, ESPCI Paris, Université PSL, Paris, France

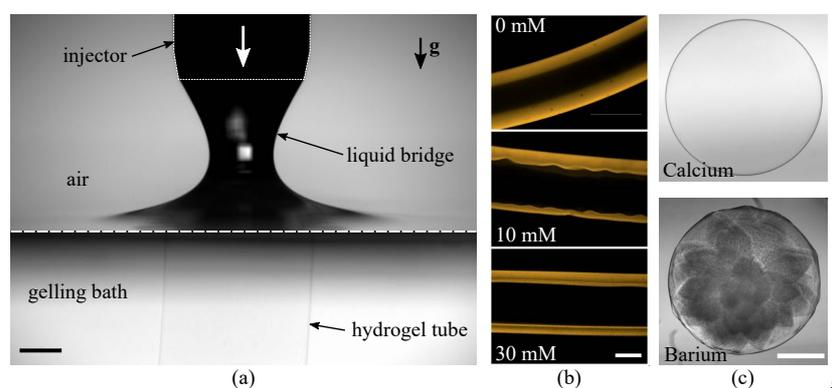
Presenting author's e-mail: [nicolas.bremond@espci.fr](mailto:nicolas.bremond@espci.fr)

Hollow microfibers, or microtubes, having a wall made of hydrogel that allows for solutes to diffuse in and out can act as bioreactors and thus find applications in cell biology [1]. The ability to create millimeter size hydrogel tubes facilitates their manipulation and connection to a perfusion system and thus widens the scope of their use.

Alginate, a natural polyelectrolyte that turns into gel in presence of divalent cations, is used to create the tube's membrane. The tube is formed by extruding the alginate solution at a moderate flow rate by placing a millimeter size injector at a few millimeters from the gelling bath (Fig. 1 a). This specific condition where liquid inertia is low and thus jet formation is not possible neither in air nor in the aqueous bath led to interesting phenomenon where gravity comes into play. The stability and shape of the liquid bridge connecting the injector and the bath is shown be a function of the distance between them, the liquid viscosities and surface tension and flow rates. It is also shown that the tube size is the result of a subtle interplay between the spreading of the viscous alginate solution at the free surface, the diffusion of cations that induce its sol-gel transition, the concomitant syneresis of the gel as well as the surface tension difference between the polymer solution and the gelling bath. In addition, the morphology of the inner surface of the hydrogel membrane can be tuned by adding divalent cations in the core solution (Fig. 1 b).

Due to the presence of various salts in a microbial culture medium that compete with the complex of alginate with divalent cations, an ionic switch strategy has been elaborated in order to create stable and transparent hydrogel tube shell that otherwise would either dissociate or be heterogeneous (Fig. 1 c).

**Keywords:** Iontropic hydrogel, sol-gel, syneresis, flow, diffusion, extrusion



**Figure 1.** (a) Process to make hydrogel tubes. (b) Confocal images of hydrogel tubes having different concentration of calcium in the core solution. (c) Alginate hydrogel beads made with calcium or barium. Scale bars are 1 mm.

## References

[1] Cheng, J., Jun, Y., Qin, J., & Lee, S. H. *Biomaterials*, 2017, **114**, 121-143.

# The role of polymer rheology modifiers in the assembly of drying binary colloidal dispersions

Timothy Murdoch<sup>1</sup>, Baptiste Quienne<sup>2</sup>, Edgar Espinosa<sup>3</sup>, Franck D'Agosto<sup>3</sup>, Muriel Lansalot<sup>3</sup>, Julien Pinaud<sup>2</sup>, Sylvain Caillol<sup>2</sup>, and Ignacio Martin-Fabiani<sup>1</sup>

<sup>1</sup>Department of Materials, Loughborough University, Loughborough, UK

<sup>2</sup>ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

<sup>3</sup> Université de Lyon, Université Lyon 1, CPE Lyon, CNRS UMR 5128, Laboratoire CP2M, Equipe PCM, Villeurbanne, France

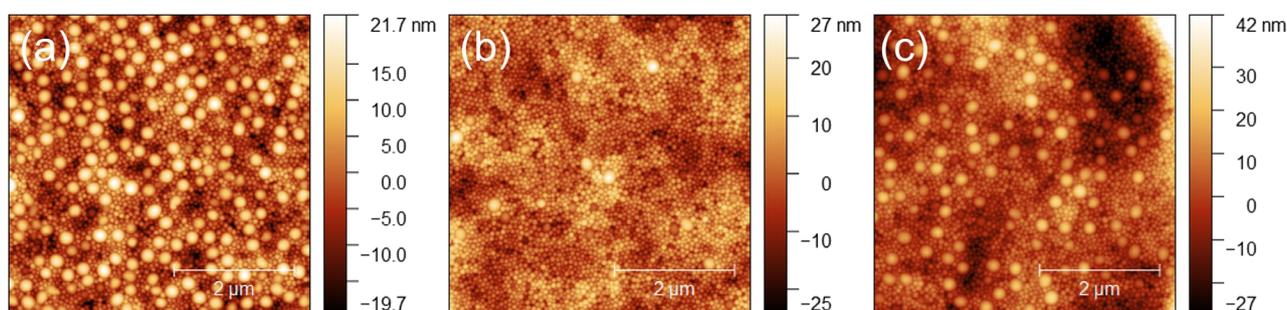
Presenting author's e-mail: [i.martin-fabiani@lboro.ac.uk](mailto:i.martin-fabiani@lboro.ac.uk)

Interest in the assembly of colloidal blends upon solvent evaporation has increased significantly in recent years. Since we reported the stratification effect which takes place in drying binary colloidal blends [1], resulting in small-on-top colloidal film structures, many experimental, modelling, and theoretical studies have been devoted to the subject [2,3]. However, most of these projects do not consider the presence of other species which are commonplace in colloidal formulations, such as rheology modifiers. The presence of these polymers might affect not only the viscosity of the water phase but also the interactions between dispersion components, potentially altering the final colloidal film architecture.

In this study, we investigate the effect of adding polymeric rheology modifiers in the assembly of drying binary colloidal blends. We demonstrate how the structure of the colloidal film obtained in the absence of these polymers (Figure 1a) can be tuned by their addition. The final film architecture is dependent on whether the rheology modifiers are associative (HEURs - Hydrophobically modified Ethoxylated Urethanes, Figure 1b) or non-associative, thickening the water phase (xanthan gum, Figure 1c). We utilize atomic force microscopy, rheology, dynamic light scattering, and solvent-relaxation NMR in a combined study to understand colloidal interactions and the mechanisms underpinning evaporation-induced assembly in these dispersions.

Our results advance the current knowledge on the assembly process of drying binary colloidal blends by studying the effects of added polymer rheology modifiers. The insights presented here will be not only valuable from a fundamental viewpoint, but also for harnessing colloidal assembly successfully in the vast range of industrial products which contain rheology modifiers.

**Keywords:** colloidal blends, stratification, colloidal assembly, polymers, rheology



**Figure 1.** Atomic force microscopy topography maps of the top surface of colloidal binary films assembled a) in the absence of rheology modifiers and in the presence of b) 0.1 wt.% HEUR, and 0.4 wt.% xanthan gum.

## References

- [1] A. Fortini, I. Martin-Fabiani *et al.* Physical Review Letters, 2016, 116, 229901.
- [2] J. Keddie and M. Schulz. Soft Matter, 2018, 14, 6181-6197
- [3] J. Tinkler *et al.*, Journal of Colloid and Interface Science, 2021, 581, 729-740.

# Organic Reactions and Radical Polymerizations in Surfactant-free, Mesostructured Liquids

Jonas Blahnik, Evamaria Hofmann, Werner Kunz

University of Regensburg, Institute of Physical and Theoretical Chemistry,  
Regensburg, Germany

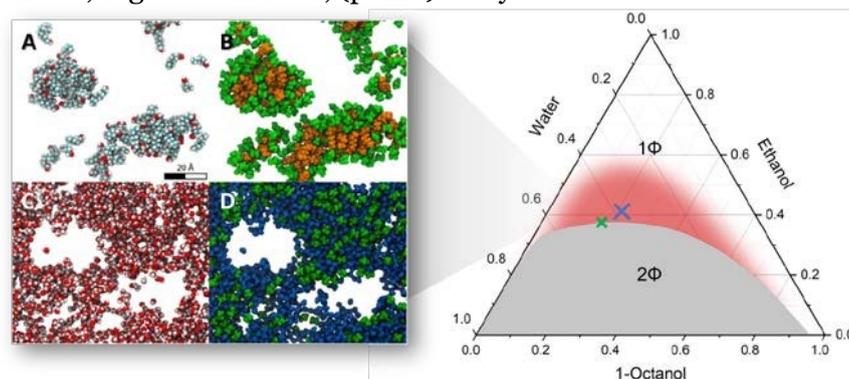
Presenting author's e-mail: [werner.kunz@ur.de](mailto:werner.kunz@ur.de)

Surfactant-free microemulsions (SFME) are ternary, mesostructured liquids consisting of an oil, water, and a hydrotrope. Even if their existence was postulated in the late 1970s, it took until the last two decades that SFMEs found their way to a broader public in the colloidal community. Nowadays, the effect is more or less investigated and understood. However, with the exception of enzymatic reactions, only a few examples for applications of SFME as a highly dynamic, mesostructured reaction medium are known. [1] We present a quite universal approach for free-radical polymerizations in SFME, as well as their use as reaction media for (photo)catalysis.

Microemulsions comprise an attractive environment for free-radical polymerizations with the possibility to tune the polymer size and morphology. However, surfactants or auxiliary colloids have an impact on the polymer properties (e.g. accelerating the release of plasticizers from a workpiece into the environment). We show simple systems consisting of water, an alcohol (propanol, tert-butyl alcohol) as hydrotrope, and vinylic monomers. By choosing the exact position in the phase diagram, which should be preferably in the pre-Ouzo region left-hand of the critical point, it is possible to affect the polymer morphology, yield, and mean molar mass [2].

In order to enable challenging organic reactions in aqueous solution, complex designer surfactants are often the method of choice. [3] Though, both their synthesis and their recycling are time- and material-consuming. Again, SFMEs represent a simple alternative as reaction media. Their dynamic structuring allows the replacement of the surfactant and their composition facilitates the recycling afterwards. In addition, we use the great solubilizing power of an SFME to dissolve otherwise poorly soluble substrates as well as an organic photocatalyst with promising redox potential. The reactions studied are relevant for both research and industrial applications.

**Keywords:** surfactant-free microemulsions, mesostructured aggregates, structured reaction media, polymerizations, organic reactions, (photo)catalysis



**Figure 1.** Snapshots from molecular dynamics (left side) and their location in a ternary phase diagram of the SFME composed of water, ethanol, and 1-octanol. [1]

**Acknowledgements:** E. Hofmann thanks the Fonds der chemischen Industrie (FCI) for her scholarship.

## References

- [1] J. Blahnik, E. Müller, L. Braun, P. Denk, and W. Kunz, *COCIS*, 2022, 57, 101535.
- [2] S. Krickl, J. Blahnik, W. Kunz, K. Schmid, EP patent application pending, 2020.
- [3] C. M. Gabriel, N. R. Lee, Fl Bigorne, P. Klumphu, M. Parmentier, F. Gallou, B. H. Lipshutz, *Org. Lett.*, 2017, 19, 1.

# Rheological properties of micellar solutions and bicontinuous micellar phases

*Gergana Radulova, Krassimir Danov, Teodora Stancheva*

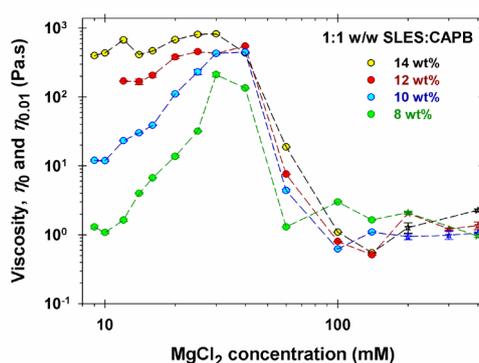
<sup>1</sup>*Department of Chemical and Pharmaceutical Engineering, Faculty of Chemistry and Pharmacy, Sofia University, Bulgaria*

Presenting author's e-mail: [gerganar@lcpe.uni-sofia.bg](mailto:gerganar@lcpe.uni-sofia.bg)

The phase separation of saturated micellar network can occur in mixed surfactant solutions (cationic and zwitterionic) in the presence of divalent counterions:  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$  [1]. In the presence of  $\text{Mg}^{2+}$ , a multiconnected micellar phase is formed that sediments and can be easily separated from the water phase. The rheological flow curves (apparent viscosity vs shear rate) show typical regions with Newtonian and shear-thinning behavior. The effects of wormlike micelles and bicontinuous micellar phases on the rheological properties are systematically studied for different (i) total concentration of surfactants, (ii) the amount of added electrolyte, and (iii) rheological regimes (oscillations at different frequencies and amplitude, shear rates and stresses, Maxwell type rheological experiments). The theoretical interpretation of the obtained rheological data shows:

- With the addition of  $\text{Mg}^{2+}$  (in the form of  $\text{MgCl}_2$  and  $\text{MgSO}_4$ ) to the surfactant mixtures, the apparent viscosity goes through a maximum. High enough concentration of added  $\text{Mg}^{2+}$  lead to the formation of bicontinuous phase;
- From the oscillatory experiments, the presence of wormlike micelles is proven;
- The deviations from the Cole-Cole plots can be used to distinguish the formation of wormlike micelles and bicontinuous micellar phases;
- The separated bicontinuous phases have significantly different rheological behavior – they exhibit Newtonian behavior up to higher shear rates with a pronounced yield stress and the values for the viscosity is independent of concentrations of the surfactant and added salt.

**Keywords:** multiconnected micellar phase, micelles with divalent ions, rheology of giant micelles, bicontinuous phases



**Figure 1.** Dependence of the viscosity of surfactant solutions (with different total surfactant concentration) at low shear rates as a function of the added amount of  $\text{MgCl}_2$ .

**Acknowledgements:** The authors gratefully acknowledge the financial support of the EXTREME project, funded by the Bulgarian Ministry of Education and Science, D01-76/30.03.2021 through the programme “European Scientific Networks”.

## References

[1] M. Georgiev, L. Aleksova, P. Kralchevsky, K. Danov, *Colloids Surf. A*, 2020, 607, 125487.

## Dynamic phase inversion as a tool to track the “optimal formulation” of microemulsions. Practical applications.

*Ontiveros Jesus F.<sup>1</sup>, Lemahieu Guillaume<sup>1</sup>, Molinier Valérie<sup>2</sup> and Aubry Jean-Marie<sup>1</sup>*

<sup>1</sup>Univ. Lille, CNRS, Unité de Catalyse et Chimie du Solide, Lille, France

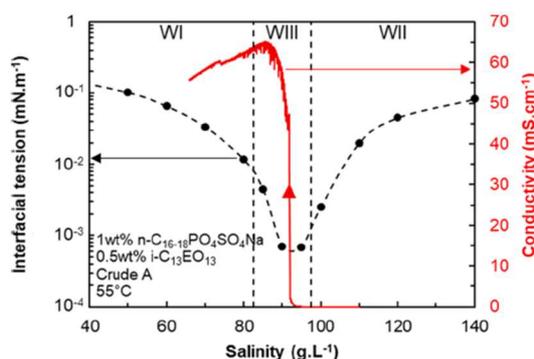
<sup>2</sup>Pôle d'Études et de Recherche de Lacq TotalEnergies Onetech, BP Lacq, France

Presenting author's e-mail: [jesus-fermin.ontiveros@centralelille.fr](mailto:jesus-fermin.ontiveros@centralelille.fr)

In chemical Enhanced Oil Recovery (EOR), surfactant mixtures must be optimized to obtain the so called “optimum formulation” characterized by a three-phase behaviour (WIII) and an ultra-low interfacial tension. To attain this condition, discontinuous formulation scans of Surfactant-Oil-Water (SOW) systems are usually performed until equilibrium. In this work, the conditions in which the dynamic transitional inversion of Surfactant/Oil/Water emulsions and equilibrium data of Surfactant/Oil/Water microemulsions matches are described, using both temperature or salinity as formulation variables.

The dynamic phase inversion temperature (PIT), initially described for systems based on ethoxylated non-ionic surfactants, proves to be relevant for systems based on typical EOR non-ionic/ionic surfactants mixtures and it allows determining the optimum formulation of crude oil based systems[1]. Dynamic salinity phase inversion (SPI) was used with well-defined surfactants and oils and, as the PIT, the inversion of emulsified systems is very close to the “optimum salinity” when the Water Oil Ratio is in the vicinity of 1. The SPI is used to track the “optimal formulation” using a mixture of an ionic EOR surfactant (sulfated propoxylated n-alcohol) and a nonionic co-surfactant (ethoxylated i-alcohol), with or without alkali and crude oil [2]. This continuous salinity scan of the stirred SOW system significantly accelerates the optimization of surfactant blends suitable for a given oil reservoir. The dynamic phase inversion also allows the determination of HLD parameters of a given surfactant in a faster and precise way.

**Keywords:** Microemulsion, Phase Inversion, Emulsion, HLD, Optimal formulation



**Figure 1.** Identification of “optimum salinity”  $S^*$  of a crude oil based SOW system by dynamic Salinity Phase Inversion monitored by conductimetry (red curve). Evolution of the W/O interfacial tension and limits of the WIII region.

### References

- [1] G. Lemahieu, J.F. Ontiveros, V. Molinier, J.-M. Aubry, Using the dynamic Phase Inversion Temperature (PIT) as a fast and effective method to track optimum formulation for Enhanced Oil Recovery, *J. Colloid Interface Sci.*, 2019, 557,746–756.
- [2] G. Lemahieu, J.F. Ontiveros, N. Terra Telles Souza, V. Molinier, J.-M. Aubry, Fast and accurate selection of surfactants for enhanced oil recovery by dynamic Salinity-Phase-Inversion (SPI), *Fuel*, 2021, 289, 119928.

**Thursday 8th September 2022**

**Design and Synthesis of Colloidal Systems and Nanoparticles**

# Polymerization-induced self-assembly and disassembly during the synthesis of thermoresponsive ABC triblock copolymer nano-objects in aqueous solution

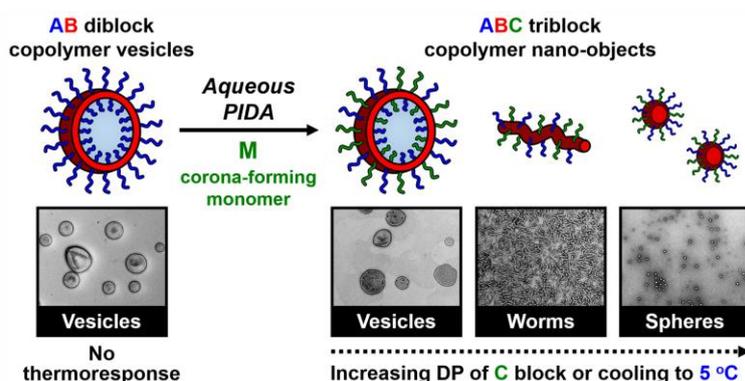
*Spyridon Varlas, Thomas J. Neal and Steven P. Armes*

*Department of Chemistry, University of Sheffield, Dainton Building, Brook Hill, Sheffield, UK*

Presenting author's e-mail: [s.varlas@sheffield.ac.uk](mailto:s.varlas@sheffield.ac.uk)

Aqueous polymerization-induced self-assembly (PISA) has been widely utilized as a powerful methodology for the preparation of various self-assembled nano-objects primarily from amphiphilic AB diblock copolymers. Moreover, it is well-studied that chain-extension of AB diblock copolymer vesicles using a range of *hydrophobic* monomers *via* seeded RAFT aqueous emulsion polymerization leads to formation of framboidal ABC triblock copolymer vesicles with adjustable surface roughness due to core-domain phase separation between immiscible blocks. However, the utilization of *hydrophilic* monomers for such syntheses has yet to be explored; this omission is addressed in the present study. Herein, poly(glycerol monomethacrylate)-*b*-poly(2-hydroxypropyl methacrylate) (G-H) diblock copolymer vesicles were used as seeds for the chain-extension of water-soluble oligo(ethylene glycol) methyl ether methacrylate (OEGMA) *via* RAFT aqueous dispersion polymerization. Interestingly, this led to polymerization-induced disassembly (PIDA), with the initial precursor vesicles being converted into lower-order jellyfish, worms or spheres depending on the targeted mean degree of polymerization (DP) for the corona-forming POEGMA block. Moreover, construction of a pseudo-phase diagram revealed an unexpected copolymer concentration dependence for this PIDA process. Previously, we have shown that the thermoresponsive behavior observed for PHPMA-based diblock copolymer nano-objects is only encountered over a relatively narrow range of compositions and DPs (see Warren *et al.*, *Macromolecules*, 2018, **51**, 8357–8371). However, introduction of the POEGMA block led to formation of thermoresponsive ABC triblock nano-objects even when the original G-H diblock copolymer vesicles proved to be thermally unresponsive (Figure 1). Thus, this versatile approach is expected to enable the rational design of new nano-objects with tunable composition, copolymer architectures and stimulus-responsive behavior.

**Keywords:** polymerization-induced self-assembly, block copolymers, thermoresponsive, vesicles



**Figure 1.** Schematic illustration for the preparation of ABC triblock copolymer nano-objects from AB diblock copolymer seed vesicles via aqueous polymerization-induced self-assembly (PIDA).

# Design of photosensitizer-based core-shell latex particles by PISA in alcoholic dispersion polymerization

*M. Ali Aboudzadeh, Mickaël LeBehec and Maud Save*

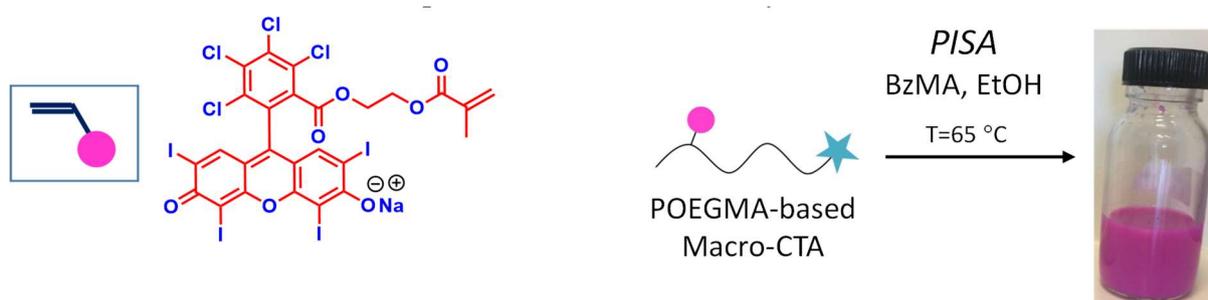
*Universite de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, Pau, France*

*Presenting author's e-mail: [m.aboudzadeh-barihi@univ-pau.fr](mailto:m.aboudzadeh-barihi@univ-pau.fr)*

Photosensitized  $^1\text{O}_2$  production has attracted much attention to produce intermediate chemicals of interest for the fine chemicals industry (*e.g.* photochemical production of Artemisinin as antimalaria intermediate), [1] photo-decontamination of air/water, [2] antimicrobial materials, [3] or photodynamic therapy (PDT). [4] Immobilization of photosensitizers on solid substrates improves their handling, recyclability, stability and facilitates purification steps to remove photocatalyst from reactants in fine chemistry. In this context, we previously described the synthesis of photosensitizing microgels [5] or film-forming latex particles [6] by polymerization in aqueous dispersed media. Due to solubility issues, relevant photo-oxygenation reactions of fine chemicals such as  $\alpha$ -terpinene or furfural have to be performed in organic solvents, among which alcohols are the less hazardous for any application. [7] To address these challenges, we describe here the synthesis of submicronic photosensitizing colloidal particles directly in alcoholic media by polymerization induced self-assembly (PISA) through implementation in dispersion process.

The commercially available Rose Bengal (RB) was selected as photosensitizer due to its high value of singlet oxygen quantum yield in ethanol ( $\Phi\Delta = 0.68-0.80$ ). [8] Then to covalently anchor RB photosensitizer, we synthesized a polymerizable methacrylate monomer that can be copolymerized with poly(ethylene glycol) methyl ether methacrylate (POEGMA) to functionalize the particle shell, while benzyl methacrylate (BzMA) was then polymerized by PISA to form the core-forming alcohol-insoluble block (Figure 1). The macromolecular features of polymers were characterized by SEC. The resulting diblock copolymer particles were analyzed by DLS and TEM and will further be assessed in terms of quantum yields of singlet oxygen production.

**Keywords:** polymerization induced self-assembly (PISA), Rose Bengal, singlet oxygen



**Figure 1.** left) Chemical structure of the synthesized RB-methacrylate based monomer (EMARB), right) synthetic strategy implemented to design shell-functionalized polymer colloids grafted by the RB organic photosensitizer.

**Acknowledgements:** European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 893426 is acknowledged.

## References

- [1] S. Triemer, K. Gilmore, P. H. Seeberger, A. Seidel-Morgenstern, *Angewandte Chemie*, 2018, 19, 5525.
- [2] M. L. Marin, L. Santos-Juanes, A. Arques, A. M. Amat and M. A. Miranda, *Chem. Rev.*, 2012, 112, 1710.
- [3] F. Vatansever, W. C. M. A. de Melo, P. Avci, D. Vecchio, M. Sadasivam, A. Gupta, R. Chandran, M. Karimi, N. A. Parizotto, R. Yin, G. P. Tegos and M. R. Hamblin, *Fems Microbiology Reviews*, 2013, 37, 955.
- [4] Z. Zhou, J. Song, L. Nie and X. Chen, *Chem. Soc. Rev.*, 2016, 45, 6597.
- [5] L. Petrizza, M. Le Behec, E. Decompte, H. El Hadri, S. Lacombe, M. Save, *Polym. Chem.*, 2019, 10, 3170.
- [6] C. Boussiron, M. Le Behec, J. Sabalot, S. Lacombe, M. Save, *Polym. Chem.*, 2021, 12, 134.
- [7] A. A. Ghogare, A. Greer, *Chem. Rev.*, 2016, 116, 9994.
- [8] F. Wilkinson, W. P. Helman, A. B. Ross, *J. Phys. Chem. Ref. Data*, 1993, 22, 113.

# Extrusion: A new method for rapid formulation of high-yield, monodisperse nanobubbles

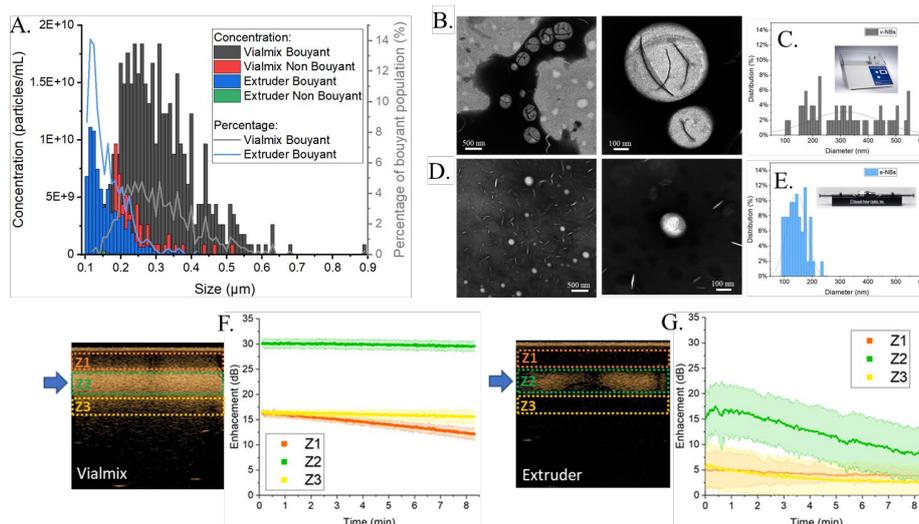
*Claire Council, Eric Abenojar, Reshani Perera, Agata A. Exner*

*Department of Radiology Case Western Reserve University, Cleveland, OH, USA*

*Presenting author's e-mail: [claire.council@case.edu](mailto:claire.council@case.edu)*

Nanobubbles (NBs) are sub-micron, shell-stabilized, gas core nanoparticles. For imaging and drug delivery, production of monodisperse, high-yield nanobubbles is desirable. Here, we present a highly efficient technique to produce NBs using a mini-extruder setup as an alternative technique to self-assembly via a conventional mechanical agitation process. C<sub>3</sub>F<sub>8</sub> gas NBs were produced from a cocktail of phospholipids dissolved in propylene glycol and hydrated in phosphate buffered saline, as previously described<sup>1</sup>. For extruder NBs (e-NBs), the phospholipid solution and C<sub>3</sub>F<sub>8</sub> gas, in each syringe were combined and then was directly extruded 30 times through a 0.8 μm membrane at 65°C, and rinsed by centrifugation followed by filtration (0.45 μm). e-NBs were compared to NBs formulated via mechanical agitation using a Vialmix (v-NBs). NB size and concentration were characterized by resonant mass measurement and transmission electron microscopy. For acoustic assessment, Pluronic NBs were imaged for 500s in an agarose phantom using a clinical US system in nonlinear imaging mode (12 MHz, MI: 0.1, 1 fps). The e-NBs produced are smaller (320 ± 100 nm vs 160 ± 50 nm) and more monodisperse than the v-NBs (Figure 1A-E). The extruder method resulted in a lower concentration compared to the Vialmix (6.2 ± 1.8 × 10<sup>10</sup> vs 3.2 ± 0.7 × 10<sup>11</sup>) (Figure 1A) at a higher volume (2.5 mL vs. 0.5 mL for v-NB). With regard to acoustic activity, v-NBs had a higher initial acoustic response, with 30 ± 1 dB compared to 17 ± 5 dB for e-NBs for focal region (Z2) (Figure 1F and G). e-NBs signal was higher in Z2, showing a stronger pressure-dependent acoustic response due to the higher monodispersity. Despite the faster signal decay under ultrasound exposure, the acoustic response of e-NBs is considerably more localized, which can have a strong appeal for precision diagnostic and theranostic applications.

**Keywords:** nanobubbles, extrusion, monodispersity, contrast-enhanced ultrasound



**Figure 1.** A. Buoyant and non-buoyant particle size and concentration distribution using resonant mass measurement (RMM). Transmission electron microscopy (TEM) images of (B) v-NBs and (D) e-NBs and distribution of size of (C) v-NBs and (E) e-NBs based on 50 particles. Contrast harmonic images (12 MHz, MI: 0.22) at  $t=0$  (left) and representation of the enhancement over 8 min (right) of v-NBs (F) and e-NBs (G).

## References

[1] A. De Leon et al. *Nanoscale*, 2019, 11,15647

# RAFT dispersion polymerization of methyl methacrylate in mineral oil

*Csilla György, Steven P. Armes*

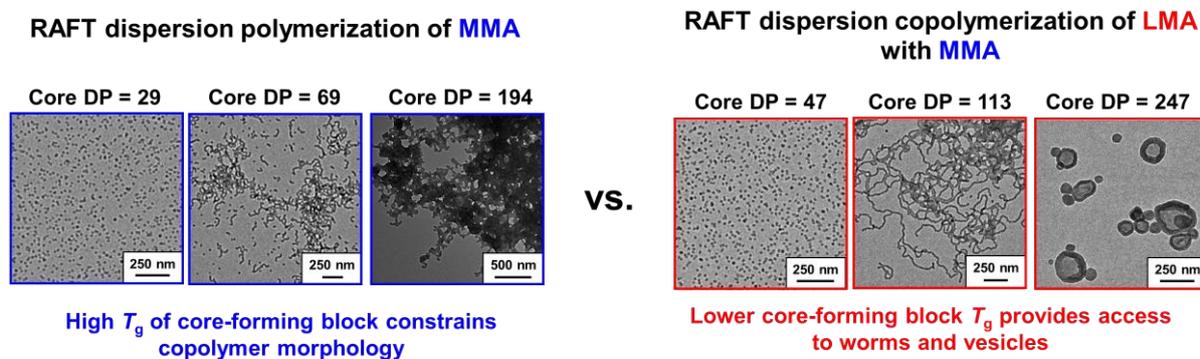
*Dainton Building, Department of Chemistry, University of Sheffield, Sheffield, U.K.*

Presenting author's e-mail: [cgyorgy1@sheffield.ac.uk](mailto:cgyorgy1@sheffield.ac.uk)

RAFT dispersion polymerization of a prototypical methacrylic monomer, methyl methacrylate (MMA), is performed in mineral oil using various poly(lauryl methacrylate) (PLMA) precursors prepared with a trithiocarbonate-based RAFT agent. The relatively high glass transition temperature ( $T_g$ ) of the corresponding core-forming PMMA block unexpectedly constrains the evolution in copolymer morphology during polymerization-induced self-assembly (PISA). More specifically, well-defined PLMA<sub>22</sub>-PMMA<sub>x</sub> spheres ( $x = 19-39$ ) and relatively short worms ( $x = 69-97$ ) can be obtained at 90 °C when using a PLMA<sub>22</sub> precursor but targeting higher  $x$  values ( $x \geq 108$ ) invariably leads to colloiddally unstable aggregates of spheres, rather than long worms or vesicles. Raising the PISA synthesis temperature from 90 to 115 °C (i.e., from below to above the  $T_g$  of the final PMMA block) does not alleviate this unexpected problem.

We demonstrate that this morphological limitation can be overcome by (i) incorporating 10 mol% LMA into the core-forming block and (ii) performing such syntheses at 115 °C. This new strategy produced well-defined spheres, worms or vesicles when using the same PLMA<sub>22</sub> precursor. Introducing the LMA comonomer not only enhances the mobility of the core-forming copolymer chains by increasing their solvent plasticization but also reduces their effective glass transition temperature to well below the reaction temperature. A reversible worm-to-sphere transition was observed for PLMA<sub>22</sub>-P(O.9MMA-*stat*-0.1LMA)<sub>113</sub> worms and a vesicle-to-worm transition for PLMA<sub>22</sub>-P(O.9MMA-*stat*-0.1LMA)<sub>228</sub> vesicles using dynamic light scattering and transmission electron microscopy.

**Keywords:** RAFT, PISA, nanoparticles, glass transition temperature



**Figure 1.** RAFT dispersion polymerization of MMA vs. RAFT dispersion copolymerization of LMA with MMA in mineral oil

# Mesoporous multicompartiment microparticles of semi-crystalline triblock terpolymers

*Nicole Janoszka<sup>1</sup>, Suna Azhdari<sup>1</sup>, Hui Chen<sup>1</sup>, Deniz Coban<sup>1</sup>, Holger Schmalz<sup>2</sup>, André H. Gröschel<sup>1</sup>*

<sup>1</sup> *Institute of Physical Chemistry, Center of Soft Nanoscience (SoN, and Center for Nanotechnology (CeNTech, University Muenster, Germany*

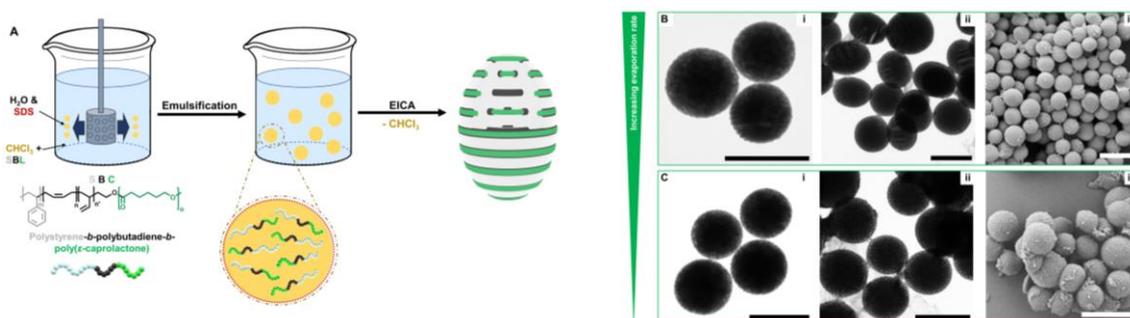
<sup>2</sup> *Macromolecular Chemistry II, and Bavarian Polymer Institute (BPI, University Bayreuth, Germany*

Presenting author's e-mail: [nicole.janoszka@uni-muenster.de](mailto:nicole.janoszka@uni-muenster.de)

Confinement assembly of block copolymers (BCPs) is a versatile way to design multicompartiment microparticles (MMs) with diverse internal structures. Until now, individual microdomains or compartments have not been utilized to create porosity for selective loading or removal despite of an explored range of MMs morphologies. Hence, generated porous MMs of ABC triblock terpolymers have promising applications in energy storage, catalysis, or nanomedicine [1]. A convenient strategy to fabricate mesoporous MMs is the selective removal of an individual microdomain.

In this work, we investigate the formation of MMs from semicrystalline polystyrene-*block*-polybutadiene-*block*-poly(*L*-lactide) (PS-*b*-PB-*b*-PLLA; SBL) or polystyrene-*block*-polybutadiene-*block*-poly( $\epsilon$ -caprolactone) (PS-*b*-PB-*b*-PCL; SBC) through evaporation-induced confinement assembly (EICA) as well as the generation of mesoporous SBL and SBC MMs by degradation of the semi-crystalline PLLA or PCL microdomain, respectively. For that, we first used a *Shirasu Porous Glass* (SPG) membrane to prepare emulsion droplets with a homogeneous size (shown in Figure 1 A). After emulsification and EICA process, we gained MMs predominantly with an inner structure of hexagonally packed core-shell cylinders consisting of a PLLA or PCL core, a PB shell, and a PS matrix. For the SBL MMs, increasing crystallinity has an influence on the inner morphology [2]. Degradation of the SBL MMs selectively removed the PLLA microdomain forming mesoporous SBL MMs with defined surface roughness [2]. Interestingly, the SBC MMs exhibit a transition from perforated into gyrodial structure when increasing the evaporation rate (see Figure 1 B and C). We foresee that mesoporous MMs will serve as platform for catalytic or nanomedical applications as the PB microdomain can be postmodified with various functionalities in a straightforward manner, e.g., click chemistry.

**Keywords:** 3D confinement, ABC triblock terpolymer, degradation, emulsification, microparticles



**Figure 1. Generation of mesoporous SBC-28 MMs.** (A) Scheme of preparation of SBC MMs via SPG membrane and EICA process. TEM (scale bar: 1000 nm) and SEM (scale bar: 2000 nm) data of SBC-28 MMs ( $d_{\text{pore}} = 2.0 \mu\text{m}$ ) at evaporation rates of  $8.6 \text{ cm}^2$  (B) and  $39.6 \text{ cm}^2$  (C) before (i) and after hydrolysis (ii) and (iii).

## References

- [1] C. K. Wong, X. Qiang, A.H.E. Müller, A. H. Gröschel, *Prog. Polym. Sci.*, 2020, 102, 101211  
[2] N. Janoszka, S. Azhdari, C. Hils, D. Coban, H. Schmalz, A.H. Gröschel, *Polymers*, 2021, 13, 4358

# Monte Carlo simulation of the microstructure of bio- versus petroleum-based (meth)acrylates synthesized by emulsion polymerization

*Shaghayegh Hamzehlou, Aitor Barquero, Jose Ramon Leiza*

*POLYMAT, Kimika Aplikatua saila, Kimika Fakultatea, Universidad del País Vasco/Euskal Herriko Unibertsitatea UPV/EHU, Donostia, Spain*

Presenting author's e-mail: [shaghayegh.hamzehlou@ehu.eus](mailto:shaghayegh.hamzehlou@ehu.eus)

In the recent years due to environmental concerns, both government regulations and consumer opinion has led to the development of polymers with a greener origin. In this context, the use of environmentally friendly processes such as emulsion polymerization and the development of new bio-sourced (or bio-based) building blocks has attracted a lot of attention. The bio-sourced monomers are mainly plant oils, carbohydrates, terpenes and lignin derivatives. Although there are industrially available bio-sourced monomers, the kinetics, microstructure and final performance of these monomers in different polymerization processes has not been studied widely.

2-Octyl acrylate and 2-octyl methacrylate are two bio-sourced (meth)acrylic monomers which are structural isomers of the 2-ethylhexyl acrylate and 2-ethylhexyl methacrylate and therefore are good candidates to replace them. 2-Octyl acrylate has successfully been used to develop waterborne adhesives and coatings, however significant difference in the microstructure of the polymer has been reported such as gel content, molar mass distribution and branching density<sup>1,2</sup>.

In this work a Monte Carlo model was used to study the kinetics and microstructure of the bio- versus petroleum-based C8 alkyl chain (meth)acrylate polymers synthesized by seeded emulsion polymerization. The model predicts detail microstructure of bio- and petroleum-based polymers such as the entire molar mass distribution (soluble and gel fraction), crosslinking and branching density as well as concentration of long and short chain branches. The model has been assessed by experimental data gathered on kinetics, branching density and molar mass distribution measured by Asymmetric-Flow Field-Flow Fractionation (AF4)<sup>2</sup>. Monte Carlo simulations were used to shed light on the mechanisms that yield notable differences in the microstructures of the oil and bio-based monomers.

**Keywords:** Bio-sourced (meth)acrylates , Monte Carlo simulation, Emulsion polymerization, Polymer microstructure

## References

- (1) Badia, A.; Movellan, J.; Barandiaran, M. J.; Leiza, J. R. s . *Ind. Eng. Chem. Res.* **2018**, 57 (43), 14509–14516.
- (2) Barrenetxe M.; Agirre A.; Santos J. I.; Badía A.; Leiza J. R.; Barquero A. *Macromol. React. Eng.* 2022,submitted.

**Friday 9th September 2022**

**Colloids in Biomaterials and Biomedical Applications**

# Colloids and interfaces: the missing link in understanding how advanced oral formulations improve drug absorption

*Zahari Vinarov, Slavka Tcholakova, Nikolai Denkov*

*Department of Chemical and Pharmaceutical Engineering,  
Faculty of Chemistry and Pharmacy, Sofia University, Sofia, Bulgaria*

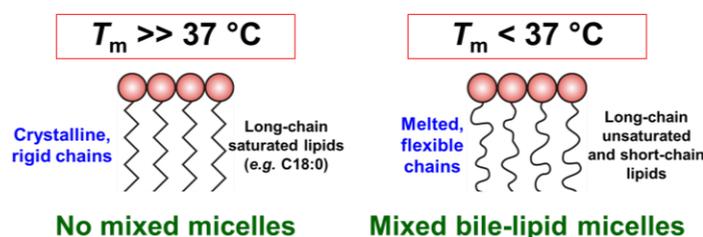
Presenting author's e-mail: [zv@lcpe.uni-sofia.bg](mailto:zv@lcpe.uni-sofia.bg)

Although oral formulations remain the first choice for drug delivery, the low aqueous solubility of the new chemical entities emerging from the drug discovery pipelines poses a significant challenge in drug development [1]. This presentation will summarize the recent progress in the physicochemical analysis of complex oral drug formulations developed to improve the oral absorption of poorly water-soluble drugs.

Lipid-based formulations are a mixture of digestible oils, surfactants (that can exceed 50 wt% of the formulation) and solvents [2]. The mechanisms of improved oral absorption include the formation of a crude emulsion, a nano- or a microemulsion in the gastrointestinal tract, followed by drug partitioning in micelles, vesicles or transient liquid-crystalline phases. However, the rapid drug release from some formulations can result in supersaturated drug solutions and precipitation, depending on the solubilization capacity of the intestinal colloids [3]. The influence of polar lipids on the solubilization capacity was found to depend on their propensity to form mixed aggregates with intestinal bile salts/phospholipids, which correlated well with the acyl chain melting point [4].

Polymer-based amorphous solid dispersions are designed to promote quick drug release and formation of supersaturated drug solutions in the intestinal fluids, which leads to liquid-liquid phase separation [5]. In some cases, drug-rich nanodroplets/nanoparticles with unexpected stability are formed, which are believed to play a role in enhancing the drug oral bioavailability. Recent progress on the impact of polymer structure and intestinal colloids on the properties of these nanoaggregates will be presented.

## Molecular mechanisms of lipid-bile salt aggregation



**Figure 1.** Physicochemical factors controlling mixed micelle formation in intestinal fluids

**Keywords:** intestinal colloids, mixed micelles, drug solubilization, oral absorption

**Acknowledgements:** The financial support of National Research Program “VIHREN” of the Bulgarian National Science Fund, project 3D-GUT (no. KP-06-DV-3/15.12.2021) is acknowledged.

## References

- [1] Z. Vinarov, B. Abrahamsson, ..., C. Wilson, P. Augustijns, *Adv. Drug. Deliv. Rev.* 2021, 171
- [2] B. Boyd, C. Bergström, Z. Vinarov, ..., A. Bauer-Brandl, V. Jannin, *Eur. J. Pharm. Sci.* 2019, 137
- [3] V. Katev, S. Tsibranska-Gyoreva, Z. Vinarov, S. Tcholakova, *Pharmaceutics*, 2021, 13
- [4] V. Katev, Z. Vinarov, S. Tcholakova, *Eur. J. Pharm. Sci.* 2021, 159, 105733
- [5] R. Ricarte, N. Zee, Z. Li, L. Johnson, T. Lodge, M. Hillmyer, *Mol. Pharmaceutics* 2019, 16, 4089

# Genetic or Chemical Conjugation Influences the Nanomechanics of Virus-Like Particle (VLP) Vaccines

*Milad Radiom<sup>1,2</sup>, Yagmur Turgay<sup>1</sup>, Swapan Preet<sup>1</sup>, Tim Keys<sup>1</sup>, Raffaele Mezzenga<sup>2</sup>, Emma Slack<sup>1</sup>*

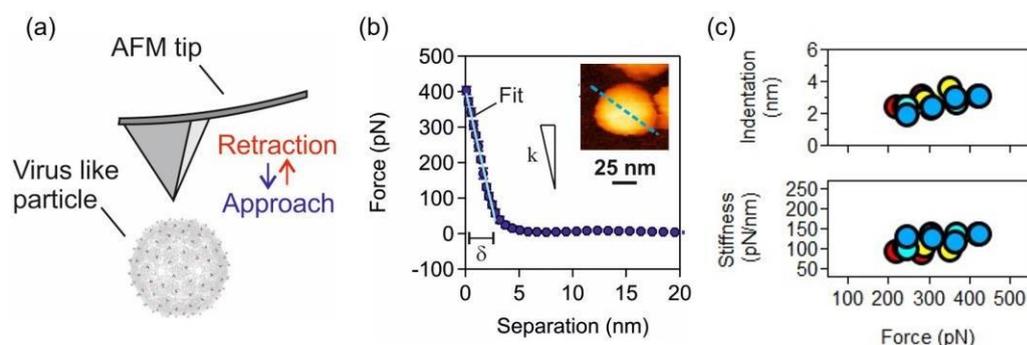
<sup>1</sup>Laboratory of Food Immunology, Institute of Food, Nutrition and Health, ETH Zürich, Zürich, Switzerland

<sup>2</sup>Laboratory of Food and Soft Materials, Institute of Food, Nutrition and Health, ETH Zürich, Zürich, Switzerland

[milad.radiom@hest.ethz.ch](mailto:milad.radiom@hest.ethz.ch)

Due to the inherent advantages of virus-like particles (VLPs) over attenuated bacteria (including size, non-infectious nature, and versatility of chemical and biosynthetic conjugation [1]), there is tendency to develop the new generation of mucosal vaccines using VLP technology. Among the design parameters for an optimal vaccine, biophysical properties are essential. To this end, we investigate the nanomechanical properties of several VLP vaccines based on *Acinetobacter* phage coat protein (AP205) using atomic force microscopy (AFM). The stiffness of AP205 VLP is justifiably interpreted in terms of standard linear solid model over a strain rate range 10–10000 (1/s). At the highest strain rate, AP205 VLP has a stiffness  $k \cong 95$  pN/nm which from the relation  $E \sim Dk/h^2$  gives an elastic modulus  $E \sim 0.27$  GPa and where the shell thickness  $h = 3.0$  nm is obtained from small angle x-ray scattering. VLP stiffness is reduced to 35 pN/nm when amine-reactive polyethylene oxide polymers are conjugated, but no significant change to the size is observed. Biosynthetic conjugation of peptides (here, antigens from SARS CoV-2 spike protein) is more complex: addition of a 36-amino acid (aa) peptide (plus 3-aa His-tag linker) is found to increase the diameter by about 5 nm, but this leads to no significant increase of the stiffness ( $k \cong 100$  pN/nm). When the peptide is repeated one more time (resulting in 72-aa) the diameter increases by an additional 5 nm, and in this case, a significant rise in stiffness is observed ( $k \cong 146$  pN/nm). Our results show that conjugation of bio-functional moieties, including non-immunogenic polymers and antigenic peptides, to scaffold VLP can induce an appreciable change to its biophysical properties including size and stiffness. It is expected that these properties influence the VLP vaccine efficacy on mucosal surfaces for vaccination.

**Keywords:** Virus-like particle; Mucosal vaccine; Biophysical property; Atomic force microscopy



**Figure 1.** (a) Schematic of AFM investigation of VLPs at single particle level. (b) Evaluation of shape and force response of VLPs. Indentation ( $\delta$ ) and stiffness ( $k$ ) are calculated from the linear part of the force curve. (c) Indentation and stiffness for several AP205 VLPs in 200–400 force range.

## References

[1] H. Tariq, S. Batool, S. Asif, M. Ali, and B.H. Abbasi, *Frontiers in Microbiology*, 2022, 12.

## Effect of red blood cell shape changes on haemoglobin interactions and dynamics: a neutron scattering study

Keyun Shou<sup>1,2,3</sup>, Mona Sarter<sup>1,6,7</sup>, Nicolas R. de Souza<sup>3</sup>, Liliana de Campo<sup>3</sup>, Andrew E. Whitten<sup>3</sup>, Philip Kuchel<sup>8</sup>, Christopher J. Garvey<sup>3,4,5</sup>, Andreas M. Stadler<sup>1,2</sup>

<sup>1</sup>JCNS-1/ IBI-8, Forschungszentrum Jülich, Jülich, Germany

<sup>2</sup>Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany

<sup>3</sup>ANSTO, Lucas Heights, New South Wales, Australia

<sup>4</sup>Faculty of Health and Society, Malmö University, Malmö, Sweden

<sup>5</sup>Lund Institute for Advanced Neutron and X-ray Science, Lund, Sweden

<sup>6</sup>I. Physikalisches Institut, AG Biophysik, RWTH Aachen, Aachen, Germany

<sup>7</sup>Current address: Rutherford Appleton Laboratory, Oxon, UK

<sup>8</sup>School of Life and Environmental Sciences, University of Sydney, Sydney, Australia.

Presenting author's e-mail: [a.stadler@fz-juelich.de](mailto:a.stadler@fz-juelich.de)

By using a combination of experimental neutron scattering techniques, it is possible to obtain a statistical perspective on red blood cell (RBC) shape in suspensions, and the inter-relationship with protein interactions and dynamics inside the confinement of the cell membrane. In this study [1], we examined the ultrastructure of RBC and protein-protein interactions of haemoglobin (Hb) in them using ultra-small-angle neutron scattering (USANS) and small-angle neutron scattering (SANS). In addition, we used the neutron backscattering method to access Hb motion on the ns time scale and Å length scale. Quasielastic neutron scattering (QENS) experiments were performed to measure diffusive motion of Hb in RBCs and in an RBC lysate. By using QENS, we probed both internal Hb dynamics as well as global protein diffusion, on the accessible time scale and length scale by QENS. Shape changes of RBCs and variation of intracellular Hb concentration were induced by addition of the Na<sup>+</sup>-selective ionophore monensin and the K<sup>+</sup>-selective one, valinomycin. The experimental SANS and QENS results are discussed within the framework of crowded protein solutions, where free motion of Hb is obstructed by mutual interactions.

**Acknowledgements:** We thank ANSTO for provision of neutron beam time. The work was supported by a DFG grant STA 1325/2-1 to AMS. MS acknowledges the support of the International Helmholtz Research School of Biophysics and Soft Matter (BioSoft).

**Keywords:** quasi-elastic neutron scattering, red blood cells, protein diffusion, small-angle neutron scattering, protein interactions, haemoglobin

**References:**[1] Shou et al. 2020 Effect of red blood cell shape changes on haemoglobin interactions and dynamics: a neutron scattering study. R. Soc. Open Sci. 7: 201507. <http://dx.doi.org/10.1098/rsos.201507>

## Adsorption kinetics of neurotrophins on polyelectrolyte multilayers- the impact of films on neuroblastoma cell viability

*Aneta Michna<sup>1</sup>, Monika Wasilewska<sup>1</sup>, Maria Dąbkowska<sup>2</sup>, Wiktoria Donerowicz<sup>2</sup>, and Bogusław Kowalski<sup>2</sup>*

<sup>1</sup> Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland

<sup>2</sup> Independent Pharmacokinetics and Clinical Pharmacy Laboratory, Pomeranian Medical University, Szczecin

Presenting author's e-mail: [aneta.michna@ikifp.edu.pl](mailto:aneta.michna@ikifp.edu.pl)

Brain-derived growth factor (BDNF) molecules, belonging to the neurotrophins family, are involved in neuronal growth and memory formation and are also targets for neurodegenerative disease therapy. Adsorption kinetics of BDNF molecules on polyelectrolyte multilayers and the BDNF layer stability were studied using streaming potential measurements (SPM), optical waveguide lightmode spectroscopy (OWLS), and atomic force microscopy (AFM).

Poly(diallyldimethylammonium chloride) (PDADMAC), of a cationic type, and heparin (HEP), of an anionic type, were used for the polyelectrolyte multilayer formation. In the first stage, bulk characteristics of the polyelectrolytes were determined by measuring diffusion coefficients and electrophoretic mobilities for various pHs. These data allowed a proper interpretation of the multilayer formation from low polyelectrolyte concentrations equal to 5 mg L<sup>-1</sup>. Periodic variations in the apparent zeta potential between positive and negative values of the layers were observed. The stabilities of the films against time (reaching 24 h) were determined using the SPM and OWLS. The performed experiments confirm the successful formation of the multilayers from low polyelectrolyte concentration on silica.

Then, SPM and OWLS were applied to determine the adsorption kinetics and the stability of BDNF -covered polyelectrolyte multilayers for defined ionic strength and pH. It was found that BDNF molecules effectively adsorb on HEP-terminated multilayers. The films, obtained in this way, were stable for at least 24 h.

The utility of the BDNF modified polyelectrolyte multilayers in human neuroblastoma SH-SY5Y cells was studied. Their effect on protein releasing profile, cell viability, mitochondrial membrane potential, and cell phenotype was determined *in vitro*. The data obtained from the sandwich ELISA assay, fluorescence spectroscopy (e.g., alamarBlue cell viability, JC-1 mitochondrial membrane potential tests), and fluorescent microscopy revealed that the cell viabilities significantly decrease when attached to the films. It is concluded that the PDADMAC/HEP multilayers can be considered versatile systems for medical applications.

**Keywords:** polyelectrolyte multilayers, poly(diallyldimethylammonium chloride), heparin, brain-derived growth factor, neurotrophins, adsorption

**Acknowledgements:** This work was financially supported by the National Science Centre, Poland, Opus Project, 2018/31/B/ST8/03277.

## Assessing suspension and infectivity times of virus-loaded aerosols involved in airborne transmission

*Kevin Roger, Tania Merhi, Omer Atasi, Clémence Coetsier and Benjamin Lalanne*

*Toulouse Chemical Engineering laboratory, CNRS, INPT, UPS*

Presenting author's e-mail: [kevin.roger@cnrs.fr](mailto:kevin.roger@cnrs.fr)

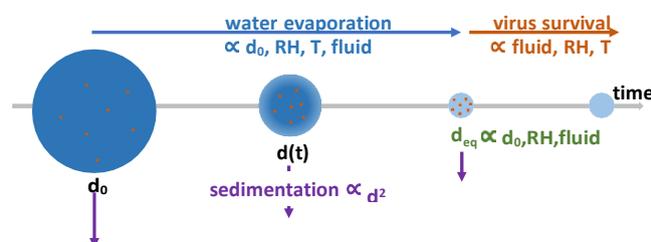
Airborne transmission occurs through droplet-mediated transport of viruses following the expulsion of an aerosol by an infected host. Transmission efficiency results from the interplay of droplet suspension time in the air, controlled by the coupling between water evaporation and droplet sedimentation, and virus survival in the drying droplet (Fig. 1). Furthermore, droplets are made of a respiratory fluid and thus display a complex composition consisting of water and non-volatile solutes.

Here, we quantify the impact of this complex composition on the different phenomena underlying transmission. Solute leads to a non-ideal thermodynamic behavior, which sets an equilibrium droplet size that is independent of relative humidity. In contrast, solutes do not significantly hinder transport due to their low initial concentration. Realistic suspension times are computed and increase with increasing relative humidity or decreasing temperature. By uncoupling drying and suspended stages, we observe that model enveloped viruses may remain infectious for hours in dried droplets. However, their infectivity decreases with increasing relative humidity or temperature after dozens of minutes.

Examining expelled droplet size distributions in the light of these results leads to distinguishing two aerosols. The first aerosol contains 0-40 micron-sized droplets, which corresponds to the majority in droplet number and remains suspended for hours. Its transmission efficiency is tuned by decreasing infectivity through increasing humidity and temperature. The second aerosol of 40-100 micron-sized droplets only remains suspended for minutes, but represents a much higher volume and thus viral load. Its transmission efficiency is tuned by decreasing suspension time through increasing humidity and decreasing temperature.

Overall, we have developed a general, quantitative and transdisciplinary methodology to approach the multi-scale problem of airborne transmission. The resulting knowledge will allow to rationally design mitigation strategies for the future.

**Keywords:** Aerosol, Evaporation, Virus, Infectivity, Saliva



**Figure 1. Phenomena involved in airborne transmission.** Droplet evaporation is a key step of airborne transmission and depends on initial droplet size, environmental conditions such as temperature and relative humidity, but also on fluid composition. The presence of non-volatile solutes in respiratory fluid droplets notably sets an equilibrium size and can also impact drying kinetics. Droplet sedimentation, which determines the aerosol suspension time, is thus directly impacted by the evaporation of this complex fluid. Furthermore, viruses' environment changes during drying, which can impact their survival.

**References:** [1] T. Merhi, O. Atasi, C. Coetsier, B. Lalanne and K. Roger\*, submitted to *PNAS*

# Dynamic Janus emulsions as foodborne bacteria sensors targeting bacterial exoenzyme production

*Agata W. Baryzewska*<sup>1</sup>, *Bradley D. Frank*<sup>1</sup>, *Christian Roth*<sup>2,3</sup>, *Peter H. Seeberger*<sup>2,3</sup>, *Markus Antonietti*<sup>1</sup>, *Lukas Zeininger*<sup>1</sup>

<sup>1</sup>*Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany*

<sup>2</sup>*Department of Biomolecular Systems, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany*

<sup>3</sup>*Institute of Chemistry and Biochemistry, Freie Universität Berlin, Berlin, Germany*

Presenting author's e-mail: [agata.baryzewska@mpikg.mpg.de](mailto:agata.baryzewska@mpikg.mpg.de)

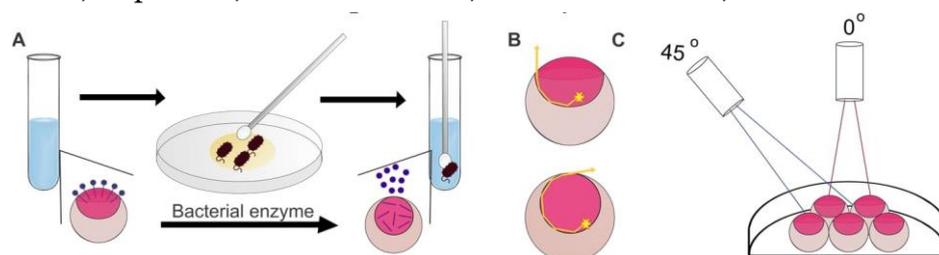
Given the predominance and threat posed by foodborne pathogens, there is a high demand for fast, sensitive, on-site detection methods, which often consist of a recognition element and a transduction element. Janus emulsions provide such output via dynamic morphological changes as a response to minute alterations in their environment and in the balance of interfacial tensions [1].

We targeted three key exoenzymes: C-8 esterase,  $\beta$ -glucosidase, and  $\beta$ -galactosidase typical for *Salmonella enterica*, *Listeria monocytogenes*, and *Escherichia coli*, respectively. To this end, we designed enzyme-cleavable surfactants, which congregate preferably at the oil-water interface, lowering the respective interfacial tension. Upon enzymatic cleavage of the surfactant, loss in the surfactant's amphiphilicity leads to an alteration of the interfacial tension at the respective interface, followed by an immediate morphological response. Morphology changes were examined using a custom-designed side-view microscope and a state-of-the-art optical setup. Our optical readout takes advantage of morphology-dependent angular light emission by placing perylene dye in the higher refractive index phase of the droplet. The scheme provides a ratiometric readout dependent only on droplet morphology rather than their size or polydispersity.

Our Janus emulsion sensor enabled extremely low detection limits for investigated foodborne bacteria, namely 10 CFU/mL within 2 hours for *Salmonella enterica* and 10<sup>3</sup> cells/mL for *Escherichia coli* and *Listeria monocytogenes*. Each of the designed enzyme-cleavable surfactants exhibited high specificity only towards its target enzyme. Additionally, we performed a series of swab tests using our detection scheme to prove its potential as an on-site aid. Our system produced a definitive response already after 2 hours, even for highly dilute bacterial samples.

Integration of enzyme-cleavable surfactants with dynamic Janus emulsions, a state-of-the-art optical readout method, and a swab test, shows high promise for dynamic Janus emulsions as future sensors of major foodborne pathogens.

**Keywords:** Janus, responsive, double-emulsion, bacteria-detection,



**Fig. 1** A) Droplet morphology change induced by enzymatic cleavage as a detection aid for swab tests. B) Morphology-dependent total internal reflection pathways in Janus droplets. C) Our state-of-the-art optical ratiometric readout.

## References

[1] Zeininger, L. *et al.* *ACS Cent. Sci.* 5, 789-795 (2019)

**Friday 9th September 2022**

**Design and Synthesis of Colloidal Systems and Nanoparticles**

## Persistent nucleation and size dependent attachment kinetics produce monodisperse PbS nanocrystals

*Benjamin Abécassis<sup>1</sup>, Matthew W. Greenberg<sup>2</sup>, Vivekananda Bal<sup>3</sup>, Brandon M. McMurtry<sup>2</sup>, Michael P. Campos<sup>2</sup>, Lilian Guillemeney<sup>1</sup>, Benoit Mahler<sup>4</sup>, Sylvain Prevost<sup>5</sup>, Lewis Sharpnack<sup>6</sup>, Mark P. Hendricks<sup>2</sup>, Daniel DeRosha<sup>2</sup>, Ellie Bennett<sup>2</sup>, Natalie Saenz<sup>2</sup>, Baron Peters<sup>3</sup> and Jonathan S. Owen<sup>2</sup>*

<sup>1</sup> *Laboratoire de Chimie, ENS de Lyon, Lyon, France*

<sup>2</sup> *Department of Chemistry, Columbia University, New York, USA*

<sup>3</sup> *Department of Chemical Engineering, University of Illinois, Urbana-Champaign, Illinois, USA*

<sup>4</sup> *Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, Villeurbanne, France*

<sup>5</sup> *Institut Laue-Langevin, 38042 Grenoble, France*

<sup>6</sup> *Department of Earth Science, University of California, Santa Barbara, USA*

Presenting author's e-mail: [Benjamin.abecassis@ens-lyon.fr](mailto:Benjamin.abecassis@ens-lyon.fr)

Modern syntheses of colloidal nanocrystals yield extraordinarily narrow size distributions that are believed to result from a rapid “burst of nucleation” (La Mer, *JACS*, 1950, **72**(11), 4847–4854) followed by diffusion limited growth and size distribution focusing (Reiss, *J. Chem. Phys.*, 1951, **19**, 482). Using a combination of *in situ* X-ray scattering, optical absorption, and <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy, we monitor the kinetics of PbS solute generation, nucleation, and crystal growth from three thiourea precursors whose conversion reactivity spans a 2-fold range. In all three cases, nucleation is found to be slow and continues during >50% of the precipitation. A population balance model based on a size dependent growth law (1/*r*) fits the data with a single growth rate constant (*k<sub>G</sub>*) across all three precursors. However, the magnitude of the *k<sub>G</sub>* and the lack of solvent viscosity dependence indicates that the rate limiting step is not diffusion from solution to the nanoparticle surface. Several surface reaction limited mechanisms and a ligand penetration model that fits data our experiments using a single fit parameter are proposed to explain the results [1,2]

**Keywords:** nanoparticles, nucleation and growth, time-resolved SAXS, synchrotron

### References

- [1] B. Abécassis et al, *Chemical Science*, 2022, advance article, [10.1039/d1sc06134h](https://doi.org/10.1039/d1sc06134h)  
 [2] Campos et al, *Chemical Science*, 2022, advance article, [10.1039/d1sc06098h](https://doi.org/10.1039/d1sc06098h)

## Multi-functional patchy SiO<sub>2</sub> particles: Fabrication via microcontact printing and directed self-assembly

*Martin Reifarth<sup>1</sup>, Pinar Akarsu<sup>1</sup>, Richard Grobe<sup>1</sup>, Matthias Hartlieb<sup>1</sup>, Marcel Sperling<sup>2</sup> and Alexander Böker<sup>1,2</sup>*

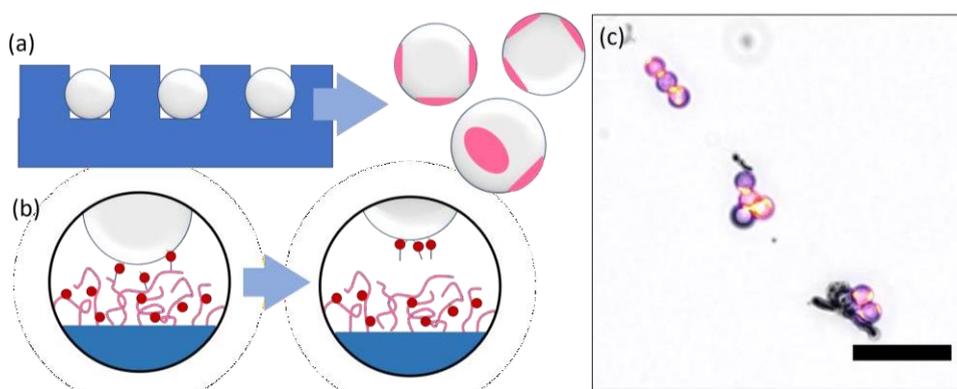
<sup>1</sup>University of Potsdam, Institute of Chemistry, Potsdam

<sup>2</sup>Fraunhofer Institute for Applied Polymer Research, Potsdam

Presenting author's e-mail: [reifarth@uni-potsdam.de](mailto:reifarth@uni-potsdam.de)

We demonstrate a method to introduce multiple locally precise enthalpic patches to spherical silicon dioxide (SiO<sub>2</sub>) microspheres. The protocol relies on a solid-phase microcontact printing ( $\mu$ CP) routine, which involves polymer-brush modified polydimethylsiloxane (PDMS) elastomers used as stamps. During the routine, highly functional trialkoxysilanes are transferred from the stamp-bound polymer brushes to the particle surface exclusively at their contact faces, enabling the precise transfer of the functionalization agent rather than its uncontrolled distribution over the entire particle area.<sup>[1]</sup> Due to the defined chemical functionalities of the patches, they can be addressed with a manifold follow-up chemistry. As this routine allows the surface modification of particles with the target molecules by keeping the current topography of the aforementioned substrate substantially constant, we anticipate that the advances might stimulate further interest in the anisotropically functionalized particles in the field of directing self-assembly of patchy particles system.<sup>[2,3]</sup>

**Keywords:** Patchy Particles, Self-assembly, Silane chemistry



**Figure 1.** Microcontact printing routine for the fabrication of patchy particles. (a) Particles are aligned in the stamp confinement. (b) Microcontact printing routine. The functionalization agent, bound to a polymer matrix attached to the stamp, is transferred to the particle faces during the printing process. (c) Corresponding results. The micrograph shows an overlay of a light transmission and a fluorescence images. Scale bars: 20  $\mu$ m.

**Acknowledgements:** We thank the European Research Council and the German Research Council for financial support.

### References:

- [1] P. Akarsu, R. Grobe, J. Nowaczyk, M. Hartlieb, S. Reinicke, A. Böker, M. Sperling, M. Reifarth, *ACS Appl. Polym. Mater.* **2021**, *3*, 2420.
- [2] Z.-W. Li, Y.-W. Sun, Y.-H. Wang, Y.-L. Zhu, Z.-Y. Lu, Z.-Y. Sun, *Nanoscale* **2020**, *12*, 4544.
- [3] A. Walther, A. H. E. Müller, *Chem. Rev.* **2013**, *113*, 5194.

## Development of double hydrophilic block copolymer/porphyrin ion complex micelles towards photofunctional nanoparticles

*Maria Karayianni, Dimitra Koufi and Stergios Pispas*

*Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece*

Presenting author's e-mail: [mkaragia@eie.gr](mailto:mkaragia@eie.gr)

Photoactive compounds such as porphyrins have been extensively used in photodynamic therapy, which emerged as a modern approach in the treatment of several types of cancers as well as non-oncological diseases [1]. At the same time, recent nanotechnological progress has been successfully incorporated in various medical applications thus leading to an increased interest for nanomedicine platforms. In this respect, synthetic block copolymers offer great potential to be utilized as tunable, versatile, responsive materials for the development of advanced nanocarriers that enable precise drug delivery and enhance therapeutic function and efficacy [2, 3].

In this work we report on the electrostatic complexation between double hydrophilic block copolymers and a model porphyrin towards the development of polyion complex micelles (PICs) that can be utilized as photosensitive porphyrin loaded nanoparticles. Specifically, we employed the poly(2-(dimethylamino) ethyl methacrylate)-*b*-poly[(oligo ethylene glycol) methyl ether methacrylate] (PDMAEMA-*b*-POEGMA) diblock copolymer, along with its quaternized polyelectrolyte copolymer counterpart (QPDMAEMA-*b*-POEGMA) and 5,10,15,20-tetraphenyl-21H,23H-porphine-*p,p',p'',p'''*-tetrasulfonic acid tetrasodium hydrate (TPPS) porphyrin. The (Q)PDMAEMA blocks enable electrostatic binding with TPPS thus forming the micellar core, while the POEGMA blocks act as the corona of the micelles and impart solubility, biocompatibility and stealth properties to the formed nanoparticles. Different mixing charge ratios were examined aiming to produce stable nanocarriers. The mass, size, size distribution and effective charge of the resulting nanoparticles, as well as their response to changes in their environment (i.e., pH, ionic strength, temperature) were investigated by dynamic and electrophoretic light scattering (DLS and ELS). Moreover, the photophysical properties of the complexed porphyrin along with further structural insight were obtained through UV-Vis and fluorescence spectroscopy measurements.

Overall, the produced porphyrin loaded nanoparticles show great potential to be used as active hybrid polymer/porphyrin photosensitizers relevant to therapeutic applications.

**Keywords:** double hydrophilic block copolymers, porphyrins, polyion complex micelles, photosensitizers

### References

- [1] S. Kwiatkowski, B. Knap, D. Przystupski, J. Saczko, E. Kędzińska, K. Knap-Czop, J. Kotlińska, O. Michel, K. Kotowski and J. Kulbacka, *Biomed. Pharmacother.*, 2018, 106, 1098-1107.
- [2] M. Qindeel, S. Sargazi, S. M. Hosseinikhah, A. Rahdar, M. Barani, V. K. Thakur, S. Pandey, R. Mirsafaei, *ChemistrySelect*, 2021, 6, 14082-14099.
- [3] M. Dickerson and Y. Bae, *Ther. Deliv.*, 2013, 4, 1431-1441.

# Fluorescent Molecularly Imprinted Polymer Particles for Direct Detection of Glyphosate in Organic Solvents and Water

*Kornelia Gawlitza, Martha Kimani, Evgeniia Kislenko, and Knut Rurack*

*Chemical and Optical Sensing Division (1.9), Bundesanstalt für Materialforschung und -prüfung, Germany*

Presenting author's e-mail: [kornelia.gawlitza@bam.de](mailto:kornelia.gawlitza@bam.de)

Glyphosate (GPS) is the most widely used pesticide in the world [1] whose use increased dramatically after the introduction of genetically modified crops engineered to resist its herbicidal action during application [1,2]. In recent years, there have been growing concerns over its toxicity following its classification by the International Agency for Research on Cancer (IARC) as a probable carcinogen [3] as well as reports of its ecotoxicological effects [4,5]. This resulted in increased efforts to develop quick and sensitive detection methods.

In this work, molecular imprinting was combined with direct fluorescence detection of GPS by improving its solubility in organic solvents using tetrabutylammonium (TBA<sup>+</sup>) and tetrahexylammonium (THA<sup>+</sup>) as counterions. To achieve fluorescence detection, a fluorescent crosslinker containing urea binding motifs was used as a probe for GPS-TBA and GPS-THA salts in chloroform, generating stable complexes through hydrogen bond formation. The GPS/fluorescent dye complexes were imprinted into 2–3 nm molecularly imprinted polymer (MIP) shells on the surface of sub-micron silica particles. Thus, the MIP binding behavior could be easily evaluated by fluorescence titrations in suspension to monitor the spectral changes upon addition of the GPS analytes. While MIPs prepared with GPS-TBA and GPS-THA both displayed satisfactory imprinting following titration with the corresponding analytes in chloroform, GPS-THA MIPs displayed better selectivity against competing molecules. Moreover, the THA<sup>+</sup> counterion was found to be a more powerful phase transfer agent than TBA<sup>+</sup>, enabling the direct fluorescence detection and quantification of GPS in water in a biphasic assay. A limit of detection of 1.45 μM and a linear range of 5–55 μM, which matches well with WHO guidelines for the acceptable daily intake of GPS in water (5.32 μM), have been obtained. The assay can be further optimized to allow miniaturization into microfluidic devices and shows potential for on-field applications by untrained personnel.

**Keywords:** Glyphosate; Molecular Imprinting; Core-Shell Particles; Fluorescent Urea Receptors

## References

- [1] M.-P. Hébert, V. Fugère and A. Gonzalez, *Front Ecol Environ*, 2019, 17, 48.
- [2] C. M. Benbrook, *Environ Sci Eur*, 2016, 28, 3.
- [3] J. V. Tarazona, D. Court-Marques, M. Tiramani, H. Reich, R. Pfeil, F. Istace and F. Crivellente, *Arch Toxicol*, 2017, 91, 2723.
- [4] E. V. S. Motta, K. Raymann, and N. A. Moran, *Proc Natl Acad Sci USA*, 2018, 115, 10305.
- [5] S. Iori, G. Dalla Rovere, L. Ezzat, M. Smits, S. S. Ferraresso, M. Babbucci, M. G. Marin, L. Masiero, J. Fabrello, E. Garro, L. Carraro, B. Cardazzo, T. Patarnello, V. Matozzo, L. Bargelloni and M. Milan, *Environ Res*, 2020, 182, 108984.

## Sequential adsorption of charged nanoobjects as a method of functionalization of drug delivery systems

Marta Szczęch<sup>1</sup>, Tomasz Kruk<sup>1</sup>, Alicja Hinz<sup>2</sup>, Natalia Łopuszyńska<sup>3</sup>, Krzysztof Jasiński<sup>3</sup>,  
Władysław P Węglarz<sup>3</sup>, Monika Bzowska<sup>2</sup>, Krzysztof Szczepanowicz<sup>1</sup>

<sup>1</sup> Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Kraków,  
Poland

<sup>2</sup> Department of Cell Biochemistry, Faculty of Biochemistry, Biophysics and  
Biotechnology, Jagiellonian University, Kraków, Poland

<sup>3</sup> Institute of Nuclear Physics, Polish Academy of Sciences, Kraków, Poland

Presenting author's e-mail: [krzysztof.szczepanowicz@ikifp.edu.pl](mailto:krzysztof.szczepanowicz@ikifp.edu.pl)

One of the first concepts of drug targeting was suggested by Paul Erlich a century ago. The hypothetical 'magic bullet' consisting of two principal components was proposed. The first component should recognize the target and bind to it, the second should perform therapeutic action. Polymeric nanocarriers (nanocapsules or nanoparticles) are promising candidates for use as a therapeutic part of the 'magic bullet' due to their potential to localize (or be targeted) in a specific manner to the site of disease and reduce or eliminate the possible side effects. Generally targeting can be broadly classified into three regimes; passive, active, and physical. In order to prepare targeted polymeric nanocarriers, the proper surface modification should be performed. The sequential adsorption of oppositely charged nanoobjects (layer by layer (LbL) method) is a powerful approach for the fabrication of multifunctional coatings. The advantages of the LbL method are the ease of manipulation and the multifunctionality that comes from the possibility of modification of the multilayer shell by organic molecules, inorganic nanoparticles, carbon nanotubes, antibodies, lipids, or nanoparticles. That multifunctionality can be utilized for the preparation of targeted drug delivery systems. The polymeric nanocarriers were prepared using a method proposed earlier [1-2]. The nanocores (actives loaded oil nanodroplets or polymeric nanoparticles) were prepared by the self-emulsification method and self-emulsification solvent evaporation method respectively. Furthermore, polymeric nanocores were functionalized by layer by layer method in order to achieve targeted drug delivery systems. The polymeric nanocores with an average size of 80-100 nm were stabilized by an AOT/Polycation surface complex. Such nanocores were encapsulated with multilayer shells formed with biocompatible polyelectrolytes (poly-L-lysine hydrobromide PLL (MW 15000-30000), poly-L-glutamic acid sodium salt PGA (MW 15000-50000)). They were further modified for passive targeting by pegylation (adsorption of pegylated polyelectrolyte PGA-g-PEG as an external layer), for active targeting by immobilization of selected antibodies, whereas for magnetic targeting by iron oxide nanoparticles incorporation into a multilayered shell. The polymeric nanocarriers were also tested as a theranostic system i.e. the MRI detectable drug delivery system. The developed systems may be considered as promising platforms for future nanomedicine.

**Keywords:** nanomedicine, nanoparticles, drug targeting, layer by layer, theranostics

**Acknowledgements:** This research was funded by the National Polish Centre, Poland, grant number 2020/39/B/NZ7/01913 and by the statutory research fund of ICSC PAS.

### References

- [1] K. Szczepanowicz, D. Dronka-Góra, G. Para, P. Warszyński, Journal of microencapsulation 27, 198-204.  
[2] M. Szczęch, K. Szczepanowicz, Nanomaterials 10 (3), 496

## Polymerization-Induced Electrostatic Self-Assembly

*Fabian Sobotta<sup>1</sup>, Théo Merland<sup>1</sup>, Chendan Li<sup>1,2</sup>, Jose R. Magana<sup>1,3</sup>, Bas G.P. van Ravensteijn<sup>1,4</sup>, Ilja Voets<sup>1</sup>*

<sup>1</sup>*Self-Organizing Soft Matter Lab, Eindhoven University of Technology, The Netherlands*

<sup>2</sup>*State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai, China*

<sup>3</sup>*Grup d'Enginyeria de Materials, Universitat Ramon Llull, Barcelona, Spain*

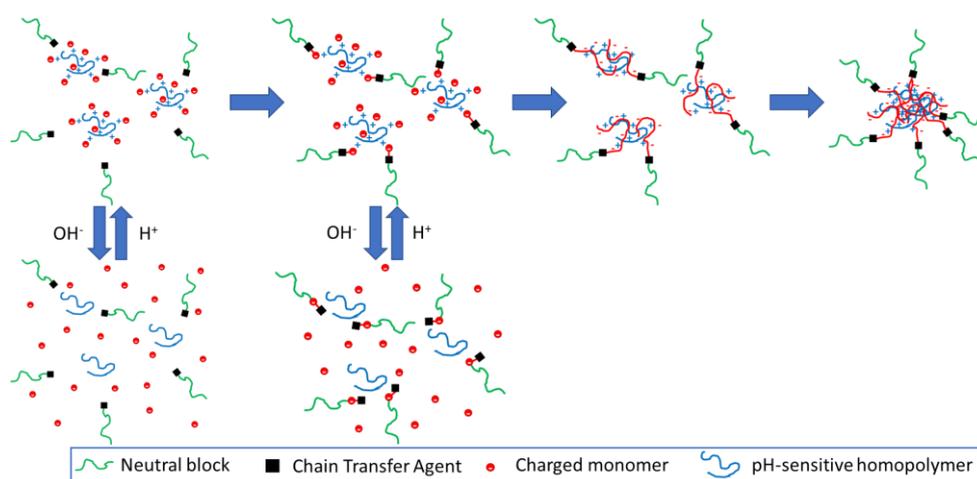
<sup>4</sup>*Utrecht Institute for Pharmaceutical Sciences, Utrecht University, The Netherlands*

Presenting author's e-mail: [t.a.merland@tue.nl](mailto:t.a.merland@tue.nl)

Mixing two polyelectrolytes with opposite charges in water leads to the formation of a complex named coacervate when it is liquid-like in nature. This complexation-induced phase separation can be stabilized by attaching a neutral hydrophilic block to at least one of the two polyelectrolytes. The neutral block forms a shell around the coacervate to stabilize it, leading to a micelle-like structure.

These co-assemblies are referred to as Polyion Complex (PIC) micelles or complex coacervate core micelles (C3Ms). Amongst others, they are used as non-viral gene vectors and for enzyme encapsulation. Similar to amphiphilic systems, the morphology and size of PIC micelles can be tuned by adjusting the neutral/charged block length ratio in the block copolymer. In many cases, out-of-equilibrium structures are formed at low salt concentrations due to strong electrostatic interactions. Consequently, the outcome of the co-assembly process strongly depends on the mixing process.

In this context, Polymerization-Induced Electrostatic Self-Assembly (PIESA) was recently developed to produce co-assemblies during synthesis.[1,2] During PIEASA, a charged monomer is polymerized from a (neutral) macro-chain transfer agent using RAFT polymerization in the presence of an oppositely charged homopolymer. The latter acts as a template as charged monomers bind to it. It is possible to carry out polymerization under dilute conditions, because of a significant increase in the local monomer concentration surrounding the homopolymer. When the template is a weak acid or base, the final co-assemblies can thus be tailored by the ionization degree of the template.



**Figure 1.** Polymerization-Induced Electrostatic Self-Assembly.

**Keywords:** Complex coacervate core micelles, polyelectrolytes, co-assembly, light scattering.

### References

- [1] Yu, Q., Ding, Y., Cao, H., Lu, X., and Cai, Y., ACS Macro Letters, 2015, 4, 1293.  
 [2] Sproncken, C.C.M., Magana, J.R., and Voets, I.K., ACS Macro Letters, 2021, 10, 167.

**Friday 9th September 2022**

**Active and Bioinspired Colloidal Systems**

# Understanding Enhanced Rotational Dynamics of Active Probes in Rod Suspensions

Meike Bos<sup>1</sup>, Narinder Narinder<sup>2</sup>, Clara Abaurrea-Velasco<sup>1</sup>,  
Clemens Bechinger<sup>2</sup>, and Joost de Graaf<sup>f</sup>

<sup>1</sup>Institute for Theoretical Physics, Center for Extreme Matter and Emergent Phenomena,  
Utrecht University, Utrecht, The Netherlands

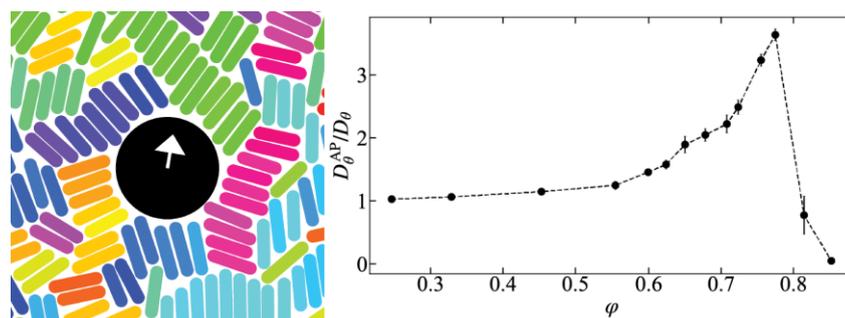
<sup>2</sup>Fachbereich Physik, Universität Konstanz, Konstanz, Germany

Presenting author's e-mail: [j.degraaf@uu.nl](mailto:j.degraaf@uu.nl)

Synthetic active particles (APs) have received considerable interest for biomedical applications and as model systems for non-equilibrium dynamics. However, because an AP's motion strongly depends on the properties of the surrounding liquid, it can additionally serve as a microrheological probe for the properties of the surrounding medium [1,2]. APs in Newtonian media have been studied in great detail, but much less is known when these particles move in complex fluids. Such a fluid's nonlinear rheological properties can lead to a drastically enhanced rotational diffusion (ERD) coefficient [1-3].

In this oral presentation, we study the motion of an AP in a polydisperse quasi-two-dimensional suspension of colloidal rods, see Fig. 1 for a simulation snapshot. Compared to previous studies [1,2], wherein we embedded APs in a spherical colloid suspension, the use of rods allows us to unlock a new mode of fast, local structural dynamics. This dynamics enabled a comprehensive understanding of the mechanism underlying ERD. Combining simulations and experiment, we conclude that minute microstructural fluctuations of rods in near contact with the AP, together with the probe's active motion, generate a fluctuating torque on the AP eventually leading to ERD. These fluctuations can be connected to a local stress relaxation, which may be used in the continuum formalism that was proposed [1,3,4] to capture ERD. Our work thus unifies the previously disjoint continuum and particle-based descriptions for this phenomenon. Beyond the rheological characterization abilities of APs, our findings are important to understand the dynamics of microorganisms in their natural (typically viscoelastic) habitat.

**Keywords:** active, self-propelled, viscoelastic, rheology



**Figure 1.** (left) Snapshot of an active probe in our simulation study. The colors indicate rod orientation. (right) The associated ERD as a function of rod area fraction.

## References

- [1] C. Lozano et al., Nat. Mater., 2019, 18, 1118.
- [2] C. Abaurrea-Velasco et al., Phys. Rev. Lett. 125, 2020, 258002.
- [3] J.R. Gomez-Solano et al., Phys. Rev. Lett. 2016, 116, 138301.
- [4] N. Narinder et al., Phys. Rev. Lett. 2018, 121, 078003.

## Controlling the structure, phase behaviour and dynamics of soft colloids by active interaction switching

Michael Bley<sup>1</sup>, Pablo I. Hurtado<sup>2,3</sup>, Joachim Dzubiella<sup>1</sup>, and Arturo Moncho Jordá<sup>3,4</sup>

<sup>1</sup> *Physikalisches Institut, Albert-Ludwigs-Universität Freiburg, Freiburg, Germany.*

<sup>2</sup> *Departamento de Electromagnetismo y Física de la Materia, Universidad de Granada, Granada, Spain.*

<sup>3</sup> *Institute Carlos I for Theoretical and Computational Physics, Universidad de Granada, Granada, Spain.*

<sup>4</sup> *Departamento de Física Aplicada, Universidad de Granada, Granada, Spain.*

Presenting author's e-mail: [moncho@ugr.es](mailto:moncho@ugr.es)

We explore the microstructure and phase behavior of a nonequilibrium system comprised by soft colloids that can actively switch their interactions between two states at a predefined kinetic rate. For this purpose, we employ a Reactive Dynamical Density Functional Theory (R-DDFT) and reactive Brownian-Dynamics simulations (R-BD). We find that the switching rate interpolates between a near-equilibrium binary mixture at low rates and a nonequilibrium monodisperse liquid for large rates, strongly affecting the one-body density profiles, adsorption, and pressure at confining walls. Importantly, we show that sufficiently fast switching impedes the phase separation of an (in equilibrium) unstable liquid, allowing the control of the degree of mixing and condensation and local microstructuring in a cellular confinement by tuning the switching rate [1, 2].

Switching activity also modifies the dynamics and diffusion coefficients of the individual particles, leading to a crossover from short to long times, with a regime for intermediate times showing anomalous diffusion [3]. The corresponding self-intermediate scattering function shows the two-step relaxation patterns typically observed in soft materials with heterogeneous dynamics such as glasses and gels. R-DDFT results are in excellent agreement with R-BD simulations and the analytical predictions of a phenomenological Continuous Time Random theory, thus confirming that R-DDFT constitutes a powerful method to investigate not only the structure and phase behavior, but also the dynamical properties of non-equilibrium active switching colloidal suspensions.

**Keywords:** active colloids, switching, dynamics, structure, phase behavior

**Acknowledgements:** We thank the Junta de Andalucía and European Regional Development Fund – Consejera de Conocimiento, Investigación y Universidad (Projects PY20-00241 and A-FQM-90-UGR20).

### References

- [1] A. Moncho-Jordá and J. Dzubiella, *Phys. Rev. Lett.*, 2020, 125, 078001.
- [2] M. Bley, J. Dzubiella and A. Moncho-Jordá, *Soft Matter*, 2021, 17, 7682.
- [3] M. Bley, P.I. Hurtado, J. Dzubiella and A. Moncho-Jordá, *Soft Matter*, 2022, 18, 397.

# Can activity in a 3D dense suspension of Quincke rotors cause thickening or dethickening?

*Edward Yong Xi Ong<sup>1</sup>, Anna Barth<sup>2</sup>, and Itai Cohen<sup>2</sup>*

<sup>1</sup> *Department of Applied Engineering and Physics, Cornell University, New York, USA*

<sup>2</sup> *Department of Physics, Cornell University, New York, USA*

*Presenting author's e-mail: [eo263@cornell.edu](mailto:eo263@cornell.edu)*

We describe our experimental findings on the ability of Quincke rotors to tune shear thickening and jamming of suspensions in 3D. Suspensions of Quincke rotors exhibit many interesting features including swarming [1], motility-induced phase separation [2-3] and chaotic dynamics [4-5]. Previous experimental investigations into how these features affect the suspension rheology revealed interesting rheological signatures such as shear thinning and negative apparent viscosities [6-7] despite accessing only a limited volume fraction of rotors ( $\phi V < 0.2$ ). Here we investigate the structure and rheology of Quincke rotors in the dense regime, where passive particles exhibit shear thickening, jamming, and yielding behavior. We propose to tune the rheology of this active dense system by carefully tuning the applied electric field, and hence the activity, for different volume fractions of rotors.

We carry out our investigations on an active suspension consisting of polyethylene particles suspended in an electrically insulating and density-matched fluid medium. These particles exhibit a range of interesting behavior dependent on the particle volume fraction and the applied electric field, ranging from classic Quincke rotation to the formation of large vortices and clusters of similar sizes and inter-cluster spacing. We first categorized and quantified the behavior of the suspension at different volume fractions and electric field strength in the absence of shear under a microscope. Using an electrorheological device, we then investigated how the shear thickening rheology of the suspension is affected as the activity of the system is varied. The addition of activity to the parameter space governing the transition between the thickened, jammed and yielding state would provide an extremely powerful and convenient tuning mechanism to rapidly modify the shear behavior of the suspension on the go.

**Keywords:** Active matter, Quincke rotors, Rheology, Dense suspensions, Field-driven

**Acknowledgements:** Agency for Science, Technology, and Research (A\*STAR Singapore) and the National Science Foundation (NSF) for funding. Anton Paar VIP program for assistance and use of the MCR-702 rheometer.

## References

- [1] Hamid Karani, Gerardo E. Pradillo, and Petia M. Vlahovska, *Physical Review Letters*, 2019, 123(20):208002
- [2] Geyer D, Martin D, Tailleur J, Bartolo D, *Physical Review X*, 2019, 9(3):031043.
- [3] Bricard A, Caussin JB, Desreumaux N, Dauchot O, Bartolo D, *Nature*, 2013, 503(7474):95-8.
- [4] Lemaire E, Lobry L, *Physica A: Statistical Mechanics and its Applications*, 2002, 314(1-4):663-71.
- [5] Peters F, Lobry L, Lemaire E., *Chaos: An Interdisciplinary Journal of Nonlinear Science*, 2005, 15(1):013102.
- [6] Pannacci N, Lemaire E, Lobry L, *Rheologica acta*, 2007, 46(7):899-904.
- [7] Lemaire E, Lobry L, Pannacci N, Peters F, *Journal of rheology*, 2008, 52(3):769-83.

# Chromatographic Separation of Active Polymer-like Worm Mixtures by Contour Length and Activity

*Antoine Deblais<sup>1</sup>, Tess Heeremans<sup>1</sup>, Daniel Bonn<sup>1</sup> and Sander Woutersen<sup>2</sup>*

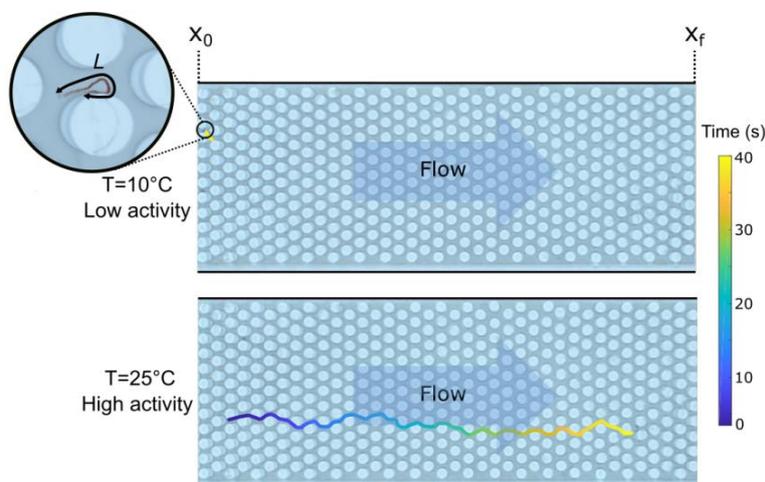
<sup>1</sup>*Van der Waals-Zeeman Institute, IoP, University of Amsterdam, , Amsterdam, The Netherlands.*

<sup>2</sup>*Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands.*

Presenting author's e-mail: [a.deblais@uva.nl](mailto:a.deblais@uva.nl)

The convective transport rate of polymers through confined geometries depends on their size, allowing for size-based separation of polymer mixtures (chromatography) [1-2]. Here, we investigate if mixtures of active polymers can be separated in a similar manner based on their activity. We use thin living worms *T. tubifex* [3-4] as a model system for active polymers and study the transport of these worms by an imposed flow through a channel filled with a hexagonal-pillar array. The transport rate through the channel depends strongly on the degree of activity, an effect that we assign to the different distribution of conformations sampled by the worms depending on their activity. Our results demonstrate a unique way to sort mixtures of active polymers based on their activity and provide a versatile and convenient experimental system to investigate the hydrodynamics of active polymers.

**Keywords:** Active matter, Active Polymers, Chromatography, Separation.



**Figure 1.** Hydrodynamic pillar array experiment with active polymerlike worms. Trajectories in the channel for the same worms at two different temperatures (top,  $T = 10^{\circ}\text{C}$  and bottom,  $25^{\circ}\text{C}$ ) in time (color gradient). The continuous line shows the tracked paths along the channel at the two different temperatures for the same amount of time (40 s); decreasing temperature increases the elution time.

## References

- [1] M. C. VandeSande, D. J. Pasut, and H. W. de Haan, *Electrophoresis* 38, 2488 (2017).
- [2] D. Berek, *Journal of separation science* 33, 315 (2010).
- [3] A. Deblais, S. Woutersen, and D. Bonn, *Physical Review Letters* 124, 188002 (2020).
- [4] A. Deblais, A. C. Maggs, D. Bonn, and S. Woutersen, *Physical Review Letters* 124, 208006 (2020).

# Role of self-generated fluid flows in active colloids moving through polymer networks

*Andreas Zöttl*

*University of Vienna, Faculty of Physics, Wien, Austria  
TU Wien, Wien, Austria*

Presenting author's e-mail: [andreas.zoettl@univie.ac.at](mailto:andreas.zoettl@univie.ac.at)

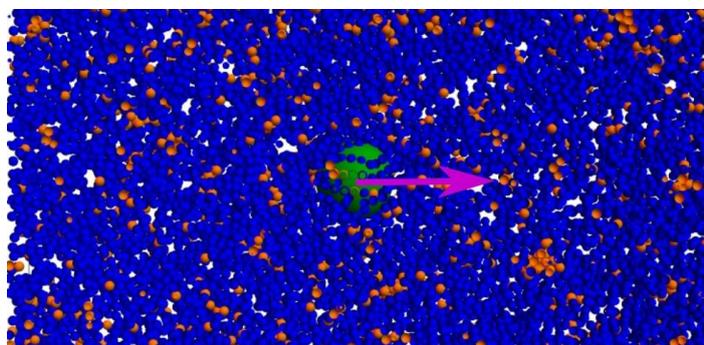
Recently, increasing interest in understanding how complex environments consisting of static or dynamic obstacles influence active colloidal transport and phase behavior has emerged. Of particular interest are polymeric environments mimicking essential structural and viscoelastic features of *in vivo* biopolymer networks. These are of importance for potential drug delivery operations carried out by active micromachines in the future, but also to understand general mechanisms of active transport in complex biologically relevant fluids.

Here we systematically investigate the transport of active colloids through explicitly modeled polymer networks using the hydrodynamic method of multiparticle collision dynamics (MPCD). In contrast to simple “dry” active Brownian particle (ABP) models self-generated fluid flows created by a self-propelled spherical squirmer – a prototypical hydrodynamic model system for active colloids – are included. Furthermore we compare our results to a passively driven particle, and to a simple ABP.

We observe that active colloids move much faster compared to driven colloids with respect to their reference speeds obtained in polymer-free Newtonian fluids. We identify different physical mechanisms responsible for our observations: First, hydrodynamic screening due to the polymer network is different for driven and active particles. Second, local polymer depletion influences transport in the presence of generated flow but is irrelevant for ABP models. We further quantify the flow field, polymer density and crosslinking around the active colloids. By allowing bonds in polymer networks to form and break transiently, we show how self-generated viscous gradients enhance bond-breaking locally, and allows active colloids to widen and enter pores in polymer networks.

In summary, we show how self-generated fluid flows enhance active transport by manipulating the local polymeric environment.

**Keywords:** microswimmers, active transport, polymer networks, screening, depletion



**Figure 1.** Active colloid moving in transiently crosslinked polymer network. Green sphere: squirmer; pink arrow: squirmer orientation; blue and orange: non-crosslinking and crosslinking monomers, respectively, forming a polymer network embedded in an MPCD background fluid

**Acknowledgements:** We acknowledge financial support from the Austrian Science Fund (FWF) through a Lise-Meitner fellowship (grant M-2458).

# Understanding the non-equilibrium interactions governing the tracer response near chemically active confined Janus particles

*Mihail N. Popescu<sup>1</sup>, Jaideep Katuri<sup>2</sup>, William E. Usual<sup>3</sup> and Samuel Sánchez<sup>4</sup>*

<sup>1</sup>Max Planck Institute for Intelligent Systems, Stuttgart, Germany

<sup>2</sup>Argonne National Lab, Lemont, IL, USA

<sup>3</sup>Dept. of Mechanical Engineering, Univ. of Hawai'i at Manoa, HI, USA

<sup>4</sup>IBEC, Barcelona, Spain

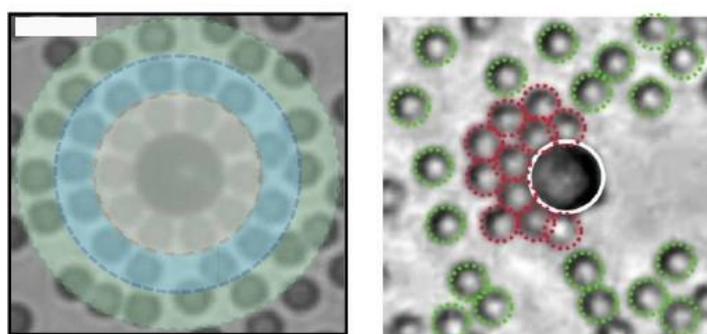
Presenting author's e-mail: [popescu@is.mpg.de](mailto:popescu@is.mpg.de)

Chemically active Janus particles sustain non-equilibrium spatial variations in the chemical composition of the suspending solution; these induce hydrodynamic flow and motility of the particles. Here we discuss a combined experimental and theoretical study that exploits the response of spherical, inert silica particles (tracers) in order to investigate the nature of the hydrodynamic and chemical fields associated with the chemical activity of a spherical Pt-silica Janus particle immobilized at a wall [1].

The active particles are immobilized with the symmetry axis being either perpendicular or parallel to the wall. This allows one to address the effect of the confining wall on the effective interactions experienced by the tracers, as well as the dependence of the effective interactions on the configuration of the active particle. Qualitatively distinct, configuration-dependent responses of the tracers are observed (see Figure 1): for an axis-perpendicular configuration, tracers are attracted to the active particle; but for an axis-parallel configuration an anisotropic response and a tracer-free exclusion zone around the Pt side emerge.

The observations can be qualitatively captured and rationalized by a simple model of a chemically active particle. This requires accounting for the distortion by the wall of the hydrodynamic and chemical fields around the particle, as well as for an osmotic flow at the wall in response to the chemical activity of the particle [1,2]. The importance of the latter is further emphasized by experiments that highlight a clear dependence of tracer dynamics on the substrate material. Last, we note that the effective attraction observed when the particles are near the wall does not carry over to the case when the particles are in unbounded solution: there the tracers would exhibit purely repulsive interactions with an active Janus particle (immobilized or motile).

**Keywords:** active colloids, diffusion, Stokes flow



**Figure 1.** Tracer response to an active Janus colloid in axis-perpendicular (left) or axis-parallel (right) configuration.

## References

- [1] J. Katuri et al, A. Name, B. Name and C. Name, *Sci. Adv.*, 2021, 7, eabdo719.  
[2] A. P. Bregulla and F. Cichos, *J. Chem. Phys.*, 2019, 151, 044706.

**Friday 9th September 2022**

**Advanced Colloid Science for Applications and Products**

# Non-aqueous foams stabilized by crystalline particles: from design to applications

*Anne-Laure Fameau<sup>1</sup> and Bhuvnesh Bharti<sup>2</sup>*

<sup>1</sup>*INRAe, PIHM, UMET, UNiversity Lille, Villeneuve d'Asq, France*

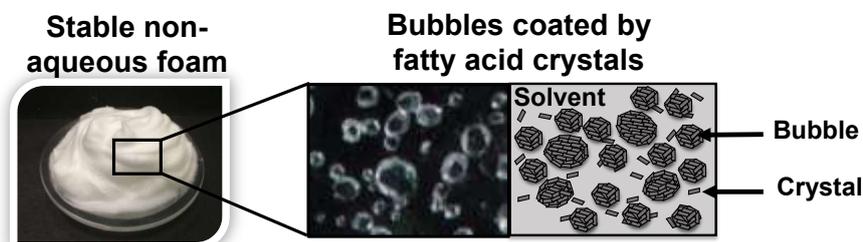
<sup>2</sup>*Louisiane State University, Cain department of Chemical Engineering, USA*

*Presenting author's e-mail: anne-laure.fameau@inrae.fr*

Liquid foams are complex colloidal systems based on gas bubbles dispersed in a liquid continuous phase. Two different categories of liquid foams exist: aqueous or non-aqueous. Non-aqueous foams represent a new promising emerging field [1]. Two types of non-aqueous foams are gaining interest: oil foams based on vegetable oil (oleofoams) and alcohol-based foams [2,3]. Oleofoams are a promising option to develop food products combining both a reduced fat content and new appealing textures and sensorial properties. Oleofoams also possess other advantages of interest for cosmetic and pharmaceutical applications: long-term stability lasts for months even above room temperature, reduction in microbial spoilage as water is absent and so preservatives are not needed [4]. Therefore, oleofoams appear to be a perfect new product regarding the increasing trend to develop “clean label” products in various industries. Alcohol-based foams are gaining interest nowadays since the global pandemic due to COVID-19 and the frequent use of alcohol-based hand sanitizers as recommended by the World Health Organization.

The main difference between aqueous and non-aqueous foams comes from the relatively large difference in the surface tension of the solvents [1]. For non-aqueous systems, the low surface tension makes the adsorption of hydrocarbon-based surfactants energetically unfavourable. One way to produce and stabilize non-aqueous foams is to use surfactant crystalline particles, which can adsorb at the air-liquid surface [5]. In this talk, we will present how crystalline particles based on fatty acids and fatty alcohols can lead to the production and stabilization of both oleofoams and alcohol-based foams [2,6]. The formation and stabilization mechanisms of these two types of non-aqueous foams are the same and based on the adsorption of crystalline particles at the air-liquid surface [5]. These foams are ultrastable due to the dense layer of adsorbed crystals at bubble surfaces that considerably reduce both disproportionation and coalescence.

**Keywords:** foam, crystal, food, cosmetic, pharmaceutical



**Figure 1.** Illustration of non-aqueous foam stabilized by the presence of fatty acid crystals both in bulk and at the interface as observed by polarized light microscopy

## References

- [1] Fameau A-L, Saint-Jalmes A. *Adv Colloid Interface Sci.* 2017;247:454–64.
- [2] Fameau A-L, Ma Y, Siebenbuerger M, Bharti B. *J Colloid Interface Sci.* 2021;600:882–6.
- [3] Fameau A-L, Saint-Jalmes A. *Front Sustain Food Syst.* 2020;4(110).
- [4] Callau M, Jenkins N, Sow-Kébé K, Levivier C, Fameau A-L. *J Cosmet Sci.* 2021;72(4):399–405.
- [5] Fameau A-L, Binks BP. *Langmuir.* 2021;37(15):4411–8.
- [6] Callau M, Sow-Kébé K, Jenkins N, Fameau A-L. *Food Chem.* 2020;333:127403.

# Mechanistic aspects of drug encapsulation in colloidal assemblies

*Eva Judy, Remco Tuinier*  
Eindhoven University of Technology, Eindhoven, Netherlands

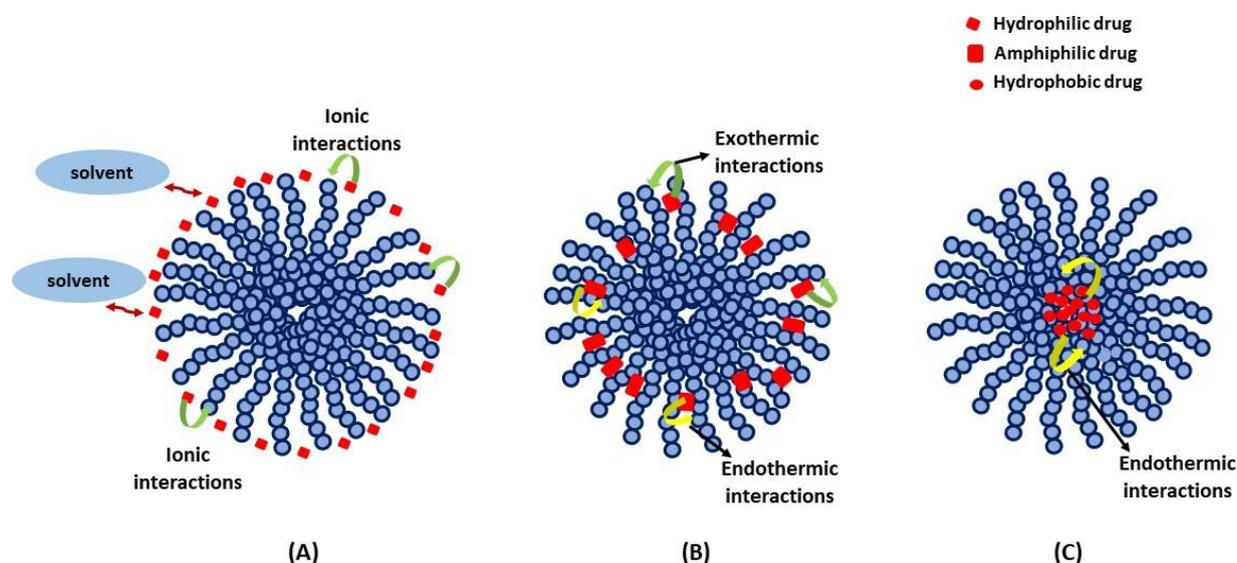
Presenting author's e-mail: [e.judy@tue.nl](mailto:e.judy@tue.nl)

Rational drug design and improved drug delivery requires continuous efforts from synthesis to target oriented desired effects. Colloidal self-assemblies have routinely been used in effective drug encapsulation and as delivery vehicles. Establishing structure-property-energetics relationships in such systems are crucial to meet the objectives of drug discovery and its delivery aspects. Majority of reported work in literature on drug encapsulation in self-assemblies and its release, is based on spectroscopic evidences making it more qualitative in nature. Direct thermodynamic signatures associated with these processes have potential to quantitatively analyze the strength and nature of intermolecular interactions thereby suggesting guidelines for synthesis of new molecular entities and improvements in the existing systems.

We have attempted to understand partitioning/encapsulation of drugs with varying functionalities in different colloidal self-assemblies, quantitatively based on thermodynamic signatures employing high sensitivity isothermal titration calorimetry, in combination with spectroscopy and microscopy. Further, the results have also been supplemented with theoretical modelling employing the self-consistent field (SCF) method. A combination of these powerful tools has enabled us in proposing a protocol that permits reliable and authentic determination of quantitative partitioning of drugs.

The work to be presented mainly focuses on partitioning of antibiotic and anti-inflammatory drugs in colloidal self-assemblies of surfactants and poloxamers. The mode of partitioning of drugs has been discussed in terms of nature of interactions and role of solvent impacting enthalpic and entropic components to overall Gibbs free energy change (Fig 1). These observations will be supplemented using SCF methods to confirm the spatial distribution of the drugs inside the self-assemblies. Such an approach applied to variety of drugs and self-assemblies is expected to provide guidelines for rational drug discovery and enhance efficacy of delivery systems over a period of time.

**Keywords:** Rational drug design, isothermal titration calorimetry, thermodynamic signatures, self-consistent field method, colloidal self-assemblies



**Figure 1.** Modes of partitioning of drugs in colloidal assemblies depending on the difference in their structure, interaction properties and functionalities.

## References

- [1] E. Judy and N. Kishore, *Langmuir*, 2021, 37, 7203.
- [2] A. Koochaki, M. R. Moghbeli, S. J. Nikkhah, A. Ianiro and R. Tuinier, *RSC Advances*, 2020, 10, 3253.

# In-situ Investigation of Ca<sup>2+</sup> Effects on Humic Acid Aggregation with Polyelectrolyte for Water Treatment

*Mingyu Yuan<sup>1</sup>, Heriberto Bustamante<sup>2</sup>, Michael Gradzielski<sup>1</sup>*

<sup>1</sup>*Stranski-Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, Berlin, Germany*

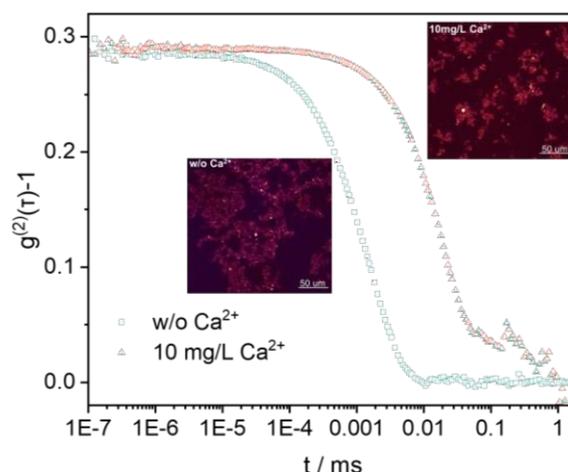
<sup>2</sup>*Sydney Water, Parramatta NSW, Australia*

Presenting author's e-mail: [m.yuan.1@campus.tu-berlin.de](mailto:m.yuan.1@campus.tu-berlin.de)

The complexation/coagulation induced by cationic polyelectrolyte (PE) is considered to be an effective method to deal with humic acid (HA) in conventional water treatment process. That is important as HA exists ubiquitously in aquatic environments as a degradation product of plants and it can negatively affect the quality of drinking water. [1]

In this study, we investigate the Ca<sup>2+</sup> effects on the interaction between HA and various polyelectrolytes, including synthetic polydiallyldimethylammonium chloride (PDADMAC) and (modified) chitosan from natural sources to develop an environmentally friendly solution. [2] A combination of UV-Vis and confocal microscopy is utilized to probe the phase behavior and colloidal morphology of the formed HA-PE aggregates as a function of mixing ratio. In addition, an in-situ observation of the HA-PE aggregation process was done via SLS, DLS, and small-angle x-ray scattering (SAXS). It was observed that by tailoring the concentration of Ca<sup>2+</sup> faster aggregation kinetics and denser aggregates can be formed even at low polyelectrolyte concentration. This insight from colloid science is promising to optimize water treatment process in industrial fields.

**Keywords:** polyelectrolyte, aggregation, ion effects, water treatment



**Figure 1.** Intensity correlation functions of HA-PDADMAC aggregates with various Ca<sup>2+</sup> concentration and the corresponding confocal reflection microscopy images.

**Acknowledgements:** We acknowledge funding from Deutsche Forschungsgemeinschaft (DFG), GR1030/26-1.

## References

- [1] Loganathan, P.; Gradzielski, M.; Bustamante, H.; Vigneswaran, S., *Environ. Sci.: Water Res. Technol.* 2020, 6 (1), 45-61.  
 [2] Renault, F.; Sancey, B.; Badot, P.-M.; Crini, G., *Eur. Polym. J.* 2009, 45 (5), 1337-1348.

## Facet-dependent surface charge and hydration of colloidal nanoparticles at variable pH

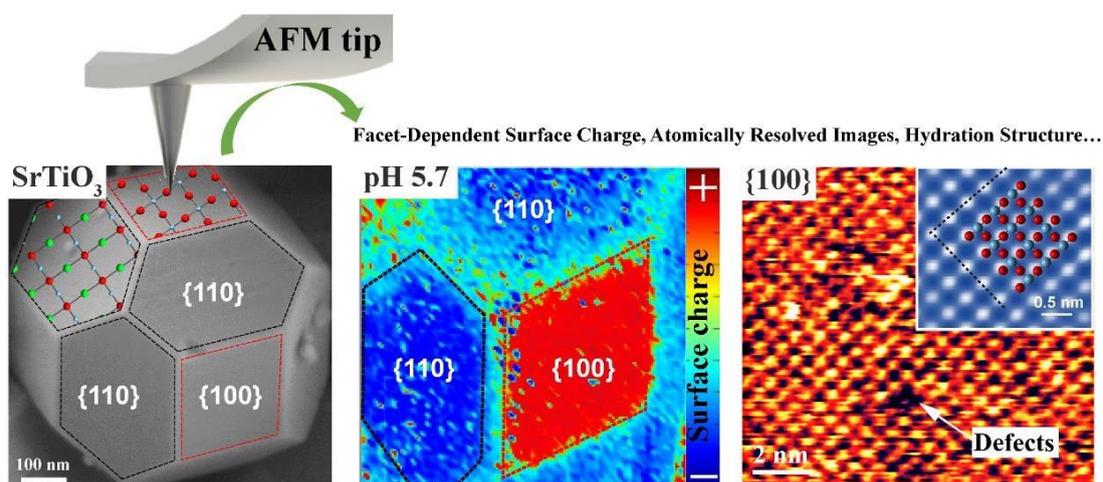
*Igor Siretanu, Shaoqiang Su, Dirk van den Ende, Bastian Mei, Guido Mul and Frieder Mugele*

*Physics of Complex Fluids Group and MESA+ Institute Faculty of Science and Technology  
University of Twente, Enschede, Netherlands*

Presenting author's e-mail: [i.siretanu@utwente.nl](mailto:i.siretanu@utwente.nl)

Anisotropy of shape and surface properties determine the functionality of faceted nanoparticles in various contexts including facet selective colloidal self-assembly, crystal growth, biosensing, improved photo/electrocatalytic activity and enhanced selective cellular and ions uptake. The characteristic anisotropy, surface properties and function of solid-liquid interfaces of crystalline faceted nanoparticles are believed to be essential for their performance but remains poorly understood and difficult to characterize and quantify. We use dual scale Atomic Force Microscopy to measure electrostatic and hydration forces of faceted SrTiO<sub>3</sub> nanoparticles in aqueous electrolyte at variable pH. We demonstrate (i) the ability to quantify strongly facet-dependent surface charges yielding isoelectric points of the dominant {100} and {110} facets that differ by as much as 2 pH units, ii) fluids composition controlled facet-dependent accumulation of oppositely charged (SiO<sub>2</sub>) particles, and iii) that atomic scale defects can be resolved but are in fact rare for the samples investigated [1]. Atomically resolved images and facet-dependent hydration structure suggest a microscopic hydration and charge generation mechanism.

**Keywords:** faceted colloidal SrTiO<sub>3</sub> nanoparticles, facet-dependent surface charges, atomically resolved images, atomic force microscopy, hydration structures



### References

[1] Su, S., Siretanu, I., van den Ende, D., Mei, B., Mul, G., & Mugele, F. (2021). Facet-Dependent Surface Charge and Hydration of Semiconducting Nanoparticles at Variable pH. *Advanced Materials*, 33(52), 2106229.

# Novolac-based microcapsules containing isocyanate reagents for self-healing applications

Efterpi Avdeliodi<sup>1</sup>, Amaia Soto Beobide<sup>1,2</sup>, Athena M. Fidelli<sup>3</sup>, Poppy Krassa<sup>3</sup>, George A. Voyiatzis<sup>2</sup>, Georgios Bokias<sup>1</sup>, Joannis K. Kallitsis<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Patras, Patras, Greece

<sup>2</sup>Foundation for Research and Technology – Hellas (FORTH), Institute of Chemical Engineering Science (ICE-HT), Patras Greece

<sup>3</sup>Megara Resins Anastassios Fanis S.A., Greece

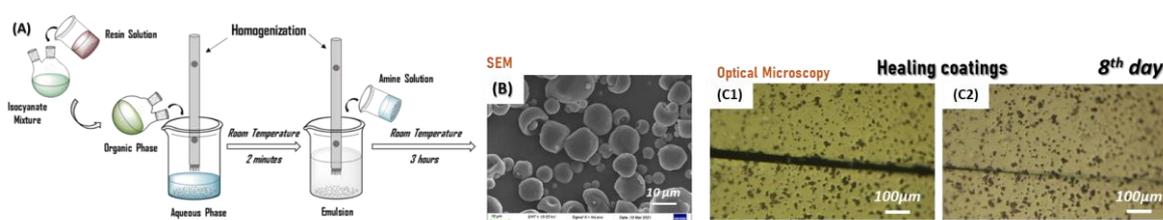
Presenting author's e-mail: [bokias@upatras.gr](mailto:bokias@upatras.gr)

Microcapsules (MCs) containing isocyanate compounds (NCO) for use as self-healing materials in waterborne polyurethane coatings were synthesized using modified Novolac resins. The concept is to combine an organic substrate based on protected Novolac resins with isocyanate reagents of different reactivity and control the reaction conditions to minimize the reaction and increase the stored amount of the less reactive isocyanate derivative. Thus, methylene diphenyl diisocyanate (MDI) and isophorone diisocyanate (IPDI) derivatives were used to react with diethylenetriamine (DETA). As the highly reactive MDI reacts for the shell formation, the less reactive IPDI is stored in the core during the interfacial polymerization performed at room temperature for short reaction times.

Based on that strategy a number of microcapsules were obtained with different morphology and sizes, depending on the agitation conditions as revealed using SEM and optical microscopies. Selective extraction was used to determine the amount of the less reactive isocyanate (IPDI) stored inside the capsules through FTIR-ATR spectroscopy and isocyanate titration (ASTM D2572). It was determined that Acetyl Microcapsules encapsulated the 96 wt.% of IPDI monomer, and that they have the ability to enclose 4.5x and 10x more IPDI compared to the amount encapsulated by Benzyl microcapsules and Novolac microcapsules, respectively. In addition, it was found that the microcapsules are stable, maintaining approximately 80% of the initial –NCO after two months storage under inert conditions.

Finally, the self-healing ability of the microcapsules was tested by adding selected IPDI-containing microcapsules in environmentally friendly waterborne polyurethane dispersions (WPUdS), based on polyether, polyether/polyester and polycarbonate polyols. As proven, the microcapsules based on Acetyl-modified Novolac have shown efficient healing behavior, in the absence of any catalyst, on the polyurethanes' surfaces when artificially scratched.

**Keywords:** Novolac resin, Microcapsules, Self-healing, Isocyanate, Polyurethane



**Figure 1.** (A) Formation process of microcapsules (B) Morphology of microcapsules using Acetyl-modified Novolac resin. Scratch on Acetyl microcapsules loaded polyurethane films on (C1) day 0 and (C2) day 8.

**Acknowledgements:** This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code:T2EΔK-00307 “Synthesis of waterborne polyurethane dispersions with encapsulation of micro/nano structures for ecological self-healing coatings”)



# Design of Colloidal Molecularly Imprinted Polymer Colloids as Biomimetic Sorbent for Recognition and Separation of Nonylphenol Pollutant

Emile Decompte<sup>1</sup>, Volodymyr Lobaz<sup>2</sup>, Mathilde Monperrus<sup>1</sup>, Elise Deniau<sup>1</sup>, Maud Save<sup>1</sup>

<sup>1</sup> Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, Pau, France

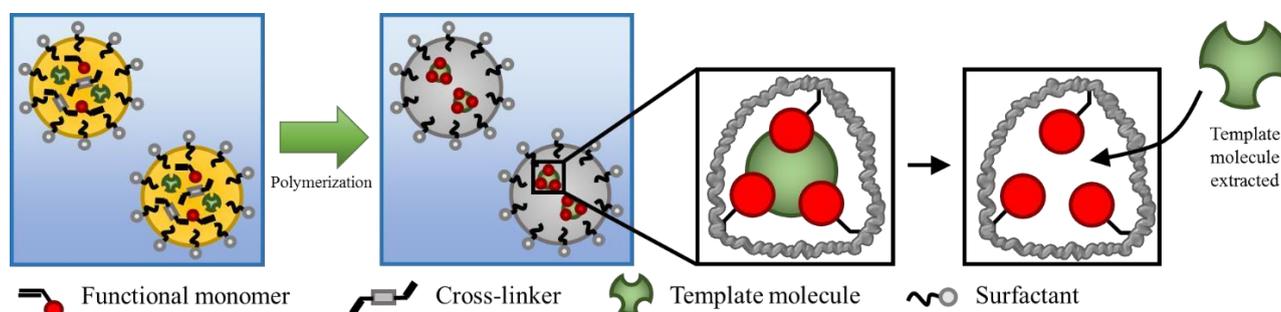
<sup>2</sup> Institute of Macromolecular Chemistry AS CR, Prague, Czech Republic

Presenting author's e-mail: [maud.save@univ-pau.fr](mailto:maud.save@univ-pau.fr)

The presence of organic micropollutants in water rivers induces adverse effects on the environment even at low concentration levels. Pre-concentration of these pollutants using methodologies associated with a level of selectivity are interesting to increase their concentrations prior analytical measurements. A very promising alternative is the use of molecularly imprinted polymers (MIPs) (see Figure.).[1] MIPs are synthetic biomimetic systems able to bind target molecules with affinities and specificities via receptor cavities. Stable colloidal MIP (microgels) have benefits among macroscopic MIP such as a good compatibility with the aqueous phase and increased exchange surface. The originality of the present work is to synthesize stable colloidal submicronic MIP particles directly in the aqueous phase by miniemulsion polymerization.[2] We focused our attention on nonylphenol micropollutant, an endocrine disruptor classified as a potentially hazardous substance,[3] with an Environmental Quality Standard (EQS) of 0.3 µg/L.[4] The low solubility of nonylphenol in water drove the choice towards miniemulsion polymerization process to load the micropollutant template in the initial monomer droplets (see Figure 1).

N-vinylcaprolactam (VCL) and hydrophobic co-monomer based microgels were synthesized by free-radical miniemulsion polymerization in the presence of nonylphenol. VCL moiety was chosen to create the molecular imprint with the template molecule via hydrogen bonding and the other liquid co-monomer ensured hydrophobic interactions and favors the initial droplet formation. In this project, we investigated the effect of the chemical structure of different hydrophobic co-monomer such as vinyl acetate (VAc), vinyl benzoate (VB) and 2-ethylhexanoic acid vinyl ester (Veova EH). We highlighted the water/ethanolic composition promoting a high selectivity of the imprinted colloids compared to the non-imprinted colloids.

**Keywords:** miniemulsion polymerization, microgel, selective adsorbent, organic micropollutant.

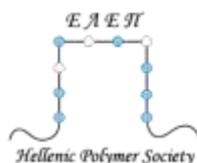


**Figure 1.** Principle of the miniemulsion polymerization and scheme of the formation of the molecular imprint.

## References

- [1] L. Chen, X. Wang, W. Lu, X. Wu, J. Li, *Chem. Soc. Rev.* **2016**, *45*, 2137-2211.  
 [2] E. Decompte, V. Lobaz, M. Monperrus, E. Deniau, M. Save *ACS Appl. Polym. Mat.* **2020**, *2*, 3543-3556  
 [3] A. Soares, B. Guieysse, B. Jefferson, E. Cartmell, J. N. Lester, *Environ. Int.* **2008**, *34*, 1033-1049.  
 [4] European Directive on water 2008/105/EC, *J. Eur. Union* L348, 84-97 (**2008**) 306

## Organizers



## Sponsors



LANGMUIR

