Novel Analysis Methods for the Nonlinear Dilatational Rheology of Complex Fluid-Fluid Interfaces

Leonard M. C. Sagis\textsuperscript{1,2,*}, Silvia E. H. J. van Kempen\textsuperscript{1}, Nam Phuong Humblet-Hua\textsuperscript{1}

\textsuperscript{1} – Food Physics Group, Wageningen University, Bomenweg 2, 6703 HD Wageningen (NL)
\textsuperscript{2} – ETH Zurich, Dept. of Materials, Polymer Physics, Wolfgang-Pauli-Str. 10, 8093 Zurich (CH)
\* - leonard.sagis@wur.nl

When fluid-fluid interfaces are stabilized by proteins, (anisotropic) colloidal particles, or polymers, the microstructure of the interface is often highly complex. These surface active components may form 2D gels, 2D glass phases, 2D (liquid) crystalline phases, or 2D dispersions. The response of complex interfaces to dilatational deformations is often nonlinear even at small deformations, as a result of structural rearrangements induced by the applied deformation. The data analysis commonly used by profile analyzing tensiometers (PAT) for the determination of surface dilatational properties cannot adequately describe highly nonlinear responses of complex interfaces [1]. Here we discuss how Lissajous curves and a generalized form of the Laplace equation can be used to obtain more meaningful measures for the dilatational properties of complex interfaces. As an example we present dilatational data, obtained with a PAT, for fluid-fluid interfaces stabilized by oligosaccharide-fatty acid esters, protein fibrils, and protein-polysaccharide complexes. At high deformation amplitudes the Lissajous curves of surface pressure versus deformation of these interfaces show remarkable asymmetries between the compression and extension part of the cycle. For example, air-water interfaces stabilized by oligosaccharide-fatty acid mono-esters display strain-thinning behavior in extension, and strain-hardening in compression. A possible explanation for this behavior is that during compression the interface is compressed to a 2D soft glassy state. Oil-water interfaces stabilized by semi-flexible protein fibrils display a highly elastic response upon compression, and a more viscous response upon extension. These interfaces may be undergoing an isotropic-to-nematic transition during compression. We analyze the Lissajous curves for these interfaces with a scheme recently introduced by Ewoldt et al. [2]. With this scheme we extract four dilatational moduli from the Lissajous curve: the moduli at minimum and maximum expansion, $E_{dM}^{ex}$ and $E_{dL}^{ex}$, and the moduli at minimum and maximum compression, $E_{dM}^{com}$ and $E_{dL}^{com}$. We also obtain the nonlinearity parameters $S^{ex} = (E_{dL}^{ex} - E_{dM}^{ex})/E_{dL}^{ex}$ and $S^{com} = (E_{dL}^{com} - E_{dM}^{com})/E_{dL}^{com}$. When these parameters are determined as a function of deformation amplitude, frequency, and droplet size, a quantification of the response of complex interfaces to dilatational deformations can be obtained, that gives insight in the microstructure of the interface. Using a generalized form of the Laplace equation [1], we show that the effective transient surface tension of a deformed complex interface may contain contributions from deviatoric surface stresses or bending stresses. Our results show that although a careful and extensive analysis of data is needed (based on Lissajous curves and a generalized form of the Laplace equation) it is feasible to explore the often exotic dilatational behavior of complex interfaces with PAT measurements.

Literature:

The Rheology of Shake Gels

Paul Luckham1*, Ann-Sophie Chevalier,1,2, Maria del Mar Ramos Tejada,1,3 Francisco José Martínez Boza1,4

1 – Dept Chemical Engineering, Imperial College London, UK
3 – Dept. de Física, Universidad de Jaen, Linares, Spain
4 – Dept de Ingeniería Química. Universidad de Huelva. 21071 Huelva, Spain

* - p.luckham01@imperial.ac.uk

Polymer adsorption to particles to enhance colloid stability has been studied extensively for at least the last five decades due to the role of polymers in stabilising particles against aggregation. It is also well known that under certain circumstances polymers can also induce the aggregation of particles either by simultaneously adsorbing on two particles, bridging flocculation, or due to the presence of non adsorbing polymer giving rise to depletion flocculation. Serendipitously we have discovered that certain formulations where we have particles in a relatively high molecular weight polymer solution are perfectly stable for many days, giving a low viscosity solution, but on shaking a gel is formed, some of which can have the consistency of silicone rubber (see the photo’s below). On standing the gel relaxes back into the liquid state of the course of seconds to days, depending on the formulation. In searching the literature we found that Zebrowski et al [1] has reported similar observations for the synthetic clay Laponite- Polyethyleneoxide-water system, however we have observed that this phenomenon is rather more general and similar systems can be formed in other inorganic oxide particulate systems, although to date we have not found another polymer which will form such a gel. (We note here that some aspects of this behavior has previously been observed by Cabane [2] and Otskubue [3] and their colleagues.)

Initially attempts to monitor the formation of this gel under simple shear in a commercial rheometer were singularly unsuccessful, despite shearing at 1000s⁻¹. However, we have found that in a rheometer shear needs to be applied for a very long time, up to 2 hours before over the course of 20 seconds a solid like gel is formed. This has enabled us to characterize the rheological and the relaxation properties of these intriguing formulations, and to propose a mechanism for their formation based around a model for the shear thickening behaviour of hydrophobically modified polysaccharide solutions.

Figure 1 The formation of a shake gel, by simply shaking the formulation which then transforms from a viscous liquid to an elastic solid

Literature:

3. Otsubo, Y. and K. Watanabe, Rheological behaviour of silica suspensions during bridging flocculation induced by shear, J. Colloid Interface Sci. 133, 491–49
Colloid Aggregation and Water Purification - Using Flocculents from Seeds of Moringa Trees

Adrian R. Rennie 1*, Maja S. Hellsing 1, Habbauka M. Kwaambwa 2, Bonang Nkoane 3, Fiona Selato 3

1 – Uppsala University
2 – Polytechnic of Namibia
3 – University of Botswana
* - Adrian.Rennie@physics.uu.se

Although flocculation has been studied for many years and the aggregate structures are understood as fractals, the different regimes of colloid aggregation are not always well-defined. Diffusion limited or reaction limited colloid aggregation of clusters is expected to give rise to mass fractals with characteristic exponents (dimensions) between 1.75 and 2.3. In order to develop alternative water purification technology we have been investigating flocculents from seeds of Moringa oleifera trees [1, 2]. Scattering experiments (reflection and small-angle scattering) with neutrons provide valuable information about how the protein binds to impurities and how flocculation occurs. New ultra-small angle neutron scattering experiments [3] have shown very dense clusters with dimensions between 2.4 and 2.95 when experiments are performed on concentrated dispersions. Interesting changes are observed with both concentration of particles (polystyrene latex) and flocculents. The increase in fractal dimension with concentration resembles some recently published simulations using Brownian dynamics [4]. The results suggest how the water purification process may be optimised and extended to larger scale purification plants.

![Fig. 1 Fractal dimensions of flocs obtained with (a) protein from two varietals of Moringa trees for various particle concentrations and (b) changes in fractal dimension with 3 wt% particles for different protein concentration.](image)

**Literature:**

On Some Experimentally Established Features of the Osmotic Kinetics and Their Interpretation

Emil Manev¹, Kiril Kolikov², Ivan Minkov¹, Boryan Radoev¹

¹ Sofia University “St. Kliment Ohridski”, Sofia, Bulgaria
² University of Plovdiv, "Paisii Hilendarski", Plovdiv Bulgaria
* - Radoev@chem.uni-sofia.bg

Osmosis, that is, the diffusion of solvent across a semipermeable membrane, has been a subject of investigation for more than a century. Although osmotic equilibrium is considered to be well understood from thermodynamic viewpoint and does not pose serious ambiguities, the dynamic aspects of the process frequently exhibit new and even surprising effects, which are difficult to explain within the frames of the traditional kinetic models. Such a non-trivial effect is the established in the present investigation maximum in the rate of solvent transferred through the membrane as a function of time, \( q(t) \). This dependence invariably takes the shape of a curve originating at the zero, with gradually increasing values reaching eventually saturation; the plateau at \( q(t \to \infty) \) reflects the equilibrium state. In our experimental investigation we obtained \( q(t) \) dependences featuring S-shaped curves, passing through inflexion, equivalent to \( \frac{d^2 q}{dt^2} = 0 \). The experiments at varied concentrations confirmed the presence of maxima in the solvent transfer rates, whose heights increase with the solute concentration.

The attempt to interpret such maxima led us to the hypothesis for the occurrence of certain polarization in the vicinity of the membrane, similar e.g. to the concentration polarization at electrolysis. The influx of solvent results in local dilution of the solution in the near-membrane space which generates reverse diffusion flow from the interior, aiming to level the concentrations. An essential assumption here is that the driving osmotic pressure is proportional to the local difference of the concentrations on either side of the membrane. In its turn, the near-membrane concentration is equal initially to the mean concentration in the chamber space. Consequently, it decreases due to dilution, but eventually again reaches the mean concentration level at equilibrium. Such a passage through a minimum in local concentration we associate with the occurrence of the maximum in the rate of solvent influx.

Acknowledgment:

This study is financially supported by Project № DTK 02/35 with the National Fund for Scientific Research at the Bulgarian Ministry of Education and Science.
Total Internal Reflection Raman Spectroscopy of the Solid-Liquid Interface

Colin D. Bain 1*

1 - Department of Chemistry, Durham University, U.K.
* - c.d.bain@durham.ac.uk

Total internal reflection (TIR) Raman spectroscopy is a recent technique for studying the adsorption of surfactants, organic molecules, polymers, biological lipids and inorganic ions at solid-liquid interfaces. The short penetration depth of the evanescent wave (typically ~100 nm) allows the discrimination of adsorbed species from those in the bulk. The combination of TIR Raman spectroscopy with chemometric analysis methods allows the acquisition of spectra in as little as one second even in multicomponent systems. A flow cell coupled to a continuous stirred tank allows the determination of complete adsorption isotherms in a few hours provided that the adsorption kinetics are sufficiently fast. If the substrate of interest is transparent, it can be used as incident medium for the pump laser light and molecules of interest adsorbed directly onto the substrate. More generally, thin films of other materials, such as cellulose or haematite, can be deposited on an optical prism and adsorption studied at the interface of the thin film with a liquid. This paper will describe the principles of TIR-Raman spectroscopy and the experimental set-up, discuss the strengths and weaknesses of the technique, and illustrate the application of TIR-Raman spectroscopy with recent examples from our laboratory.

![Diagram](image)

**Fig. 1** Schematic illustration of a hydrodynamic flow cell for total internal reflection Raman spectroscopy.

**Literature:**

The Effects of Aggregation and Protein Corona on the Cellular Internalization of Oxide Nanoparticles

N. OuldMoussa, M. Safi, E. Seyrek, H. Conjeaud and J.-F. Berret*

Matière et Sytèmes Complexes, UMR 7057 CNRS Université Denis Diderot Paris-VII, Batiment Condorcet, 10 Rue Alice Domon et Léonie Duquet, 75205 Paris, France

* - jean-francois.berret@univ-paris-diderot.fr

Engineered nanoparticles are essential components in the development of nanotechnologies. For applications in nanomedicine, particles need to be functionalized to ensure a good dispersibility. In many cases however, functionalization is not sufficient. Particles dispersed in biological fluids become either coated by a corona of serum proteins or precipitate out of the solvent. In the present study, iron and cerium oxide particles of size 10 nm are put under scrutiny. These particles have important biological applications in magnetic resonance imaging or regenerative medicine. As for living cells, murine fibroblasts, human lymphoblasts and macrophages are examined [1]. The interactions between oxide nanoparticles and cells are studied by electron microscopy (Figure 1) and flow cytometry. The previous studies were complemented by cytotoxicity assays.

We first show that by changing the coating of oxide particles from citrate ligands to small carboxylated or pegylated polymers, the colloidal stability of the dispersion is improved and the adsorption/internalization towards living cells is profoundly affected. As shown by time-resolved light scattering, citrate-coated particles in cell culture media are spontaneously covered by plasmic proteins and destabilize, whereas the polymer-coated particles exhibit an outstanding dispersibility and a structure devoid of protein corona. As a result of their precipitation, citrate-coated particles interact more strongly with cells. The present approach shows that the surface chemistry and coating of engineered particles are the key parameters in the nanoparticle/cell interactions, and have moreover a strong impact on the toxicity and cell viability.

Literature:

Fluorescence Correlation Spectroscopy of Repulsive Systems: Theory, Simulation and Experiments

Jingfa Yang, Ligang Feng, Jiang Zhao\textsuperscript{1*}, Kaloian Koynov\textsuperscript{2**} Hans-Jürgen Butt\textsuperscript{2}

\textsuperscript{1} – Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
\textsuperscript{2} – Max-Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
\* - jzhao@iccas.ac.cn; ** - koynov@mpip-mainz.mpg.de

The dynamics and structures of soft matter systems with multiple charges have been attracting intensive research attention for decades. One of the most uniqueness is the multiple modes in the fluctuation dynamics, which should be originated from the long-range electrostatic interaction. However, a clear picture of such a complex dynamics is unclear, especially on its correlation with the structures. In this research, a systematic investigation into this problem has been performed by dual-color fluorescence correlation spectroscopy (FCS), taking charged colloids as the model system. The research consists of development of theory, Brownian simulation and FCS experiments.

The theoretical basis of FCS for repulsive systems is further expanded and developed. The results of the theoretical analysis are further proved by Brownian simulation and most importantly, by the experimental observation. It is found that the collective correlation function can be divided into the self-part and the distinct-part. The former shows the self-diffusion of the objects while the latter describes the mutual interactions. Dual-color fluorescence cross-correlation spectroscopy provides the direct measurements, from which these two parts can be separated. The particle concentration and the mean squared displacement of single particles can be derived from the self-correlation function while the correlation volume between particles can be approximately estimated from the cross-correlation function. The Debye length of the solution and the surface charge number of particles can be fitted from the cross-correlation function in the case of charged colloids.

![Fig. 1 The cross-correlation function of charged polystyrene colloids by dual-color fluorescence correlation spectroscopy.](image)

**Literature:**

**Acknowledgements:**
Financial supports by National Natural Science Foundation and the Joint Scholarship of Max-Planck Society and Chinese Academy of Science.
Determination of the Hydrodynamic Friction Matrix for Various Anisotropic Particles

Daniela J. Kraft\textsuperscript{1*}, Raphael Wittkowski\textsuperscript{2}, Kazem V. Edmond\textsuperscript{1}, Borge ten Hagen\textsuperscript{2}, David Pine\textsuperscript{1}, Hartmut Löwen\textsuperscript{2}

\textsuperscript{1} – Center for Soft Matter Research, New York University, USA
\textsuperscript{2} – Heinrich Heine University Düsseldorf, Germany
* - kraft@physics.leidenuniv.nl

The relationship between the shape of a colloidal particle and its Brownian motion can be captured by the hydrodynamic friction matrix. It fully describes the translational and rotational diffusion along the particle's main axes as well as the coupling between rotational and translational diffusion. We observed a wide variety of anisotropic colloidal particles with confocal microscopy and calculated the hydrodynamic friction matrix from the particle trajectories. We find that symmetries in the particle shape are reflected in the entries of the friction matrix. We compare our experimentally obtained results with numerical simulations and theoretical predictions.

Literature:

1. Daniela J. Kraft, Raphael Wittkowski, Borge ten Hagen, Kazem V. Edmond, David J. Pine, Hartmut Löwen, Brownian motion and the hydrodynamic friction tensor for colloidal particles of arbitrary shape (submitted)
The Short Time Dynamic Signature of the Liquid-Crystal-Glass Transition in Charged Spherical Colloidal Suspension

P. Holmqvist*

1Institute of Complex Systems (ICS-3), Forschungszentrum Jülich, D-52425 Jülich, Germany
* - p.holmqvist@fz-juelich.de

We present the short time dynamic transition of the liquid – crystal - glass transition. Applying dynamic light scattering (DLS) the short time dynamic function, D(q), has been determined from the intensity autocorrelation function, g_2(q,t), at different concentrations in both the crystal and glass region. From D(q) the short time self diffusion, d_s, was determined as a function of concentration. We found that d_s speeds up in the crystal state but has very similar characteristics in the liquid and the glass region. The corresponding structure factor, S(q), will also be presented and we show similarity between the glass and the liquid. This investigation shows that the liquid – crystal and crystal-glass transitions can be identified in addition to the appearance or no appearance of Bragg peaks with the short time dynamics. However no sharp transition in the short time dynamics or S(q) can be found between the glass and the liquid.
Driving Mechanisms Leading to the Dry-out of Nanofluids Droplets

Carle Florian, Brutin David*

Aix Marseille University, IUSTI UMR 7343, 13013, Marseille, France
* - david.brutin@univ-amu.fr

The dry-out after the evaporation of a droplet of nanofluids is of great interest since it is the consequence of several mechanisms including convection, wetting, fracturation and delamination. We investigate the role of each contribution in the final pattern by changing: - the humidity to increase or decrease the evaporation rate, the concentration to change the type of pattern observed, the substrate chemical nature to analyze the interaction between the substrate and the nanoparticles, the surface function groupment at the nanoparticles surface to quantify the role of nanoparticles-nanoparticles interaction on the final dry-out.

![Image](image.png)

**Figs. 1** Droplets of 24 nm diameter of polystyrene dry-out – Left picture: different substrates and nanofluids surface functional charges – Right picture: Teflon substrate and different concentrations.

We will present a summary of the driving mechanism leading to the dry-out of nanofluid droplet using quantitative example recently published or submitted for publication [1,2].

**Literature:**


Theoretical Analysis on the Orientational Characteristics and Rheological Properties of a Rod-like Hematite Particle Suspension in a Simple Shear Flow

Akira Satoh 1*, Yasuhiro Sakuda 1

1 – Faculty of System Science and Technology, Akita Prefecture University
* - asatoh@akita-pu.ac.jp

We have theoretically investigated the particle orientational and rheological properties of a dilute suspension composed of spindle-like hematite particles. This spindle-like hematite particle has a characteristic feature that the particle is magnetized in a direction normal to the major particle axis [1]. We have derived the basic equation of the orientational distribution function by taking into account the spin rotational Brownian motion about the particle axis [2] and this basic equation has been solved numerically. For a very strong magnetic field applied in the shear flow direction, the particle inclines in the direction normal to the flow direction. Also, the particle is restricted in a plane normal to the shearing plane due to the spin Brownian motion. Although the negative viscosity was observed in the previous study [2], in the present case these orientational properties of the particle give rise to positive viscosity. The viscosity becomes large with increasing magnetic field strength. In the case of an external magnetic field applied in the direction of the angular velocity of a simple shear flow, the particle inclines toward a plane normal to the shearing plane, while the magnetic moment is restricted in the direction of the magnetic field. For a strong shear flow, the particle inclines in the shear flow direction and does not rotate around the magnetic moment. The viscosity due to magnetic properties does not occur under the situation of the present magnetic field direction.

Fig. 1 Dependence of the viscosity on the magnetic field strength $\zeta$ for three cases of Peclet number (shear rate), $Pe$.

Fig. 2 Orientational distribution function for $Pe=5$ and $\zeta=20$; the particle has a stronger tendency to incline in a direction normal to the shear flow direction with the magnetic moment aligning in the magnetic field direction.

Literature:

Janus Particles in Confined Geometries: Density Functional Theory and Monte Carlo Simulations

Jaroslav Ilnytskyi¹, Andrzej Patrykiejew², Stefan Sokołowski²*

¹ – Institute for Condensed Matter Physics, National Academy of Sciences of Ukraine, 1 Sviantsitkii Street, 79011 Lviv, Ukraine
² – Department for the Modelling of Physico-Chemical Processes, MCS University, 20031 Lublin, Poland
* - stefan.sokolowski@gmail.com

We propose a Density Functional Approach to calculate the structure, thermodynamic properties and phase transitions in the system of Janus particles at a single wall and confined in slit-like pores. The Janus molecules are modelled as spheres composed of a hydrophilic and hydrophobic part. Both lattice, as well as lattice-off models are considered. The results of theoretical predictions are compared with Monte Carlo data, as well as with the results of previous Density Functional calculations.¹,² Moreover, in the case of lattice-off model we investigate how the solvation force between two plates changes with fluid chemical potential, temperature and the strength of the interparticle interactions. We also present a theory that describes Janus particles at planar walls modified by tethered chain molecules.³ The pinned chains are treated as tangentially jointed spheres that can interact with fluid molecules via orientation-dependent forces. In this case we study the adsorption of the particles, focusing on the competition between the external field (due to the surface and due to attached chain molecules) and the interaction-induced ordering phenomena.

Literature:


Acknowledgements: This work was supported by the EU under IRSES Project STCSCMBS 268498.
Microstructure Formation in Freezing Nanofluid Droplets

Renaud Denoyel and Mickaël Antoni*

Aix-Marseille Université, CNRS, MADIREL UMR 7246, 13397 Marseille cedex 20, France
* - m.antonii@univ-amu.fr

Nanofluids consist in suspensions of nanoparticles with specific interfacial properties that can be tuned by the addition of surface active molecules. When submitted to fast temperature changes, like for example quenching in slushed nitrogen, nanofluids can present important artifacts as illustrated in figure (a) [1,2]. In this work, the freezing kinetics of nanofluid droplets consisting in a suspension of 15 nm diameter silicon oxide nanoparticles is studied. When surfactant free, these nanoparticles are soluble in water up to 300 g/L. The droplets have few microliters volume and are kept at the end of a hydrophobic capillary tip immersed in a pure hexane continuous phase. This system is maintained in the field of view of an optical microscope and cooled down to -40°C. A high resolution image grabber and a temperature regulated device finally give a straightforward access to the solidification kinetics.

(a) Cryo-SEM image of a silicon oxide nanofluid after freezing in slushed nitrogen. The white pattern corresponds to nanoparticle microstructures. (b) and (c) freezing kinetics at two successive times at temperature T=−30°C. The black growing structure corresponds to propagating dendrites of frozen liquid. Time interval between the two images is 2.10−3 s and the field of view is 1 mm².

Depending on the silica nanoparticles concentrations and on the cooling rates (1 to 5°C/min), under cooled regimes up to 25°C can be achieved. Well known thermodynamical conditions are then reached for the formation of nucleation germs that will trigger the freezing of the complete droplets. Freezing starts either nearby the capillary tip or at the droplet interface (see figures (b) and (c)). A first regime then shows up. It is fast (few milliseconds) and displays rapidly growing dendrites that will fill out the droplet with a typical velocity that depends on the concentration of nanoparticles. This first regime is followed by a slow one (about one second) where the residual liquid between the dendrites progressively solidifies. It corresponds to the regime where the latent heat is evacuated from the inner part of the droplet to its periphery. When increasing the temperature back above 0°C, the droplets melt and flocculated silicon oxide microstructures can be evidenced.

Literature:
1. Limage, S., et al., Colloids and Surfaces A, 2009, 365, 154-161

Ángel V. Delgado*, S. Ahualli, M.M. Fernández, G. Iglesias, M.L. Jiménez

Department of Applied Physics, School of Sciences, University of Granada
18071 Granada, Spain
* - adelgado@ugr.es

Blue energy, or energy associated to salinity differences has recently gained interest as a true potential route for obtaining renewable energy by clean methods. Several procedures have been proposed to take this possibility to practical grounds [1-3], known under the common name of Capmix (Capacitive Mixing) techniques. In one of them (CDLE, [3]), a pair of porous electrodes (typically, activated carbon) are externally charged in contact with salty water (sea for example) and discharged in fresh water (river, for example). Since the interfacial potential increases when the ionic concentration is reduced at constant charge, the charge returns at higher potential, hence, gaining an amount of energy roughly equal to the product of the charge transferred times the potential increase. In practical terms [1,4], the typical values are, respectively, 100 mC and 50 mV, so the energy amounts to some hundred µJ. In this work, we present a model of the processes involved, and give clues as to the optimum working conditions. We will provide results of the simulations carried out at steady state and on the kinetics of the charging-discharging process, assuming cylindrical, parallel pores. As illustration, Fig. 1 shows the cycle and the predicted energy production as a function of the charging voltage for different values of pore radius. Experimental data will also be considered, and in particular we will analyse the main characteristics of the electrode material (pore size distribution, wettability) aimed at maximizing energy production.

![Fig. 1. Schematics representation of the working cycle and predicted energy production.](image)

**Literature:**


**Acknowledgements:** Financial support from EU (7th FP, Project CAPMIX) is gratefully acknowledged.
Gel Point Determination Thanks to Microrheology Measurement at Rest

Roland Ramsch, Christelle Tisserand*, Giovanni Brambilla, Gérard Meunier

* tisserand@formula.com

This work presents a new technique of the passive microrheology for the study of the microstructure properties of soft materials like emulsions, polymers, hydrogels. Our technology uses Multi Speckle DWS (MS-DWS) set-up in backscattering with a video camera. It allows to measure the mean displacement of the microstructure particles in a spatial range between 0,1 and 100 nm and a time scale between $10^{-3}$ and $10^5$ seconds. Displacement of probe particles is monitored to obtain directly the Mean Square Displacement (MSD) curve, which is the signature of the viscoelastic properties of a product. This technique allows to monitor the evolution of the microstructure, the restructuration after shearing, the variation of the viscoelastic properties versus temperature, pH...

This work focuses on viscoelastic properties evolution and particularly gel point transition. A new method called Time Cure Superposition is used to rescale MSD curves and obtain a master curve. From this curve can be automatically and precisely determined the liquid/solid transition. We will explain this rescaling method and show application examples and advantages of using a non intrusive method for:

- Gelation process of food products to measure gel point of yoghurt
- Carraghenan networks formation and comparison of their viscoelastic properties versus concentration.

Literature:

2. M.L. Gardel, M.T. Valentine and D.A. Weitz, “1 Microrheology”, Department of Physics and Division of Engineering and Applied Sciences, Harvard University, Cambridge MA 02138
Electrokinetic Properties of Biodegradable Conducting Polyaniline-

graft-Chitosan Copolymer in Aqueous and Non-aqueous Media

Mehmet Cabuk\(^1\)*, Mustafa Yavuz\(^2\), Halil Ibrahim Unal\(^3\)

\(^1\)Department of Chemistry, Faculty of Arts and Sciences, Mus Alparslan University, Mus, Turkey
\(^2\)Department of Chemistry, Faculty of Arts and Sciences, S. Demirel University, Isparta, Turkey
\(^3\)Gazi University, Chemistry Department, Smart Materials Research Lab. Ankara, Turkey

* - mcabuk@alparslan.edu.tr

Zeta (\(\zeta\))-potential measurements are one of the most powerful tools to investigate the colloidal properties. Electrokinetic data are used to determine the \(\zeta\)-potential characteristics of the materials [1,2]. In this study, electrokinetic properties of polyaniline-graft-chitosan (PAni-g-CS) copolymer, synthesized by chemical oxidative radicalic polymerization, were investigated. The effects of time, pH, electrolytes, various surfactants, and temperature onto \(\zeta\)-potentials of the dispersions prepared in polar (water) and non-polar (silicone oil) media were examined. The \(\zeta\)-potential of PAni shifted to more positive regions after grating with chitosan (Fig. 1). Concomitantly, the isoelectric point of the PAni homopolymer shifted to higher pH value. In acidic medium, \(\zeta\)-potential of the copolymer was observed to increase up to +44 mV. It was concluded that the presence of monovalent (\(NaCl\)) electrolyte had no impact on \(\zeta\)-potentials of the copolymer whereas; divalent (\(BaCl_2\)) and trivalent (\(AlCl_3\)) electrolytes caused the \(\zeta\)-potentials to shift to more positive regions. Mastery of this study will be very helpful for designing, fabricating, and developing further new materials based on biodegradable chitosan and conducting polymers.

![Fig. 1](image_url)

**Fig. 1** Effect of pH on \(\zeta\)-potentials of the materials, \(c_{\text{samples}} = 0.1 \text{ g/L, } T = 25 ^\circ \text{C}\)

**Literature:**


**Acknowledgements:**

The authors thanks to SDU-BAP (project No: 2224-D-10), COST Action CM1101 and TUBITAK (111T637) for the financial support of this work.
The classical theory of the laminar electro-Brownian coagulation of charged particles in the transition regime has been founded by N. Fuchs and based on his “boundary sphere” concept. However, this theory missed the hydrodynamic factor, i.e., dependence of a diffusion coefficient of closing particles on their separation. First, this factor was proposed by B. Derjaguin in his theory of colloidal stability. But its relevant incorporation into the theory of coagulation of aerosol particles is still under a question. In our theoretical studies, we considered this problem and proposed a “refined classical model” (RCM) of coagulation of charged nano-sized aerosols with correct including this missed factor. In an initial model, we consider van der Waals’, Coulomb’s and “image” driving forces. The RCM and the corresponding refined classical theory (RCT) of aerosol coagulation are used for describing coagulation and stability of charged and uncharged nano-aerosols in the transition Knudsen range (0.1 < Kn < 10) that is typical for motion of nanoparticles in the air.

The major new results of this approach are (1) the criteria of RCM/RCT validity and their limits, (2) the exact steady-state charge distribution function describing aerosol ensemble in the bipolar ion atmosphere, (3) the DLVO-type criterion of preventing coagulation of charged particles, and (4) the refined electro-Brownian coagulation coefficient with the enhancement factor in the Knudsen transition regime. A comparison of the theory with other theoretical and experimental data on soot nanoparticles shows a good semi-quantitative agreement in most important cases [1,2].

**Literature:**


**Acknowledgements:** The Russian Foundation for Basic Research (grant 12-07-00654).
Microemulsions as Carrier Media for Environmentally Friendly Enzymatic Decontamination of Lipophilic Toxic Compounds

Christoph Schulreich¹, Salomé Vargas Ruiz², Martin Jung³, André Richardt³, Stefan Wellert²*, Thomas Hellweg¹

¹ Physical Chemistry III, University Bielefeld, Universitätsstraße 25, 33615 Bielefeld, Germany
² Stranski Laboratory, Technical University Berlin, Str. d. 17.Juni 124, 10623 Berlin, Germany
³ Armed Forces Scientific Inst. f. NBC Protection, Humboldtstraße1, 29633 Munster, Germany
* - s.wellert@tu-berlin.de

Decontamination is the process of removal or neutralization of surface hazards resulting from a chemical attack or an accidental release of toxic chemicals, e.g. organophosphates as insecticides and chemical warfare agents. Modern decontamination media have to match requirements, which allow to reconstitute personnel and equipment rapidly. Their ability to extract penetrating chemical agents and industrial chemicals out of sorptive surfaces is of importance and they have to be noncorrosive, nontoxic and environmentally friendly. In recent years natural surfactants, e.g. alkyl polyglucosides attract increasing interest for new applications of liquid decontamination agents. For example, microemulsions based on sugar surfactants and plant and food grade oils combine a soft and "green" performance with a phase behaviour of low temperature sensitivity.

For a series of such bicontinuous microemulsions, we discuss extraction and wetting properties for model and realistic surfaces of different degrees of hydrophobicity. These systems overcome the problem of solubilisation of the hydrophobic contaminant. Additionally, the effect of enzyme addition to these microemulsions was investigated. The enzyme Diisopropyl fluorophosphatase (DFPase) from the squid Loligo vulgaris efficiently detoxifies highly toxic organophosphorus compounds. DFPase can be used in bicontinuous microemulsions where it remains catalytically active which can be shown by the use of NMR and FTIR spectroscopy. Scattering techniques allow us to confirm that structure and dynamics of the amphiphilic interface are not affected by the presence of the enzyme. Hence, these sugar surfactant based bicontinuous microemulsions are promising environmentally friendly compartmentalized reaction media providing interesting properties for biotechnological applications in general.
Synergism by Co-assembly at the Origin of Ion Selectivity in Solvent Extraction

S. Dourdain¹*, I. Hofmeister¹, O. Pecheur², J-F. Dufrêche¹, R. Turgis¹, A. Leydier¹, J. Jestin³, F. Testard⁴, S. Pellet-Rostaing†¹, T. Zemb†¹

¹ – ICSM/LTSM, CEA/CNRS/UM2/ENSCM UMR5257, Site de Marcoule, Bat 426, 30207 Bagnols sur Ceze, France
² – CEA, Nuclear Energy Division, RadioChemistry & Processes Department, 30207 Bagnols sur Cèze, France
³ – Laboratoire Léon Brillouin CEA/CNRS, CEA Saclay, 91191 Gif-sur-Yvette, France
⁴ – DSM/IRAMIS/SIS2M/LIONS, CEA Saclay, Bat 125, 91191 Gif-sur-Yvette, France

* - sandrine.dourdain@cea.fr

In solvent extraction, synergism emerges when for a defined formulation of the solvent phase, there is an increase of distribution coefficients for some cations in a mixture. To characterize the synergistic mechanisms, we determine free energy of mixed co-assembly in aggregates. Aggregation in any point of a phase diagram can be followed not only structurally by SANS, SAXS and SLS, but also thermodynamically by determining the concentration of monomers coexisting with reverse aggregates. Using the industrially used couple HDEHP/TOPO forming mixed reverse aggregates, and the representative couple U/Fe¹, we show that there is no peculiarity in the aggregates microstructure at the maximum of synergism. Nevertheless the free energy of aggregation necessary to form mixed aggregates containing extracted ions in their polar core, is comparable to the transfer free energy difference between target and non-target ions, as deduced from the synergistic selectivity peak.² The effect of extracted ions and solvents on aggregation will be discussed in this talk.

Fig. 1 Aggregation and transfer energy correspondence in and out of synergism.

Literature:

Acknowledgements:
Fruitful discussions with O. Diat, P. Bauduin, K. Nash, M.C. Charbonnel, D. Guillaumont and H. Moewald are deeply acknowledged. We also thank the GUTEC foundation for its support.
Ultrasonic Approach for Nanoparticles in Water

Darya Radziuk1*, Dmitry Shchukin,2 Wei Zhang,3 Andre Skirtach,4 Michael U. Kunke,5 Peter Weßels6 and Helmuth Möhwald1

1 – Max-Planck Institute of Colloids and Interfaces, Department of Interfaces am Mühlenberg 1, DE-14467 Potsdam, Germany
2 – University of Liverpool, Department of Chemistry, Crown Street, Liverpool L69 7ZD, United Kingdom
3 – Technical University of Denmark, Department of Energy Conversion and Storage, Risø Campus, 4000 Roskilde, Denmark
4 – University Gent, Department of Molecular Biotechnology, Coupure Links 653 Bl. B 9000 Gent, Belgium
5 – University of Potsdam, Institute of Chemistry and Physical Chemistry, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam, Germany
6 – Laser Center Hannover e.V., Hollertithalle 8, 30419 Hannover, Germany
* - darya.radziuk@mpikg.mpg.de

Acoustic cavitation is widespread in both research and industry with the emphasis on water purification, cleaning of surfaces and formation or design of novel materials as a green and environmentally friendly technology. The remarkable effects of cavitation arise from tiny bubbles that act as hot spots with supersonic extremes far above molecular level in otherwise cold bulk. Typically the surface energy of ultrasound is transformed into chemical (sonochemistry), mechanical (shock waves or jets) or thermal (thousand K and atm) energy avoiding chemical pollution, expensive apparatus and long time processing.

Here we demonstrate several designed ultrasonic approaches to form amorphous materials (relevant for catalysis),1 modify plasmonic surfaces2 (important for SERS) and synthesize fluorescent geometries3 at the nanoscale of colloidal solutions in water. Figure 1 shows electron images of ultrasonic amorphous platinum nanoparticles, gold-silver nano-alloys and fluorescent erbium oxide nanoparticles in organic-free water. To note, the latter normally requires organic substances to form well-defined morphology that exhibit optical properties.

Fig. 1 In water (A) TEM image of amorphous Pt nanoparticles after 20 min of sonication, (B) STEM images of ultrasonic Au-Ag alloy and (C) SEM image of erbium oxide nanoparticles.

Literature:

Acknowledgements:
Joint German-French “LEA” laboratory and PROCOPE-2008 project, Nanofuture (BMBF) and Gay-Lussac award to prof. H. Möhwald
Humic substances form the key constituent of natural organic matter in numerous natural environments (soils, sediments, water aquifers), where they take responsibility for crucial ecological effects (e.g. self-detoxification of soils). As they are formed primarily from the biodegradation of plant residues, they are characterized by a complex molecular structure with plenty of diverse functional groups which result in unusual and versatile reactivity and sorption ability of natural humic matrices. This interesting nature of humic substances stands behind their ability to control the transport of low-molecular compounds in the environment (e.g. transport of nutrients, pollutants or pesticides in soils) and motivate reactivity-mapping studies on humics. Recently, various laboratory diffusion techniques were introduced [1-2] in order to illustrate an effect of interactions with humic substances on the transport of ionic compounds in model humic matrices (i.e. humic hydrogels). This contribution summarizes most recent experiments utilizing diffusion cells technique and non-stationary diffusion experiments (Fig. 1) in reactivity-mapping on humic substances, applied in agarose-supported hydrogel. In the experimental part, effect of numerous experimental parameters (concentration of humic substances in the hydrogels, pH, ionic strength, selective masking some reactive groups) on representative transport parameters of low-molecular compounds (effective diffusion coefficients, partition coefficients) have been systematically studied. As was experimentally confirmed, two opposing effects take place in these reactive systems— on the one side, interactions between HAs and the diffusing dyes causes improved partitioning of the dye in the gel (characterized by high concentration jump at the solution-gel interface) but at the same time, it strongly suppress the mobility of the dye in the gel (characterized by value of diffusion coefficient)

![Fig. 1 Picture of diffusion cells apparatus (left) and samples from non-stationary diffusion experiments (right)](image)

**Literature:**


**Acknowledgements:**

This work has been supported by Czech Science Foundation, project P106/11/P697.
Rotational Diffusion in Concentrated Platelet Systems Measured with X-ray Photon Correlation Spectroscopy

1 P. Holmqvist*, 2 V. Meester, 3 F. Westermeier and 2,†D. Kleshchanok

1 Institute of Complex Systems (ICS-3), Forschungszentrum Jülich, D-52425 Jülich, Germany
2 Van ’t Hoff Laboratory for Physical and Colloid Chemistry Debye Research Institute Utrecht University Utrecht, The Netherlands
3 Hasylab, Deutsches Elektronen-Synchrotron, D-22607, Germany
†current address: Science and Technology centre Geleen, Sabic Europe, The Netherlands
* - p.holmqvist@fz-juelich.de

Using X-ray Photon Correlation Spectroscopy (XPCS) we have measured the rotational modes of concentrated charged gibbsite platelets in the isotropic regime. This has been done by analyzing the data qualitatively using available theories for non interacting systems. The relaxation spectra do not follow the same pattern as for spherical particles at larger wave vectors. It will be shown that this deviation from the behavior of spherical systems arises from the influence of the rotational modes. In addition, in the isotropic state a pre-transitional peak in the static q-dependent intensity at large q values is discussed. We suggest that this peak originates from a strong local alignment between platelets before the actual phase transition takes place.
Starch-assisted Green Synthetic Route of Nanosized Zinc Oxide with Promising Photocatalytic Properties

P. Vasileva*, N. Stamenov, B. Cherkezov

1 - Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia, Bulgaria
* - pvasileva@chem.uni-sofia.bg

Gel matrix of the natural polysaccharide starch has been employed as a template for the sol-gel synthesis of zinc oxide nanoparticles via solution-solid technique. The template offers selective binding sites for Zn (II) under aqueous conditions. Controlled solvent-exchange, further isolation of solid product by microfiltration and drying, and subsequent removal of the template backbone enable the synthesis of spatially separated zinc oxide nanocrystals with smaller crystallite size and higher surface area.

The crystalline character of the zinc oxide and near narrow particle size distribution pattern have been confirmed through powder XRD measurements and TEM with SAED observation. The average crystallite size of the particles obtained at optimal synthesis conditions was found to be 16 nm irrespective of the nature of the template. The morphology, surface and optical properties of ZnO samples were characterized by SEM observation, BET-surface area and ζ-potential measurements, UV–Vis and PL spectra.

The UV photocatalytic activity of zinc oxide nanoparticles was studied and compared with TiO₂ (P25) by analyzing the degradation of methylene blue (MB) in aqueous solution. The nanosized ZnO sample showed greater photocatalytic activity than commercial TiO₂ photocatalysts. The size and shape factors seem to be of great importance in the observed photocatalytic performance.

Fig. 1 (A) SEM and (B) TEM images of nanocrystalline ZnO; inset in (B): SAED pattern; (C) Evolution curves of MB photocatalytic degradation on TiO₂ (Degussa P25) and ZnO nanoparticles.

Acknowledgements: The Scientific Research Fund of Sofia University “St. Kliment Ohridski” (Project 118/2013) has supported this work.
Gold and Silver Nanoparticles: Green Synthesis, Immobilization onto Silica Spheres and Analytical Applications

P. Vasileva¹*, T. Yordanova², L. Djerahov², I. Karadjova²

¹ - Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry
² - Department of Analytical Chemistry
Faculty of Chemistry and Pharmacy, University of Sofia, Bulgaria

* - pvasileva@chem.uni-sofia.bg

In this work, aqueous dispersions of silver (Ag NPs, $D_{av}=14$ nm) and gold (Au NPs, $D_{av}=11$ nm) nanoparticles were synthesized by green chemical reduction method using carbohydrates as reducing and stabilizing agents. The colloid mixing method were applied to immobilize the starch-coated Ag NPs and Au NPs onto the surface of amine-functionalized silica (SiO₂) submicrospheres ($D_{av}=400$ nm). The size, morphology, structure, surface and optical properties of nanoparticles and nanocomposites were characterized by transmission electron microscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, dynamic light scattering, zeta potential measurements, UV-vis spectroscopy.

Simple, fast and low cost procedures were developed for highly sensitive and selective quantitative sensing of Hg (II) and Cr (VI) using aqueous dispersions of starch-stabilized and raffinose-stabilized silver nanoparticles as optical sensing systems. Colorimetric probes developed are based on various mechanisms including sorption of analytes, redox reaction and/or aggregation of silver nanoparticles. The sensitivity and selectivity of colorimetric sensors proposed towards interferent transition-metal ions, alkali metal ions and alkaline earth metal ions were studied. The effect of the analyte concentrations to the Ag NPs optical response was considered and the LODs for analyte determination were defined.

Nanocomposite particles SiO₂-AgNPs and SiO₂-AuNPs were characterized as sorbents for speciation and determination of iHg and methylHg in surface waters. Several parameters such as acidity of the sorption media, amount of sorbent, time of sorption, type and concentration of the eluent were optimized in order to define chemical conditions for selective separation and enrichment of both iHg and methylHg. Analytical schemes for speciation and determination of Hg were developed.

Acknowledgements: to BeyondEverest project FP7-REGPOT-2011-1
Highly Water Repellent Coatings in Marine Environment

Michele Ferrari*, Libero Liggieri, Francesca Ravera, Francesca Cirisano, Eduardo Guzmán, Alessandro Benedetti

CNR - Istituto per l’ Energetica e le Interfasi, Italy
* - m.ferrari@ge.ieni.cnr.it

Highly water repellent coatings with wettability properties known as superhydrophobicity (SH) are related to surfaces with contact angle above 150° and a very small hysteresis. The small area available for these surfaces when in contact with water address to be exploited in many applications where interactions with aqueous environment are usually strongly to be avoided like for protection and friction reduction in marine environment. With the aim to provide more resistant and long lasting coatings, the SH surfaces under investigation have been prepared by different preparation methods and studied in presence of pure water, marine waters, solutions and dispersions. Depending on the preparation SH surfaces show different aging resistance due to the composition and thickness of the coating. Wetting studies and surface characterization show how the use of patterned and non patterned surfaces can be used to achieve different aims in terms of fouling prevention and protection of metals in underwater conditions.

Literature

Acknowledgements:
The Authors acknowledge the RITMARE( La Ricerca Italiana per il Mare) Project for the financial support.
Uptake of Six Heavy Metal Cations by Synthetic Goethite

Edward Maćzka¹ and Marek Kosmulski¹,*

¹ – Lublin University of Technology, Lublin, Poland
* - mkosmuls@hektor.umcs.lublin.pl

Synthetic goethite [1] was characterized by means of XRD, SEM, BET, electrophoretic mobility, electric sonic amplitude, and Mössbauer spectroscopy [2-4]. The particles had an acicular shape (470 nm long, and 66 nm wide), the specific surface area was 40 m²/g, and the IEP was at pH 9.4. The uptake of heavy metal cations at various pH and initial concentration of metal cations of 10⁻² M was studied by ASA. The uptake decreased in a series Cu>Pb>Zn>Co>Ni=Cd, which is typical for other studies of uptake of metal cations by iron (hydr)oxides [5], and which is correlated with the 1st hydrolysis constants of metal cations.

Literature:

Gravity Effects on Particle-bubble Interactions in Granulometric Separation Processes

L. Nikolov*

Institute of Physical Chemistry, Bulgarian Academy of Sciences
"Acad.G.Bonchev" Str., bl.11, Sofia 1113, Bulgaria
* - liubo_nik@yahoo.com

The influence of the gravity effects on the behaviour of fine particles in the boundary layer of rising bubbles is presented. By scaling analysis the role of the gravity in addition to the dynamic interaction, caused by the finite dimensions of the particles is explained. An asymptotic model for the disturbance field caused by fine heavy solid is obtained and solved analytical. The trajectories of sub- and micron sized heavy particles in the boundary layer are calculated. It is found that the rejection outside of the boundary layer or “capturing” particle-bubble effect is observed (may be expected) with increasing the density of the solid. An idea it is also given about granulometric separation of particles by the bubble. A criterion for separation, which may be experimentally clarified is found.
Adsorption Properties of Surfactants and Their Mixtures – Potential Components of Industrial Degreasing Agents

Katarzyna Radwan\textsuperscript{1}, Monika Rojewska\textsuperscript{2}, Joanna Rakowska\textsuperscript{1}, Bożena Twardochleb\textsuperscript{3}, Krystyna Prochaska\textsuperscript{2}\textsuperscript{*}

\textsuperscript{1} – Research Centre for Fire Protection – National Research Institute, Józefów, Poland.
\textsuperscript{2} – Poznan University of Technology, Institute of Chemical Technology and Engineering, Poland,
\textsuperscript{3} – Institute of Heavy Organic Synthesis "Blachownia", Kędzierzyn-Koźle, Poland,
\textsuperscript{*} - krystyna.prochaska@put.poznan.pl

Eco-friendly degreasing agents useful in various branches of industry should be effective at very low dosage, should exhibit a low tendency to foaming and should possess very high emulsion stability at any pH. Furthermore, it should be readily biodegradable. The main components of degreasing agents are surfactants which are responsible mainly for the decrease of surface/interfacial tension and increase of the wettability. Usually degreasing systems contain two or three surfactants because the mixed systems exhibit much better adsorption/wetting properties than the individual components. In order to obtain a recipe of effective degreasing agent, a selection of suitable surfactants is required.

The main goal of presented investigations was the determination and comparison of adsorption properties at the air/water interface of selected commercial surfactants and their binary mixtures which are potential components of the industrial degreasing compositions. Surface and micellar properties of surfactants and their mixtures were discussed on the basis of equilibrium surface tension measurements and study of kinetics of adsorption.

Five commercial surfactants were investigated: two anionic compounds and three non-ionic derivatives. All measurements were carried out at 294 K. Equilibrium surface tension at the air/water system for individual compounds and their binary mixtures was measured by du Noüy ring method using K12 Krüss and KSV Sigma 701 tensiometers. Dynamic surface tension measurements were performed using the bubble pressure tensiometer (Sita t60, Germany), which registered change of surface tension in time from 30 ms to 60 000 ms.

The application of Frumkin's equation to approximate the experimentally obtained equilibrium surface tension isotherms allows estimation of adsorption parameters, as: the partial molar area of a surfactant molecule at the surface ($\omega$), surface excess at the saturated interface ($\Gamma^\infty$) and free energy of adsorption ($\Delta G_{ads}$). On the basis of the dynamic surface tension data for micellar solution the magnitude of micelle dissociation rate constant were estimated.

The experimentally obtained surface tension isotherms in the air/water system for all surfactants investigated allowed to compare the surface activity of these compounds. Observed differences of the kinetics of adsorption and the abilities for lowering the surface tension are significant. Compounds studied reveal both different efficiency as well as different effectiveness of adsorption in the air/water system. The results of study of surface activity for binary systems indicated that some of investigated mixtures showed strong synergistic effect in reducing of surface tension in the air/water system.

Acknowledgements:

The research was financially supported by DS-PB/32/067/2013 and 016/BC/CNBOP-PIB/2013.
Supramolecular Solvent-Free Nanofluids

John Texter*

Coatings Research Institute, Eastern Michigan University, Ypsilanti, MI 48197, USA
* - jtexter@emich.edu

We show that auto-condensation of organoalkoxysilanes, followed by suitable anion exchange, produces solvent-free nanoparticle nanofluids we call organosiloxane supramolecular liquids. We find that classical liquid properties are exhibited with some distinct differences. We observe heat capacity anomalies manifested as lambda transitions in excess heat capacity centered around a glass transition ($T_g$) and around a freezing transition. The $T_g$-proximal lambda transition is the first experimental realization of an enthalpic phase transition overlying a glass transition. The existence of such a connection or coincidence has undergone decades of theoretical conjecture. The second anomaly spanning the melting/freezing range is the first reported excess enthalpy ever reported for an experimental particulate fluid undergoing a phase transition. The integral enthalpy from these lambda transitions is quantitatively accounted for by the loss of specific surface area of the particles, and the associated surface free energy, upon freezing and upon cooling beneath the glass transition temperature. This new material and cousins to be similarly derived promise to become useful in developing soft-sphere potentials in the thermodynamics of polymeric liquids.\(^1\)

Similarly composed nanofluids obtained by condensation on nanosilica core templates and surface decorated with both ionic liquid organic salt groups and with various reactive groups are exotic cross-linking agents that define new types of resins. Such agents can be used to counter embrittlement provided by nanofillers while increasing toughness. We show that such materials can be used to produce thin films including UV protective clearcoats and an interesting new family of adhesives.\(^2,3\)

![Fig. 1 TEM of nanofluid (20 nm scale bar)](image)

Literature:

Laplace Equation of Capillarity Extension for Non-Localized Situations to Included Capillary Systems Containing Surface and Line Boundaries

J. Gaydos*

Department of Mechanical and Aerospace Engineering, Carleton University, 1125 Colonel By Drive, Ottawa, K1S 5B6, CANADA
* - jgaydos@mae.carleton.ca

Classical expressions for mechanical equilibrium in capillary systems such as the Laplace, Young and Neumann triangle relation can be derived using a calculus of variations approach that minimizes the composite system’s free energy subject to constraints to obtain extremals. These free energy expressions are functionals of the equations that characterize the system’s boundaries and they yield localized expressions between the intensive properties (e.g. pressure, surface tension, etc.) and the boundary geometry. However, for very small systems with nonlocalized behaviour new approaches or extensions are required. These extensions provide for consideration of functionals of functional that lead to Euler-Lagrange equations that are integro-differential in character. This expands the ability to describe capillary systems beyond solely differential equations and permits a description of interfacial forces such as disjoining pressure, etc. within a consistent formulation.
Shear Microrheology of Complex Fluids Using Magnetic Wires

L. Chevry, R. Colin, B. Abou and J.-F. Berret*

Matière et Systèmes Complexes, UMR 7057 CNRS Université Denis Diderot Paris-VII, Batiment Condorcet, 10 Rue Alice Domon et Léonie Duquet, 75205 Paris, France

* - jean-francois.berret@univ-paris-diderot.fr

Rheology is the study of the deformation and flow of matter. It is usually performed on macroscopic samples to determine a value of the viscosity, or a frequency-dependent response. Rheology on biological fluids is more challenging because of the small amounts of fluid available. Living cells for instance have volumes of the order of 10^{-12} L, and can only be studied with specific micro-rheology techniques, e.g. by embedding colloids in the cell interiors and monitoring their motion by microscopy [1]. Here, we present a micro-rheology technique based on the use of magnetic wires. Micron-sized wires of diameter 0.5 µm were synthesized following the electrostatic assembly of iron oxide nanoparticles. Passive/active micro-rheology was first conducted on model liquids, such as Newton and Maxwell fluids. These experiments reveal excellent agreement with theory [2].

Experiments were then carried out with wires embedded in the intracellular medium of murine fibroblasts [1] and of canine kidney epithelial cells (Figure 1). The mean-squared angular displacement (MSAD) of wires was obtained as a function of the time using an original tracking technique. The MSAD reveals a Brownian-like diffusive regime and a rotational diffusion constant varying as \( \ell^{-2} \), where \( \ell \) is the wire length. This scaling suggests that for the fibroblasts and for the epithelial cells, an effective viscosity of the cell interior can be determined. Values of viscosity were found at 0.16 and 1.4 Pa s, respectively, i.e. 200 and 1800 times the viscosity of water (T = 37°C). These results are discussed in the light of previous cell mechanics experiments, and demonstrate the importance of innovative probes for studying fluids in confined environments.

Literature:

Viscoelastic Instabilities of Core Annular Flows

Hugo Doméjan 1*, Jérôme Bibette 1 and Nicolas Bremond 1.

1 – LCMD, ESPCI ParisTech
* - hugo.domejean@espci.fr

Making materials via an extrusion step usually involves complex liquids that are known to exhibit bulk and interfacial instabilities. Here, we present an experimental study on the stability of the co-extrusion of two miscible liquids. The existence of a liquid core that is miscible with the surrounding layer, which is more viscous or has viscoelastic features, leads to a partial mixing inside the injector. Then, a flapping instability of the resulting free compound jet, which is formed in air at rest, is observed. Understanding and controlling such instabilities should enable to create new kind of core-shell materials.

We use concentric round glass capillaries in order to visualize the primary destabilization before formation of the compound free jet. Moreover, a harmonic perturbation of the flow rates can be superimposed. In that way, the frequency response of this co-flow can be assessed. The interface position between the two liquids, which is controlled by the flow rate ratio, is a key parameter that controls the transition between a stable regime towards an unstable one. Different flow patterns have been identified as a function of the liquid and flow properties. In particular, we observe a spiral motion of the core when polymers are added into the shell liquid.

The destabilization of the core directly impacts on the formation of the resulting compound jet in air. A flapping motion is observed when the core is subjected to azimuthal fluctuations. The polymer chains of the shell fluid are elongated under shear inside the injector. Then, in air, the relaxation of the associated normal stress induces a swelling of the free jet. The spiraling motion of the core leads to an anisotropic stress relaxation that deviates laterally the jet and thus induces a flapping movement. All these flow instabilities preclude any controlled fragmentation of the resulting compound jet for making core-shell objects. By damping the flow fluctuations inside the injector and by using a polymer solution that can be further solidified, we managed to produce monodisperse micrometric capsules having a liquid core.

Fig. 1 The core fluid is water with ink and the shell one is a polymer solution. Scale bar = 500µm. (a) Spiraling mode of the shear instability of a confined co-flow. (b) Flapping instability of a compound free jet. (c) Controlled fragmentation of the compound free jet without the flapping motion.
Drops Impacting Water- and Oil Repellent Coatings
Doris Vollmer*, Xu Deng, Frank Schellenberger, Periklis Papadopoulos, Hans-Jürgen Butt

1 Max Planck Institute for Polymer Research, 55128 Mainz, Germany
* - vollmerd@mpip-mainz.mpg.de

Impact dynamics of liquid drops is of high importance in a variety of industrial processes such as rapid spray cooling, spray painting and coating, or deposition of pesticides on plant leaves. Of special importance is the transition regime between complete rebound and pinning since it goes in hand with a change of the wetting behavior.

Here, we study impact dynamics of drops on so called “superamphiphobic” coatings, i.e. coatings that repel both, water and oil.[1] Superamphiphobic coatings extend the properties of superhydrophobic coatings towards low interfacial tension liquids. Both, water and oil drops do not wet a superamphiphobic surface but roll-off, when tilting the coating by less than 5°.

We fabricated superamphiphobic coatings that consist of a fractal-like fluorinated silica network.[2] Mixtures of ethanol-water and glycerin-water are chosen to investigate the influence of interfacial tension and viscosity on spreading and retraction dynamics. At low impact velocity the drops completely rebound. However, the contact time increases with impact velocity. Now, the drops temporarily impale the superamphiphobic coating (Fig. 1). Further increase of the impact velocity causes partially pinning. An increasing amount of liquid remains on the coating. The depth of impalement increases with impact velocity, where impalement is confined to the initial impact zone of the drop. From an estimate of the pressure is can be concluded that impalement is dominated by depinning.

Fig. 1 Sketch of the evolution of a retracting drop, after impacting a superamphiphobic surface

Literature:
1. Xu Deng, Frank Schellenberger, Periklis Papadopoulos, Doris Vollmer, Hans-Jürgen Butt; Liquid drops impacting superamphiphobic coatings, submitted
2. X. Deng, L. Mammen, H.-J. Butt, and D. Vollmer; Transformation of black candle soot into a transparent robust superamphiphobic coating, Science 335, 67 (2012)
Ultrasonic Approach for Nanoparticles in Water

Darya Radziuk, Dmitry Shchukin, Wei Zhang, Andre Skirtach, Michael U. Kunke, Peter Weßels and Helmut Möhwald

1 – Max-Planck Institute of Colloids and Interfaces, Department of Interfaces am Muhlenberg 1, DE-14467 Potsdam, Germany
2 – University of Liverpool, Department of Chemistry, Crown Street, Liverpool L69 7ZD, United Kingdom
3 – Technical University of Denmark, Department of Energy Conversion and Storage, Risø Campus, 4000 Roskilde, Denmark
4 – University Gent, Department of Molecular Biotechnology, Coupure Links 653 Bl. B 9000 Gent, Belgium
5 – University of Potsdam, Institute of Chemistry and Physical Chemistry, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam, Germany
6 – Laser Center Hannover e.V., Hollerithallee 8, 30419 Hannover, Germany
* - darya.radziuk@mpikg.mpg.de

Acoustic cavitation is widespread in both research and industry with the emphasis on water purification, cleaning of surfaces and formation or design of novel materials as a green and environmentally friendly technology. The remarkable effects of cavitation arise from tiny bubbles that act as hot spots with supersonic extremes far above molecular level in otherwise cold bulk. Typically the surface energy of ultrasound is transformed into chemical (sonochemistry), mechanical (shock waves or jets) or thermal (thousand K and atm) energy avoiding chemical pollution, expensive apparatus and long time processing.

Here we demonstrate several designed ultrasonic approaches to form amorphous materials (relevant for catalysis), modify plasmonic surfaces (important for SERS) and synthesize fluorescent geometries at the nanoscale of colloidal solutions in water. Figure 1 shows electron images of ultrasonic amorphous platinum nanoparticles, gold-silver nano-alloys and fluorescent erbium oxide nanoparticles in organic-free water. To note, the latter normally requires organic substances to form well-defined morphology that exhibit optical properties.

![Figure 1](image_url)

**Fig. 1** In water (A) TEM image of amorphous Pt nanoparticles after 20 min of sonication, (B) STEM images of ultrasonic Au-Ag alloy and (C) SEM image of erbium oxide nanoparticles.

**Literature:**

**Acknowledgements:**
Joint German-French “LEA” laboratory and PROCOPE-2008 project, Nanofuture (BMBF) and Gay-Lussac award to prof. H. Möhwald
The world of drug delivery is getting every day more efficient with new product forms, which are directly targeting the deficient organs. Colloidal systems such as emulsions (simple or multiple) or nanoparticle suspensions are now widely used as drug carriers or nutritional solutions in this respect. These new product forms allow better targeting and assimilation for the patient, and give rise to new solutions for the drug designers. However, the stability of these inherently unstable colloidal systems makes them complex to formulate and study. Despite the existence of models and increasing knowledge on physical chemistry to help the formulator to tend towards more stable formulations, he cannot take the risk to select an industrial formula for its sole end-use properties without testing the stability experimentally, when an unstable formulation can risk the life of the patient he is trying to cure. Therefore, the companies developing instruments have worked in collaboration with the physical chemists, from industry and research, to develop new techniques of analysis for either predicting the stability of these mixtures, or reducing times of ageing tests. These techniques, although very powerful, require a good knowledge of measurement to interpret the results. This presentation aims to review the main examples of multiple light scattering to monitor the physical stability of colloidal systems for pharmaceutical applications.