Osmotic Equations of State of Dipolar Fluids from Analytical Centrifugation

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The dipolar hard sphere (DHS) model is of fundamental importance in the statistical thermodynamics of polar liquids such as ethanol, hydrogen fluoride, water, and apolar ferrofluids. Despite the apparent simplicity of the DHS-model, it confronts us with puzzling phase behavior, especially regarding the longstanding controversy about the existence of isotropic gas-liquid phase separation. There are no molecular dipolar hard spheres, since permanently dipolar molecules cannot be spherical and any dipolar interaction is always supplemented by the Van der Waals attraction. Our approach is to use apolar ferrofluids as an experimental model system for dipolar hard spheres and to determine experimental osmotic equations of state from sedimentation-diffusion equilibrium concentration profiles in the centrifugal field of an analytical centrifuge.

Monodisperse single-domain magnetite nanoparticles (Fe₃O₄) with diameters in the 4-20 nm range were prepared by a seed-mediated growth procedure [1] and dispersed in an apolar organic solvent. Sedimentation-diffusion equilibrium profiles were integrated, which is shown to be an extremely sensitive and model-independent way to determine the osmotic pressure as a function of concentration even below one pascal [2, 3]. We have previously demonstrated that sedimentation velocity is strongly depends on interactions between magnetic nanoparticles [4]. Here, we will present the first experimental equations of state for apolar ferrofluids and compare these with theory.