Improved Models of Colloidal Gels: Kinetic Arrest, Relaxation Dynamics, Structural Breakdown and the Role of Hydrodynamic Interactions

by

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Abstract

Colloidal gels, composed of sub-micron, mutually attractive particles that aggregate to form a system spanning network, are the most abundant and diverse soft matter in society with numerous familiar, yet also many exotic applications, ranging from common dairy products to novel medical implants. Despite this profusion, the link between network microstructure and macroscopic behavior and function remains a mystery. Computational models of the microstructural evolution of colloidal gels present one opportunity to efficiently study the emergence of bulk material properties. However, these simulations often fail to match experimental results and are unable to reproduce landmark observations set as benchmarks. This thesis is concerned with the systematic study of the influence of hydrodynamic interactions on colloidal gelation to explain the prevailing experimental-theoretical mismatch in the literature. The novel insights drive the development of improved models that can accurately describe the physics of colloidal gels.

A series of computational studies carefully investigate the role of hydrodynamic interactions in determining the conditions for kinetic arrest of attractive dispersions. The collective dynamics enabled by fluid mechanics are shown to enhance coagulation leading to a shift in the gel boundary to lower strengths of attraction and lower particle concentrations when compared to models that neglect hydrodynamic forces. Simulations with long-ranged hydrodynamic interactions are found to faithfully reproduce experimental phase diagrams. This is shown to hold true both for purely attractive dispersions as well as in systems with repulsive barriers. Perturbation analysis is used to study the rheology of semi-dilute, attractive colloidal dispersions and it is demonstrated that both hydrodynamic interactions and the interparticle potential critically affect the viscoelasticity of the material. A normal mode analysis on colloidal gels is conducted using different models of the hydrodynamic interactions between suspended particles to investigate the relaxation rates and energy dissipation in the network. It is established that computational models neglecting long-ranged hydrodynamic interactions critically fail to compute accurate values of rheological properties of interest.

These findings are then integrated to study experimentally observed instabilities of attractive dispersions under shear and during sedimentation. Models accounting for the prevalent hydrodynamic forces are used to show that the phenomena of vorticity alignment and log-rolling are fluid mechanical in origin. Experimental measurements of density fluctuations and shear anisotropy are faithfully reproduced in simulations for the first time. Finally, a theory is developed to quantitatively predict the collapse dynamics of freely settling colloidal gels and new engineering strategies for extending the process lifetime of gel networks are presented. The observations and results discussed in this thesis leave no doubt that the properties and the mechanical response of gels are fundamentally altered by many-body hydrodynamics. These will have to be properly accounted for in the first generation of predictive computational models employed in the engineering design of colloidal gels.

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