Colloidal Stability in Complex Fluids

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Objectives

The broad objective of this ground-based research program is to develop a fundamental understanding of factors governing the stability of complex colloidal suspensions. Such systems are utilized in numerous applications including advanced ceramics, coatings, inks, and paints. Specifically, this research aims to investigate the effects of depletion phenomena, which arise between large colloidal particles in solutions containing smaller particles, on the stability, structural evolution, and rheological properties of such complex systems.

Microgravity Relevance

This ground-based research effort will benefit greatly from a microgravity environment because complications arising from particle-size or density-driven segregation in suspension would be minimized allowing for a broader range of experimental conditions to be probed.

Background

Colloidal processing is well known to be the optimal approach for tailoring the structure and, hence, properties of ceramic films and bulk forms. Through careful control of the interparticle interactions, suspensions can be prepared in the dispersed, weakly flocculated, or strongly flocculated state. In the dispersed state, discrete particles exist which repel each other upon close approach when the repulsive barrier $>>kT$. In the weakly flocculated state, particles aggregate in a shallow secondary minimum (well depth ≈ 1 - 20 kT) forming clusters (or flocs) of non-touching particle networks, where the minimum equilibrium separation distance between particles is given by h_o. In contrast, particles aggregate into a deep primary minimum in the strongly flocculated state forming clusters of touching particle networks.

Depletion interactions arise between large colloids suspended in a solution containing smaller particles, known as depletants. Such species may promote flocculation *or* stabilization of primary colloidal particles. The term "depletion" denotes the existence of a negative concentration gradient near primary particle surfaces. For rigid depletant species, their concentration is reduced at bare particle surfaces and increases to its bulk solution value at some distance away from these surfaces. This distance, known as the depletion layer thickness, is of the order of the depletant diameter ($D_{depletant}$).

The emergence of new and/or improved technologies hinge critically on rational improvements in wet (or suspension) processing of ceramic powders. It has become increasingly clear that *relevant* ceramic systems will be complex in nature, consisting of single or multiphase particles with engineered size distributions (e.g., bimodal, trimodal) and a myriad of processing additives (e.g.,

soluble polymeric species, insoluble polymer lattices, etc.). However, little is known about how colloidal interactions driven by particle size differences (i.e., depletion phenomena) affect the processing-structure-property relations of particulate-derived ceramic films and bulk forms. Successful completion of this research program will establish this critical knowledge base.

Significant Results

Preliminary experiments have focused on how depletant species influence the stability and properties of model ceramic suspensions. Such systems consist of monosized silica (SiO_2, $D_{colloid}$ = 500 nm) spheres, which serve as large colloids, in an aqueous solution of monodisperse, zirconia (ZrO_2, $D_{depletant}$ = 8 nm) spheres, which serve as depletant species. The rheological behavior of these suspensions as a function of varying colloid and depletant volume fraction have been measured using controlled stress rheometers (Bohlin CVO and CS-10). In the absence of depletant species, SiO_2 suspensions (prepared at pH = 0.5 and high electrolyte concentrations) exhibited strong shear thinning behavior indicative of a weakly flocculated system. Upon the addition of depletant species, the suspension rheology changed dramatically. Both the low shear apparent viscosity and degree of shear thinning behavior decreased as a result of depletion stabilization effects. To complement these studies, sedimentation experiments have been carried out to probe their settling behavior as a function of depletant volume fraction. Similar trends were observed. In the absence of depletant additions, the suspensions settled to produce a relative open structure (packing density ~ 20% of theoretical), as expected for an unstable system. Above a critical depletant volume fraction, the suspensions settled to produce a dense structure whose density approached that expected for random close-packing (~ 60% of theoretical) of monosized particles, as expected for a stabilized system.

Modeling of Colloidal Interactions

The stability of a given colloidal system is determined by the total interaction potential energy. To model the experimental systems described above, we account for long range van der Waals, electrostatic, and depletion interactions. The attractive van der Waals interaction potential energy, V_{vdw}, exhibits a power law distance dependence whose strength depends on the dielectric properties of the interacting colloidal particles and intervening medium. The repulsive electrostatic interaction potential energy, V_{elect}, exhibits an exponential distance dependence whose strength depends on the surface potential induced on the interacting colloidal particles and the dielectric properties of the intervening medium. Exact analytical expressions for the electrostatic potential energy cannot be given, thus analytical approximations or numerical solutions were used. The depletion interaction potential energy, V_{dep}, is calculated using the approach developed by Walz and Sharma, which predicts the depletion force between two charged spheres in a solution of smaller, charged spheres and accounts for second-order effects arising from two-body depletant interactions through a virial expansion of the single particle distribution function correct to O ($p\infty^2$), where $p\infty$ is the bulk depletant concentration. A comparison of the predicted stability to their experimentally observed behavior will be made.