MAR09-2008-004217

Abstract for an Invited Paper
for the MAR09 Meeting of
the American Physical Society

Sublimation dynamics of colloidal microgel crystals[1]

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Polymer microspheres in suspension serve as a powerful model system for probing thermodynamic phase transitions. These particles are large enough to visualize using optical microscopy and the particle trajectories can be obtained with nanometer-scale resolution from the images. Equally important is the ability to tune the interactions among the particles using charge or adsorbed polymers to induce repulsion, or non-adsorbing polymers to induce attraction by the depletion effect. I will focus on short-ranged depletion attraction induced by micelles of molecular surfactants or triblock copolymer (Pluronic). Because the micellar size and concentration depend sensitively on temperature, the magnitude and range of the attraction can be tuned in situ. This approach lets us track individual microspheres as they form crystals following a quench, or as crystals sublimate when superheated. We focus on systems where the particles are attracted to a flat surface by depletion and thus confined to two dimensions. We find that when crystallites are superheated, they first sublimate by thermally-excited bond-breaking at the perimeter. Below a cross-over size, however, the crystallites rapidly become amorphous throughout, then evaporate very fast at an approximately diffusion-limited rate. The cross-over size varies from 20-100, depending on temperature and concentation. A similar two-stage process is followed during crystallization. During nucleation, we measure the free energy as a function of cluster size and thereby obtain interfacial tensions and chemical potentials. The results point to a thermodynamically meta- or unstable fluid phase, which is not found in equilibrium but which plays a key role in phase-separation dynamics according to Ostwald's Rule. Results will be compared to experiments, simulations, and theory of crystallization of globular proteins.

[1]This work was done in collaboration with Liquan Pei and John R. Savage. We gratefully acknowledge support from Research Corporation and from the NSF through grant DMR-0605839.