55c Equilibrium and Constrained-Equilibrium States in Stratified Particle-Stabilized Thin Liquid Film

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Drainage of thin liquid films often involves spontaneous formation of coexisting regions of different, but uniform thickness. For example, circular black-film spots can be seen in soap bubbles prior to breakup. Such a stratification phenomenon is particularly interesting in films stabilized by colloidal particles, micelles, or polyelectrolytes, where the thinning occurs through a series of stepwise transitions between film states characterized by the thickness commensurate with the size of the stabilizing particles.

A number of experimental studies of stratified films have been reported, but a complete theoretical understanding of such systems is still lacking. In this talk we present a comprehensive phenomenological theory of formation of stratified films and the subsequent evolution of the coexisting phases. The description is based on a quasi-two-dimensional thermodynamic formalism in which an essential role is played by the nonisotropic microscopic pressure tensor in the film.

We formulate appropriate equilibrium conditions for the film tension, normal pressure, and chemical potential of the particles in the film. Using scaling arguments and Stokesian-dynamics calculations, it is shown that the relaxation of these parameters occurs consecutively on three distinct time scales. This time-scale separation implies that stratified films with coexisting phases of different thickness evolve through a set of constrained equilibrium states. In such states, the individual film phases are in thermodynamic equilibrium, but only some of the equilibrium conditions between these phases are satisfied---the others are not, due to dynamical constraints. Film stratification is described quantitatively for a hard-sphere suspension using Monte-Carlo simulations to evaluate thermodynamic equations of state. A trajectory of the system in the thermodynamic space of states is discussed.