HYDRODYNAMICS OF PARTICLE-STABILIZED THIN LIQUID FILM

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Summary Thermodynamic and hydrodynamic properties of thin liquid films stabilized by colloidal particles are investigated theoretically and numerically. A thermodynamic description of the film is formulated, in which the system is treated as an effective two-dimensional medium. Equilibrium equations of state were evaluated via a Monte-Carlo method for a film stabilized by a suspension of hard spheres. Our results provide basis for quantitative description of stepwise structure of films with coexisting regions of different thickness. We also evaluated the effective viscosity coefficients for two-dimensional compressional and shear flows of a film and the self and collective mobility coefficients of the stabilizing particles. The hydrodynamic calculations were performed using a multiple-reflection representation of Stokes flow between two free surfaces. In this approach, the particle-laden film is equivalent to a periodic system of spheres with a unit cell that is much smaller in the transverse direction than in the lateral direction.

INTRODUCTION

We present results of our study of equilibrium and nonequilibrium behavior of thin liquid films stabilized by suspended colloidal particles. Such particles (e.g., micelles or charged silica spheres) can hinder the drainage of liquid films separating drops or bubbles, and thus they are often used to control emulsion and foam stability. In fact, micelles in surfactant solutions provide one of the most important stabilizing mechanisms. Moreover, particle-stabilized films exhibit an interesting equilibrium and nonequilibrium behavior that can be observed in experiments. Thus, such films can be used as a model system to study confinement effects in colloidal systems.

THERMODYNAMIC DESCRIPTION

Colloidal particles affect equilibrium states of a film by producing an oscillatory effective potential between the interfaces. The minima of this potential are associated with a layered suspension structure in the film [1]. Due to the layered structure, the film can develop coexisting regions of a different thickness H; such stratification has been observed in numerous experiments [2, 3].

In this study we propose an effective thermodynamic description of a particle-stabilized film. In our approach, the film is treated, essentially, as a two-dimensional medium. The details of the suspension structure across the gap are averaged out, and included in the thermodynamic description only through the contribution to the surface free energy, similar to the Gibbs theory of interfacial thermodynamics.

An analysis of the expression for work associated with the change of the thickness h and area A of the film yields the following fundamental relation for the free energy

$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V - \bar{P}\,\mathrm{d}A + \mu_c\,\mathrm{d}N_c + \mu_f\,\mathrm{d}N_f. \tag{1}$$

Here S is the entropy, T is the temperature, p is the transverse component of the pressure tensor, $V = Ah$ is the volume of the film, and $\bar{P}$ is the effective surface pressure. The surface pressure is defined by the relation

$$\bar{P} = h(p' - p) - 2\sigma, \tag{2}$$

where p' is the lateral component of the pressure tensor averaged across the film, and σ is the surface tension of the film interfaces. We note that in the film the pressure tensor is not isotropic, but has two independent components due to the cylindrical symmetry. The last two terms in equation (1) describe the change of the free energy due to a variation of the number of colloidal particles N_c and fluid molecules N_f, where μ_c and μ_f are the corresponding chemical potentials. For an incompressible suspension the last term can be eliminated using appropriate variable change.

According to equation (1) the film behaves as a *compressible* two dimensional fluid, even when the the suspension between the film interfaces is incompressible. The film thickness $h = V/A$ plays a role similar to the two dimensional fluid density. In what follows we focus on a suspension of hard-sphere colloidal particles suspended in and incompressible fluid treated as a thermodynamically passive continuum medium. Thus, free energy includes only contributions from the colloidal particles. The coexistence of of film regions of different thickness require that the equilibrium conditions

$$p^{(1)} = p^{(2)} = p^{(e)}, \quad \bar{P}^{(1)} = \bar{P}^{(2)}, \quad \mu_c^{(1)} = \mu_c^{(2)} \tag{3}$$

are satisfied, where $p^{(e)}$ is the externally applied pressure, and the indices (1) and (2) refer to the coexisting regions.

Using Monte-Carlo simulations we have evaluated particle contributions to the pressures p and $\bar{P}$ in films with different thickness h and particle volume fractions ϕ. The oscillatory character of the functions $p(h)$ and $\bar{P}(h)$, illustrated in figure 1, indicates that regions of different thickness can exist in mechanical equilibrium. Calculations of the chemical potential μ_c as a function of film thickness and volume fraction are underway; the result of these calculations will complete our thermodynamic description of the system.

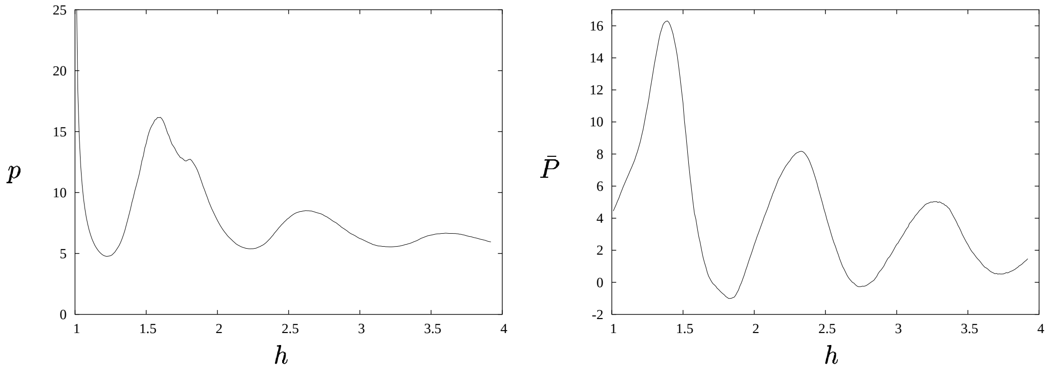

Figure 1. The transverse component to the pressure p and the effective surface pressure $\bar{P}$ versus film thickness h of particle volume fraction $\phi = 0.4$.

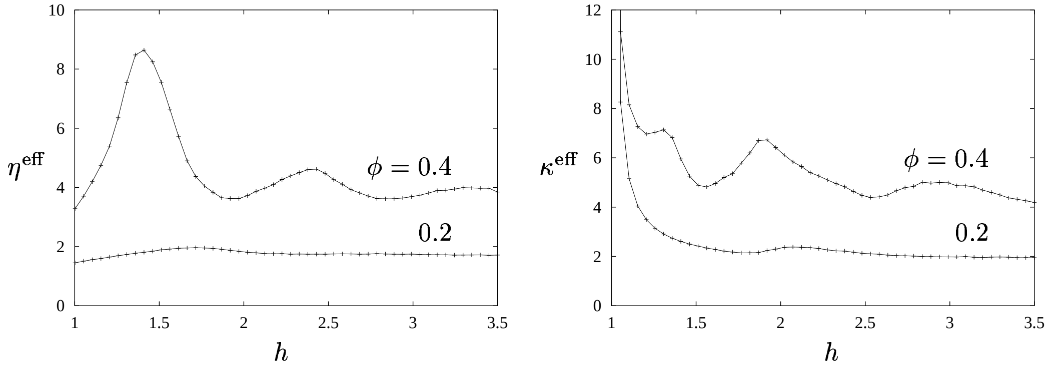

Figure 2. The effective shear viscosity η^{eff} and compressional viscosity κ^{eff} versus film thickness h for two particle volume fractions (as labeled)

HYDRODYNAMIC PROPERTIES

As discussed in the previous section a particle stabilized thin liquid film behaves as a compressible two-dimensional fluid. A compressional flow results in a change of film thickness, which is an analogue of the density. Accordingly, in the hydrodynamic (long-wavelength) limit, the motion of the film is characterized by the shear and bulk viscosity coefficients. Particle diffusion in the film is characterized by the self and mutual diffusion coefficients.

We have evaluated the short-time viscosities and the particle diffusivities using a Stoksian-dynamics approach. The presence of the planar fluid interfaces was incorporated using a reflection method. Assuming negligible viscosity of the gas surrounding the film, the reflected flow field from the interface has the same form as the original flow. Thus, the system can be represented by a three dimensional periodic array of particles with a flat unit cell of a thickness $2h$. Our results for the shear and compressional viscosities are illustrated in figure 2. Similarly to the results presented in figure 1, the viscosity coefficient are oscillatory functions of film thickness h, especially at high volume fractions.

CONCLUSIONS

We formulated a theoretical description for equilibrium states and non-equilibrium processes in thin liquid films stabilized by colloidal particles. The effective two-dimensional equations of state and transport coefficients were evaluated for a hard-sphere suspension. Generalizing our results to continuous interparticle potentials and incorporating the van der Waals attraction between interfaces is straightforward. Thus our theory forms a basis for quantitative description of equilibrium properties and nonequilibrium dynamics of particle stabilized films observed in experiments.

References

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