GRADIENT DYNAMICS FORMULATION OF EVOLUTION EQUATIONS FOR THIN FILMS OF COMPLEX FLUIDS

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Summary We propose a way to construct dynamical models for liquid films of suspensions and solutions, as well as for films covered by insoluble surfactants. First, we briefly review the 'classical' hydrodynamic form of the coupled evolution equations for the film height and (solute or surfactant) concentration that are well established for small concentrations; and mention recent results on line deposition from evaporating suspensions.

Then we re-formulate both basic models as a gradient dynamics based on an underlying free energy functional that accounts for wettability and capillarity of the solvent. Based on this re-formulation in the framework of nonequilibrium thermodynamics, we propose extensions of the basic hydrodynamic models that may account for (i) surfactant- or solute dependent wettability, and (ii) surfactant or solute phase transitions. Other possibilities are mentioned and examples are sketched for (i) and (ii).

INTRODUCTION

The effects of capillarity and wettability are important interfacial phenomena whose detailed understanding is relevant to many small scale fluidic systems that occur naturally in biological contexts or that are employed in modern technology, such as microfluidics. Paradigmatic physical processes where both effects are involved are, for instance, the dewetting of very thin films on solid substrates, the spreading of droplets on solid or liquid substrates and the meniscus dynamics at a plate that moves slowly in or out of a bath. For reviews see [1, 2]. In the case of simple liquids many of the observed effects are well described employing long-wave evolution equations (see reviews in [3, 4]).

However, many recent experiments are performed with complex liquids, e.g., dewetting of drops and films of (evaporating) solutions of polymers or of nanoparticle suspensions [5, 6], dewetting and decomposing films of polymer mixtures [7], and the spreading of drops covered by soluble or insoluble surfactants [8], the spreading of nanoparticle suspensions [9]. The interfacial effects of capillarity and wettability are still important driving forces, however, they may now interact with the dynamics of internal degrees of freedom. The theoretical description of many of the observed dynamical processes is only well established for a restricted number of cases, e.g., for low solute or surfactant concentrations.

HYDRODYNAMIC DESCRIPTION

Consider a thin film of a partially wetting suspension or solution in contact with its vapour on a flat solid substrate. In long-wave approximation [3] the evolution equations for the film thickness profile $h(x, y, t)$ and the vertically averaged solute concentration field $\phi(x, y, t)$ are

$$\partial_t h = \nabla \cdot [Q(h, \phi) \nabla p(h)] \tag{1}$$

$$\partial_t (\phi h) = \nabla \cdot [\phi Q(h, \phi) \nabla p(h)] + \nabla \cdot [D(\phi) h \nabla \phi] \,. \tag{2}$$

Here the mobility is $Q(h, \phi) = h^3/3\eta(\phi)$. The dynamic viscosity may be a constant $\eta(\phi) = \eta_0$ or exhibit a (possibly strong non-linear) dependence on the local solute concentration as, e.g., given by the Krieger-Dougherty law [10]. The pressure p may contain Laplace and Derjaguin (disjoining) pressure contributions (beside others) ϕ is a dimensionless *per volume* concentration. Such equations are widely used to model particle-laden films or films of solutions. For instance, adding the influence of evaporation one may model the deposition of line patterns from (evaporatively) receding contact lines of suspensions or solutions [11]. The approach is limited to non-interacting particles (i.e. particles that have no net attractive forces between them). Below we propose a 'thermodynamic' re-formulation that removes this limitation.

Similarly, the evolution equations that relate the material properties of the insoluble surfactant and the resulting hydrodynamic film flow are well established for low surfactant concentrations [3, 4]. The equations for the film thickness h and surfactant concentration Γ read

$$\partial_t h = -\nabla \cdot [Q(h) \nabla p(h)] - \nabla \cdot \left[\widetilde{Q}(h, \Gamma) \nabla \Gamma \right] \tag{3}$$

$$\partial_t \Gamma = -\nabla \cdot \left[\widetilde{Q}(h, \Gamma) \nabla p(h) \right] - \nabla \cdot \left[\widehat{Q}(h, \Gamma) \nabla \Gamma \right] + \nabla \cdot [D \nabla \Gamma] \,, \tag{4}$$

where the mobilities related to the solutal Marangoni term are $\widetilde{Q}(h, \Gamma) = \gamma_\Gamma h^2/2\eta$ and $\widehat{Q}(h, \Gamma) = \gamma_\Gamma h \Gamma/\eta$. The parameter γ_Γ is defined through the linear equation of state $\gamma(\Gamma) = \gamma_0 + \gamma_\Gamma \Gamma$ that describes how the surface tension deviates from its reference value for a bare free surface $\gamma(0) \equiv \gamma_0$.

This approach is valid for low surfactant coverages where the linear equation of state applies. However, many works adapt the approach to large surfactant concentrations by replacing the linear equation of state by a nonlinear one. We

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argue below that this may be thermodynamically inconsistent. Next we propose a 'thermodynamic' re-formulation that allows for various extensions of the governing equations.

RE-FORMULATION AS GRADIENT DYNAMICS

In both discussed cases, the two coupled hydrodynamic evolution equations can be re-written in a 'thermodynamic' form: as a gradient dynamics based on an underlying free energy functional $F[h, \psi]$ (case of suspension/solution, $\psi = h\phi$) and $F[h, \Gamma]$ (case of insoluble surfactant). For details regarding the free energy functional see [12] and [13], respectively. In the following we use the symbol ξ to stand for either ψ or Γ depending on the system considered.
Using the respective $F[h, \xi]$, the long-wave hydrodynamic equations given above exactly correspond to the general gradient dynamics form (equivalent to a formulation in the context of linear non-equilibrium thermodynamics).

$$\begin{aligned} \partial_t h &= \nabla \cdot \left[Q_{hh} \nabla \frac{\delta F}{\delta h} + Q_{\xi h} \nabla \frac{\delta F}{\delta \xi} \right] \\ \partial_t \xi &= \nabla \cdot \left[Q_{h\xi} \nabla \frac{\delta F}{\delta h} + Q_{\xi\xi} \nabla \frac{\delta F}{\delta \xi} \right] \end{aligned} \tag{5}$$

where the Q_{ij} form a symmetric positive definite mobility matrix [12, 13].
With this we have provided a gradient dynamics re-formulation of the hydrodynamic long-wave models. The gradient dynamics form is based on a usage of nonequilibrium thermodynamics somewhat similar to the approach taken in DDFT in its local approximation [14].
However, the re-formulation only shows its potential when applied to expand the hydrodynamic model to incorporate the case of solute molecules/particles with net attractive interactions, decomposing solute-solvent systems, solute-dependent wettability, nonlinear equations of state for surfactants, surfactant-dependent wettability, phase transitions at high surfactant concentrations, or substrate mediated surfactant condensation [12, 13].
As an example, we focus on a concentration-dependent wettability. We employ homogenisation techniques (effective medium approximation) to obtain effective optical characteristics. Combining this with classical theory of effective molecular interactions between the film surface and the substrate, we arrive at a Derjaguin (disjoining) pressure that depends on film height and concentration. The derived model is employed to analyse how the stability thresholds of flat homogeneous films are influenced by the incorporation of the additional degree of freedom related to the concentration field. We also give examples of nonlinear thickness and concentration profiles for steady droplets.
As an outlook we consider the influence of net attractive interactions of solute particles on deposition patterns and discuss applications of the amended surfactant models

CONCLUSIONS

We have presented gradient dynamic formulations of the coupled thin film long-wave evolution equations that are employed to describe (i) thin films of solutions or suspensions, (ii) films covered by insoluble surfactants. We have argued that based on the re-formulation in both cases one may incorporate several additional 'energetic' effects directly into the thin film model. It is encouraging that the approach for instance allows us to obtain the thin film equations for coupled decomposition and dewetting of a film of a binary mixture that are in [15] derived from model-H employing a formal long-wave approximation, and as well equations used to model substrate-mediated condensation in Langmuir-Blodgett transfer [16, 17].

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