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Thermodynamically consistent description of the hydrodynamics of free surfaces covered by insoluble surfactants of high concentration

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In this paper, we propose several models that describe the dynamics of liquid films which are covered by a high concentration layer of insoluble surfactant. First, we briefly review the "classical" hydrodynamic form of the coupled evolution equations for the film height and surfactant concentration that are well established for small concentrations. Then we re-formulate the basic model as a gradient dynamics based on an underlying free energy functional that accounts for wettability and capillarity. Based on this re-formulation in the framework of nonequilibrium thermodynamics, we propose extensions of the basic hydrodynamic model that account for (i) nonlinear equations of state, (ii) surfactant-dependent wettability, (iii) surfactant phase transitions, and (iv) substrate-mediated condensation. In passing, we discuss important differences to most of the models found in the literature. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4758476]

I. INTRODUCTION

Small volumes of simple and complex fluids that occur naturally in biological contexts or that are employed in modern technology, such as in microfluidics, are often (partly) confined by a free surface that may be covered by surface active agents. These so-called surfactants may be detergents, lipids, certain nano-particles, or particular polymeric compounds. Because they decrease the surface tension of the free surface, gradients in their concentration correspond to gradients in the surface tension. These gradients result in tangential forces at the free surface that drive flows in the bulk liquid. This is the so-called solutal Marangoni effect, that is, e.g. responsible for the tears of wine.[1,2]

All surface active agents are to some extent soluble in the bulk liquid, implying that a complete dynamical model needs to describe the motion of the bulk liquid, bulk concentration of surfactant, the surface concentration of surfactant, and the adsorption/desorption processes that exchange surfactant molecules between the bulk liquid and the free surface. However, for many practically important surfactants, the bulk solubility is actually very small. Then one speaks of "insoluble surfactants" and only considers the dynamics of the surfactant that is adsorbed at the free surface. Here, we consider moderately high surfactant concentrations. By this, we mean concentrations for which a description of the surfactant molecules as non-interacting independent particles (the gaseous state) is not appropriate, but which are still well below the close-packing limit or the transition to a surfactant layer of more than one molecule in thickness. In particular, we restrict our attention to insoluble surfactants at concentrations at which no micelles are formed in the bulk liquid.[3]

The governing transport equations that relate the material properties of the insoluble surfactant and the resulting hydrodynamic flow are well established for low values of the surfactant surface

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coverage Γ.[4–6] In this case, the linear equation of state

$$\gamma(\Gamma) = \gamma_0 + \gamma_\Gamma \Gamma \tag{1}$$

describes how the surface tension deviates from its reference value $\gamma(0) \equiv \gamma_0$, for a bare free surface. The coefficient γ_Γ is a material constant that is negative for most combinations of liquid and surfactant. The resulting tangential Marangoni force at the free surface is $\nabla_s \gamma = \gamma_\Gamma \nabla_s \Gamma$, where $\nabla_s = (\underline{I} - \mathbf{nn}) \cdot \nabla$ is the derivative along the free surface and $\mathbf{n}$ is the unit normal vector. For any (linear or nonlinear) equation of state, the surface tension gradient $\nabla_s \gamma$ enters the tangential stress boundary condition of the momentum transport equation. The latter is accompanied by a transport equation for Γ that accounts for advective and diffusive transport of the surfactant.[7,8] The resulting system of equations may be simplified in order to apply them to various physical situations, such as the dynamics of surfactant-laden drops or bubbles immersed in (another) liquid,[9,10] free-standing soap films,[11] liquid bridges covered by a surfactant monolayer,[12] surfactant-covered vertical falling liquid films,[13] films on horizontal solid substrates,[4,5,14] and drawn menisci.[15] In particular, the latter geometry allows for an asymptotic treatment which results in a long-wave or lubrication description of the dynamics, via two coupled evolution equations for the film height and the surfactant surface coverage.[4,5] In the following, we focus on this geometry, but we should emphasise that our main arguments also apply to the general case.

Many works only treat the case of low surfactant surface coverages and employ the linear equation of state in Eq. (1). The surface tension driven flow is then said to result from a linear solutal Marangoni effect. However, there is a growing literature where a similar approach is used to treat the dynamics of free surfaces covered by large concentrations of insoluble surfactants. It is common practice to replace the linear equation of state (1) by a nonlinear one and leave all other terms in the dynamical equations unchanged. We argue below that this may result in governing equations that are thermodynamically inconsistent, since one must also amend the surfactant surface diffusion term. The basic equations should also be amended to be able to describe the influence of the surfactant coverage on wettability, relevant for very thin films and close to three-phase contact lines where ambient gas, surfactant-covered liquid, and solid substrate meet. Another amendment should account for the effects of phase transitions in the surfactant layer at high concentrations, and also the influence of a nearby solid substrate on such phase transitions that may result in substrate mediated condensation (surfactant aggregation). The approach that we propose in this paper allows one to deal with all these cases in a thermodynamically consistent manner.

The structure of the paper is as follows: First, we review in Sec. II the "classical" thin-film hydrodynamic coupled equations of motion for a thin liquid film covered by a low concentration surfactant. Then, in a preparatory step we decouple and re-formulate the two individual equations in a "thermodynamic form." In particular, Sec. III gives the gradient formulation of the evolution equation for a thin-film of pure liquid on a solid substrate, for the case where capillarity and wettability are the dominant influences, while Sec. IV briefly reviews the classical diffusion equation and places it in the thermodynamic context that we employ. In Sec. V, the full coupled system is re-formulated as a gradient dynamics based on an underlying free energy functional. This thermodynamic form is used in Sec. VI to extend the thin-film model to consistently account for (i) nonlinear equations of state, (ii) surfactant-dependent wettability, (iii) surfactant phase transitions, and (iv) substrate mediated condensation. We also note some differences to the models in the literature. In Sec. VII we note some of the consequences of the gradient-dynamics formulation. Finally, Sec. VIII concludes and discusses the limitations of our approach.

II. THIN-FILM EQUATION FOR LOW SURFACTANT SURFACE COVERAGE

If a hydrodynamic system involves a free surface that is covered by an insoluble surfactant, the boundary conditions for the momentum equation have to be supplemented by an evolution equation for the surfactant concentration on the free surface that accounts for transport of the surfactant by advection and diffusion and also for shape changes of the surface that act as effective source/sink terms.[6,7] This equation must be solved in conjunction with the hydrodynamic equations and boundary conditions for the liquid film. These equations can be greatly simplified for the case of a thin film
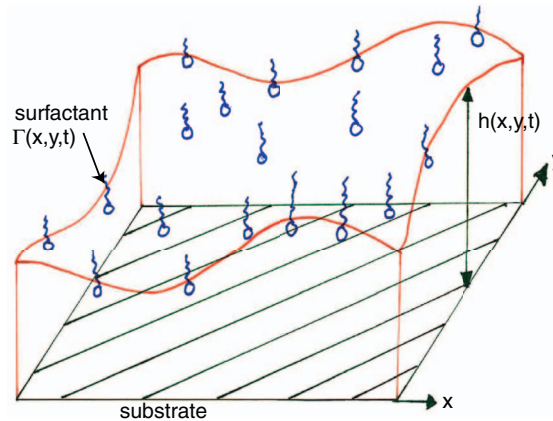
FIG. 1. Sketch of a surfactant covered liquid film.

of liquid on a solid substrate. If all quantities in the film vary over distances with a length scale parallel to the substrate that is large as compared to all length scales perpendicular to it, one may make a long-wave approximation[4,5] to obtain coupled evolution equations for the film thickness profile $h(\mathbf{r}, t)$ and the surfactant surface coverage profile $\Gamma(\mathbf{r}, t)$, which is a dimensionless surface packing fraction (or concentration), where $\mathbf{r} = (x, y)$ is a cartesian coordinate over the substrate. The surface concentration is defined as $\Gamma(\mathbf{r}, t) = l^2 \rho(\mathbf{r}, t)$, where $\rho(\mathbf{r}, t)$ is the surface number density (number per area) and l^2 is the surface area per surfactant molecule when the surfactant molecules are at maximum packing on the surface (i.e., l is a molecular length scale), so that close packing corresponds to $\Gamma = 1$. For the three-dimensional physical situation illustrated in Fig. 1, the equation for the film height is

$$\partial_t h = -\nabla \cdot \left[\frac{h^3}{3\eta} \nabla \left(\gamma_0 \Delta h - p_{\text{add}}(h) \right) \right] - \nabla \cdot \left(\frac{\gamma_\Gamma h^2}{2\eta} \nabla \Gamma \right). \tag{2}$$

Note that this equation is equally valid if one uses ρ instead of the dimensionless Γ or indeed any other measure of the surfactant surface density. Only the quantity γ_Γ needs to be redefined so that the product of γ_Γ with the surface density yields a quantity with the dimensions of an energy per area [cf. Eq. (1)]. As a result, many papers in the literature do not mention what units they choose for Γ. The time evolution equation for Γ is

$$\partial_t \Gamma = -\nabla \cdot \left[\frac{h^2 \Gamma}{2\eta} \nabla \left(\gamma_0 \Delta h - p_{\text{add}}(h) \right) \right] - \nabla \cdot \left(\frac{\gamma_\Gamma h \Gamma}{\eta} \nabla \Gamma \right) + \nabla \cdot (D \nabla \Gamma), \tag{3}$$

where γ_0 is the liquid-gas surface tension, and η is the dynamic viscosity of the pure liquid. Partial derivatives with respect to time and space are denoted ∂_t and ∂_x, respectively, $\nabla = (\partial_x, \partial_y)$ is the planar gradient operator and $\Delta = \partial_{xx} + \partial_{yy}$ is the Laplace operator. The mobility $Q(h) = h^3/3\eta$ results from Poiseuille flow in the film without slip at the substrate. The pressure $p = -\gamma_0 \Delta h + p_{\text{add}}(h)$ contains the Laplace surface curvature contribution to the pressure and additional contributions such as a hydrostatic or a disjoining pressure.[4,11,14,16,17] Note that the latter is normally assumed to be independent of Γ. Exceptions are discussed below. The diffusive transport of the surfactant in Eq. (3) follows from Fick's law for the flux $J_{\text{diff}} = -D \nabla \Gamma$. In most papers, it is assumed that the diffusion constant D does not depend on the surfactant concentration, i.e., the term $\nabla \cdot (D \nabla \Gamma)$ in Eq. (3) becomes $D \Delta \Gamma$.

Note that Eq. (3) is an equation obtained in the long-wave approximation and, therefore, does not include the source-like surface dilatation term. Different forms for such a term are discussed in Refs. 7, 18, and 19. For the same reason, the ∇ operator in the diffusion term is the planar operator and not the operator ∇_s that acts tangentially to the free surface. To extend the present ideas to more general geometries, these contributions must be taken into account.

To obtain Eqs. (2) and (3), we have related the surfactant surface coverage Γ to the surface tension γ by the linear equation of state in Eq. (1), i.e., a linear solutal Marangoni effect is assumed. In deriving Eq. (2), one also assumes that $\gamma_0 \gg \gamma_\Gamma(\Gamma_0 - \Gamma)$ and that therefore the Laplace pressure term $(-\gamma_0 \Delta h)$ only depends on γ_0.

To incorporate effects of high surfactant concentration, the equations are often extended by translating $\gamma_\Gamma \nabla \Gamma$ back into $\nabla \gamma(\Gamma)$, and then replacing the linear equation of state in Eq. (1) by some nonlinear equation of state. There are problems with doing this, as we show below. Another extension is to incorporate a surfactant-dependent wettability into the evolution equations (2) and (3). This is sometimes done in an *ad hoc* manner by simply replacing $p_{\text{add}}(h)$ by some $p_{\text{add}}(h, \Gamma)$. However, it turns out that this leaves the equation incomplete and may even result in qualitatively incorrect predictions. After re-formulating the evolution equations as a gradient dynamics in Sec. V, we discuss such extensions in Sec. VI. First, however, we introduce the gradient formulation for the decoupled thin-film equation (Sec. III) and surfactant surface diffusion equation (Sec. IV).

III. THIN-FILM OF PURE LIQUID-EVOLUTION EQUATION AS A GRADIENT DYNAMICS

It was noted some time ago that the time evolution equation for the film thickness in the case without surfactant [Eq. (2) with $\Gamma = 0$] can be written in a variational form.[20,21] This allows one to appreciate that Eq. (2) corresponds to a time evolution equation for a conserved order parameter field $h(\mathbf{r}, t)$ (cf. Ref. 22) that follows a dissipative gradient dynamics governed by the following equation:

$$\partial_t h = \nabla \cdot \left[Q_{hh} \nabla \frac{\delta F_{\text{film}}}{\delta h} \right]. \tag{4}$$

This equation describes how the field h evolves towards a minimum of the free energy functional

$$F_{\text{film}}[h] = \int \left[\gamma_0 + \frac{\gamma_0}{2} (\nabla h)^2 + f(h) \right] dA, \tag{5}$$

where $f(h) = \int p_{\text{add}}(h) dh$, the mobility function $Q_{hh} = h^3/3\eta$ (cf. also Ref. 23), and dA is a cartesian area element along the substrate.

Note that the free energy in Eq. (5) corresponds to the one that is obtained making a small slope approximation in the free energy $F_{\text{film}} = \int f(h) dA + \int \gamma_0 dS$, where the surface element $dS = \sqrt{1 + (\nabla h)^2} \, dA \equiv \xi dA$ is approximated using $\xi \approx 1 + (\nabla h)^2/2$. The constant part $\int \gamma_0 dA$ of the free energy in Eq. (5) is normally omitted since it does not contribute to the dynamics, as one can see from Eq. (4). A similar formulation is given in Sec. IV for the surfactant surface diffusion equation.

IV. DIFFUSION EQUATION AS A GRADIENT DYNAMICS

The diffusive transport of a species with small surface coverage Γ on a flat interface is described by the diffusion equation

$$\partial_t \Gamma = -\nabla \cdot J_{\text{diff}} = D \Delta \Gamma, \tag{6}$$

where the diffusive flux is given by Fick's law $J_{\text{diff}} = -D \nabla \Gamma$. The time evolution equation for the surfactant density in Eq. (3), reduces to the diffusion equation in Eq. (6) in the limit when the liquid film thickness $h(\mathbf{r}, t)$ is a constant and the coefficient $\gamma_\Gamma = 0$; i.e., when there is no Marangoni effect.

The form in Eq (6) can easily obscure the underlying thermodynamics, which can be seen when this equation is formulated as a gradient dynamics based on the Helmholtz free energy for an ideal gas (i.e., a system of non-interacting particles),

$$F_{\text{id}}[\Gamma] = \frac{kT}{l^2} \int \Gamma[\log(\Gamma) - 1] \, dA, \tag{7}$$

where k is Boltzmann's constant, T is the temperature, and l is the molecular length scale defined in Sec. II. The transport equation for Γ is of the same form as Eq. (4) and reads[24–28]

$$\partial_t \Gamma = \nabla \cdot \left[Q_{\Gamma\Gamma} \nabla \frac{\delta F_{\text{id}}}{\delta \Gamma} \right], \tag{8}$$

where the mobility $Q_{\Gamma\Gamma} = \widetilde{D}\Gamma$. Here, $\widetilde{D}$ is the molecular mobility related to the diffusion process and may in principle depend on all the independent variables, although in the following we will assume that $\widetilde{D}$ is constant.

The equivalence of the formulation in Eq. (6) and in Eqs. (7) and (8) is easily established. The advantage of the gradient dynamics form in Eq. (8) is the "built-in" straightforward way to extend the description, e.g., to incorporate attractive forces between the diffusing molecules and the effects of higher concentrations. For instance, replacing the functional in Eq. (7) by the one discussed by Cahn and Hilliard[29] (their Eq. (2.4) with (3.1)) results in the nonlinear diffusion equation (or Cahn-Hilliard equation), Eq. (9) of Ref. 30 (when $Q_{\Gamma\Gamma} = \widetilde{D}\Gamma(1-\Gamma)$ is expanded about $\Gamma = 1/2$ and only the lowest order term is kept). More recently, Marconi and Tarazona[25,26] showed that one can derive Eq. (8), starting from over-damped stochastic equations of motion for the (surfactant) particles. They showed that the diffusive fluid dynamics is described by Eq. (8), taken together with a suitable approximation for the Helmholtz free energy functional taken from equilibrium density functional theory.[24,31] This so-called dynamical density functional theory[25–28] is now a growing body of work, allowing one to go beyond Cahn-Hilliard theory, and to develop a theory which includes a microscopic (on the scale of the particles) description of the dynamics of particles suspended in a fluid medium, or in the present case of surfactant particles on the surface of the liquid.

To our knowledge, no gradient dynamics formulation has yet been given for the evolution of a thin-film covered by insoluble surfactant as described by Eqs. (2) and (3). Since the system is relaxational, i.e., there is no energy influx, a variational formulation in terms of a pair of coupled evolution equations for two conserved order parameter fields must exist and in fact is presented in Sec. V.

V. EVOLUTION OF A SURFACTANT-COVERED FILM AS GRADIENT DYNAMICS

To construct a gradient dynamics description for the full coupled system, Eqs. (2) and (3), we start by considering the Helmholtz free energy for the system $F[h, \Gamma]$, that also turns out to be the Lyapunov functional for a surfactant covered thin liquid film. It contains contributions that result from wettability (adhesion), expressed in terms of the height profile of the film, $\int f(h)dA$, *and* contributions from the surface $\int g(\Gamma)dS$, where $g(\Gamma)$ is the Helmholtz surface free energy density (i.e., an energy per area), and $dS = \sqrt{1 + (\nabla h)^2}dA = \xi dA \approx [1 + (\nabla h)^2/2]dA$ is a surface element. The contribution of the height profile are similar to those in Eq. (5). In the parameter regime where the linear equation of state (1) for the surfactant is valid, i.e., when the surfactant density is low, then the surfactant layer corresponds to a two-dimensional gas of surfactant molecules on the film surface. The corresponding contribution to the free energy density is the entropic (ideal-gas) term $(kT/l^2)\Gamma(\log \Gamma - 1)$ that on its own leads to a diffusion equation for Γ, as discussed in Sec. IV. However, one may add other contributions that are relevant at higher concentrations, resulting from the interactions between surfactant molecules. Such contributions are discussed below in Sec. VI. For the non-interacting case we obtain

$$F[h, \Gamma] = \int \{f(h) + g(\Gamma)\xi\} \, dA, \tag{9}$$

where

$$g(\Gamma) = \gamma_0 + \frac{kT}{l^2} \Gamma[\log(\Gamma) - 1]. \tag{10}$$

It should be noted that variations in h and in Γ are not independent: If locally the slope of h changes, the area of the liquid surface changes and thus the surface coverage Γ may change without any surfactant transport. To derive evolution equations that are of a gradient dynamics form, one needs
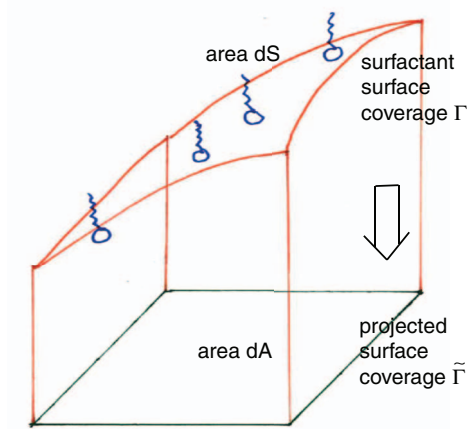
FIG. 2. Sketch that indicates the relation between the projected surface coverage $\widetilde{\Gamma}$ and the coverage Γ on the modulated free surface, defined in Eq. (11).

a concentration variable that is independent of the film height profile h. We introduce a surface coverage $\widetilde{\Gamma}$, as sketched in Fig. 2, that corresponds to the coverage Γ "projected" onto the flat substrate (thus, in principle, $\widetilde{\Gamma}$ can become larger than one). It is given by

$$\widetilde{\Gamma} = \frac{dS}{dA}\Gamma = \xi\Gamma. \tag{11}$$

Using $F[h, \widetilde{\Gamma}/\xi]$ from Eq. (9), the long-wave hydrodynamic equations (2) and (3) are equivalent to the following general form for the time evolution equations:

$$\partial_t h = \nabla \cdot \left[Q_{hh}\nabla\frac{\delta F}{\delta h} + Q_{\Gamma h}\nabla\frac{\delta F}{\delta\widetilde{\Gamma}} \right],$$

$$\partial_t \widetilde{\Gamma} = \nabla \cdot \left[Q_{h\Gamma}\nabla\frac{\delta F}{\delta h} + Q_{\Gamma\Gamma}\nabla\frac{\delta F}{\delta\widetilde{\Gamma}} \right]. \tag{12}$$

Note that $\delta F/\delta h$ and $\delta F/\delta\widetilde{\Gamma}$ correspond to volume and surface forces, respectively. The ∇ operator in the equation for $\widetilde{\Gamma}$ is the cartesian operator and not the surface operator as, e.g., in Ref. 7 because this equation describes the evolution of the projected surface coverage $\widetilde{\Gamma}$. This is valid for the film geometry considered here, but would need to be amended in an extension of our approach to arbitrary free surface shapes.

The symmetric positive definite mobility matrix in Eqs. (12) is given by

$$\mathbf{Q} = \begin{pmatrix} Q_{hh} & Q_{\Gamma h} \\ Q_{h\Gamma} & Q_{\Gamma\Gamma} \end{pmatrix} = \begin{pmatrix} \frac{h^3}{3\eta} & \frac{h^2\Gamma}{2\eta} \\ \frac{h^2\Gamma}{2\eta} & \frac{h\Gamma^2}{\eta} + \widetilde{D}\Gamma \end{pmatrix}. \tag{13}$$

Note that we have written $\mathbf{Q}$ in terms of Γ and h. The justification for using Γ and not $\widetilde{\Gamma}$ in the long-wave approximation mobilities will become clear below. To fully appreciate the equivalence of Eq. (12) [with Eqs. (9), (10), and (13)] to Eqs. (2) and (3), we calculate the variations of the free energy in Eq. (9),

$$\frac{\delta F}{\delta h} = \partial_h f(h) - \nabla \cdot [\omega\nabla h],$$

$$\frac{\delta F}{\delta\widetilde{\Gamma}} = g', \tag{14}$$

where we have introduced the local surface grand potential density $\omega = g - \Gamma g'$. Inserting these results into Eq. (12), we obtain the following time-evolution equations:

$$\partial_t h = \nabla \cdot \left[\frac{h^3}{3\eta} \nabla[\partial_h f(h) - \nabla \cdot (\omega \nabla h)] + \frac{h^2 \Gamma}{2\eta} \nabla g' \right],$$

$$\partial_t \widetilde{\Gamma} \approx \partial_t \Gamma = \nabla \cdot \left[\frac{h^2 \Gamma}{2\eta} \nabla [\partial_h f(h) - \nabla \cdot (\omega \nabla h)] + \left(\frac{h \Gamma^2}{\eta} + \widetilde{D} \Gamma \right) \nabla g' \right],$$

(15)

where we have used the fact that $(\nabla h)^2 \ll 1$ to approximate $\xi \approx 1$ in the left-hand side of the second equation, as is appropriate in the long-wave limit. Used at this stage, this approximation leads to $\widetilde{\Gamma} \approx \Gamma$. Note, however, that this approximation should be applied with caution.[32] The equations for $\partial_t h$ and $\partial_t \Gamma$ exactly correspond to the hydrodynamic model [Eqs. (2) and (3)] if (i) one identifies the local surface grand potential density ω with the surface tension γ (see further discussion in Sec. V A below) and (ii) employs Eq. (10) for $g(\Gamma)$, i.e., one only includes the ideal-gas contribution to the free energy, which is a reasonable approximation to make for low concentrations of surfactant. As a result

$$\nabla \gamma = -\Gamma \nabla \frac{\delta F}{\delta \widetilde{\Gamma}} = \Gamma \nabla g' = \left(\frac{kT}{l^2} \right) \nabla \Gamma,$$

(16)

and so one finds that the diffusion coefficient D and the solutal Marangoni coefficient γ_Γ in Eqs. (2) and (3) are given by $D = kT \widetilde{D}/l^2$ and $\gamma_\Gamma = -kT/l^2$, respectively.

Note that the hydrodynamic community often assumes that the change of the surface tension with concentration is small as compared to the reference surface tension γ_0 and, therefore, only uses γ_0 in the Laplace pressure term, i.e., $\nabla \cdot (\omega \nabla h) \approx \gamma_0 \Delta h$.

A. Equation of state – surface tension

Before presenting several extensions to the hydrodynamic equations (2) and (3), based on our reformulation in Eq. (15), we put our gradient dynamics formulation in its proper thermodynamic context. First, we discuss the equation of state that relates surface tension γ to surfactant concentration Γ, and show that the thermodynamic and hydrodynamic approaches are fully consistent for any dependence $g(\Gamma)$.

To this end, we review first some elementary considerations concerning the relation between the surface tension and the surface free energy density. The latter is defined as the excess free energy per unit area that is due to the presence of a surface. In analogy to bulk thermodynamics, this excess may be defined for different thermodynamic ensembles and may, therefore, depend on different surface thermodynamic variables. Moreover, this surface excess acts as the thermodynamic potential for surface variables (for an enlightening general discussion of surface excesses, see Ref. 33). The surface tension is the derivative of this surface thermodynamic potential with respect to the area – it is the equivalent of the pressure in bulk thermodynamics (up to a sign convention: a positive pressure generates an outward force on the container walls, whereas a positive surface tension creates an inward force on the lines bordering a surface element).

It is easy to show that the surface tension is always given by the surface excess grand potential density, regardless of whether the surface free energy is defined in the canonical or grand-canonical ensemble. In the canonical case, the surface free energy is the surface (excess) contribution to the Helmholtz free energy, $F_{surf} = Sg(\Gamma)$, for a surface element of area S. The variation of this free energy is $dF_{surf} = g(\Gamma)dS + Sg'(\Gamma)d\Gamma$. The second term arises from the fact that the variation in the canonical ensemble has to be taken for a fixed number of surfactant molecules, $N = S\Gamma/l^2$ (recall that $\Gamma = \rho l^2$), and thus the variation of the surface area creates a variation in the local concentration equal to $d\Gamma = d(l^2 N/S) = -(l^2 N/S^2)dS = -(\Gamma/S)dS$, and the surface tension becomes $\gamma = \omega(\Gamma) = dF_{surf}/dS = g(\Gamma) - g'(\Gamma)\Gamma$, where we have introduced the surface grand potential density $\omega(\Gamma) = g(\Gamma) - \mu \Gamma$, with $\mu = g'(\Gamma) = \partial g/\partial \Gamma$ the chemical potential.[34] Alternatively, if the surface excess is defined in the grand-canonical ensemble, the surface free energy is directly given

by $F_{\text{surf}} = S\omega$. Now, the variation has to be taken at constant chemical potential (the surface element is connected to a reservoir of surfactant molecules). Since Γ is a function of the chemical potential in the grand-canonical ensemble, it remains fixed, and therefore the surface tension is directly given by $\gamma = dF_{\text{surf}}/dS = \omega$.[35]

For flat interfaces with a small surfactant concentration, the surface-related part of the local Helmholtz free energy g is given by Eq. (10), and so the chemical potential $\mu = (kT/l^2)\log\Gamma$. With this, the surface tension becomes

$$\gamma = \omega = g(\Gamma) - \mu\Gamma, \tag{17}$$

$$= \gamma_0 - \frac{kT}{l^2}\Gamma, \tag{18}$$

i.e., one recovers the linear dependence, Eq. (1), used in hydrodynamics with $\gamma_\Gamma = -kT/l^2$ and $\Gamma_0 = 0$. Note that if the surface tension is defined (incorrectly) as the local Helmholtz free energy $g(\Gamma)$, the logarithmic terms entail that one does not recover the linear dependence in Eq. (1).

By identifying the surface tension with the local grand potential, the thermodynamic and hydrodynamic formulations are fully consistent for any convex local $g(\Gamma)$. In the hydrodynamic formulation [Eqs. (2) and (3)], the Marangoni force contributes to the advective flux as $-(h^2/2\eta)\nabla\gamma(\Gamma)$, and normally the equation of state $\gamma(\Gamma)$ is given directly. With $\gamma = \omega = g - \mu\Gamma$, the Marangoni term becomes $(h^2\Gamma/2\eta)(\partial_{\Gamma\Gamma}g)\nabla\Gamma$. This expression is identical to the term one obtains in the variational formulation (12), i.e., $Q_{\Gamma h}\nabla(\delta F/\delta\tilde{\Gamma}) = (h^2\Gamma/2\eta)\nabla(\delta F/\delta\tilde{\Gamma})$. For any F of the form in Eq. (9), this equals $(h^2\Gamma/2\eta)(\partial_{\Gamma\Gamma}g)\nabla\Gamma$. The equivalence of the Marangoni term in the hydrodynamic and thermodynamic formulations is valid for any convex local $g(\Gamma)$. In other words, the surface tension gradient $\nabla\gamma$ may be expressed either as $\nabla\omega$ or as $-\Gamma\nabla g'$. This implies that Eq. (15) may be written as

$$\partial_t h = \nabla \cdot \left[\frac{h^3}{3\eta}\nabla[\partial_h f(h) - \nabla\cdot(\gamma\nabla h)] - \frac{h^2}{2\eta}\nabla\gamma \right],$$

$$\partial_t \Gamma = \nabla \cdot \left[\frac{h^2\Gamma}{2\eta}\nabla[\partial_h f(h) - \nabla\cdot(\gamma\nabla h)] - \left(\frac{h\Gamma}{\eta} + \widetilde{D}\right)\nabla\gamma \right]. \tag{19}$$

Thus, the diffusion term is expressed in terms of $\nabla\gamma$ and the molecular mobility $\widetilde{D}$. Note, however, that this argument no longer holds if the free energy functional contains non-local terms in Γ, such as $(\nabla\Gamma)^2$. Then the formulation in Eq. (19) cannot be used and one must start directly with Eqs. (12).

VI. EXTENSIONS

Up to this point, we have presented a gradient dynamics re-formulation of the hydrodynamic long-wave model for the evolution of a thin-film that is covered by a low concentration of insoluble surfactants, that has several connections to the approach taken in dynamical density functional theory, with a local approximation for the free energy.

The present re-formulation really demonstrates its advantages when seeking to make (common) extensions of the hydrodynamic model, such as to incorporate nonlinear equations of state, surfactant-dependent wettability, phase transitions at high surfactant concentrations, or substrate mediated surfactant condensation. Such effects are often included into the hydrodynamic formulation (2) and (3) in an *ad hoc* manner that easily results in the omission of important terms and sometimes leads to qualitatively incorrect behaviour. The thermodynamic variational framework presented here, i.e., Eqs. (15), allows us to make extensions stemming from changes (extra terms) in the free energy functional (9) in a systematic and thermodynamically consistent manner. In the following, we discuss several examples.

A. Nonlinear equation of state

The most common extension is to replace the linear equation of state in Eq. (1) by various nonlinear expressions. Examples include the exponential (Gaussian) dependence $\gamma = C_1 + C_2 \exp(-\Gamma^2/C_3)$;[36] a smoothed stepwise change $(\gamma = C_1 + C_2 \tanh[C_3(\Gamma - 1)])$;[12,37,38] Langmuir-Szyszkowski $(\gamma = C_1 + C_2 \log(1 - \Gamma))$[9,10,12,39,40] or Frumkin $(\gamma = C_1 + C_2 \log(1 - \Gamma) + C_3\Gamma^2)$[12,39,41] equations applied to insoluble surfactants; expressions related to power laws (such as $\gamma = C_1 + C_2(1 + C_3\Gamma)^{-3})$[14,42–45]; and fits to experimentally obtained isotherms.[46] In all cases the C's represent various constants. In most works, the extension is done by solely replacing the parameter γ_Γ in Eqs. (2) and (3) by the function $\gamma' = \partial\gamma(\Gamma)/\partial\Gamma$. This, however, does not take into account that in addition to the convective transport due to the Marangoni force, the diffusive transport of the surfactant is also affected when the underlying free energy functional changes. Thus, most works assume that the diffusion constant D remains independent of the surfactant concentration, even when working with highly nonlinear equations of state. An exception is Ref. 42 that uses a $D(\Gamma)$.

Based on our thermodynamic reformulation, the proper relation between γ and D (discussed at the end of Sec. V A) results in the amended hydrodynamic equations (19) that are expressed in terms of $\gamma(\Gamma)$. One may define a non-constant $D(\Gamma)$ by enforcing Ficks's law

$$J_{\text{diff}} = -D\nabla\Gamma \tag{20}$$

to hold. From a comparison of Eqs. (3) and (15), one obtains $D\nabla\Gamma = \widetilde{D}\Gamma\nabla g' = \widetilde{D}\Gamma g''\nabla\Gamma$, i.e., $D = \widetilde{D}\Gamma g''$. With this D the hydrodynamic formulation (2) and (3) is consistent with the gradient dynamics form (15). To obtain D in terms of the equation of state, one differentiates the relation $\gamma = g - \Gamma g'$ with respect to Γ. The result $\gamma' = -\Gamma g''$ implies

$$D = -\widetilde{D}\gamma'. \tag{21}$$

Note, however, that in principle $\widetilde{D}$ itself might also be a function of Γ (and other state variables). The relations $\gamma(\Gamma)$ and $D(\Gamma)$ employed in Ref. 42 are only consistent with the general thermodynamic framework given here, if particular dependencies of $\widetilde{D}$ on Γ are assumed. Note that Fick's law in Eq. (20) is only true in the low density $\Gamma \to 0$ limit. More generally, one should have

$$J_{\text{diff}} = -M\nabla\mu, \tag{22}$$

where $M(\Gamma)$ is a mobility coefficient.[25–28,47] This form is universally valid, whereas Eq. (20) does not always hold (e.g., in the "uphill diffusion" observed in spinodal decomposition).

Note also that many authors correctly employ the hydrodynamic form in Eqs. (3) and (15) with a linear equation of state, but give the Marangoni flux in its general form as $J_{\text{mar}} = (h^2/2\eta)\nabla\gamma(\Gamma)$ in combination with a surfactant-independent diffusion constant.[5,48–51] While this approach is indeed correct for a linear equation of state, it should be stressed that it is not valid for arbitrary (nonlinear) equations of state.

B. Surfactant-dependent wettability

It is widely accepted that wettability depends on the surface density of the surfactants.[52,53] However, the literature is less clear on how such effects may be incorporated in a hydrodynamic thin-film description by extending the model given in Eqs. (2), (3) and (15). In all the contributions, we are aware of, this is done by replacing the film-thickness dependent Derjaguin (or disjoining) pressure $\Pi(h)$, that is contained in the pressure $p_{\text{add}}(h)$ in Eqs. (2) and (3), by a disjoining pressure $\Pi(h, \Gamma)$ that depends on film thickness and surfactant concentration.[54–57] The influence of surfactants on the various components of Derjaguin's pressure for thin-films are discussed in detail in Refs. 53 and 58 in the context of free standing (soap) films. For a simple model for forces between surfaces with adsorbed layers see Ref. 59.

Based on our thermodynamic re-formulation, one can now see how the hydrodynamic equations (2) and (3) must be amended to account for any dependency of the adhesion energy on film thickness and surfactant concentration. Replacing $f(h)$ in the free energy functional (9) by $f(h, \Gamma)$ results in the additional contribution $\partial_\Gamma f$ to $\delta F/\delta\Gamma$ that affects both evolution equations. The resulting

hydrodynamic form is

$$\partial_t h = \nabla \cdot \left[\frac{h^3}{3\eta} \nabla[\partial_h f(h, \Gamma) - \nabla \cdot (\gamma \nabla h)] - \frac{h^2}{2\eta}[\nabla \gamma - \Gamma \nabla \partial_\Gamma f(h, \Gamma)] \right],$$

$$\partial_t \Gamma = \nabla \cdot \left[\frac{h^2 \Gamma}{2\eta} \nabla[\partial_h f(h, \Gamma) - \nabla \cdot (\gamma \nabla h)] - \left(\frac{h\Gamma}{\eta} + \widetilde{D} \right)[\nabla \gamma - \Gamma \nabla \partial_\Gamma f(h, \Gamma)] \right].$$

(23)

The extra terms should be interpreted as an additional contribution to the Marangoni force that must be taken into account for small film thicknesses. The effective Marangoni force is $\nabla \gamma + \Gamma \nabla \partial_\Gamma f(h, \Gamma)$. It also becomes the effective driving force for diffusion of the surfactant. To our knowledge, these terms have not been included in any of the thin-film evolution equations that model surfactant-covered ultrathin films. However, they are necessary in any model that involves a surfactant-dependent Derjaguin pressure. Without them, the model may exhibit qualitatively incorrect behaviour, such as oscillatory instability modes,[56] as discussed in more detail below. Furthermore, as the system evolves in time, it does not tend to the correct equilibrium state, particularly in the contact line region. In short, to treat such effects correctly one must determine a suitable form for $f(h, \Gamma)$, obtained from the surfactant-dependent Derjaguin pressures discussed in the literature.[52,53,58]

C. Surfactant phase transitions

A third example is the description of phase separating surfactant mixtures or phase transitions at high surfactant concentrations. The simplest case of surfactant molecules that slightly attract each other is already addressed by the discussion above, as it only results in a nonlinear equation of state. For instance, for weakly attracting surfactant molecules, one replaces the purely entropic form in Eq. (10) by $g(\Gamma) = \gamma_0 + \frac{kT}{l^2} \Gamma[\log(\Gamma) - 1] - (a/2)\Gamma^2$, where the attraction strength parameter $a > 0$. This results in $\gamma = \gamma_0 - (kT/l^2)\Gamma + (a/2)\Gamma^2$ and so the effective diffusion constant depends linearly on Γ.

The situation becomes more involved for surfactant layers that can undergo a phase transition when the concentration changes, e.g., between the gaseous and the liquid-expanded or between the liquid-expanded and the liquid-condensed phases.[60,61] We emphasise that these phase-transitions all occur for sub-monolayer surfactant coverages. Therefore, the surfactant layer does not need to be treated as a film with a vertical velocity profile. Only for surfactant coverages of several monolayers does one need to devise a two-layer model similar to Ref. 62. This case is not treated here.

Beside a function $g(\Gamma)$ that accounts for the particular surfactant isotherm, one also needs to incorporate a surface gradient term $(\kappa/2)(\nabla_s \Gamma)^2 \xi$ in the free energy functional (9) to account for the finite width and line tension of the interface between the various surfactant phases. If a double-well potential is used for g, this amounts to a description of the surfactant layer using a convective Cahn-Hilliard-type equation. A similar approach is employed in Ref. 63 to describe a thin liquid film covered with an insoluble surfactant in the vicinity of a first-order phase transition. However, as explained below, our formulation differs on a number of important points.

As the algebra is involved, we illustrate this for the one-dimensional case, where x is the only spatial coordinate. The free energy functional is

$$F[h, \widetilde{\Gamma}/\xi] = \int \left\{ f(h) + g\left(\frac{\widetilde{\Gamma}}{\xi} \right) \xi + \frac{\kappa}{2} \left(\partial_x \frac{\widetilde{\Gamma}}{\xi} \right)^2 \frac{1}{\xi} \right\} dx,$$

(24)

where we use $\partial_s = (1/\xi)\partial_x$, $\widetilde{\Gamma} = \xi\Gamma$, $ds/dx = \xi$, and s is the arc-length coordinate along the free surface. Note that the final contribution to the integral in Eq. (24) is simply the term $(\kappa/2)\int(\partial_s \Gamma)^2 ds$. We keep $\xi = \sqrt{1 + (\partial_x h)^2}$ exact throughout the derivation and only use $(\partial_x h)^2 \ll 1$ at the end. Employing the approximation too early can lead to neglecting physically essential terms, such as the Laplace pressure. Details of the calculation of the functional derivatives are given in the

Appendix. The resulting expressions are

$$\frac{\delta F}{\delta h} = f' - \partial_x \left[\left(\omega - \frac{\kappa}{2} (\partial_x \Gamma)^2 + \kappa \Gamma \partial_{xx} \Gamma \right) \partial_x h \right],$$

$$\frac{\delta F}{\delta \widetilde{\Gamma}} = g' - \kappa \partial_{xx} \Gamma,$$

(25)

where we have used $(\partial_x h)^2 \ll 1$ [see the Appendix – in particular Eqs. (A19) and (A20)] and $\omega = g - \Gamma g'$. The time evolution equations for h and Γ are obtained by substituting Eqs. (25) into Eqs. (12). On inspecting the resulting equations, one notices that we have again obtained the form in Eq. (19), but now the surface tension is

$$\gamma = \widetilde{\omega} \equiv \omega - \frac{\kappa}{2} (\partial_x \Gamma)^2 + \kappa \Gamma \partial_{xx} \Gamma. \tag{26}$$

Recall that above, for the case without the gradient terms in Γ, we had that $\partial_x \gamma = -\Gamma \partial_x \delta F / \delta \tilde{\Gamma}$ [Eq. (16)]. It turns out that in the present case this result still holds. The surface grand potential density for the nonlocal case is $\widetilde{\omega} = g + (\kappa/2)(\partial_x \Gamma)^2 - \Gamma \delta F / \delta \tilde{\Gamma}$. This observation implies that with the proper definition of surface tension, the evolution equations in Eq. (19) are valid for both the extension to include nonlinear equations of state and the present extension that incorporates gradient terms in Γ in the free energy.

This issue explains the differences between our formulation and that in Ref. 63, that starts from a hydrodynamic formulation somewhat similar to that in Eq. (19).[64] We expect the formulation presented here to be useful for studying the dynamics of surfactant phase transitions on thin films, for the case of insoluble surfactants. For instance, incorporating gradient terms may enable one to explain the spatially non-monotonic distribution of a spreading surfactant drop that has been observed in recent experiments.[65]

D. Substrate-mediated phase transitions

As final example, we mention the so-called substrate-mediated phase transitions of surfactant layers that may occur when surfactant monolayers are transferred from a deep trough onto a solid substrate, i.e., during a Langmuir Blodgett transfer.[66, 67] Often, the substrate triggers a phase transition from the liquid-expanded phase to the liquid-condensed phase of the surfactant monolayer. Within the framework presented here, this transition may be described by replacing the surfactant contribution to the free energy (9), $g(\Gamma)$, by a term that depends on both the surfactant concentration and film height, $g(h, \Gamma)$. Doing this, one obtains additional contributions to the free energy variations: The g' has to be replaced by $\partial_\Gamma g$ and a term $\partial_h g$ is added to $\delta F / \delta h$ in Eq. (14). For the full expressions, see the Appendix. Such a surfactant concentration and film-height dependent contribution to the free energy is employed in Refs. 68 and 69 to describe substrate-mediated condensation, but without incorporating the additional $\partial_h g$ term. For their choice of $g(h, \Gamma)$, the omission is of no major consequence; it only amounts to a redefinition of the parameters in the disjoining pressure.

VII. CONSEQUENCES OF THE GRADIENT DYNAMICS FORMULATION

The advantage of the gradient dynamics formulation, besides its thermodynamic consistency, is that one may readily use general results obtained for other systems having governing equations of the form of Eq. (12). Similar formulations exists, for instance, for two-layer thin-film systems (where the two conserved fields are the two film thicknesses)[62, 70] and for thin-films of solutions or suspensions (where the two conserved fields are the film thickness h and the effective solute layer thickness $\psi = h\phi$, where ϕ is the vertically averaged concentration).[71]

A. Lyapunov functional

Just as in the above-mentioned cases, one can show that the free energy functional $F[h, \Gamma]$ in Eq. (12) is a Lyapunov functional: The total time derivative of $F[h, \Gamma]$ is dF/dt

$= \int \left(\frac{\delta F}{\delta h} \partial_t h + \frac{\delta F}{\delta \widetilde{\Gamma}} \partial_t \Gamma \right) dS$. Expressing the partial derivatives $\partial_t h$ and $\partial_t \Gamma$ by the expressions in Eq. (12) and after integration by parts and assuming periodic or no-flux boundary conditions, one obtains

$$\frac{dF}{dt} = - \int \left[Q_{hh} \left(\nabla \frac{\delta F}{\delta h} \right)^2 + 2 Q_{h\Gamma} \left(\nabla \frac{\delta F}{\delta h} \right) \cdot \left(\nabla \frac{\delta F}{\delta \widetilde{\Gamma}} \right) + Q_{\Gamma\Gamma} \left(\nabla \frac{\delta F}{\delta \widetilde{\Gamma}} \right)^2 \right] dx. \qquad (27)$$

Because [cf. Eq. (13)]

$$\det \mathbf{Q} = \frac{h^4 \Gamma^2}{12 \eta^2} + \frac{\widetilde{D} h^3 \Gamma}{3 \eta} > 0, \qquad (28)$$

and $Q_{hh} > 0$ and $Q_{\Gamma\Gamma} > 0$, the quadratic form in Eq. (27) is positive definite and therefore $dF/dt < 0$, and F is a proper Lyapunov functional. Furthermore, one may identify the stationary solutions of Eqs. (12) with the extrema of F.

B. Stability of flat films

Next, we briefly discuss a general result for the linear stability of flat films $h(x, t = 0) = h_0$, that are covered by a homogeneous layer of surfactant $\Gamma(x, t = 0) = \Gamma_0$. For a system of infinite size, one may decompose any fluctuation disturbances of the film height and surfactant concentration of this homogeneous state into Fourier modes and consider their time evolution. We employ the ansatz $h(x, t) = h_0[1 + \epsilon \exp(\beta t + kx)]$ and $\Gamma(x, t) = \Gamma_0[1 + \epsilon \chi \exp(\beta t + kx)]$, where k and $\beta(k)$ are the wave number and growth rate of the harmonic mode, respectively. The overall amplitude of the disturbance is ϵ, while χ is the amplitude ratio of the disturbances in the surfactant concentration and film thickness profiles. In short, the amplitudes may be written in vector notation as $\epsilon \boldsymbol{\chi} = \epsilon(h_0, \chi \Gamma_0)^T$.

Employing these ansatzes for $h(x, t)$ and $\Gamma(x, t)$ in Eqs. (12), and then linearising in $\epsilon \ll 1$, as is appropriate for small amplitude disturbances, leads to the following eigenvalue problem:

$$(\mathbf{J} - \beta \mathbf{I}) \boldsymbol{\chi} = 0, \qquad (29)$$

where $\mathbf{J}$ is the *non*-symmetric Jacobian given by

$$\mathbf{J} = -k^2 \mathbf{Q}_0 \mathbf{E}_0 \qquad (30)$$

and where $\mathbf{E}_0$ and $\mathbf{Q}_0$ are the matrix of the second variations of F in Fourier space and the mobility matrix, respectively, both evaluated at h_0 and Γ_0. Since $\det \mathbf{Q} \neq 0$ for $h, \Gamma > 0$, Eq. (29) can be written as the generalised eigenvalue problem

$$(k^2 \mathbf{E}_0 + \beta \mathbf{Q}_0^{-1}) \boldsymbol{\chi} = 0. \qquad (31)$$

Because $\mathbf{E}_0$ and $\mathbf{Q}_0^{-1}$ are both symmetric and $\mathbf{Q}_0^{-1}$ is positive definite, one can deduce that all eigenvalues β are real,[72] as one should expect for a variational problem. Inspecting Eq. (31) further indicates that the stability of the system is completely determined by the eigenvalues of $\mathbf{E}_0$, i.e., by the second variations of the free energy functional. The stability threshold is given by $\det \mathbf{E}_0 = 0$. However, having $\mathbf{E}_0$ is not sufficient to obtain the actual growth rate $\beta(k)$ of the unstable modes (i.e., the dispersion relation) and the amplitude ratio χ. These are obtained by solving Eq. (29). A remarkable effect that arises from the coupling of the two fields, i.e., when $\delta^2 F / \delta \Gamma \delta h \neq 0$, is that the system becomes unstable for a larger range of parameter values than the individual (decoupled) systems on their own. This effect is discussed in many other contexts – see, e.g., Refs. 73, 70, and 74.

The fact that the present system has a non-diagonal mobility matrix $\mathbf{Q}$ in Eq. (13) (as do the models in Refs. 70 and 71) distinguishes it from many other systems with evolution equations for two coupled order parameter fields having a gradient dynamics. This means that the equations for both fields depend on variations of the free energy with respect to each of the fields h and Γ. Thus, for a non-diagonal $\mathbf{Q}$ and when $\delta^2 F / \delta \Gamma \delta h \neq 0$, the evolution of the two fields are coupled both through the free energy functional and through the dynamical mobility coefficients in $\mathbf{Q}$. In contrast, many such

systems have a diagonal mobility matrix, and then the evolution of the two fields is solely coupled by the off-diagonal term in the matrix of second derivatives, $\delta^2 F/\delta\Gamma\delta h$. Examples are the equations in Ref. 75, that describe the spinodal decomposition in ternary systems, the dewetting of nanoparticle suspensions in Ref. 76, the coupled demixing and dewetting of a binary mixture discussed in Ref. 77, the electric field driven surface instability of two air-gap separated polymer layers in a capacitor,[78] and the model equations employed in Ref. 73 to describe the interplay between ordering and spinodal decomposition in binary systems.

VIII. CONCLUSIONS

We have proposed several amendments and extensions for models describing the dynamics of liquid films that are covered by high concentrations of insoluble surfactant. After briefly reviewing the "classical" hydrodynamic form of the coupled evolution equations for the film height and the surfactant concentration profile, that are well established for small concentrations, we have re-formulated the model in three stages as a gradient dynamics. We refer to this as the "thermodynamic form" of the evolution equations.

In the first stage, we have given the gradient dynamics form of the evolution equation for a thin film of a pure liquid on a flat substrate without surfactant, in the case where capillarity and wettability are the dominant influences. This formulation was discussed before, e.g., in Refs. 21 and 23, and is of the standard form suitable for conserved dynamics, of which a classic example is the Cahn-Hilliard equation[30] for the demixing dynamics of a binary mixture. In the second stage, we have briefly reviewed the classical diffusion equation and have noted the existence of a gradient dynamics formulation that puts it in the context of nonequilibrium thermodynamics and dynamical density functional theory. Finally, in the third stage, we have re-formulated the full coupled system of equations for the liquid film height and surfactant concentration profile in a gradient dynamics form, based on an underlying free energy functional that accounts for wettability, capillarity, and entropic contributions for the surfactant. The resulting equations are equivalent to the hydrodynamic form for the case of a linear equation of state for the surfactant.

Based on this thermodynamic re-formulation, we have proposed amendments to the basic hydrodynamic model that account for four different physical effects that all may be included through changes to the free energy functional. In particular, we have extended the thin-film model to consistently account for (i) nonlinear equations of state, (ii) surfactant-dependent wettability, (iii) surfactant phase transitions, and (iv) substrate-mediated condensation. The ideas that we have presented can also be directly applied to films covered by monolayers of nano-sized particles that are not soluble in the liquid film,[79] or any substance that remains on the surface of the liquid film.

Our results indicate that nearly all long-wave models found in the literature that extend the hydrodynamic equations for thin liquid films covered by insoluble surfactants by including nonlinear equations of state are either not fully consistent or not complete. The most important differences between our model and those in the literature, as discussed above in Sec. VI, are as follows:

(i)   When incorporating a nonlinear equation of state, most authors fail to note that one must also amend the surfactant diffusion term in the governing dynamical equations.
(ii) To account for a surfactant-dependent wettability, it is not sufficient to just adapt the Derjaguin (or disjoining) pressure. The Marangoni and diffusion term must also be amended.
(iii) To account for surfactant phase transitions, square gradient, or other non-local terms for the surfactant concentration must be incorporated into the free energy functional. In these, the gradient should be taken along the free surface.
(iv) When incorporating terms to describe a surfactant phase transition that depend on the distance between the film surface to the solid substrate (e.g., to describe substrate mediated condensation), the added coupling terms lead to additional terms in the equation of state *and* the Derjaguin pressure.

The corrections to models in the literature that result from following our approach will in many cases only result in quantitative (rather than qualitative) changes to the results that may also be rather small. In some cases, however, the differences will be qualitative and significant. For instance, we

believe that the oscillatory dewetting modes ("dewetting waves") described in Ref. 56 for one- and two-layer films with surfactant are present in the model as a consequence of a broken variational structure of the governing equations that stems from omitting terms in the equation for the time evolution of the surfactant concentration profile. Using the complete equations, all eigenvalues of the linearised problem are real, and thus all instability modes are monotonic.

The various extensions that we have proposed may all be simultaneously included so as to account for more complex situations. The corresponding free energy functional is

$$F[h, \Gamma] = \int \left\{ f(h, \Gamma) + g(\Gamma, h)\,\xi + \frac{\kappa}{2} (\nabla \Gamma)^2 \frac{1}{\xi} \right\} dA, \tag{32}$$

where $f(h, \Gamma)$ is a generalised wetting interaction term, and $g(\Gamma, h)$ is a generalised local free energy of the surfactant on the free surface. Note that future work should identify the connections that must exist between these more general functions f and g because they both arise from the same molecular interactions; this is an issue that we have not touched upon here.

Actually, the question might arise whether it is correct to keep surface part $g(\Gamma, h)$ and wetting part $f(h, \Gamma)$ of the free energy separate, even though both may depend on the surfactant concentration and film thickness. For a free film of constant height at equilibrium, one might follow Ref. 80 and introduce a film tension that comprises Derjaguin pressure and surface tension contributions in a single function that depends on the film height h and concentration Γ (but not on their gradients). This is, however, not possible for general interface geometries out of equilibrium. The reason is that both the entropic and energetic contributions to the surface part of the free energy are proportional to the surface area $ds = \xi\,dx$ of the free surface, whereas the contribution of the wetting energy (from the interactions with the substrate) is proportional to the substrate area dx and, of course, depends on the local film thickness $h(x, t)$. As a result, to leading order, the wetting energy (Derjaguin pressure) does not contribute to the surface tension relevant in the Laplace pressure term. Furthermore, it is impossible to employ such a film tension in the dynamical equations as it contains two contributions that correspond to surface forces [$\nabla \delta F/\delta \Gamma$ in Eqs. (12)] and to volume forces [$\nabla \delta F/\delta h$ in Eqs. (12)], respectively, that come with different mobility functions [Eq. (13)].

Our approach may also be further extended to accommodate more general terms that one should expect to be present in the free energy functional, including non-local integral (convolution) contributions to F, which are commonly used in dynamical density functional theory,[25–28,81] which uses as input the free energy functionals coming from equilibrium density functional theory.[24,31]

We emphasise that points (i) and (iii) above are particularly important for a number of biophysical systems, such as the description of the surfactant layers that reside on the aqueous thin-film of the lung lining,[14] where (a) the equations of state that are used are strongly nonlinear and (b) experiments show that phase transitions frequently occur, e.g., in layers of porcine lung surfactant at the air-water interface at physiologically relevant concentrations and temperatures.[82] Similar results are found for calf lung surfactant, where an expanded-to-condensed phase transition is observed as the surfactant concentration is increased.[83] The dynamics of the ongoing surfactant phase transitions and their interaction with the hydrodynamics of the thin liquid film is highly important. The formulation and extensions we present here allows one to extend the "classical" hydrodynamic thin-film models to include the more intricate thermodynamic effects based on equations of state (obtained from suitable free energy functionals) that are observed experimentally. Note, however, that a real layer of lung lining is much more complicated than the idealised situations mentioned above,[84] as it consists of mixtures of soluble surfactants. This indicates that our approach should be extended to allow for a description of soluble surfactants. The extension towards mixtures of insoluble surfactants is more straightforward, but including a third field in the system makes the algebra somewhat tedious.

Further extensions that should be considered in the future concern the dynamical aspects. Here, we have employed the mobility matrix **Q** in Eq. (13), which is derived from the well-known hydrodynamic transport equations obtained for the simplest case of an insoluble surfactant with a linear equation of state. Although we believe this approximation should hold over a large parameter range, at very high surfactant concentrations one must make corrections. Although, slip at the solid substrate can easily be accounted for, it is not clear what changes to the mobility matrix **Q** should

arise from incorporating surface viscosity effects and/or a no-slip condition at the surfactant-covered surface.

Here, we have only discussed the gradient dynamics formulation in the context of surfactant-covered liquid films on solid substrates, because the mathematical formulation is most convenient. However, it is important to note that most of the effects that we mention also occur in other geometries. A prominent example where our considerations also apply are soap films based on insoluble surfactants. This is important for many systems, such as those reviewed in Ref. 53, that involve, for instance, surfactant-dependent Derjaguin pressures and highly nonlinear equations of state. Another example is surfactant-covered drops of liquid immersed in another fluid where issue (i) is particularly relevant when, for example, studying the shear-driven deformation and/or breakup of such droplets[9, 10, 39, 85] or liquid bridges or threads.[12, 86–88] In this case, for instance, incorporating a nonlinear equation of state should also be accompanied by the corresponding amendment of the surfactant diffusion term.

ACKNOWLEDGMENTS

APPENDIX: VARIATIONAL CALCULUS IN THE GENERAL CASE

The free energy for the surfactant covered thin liquid film is

$$F[h, \widetilde{\Gamma}/\xi] = \int \left\{ f(h, \widetilde{\Gamma}/\xi) + g(\widetilde{\Gamma}/\xi, h)\xi + \frac{\kappa}{2} \left(\nabla(\widetilde{\Gamma}/\xi) \right)^2 \frac{1}{\xi} \right\} dA. \tag{A1}$$

We define

$$F[h, \widetilde{\Gamma}/\xi] = F_{\text{wet}} + F_{\text{surf}} + F_{\text{grad}} \tag{A2}$$

so as to be able to calculate the variations of the three terms in the free energy separately. In the following, we limit ourselves to the one-dimensional case and we often need to use the result

$$\partial_x \xi = \partial_x \sqrt{1 + (\partial_x h)^2} = \frac{1}{\xi}(\partial_x h)(\partial_{xx} h). \tag{A3}$$

1. Variations with respect to *h*

$$\frac{\delta F_{\text{wet}}}{\delta h} = \partial_h f, \tag{A4}$$

$$\frac{\delta F_{\text{surf}}}{\delta h} = \partial_h g - \frac{d}{dx} \left[-\xi(\partial_\Gamma g)\widetilde{\Gamma} \frac{1}{\xi^3} \partial_x h + g \frac{1}{\xi} \partial_x h \right], \tag{A5}$$

$$= \partial_h g - \frac{d}{dx} \left[\frac{1}{\xi}(g - \Gamma \partial_\Gamma g)\partial_x h \right]. \tag{A6}$$

For the next term, we need to use

$$\frac{\delta(\int \star dx)}{\delta h} = \frac{\partial \star}{\partial h} - \frac{d}{dx} \frac{\partial \star}{\partial(\partial_x h)} + \frac{d^2}{dx^2} \frac{\partial \star}{\partial(\partial_{xx} h)}. \tag{A7}$$

We also need

$$\frac{\partial}{\partial h} \xi = 0, \tag{A8}$$

$$\frac{\partial}{\partial(\partial_x h)} \xi = \frac{1}{\xi} \partial_x h, \qquad \text{and} \qquad \frac{\partial}{\partial(\partial_x h)} \frac{1}{\xi} = -\frac{1}{\xi^3} \partial_x h \tag{A9}$$

and

$$\partial_x \frac{\widetilde{\Gamma}}{\xi} = \frac{\partial_x \widetilde{\Gamma}}{\xi} - \frac{\widetilde{\Gamma}}{\xi^2}\partial_x\xi \tag{A10}$$

$$= \frac{\partial_x \widetilde{\Gamma}}{\xi} - \frac{\widetilde{\Gamma}}{\xi^3}(\partial_x h)\partial_{xx}h, \tag{A11}$$

$$\frac{\delta F_{\text{grad}}}{\delta h} = -\frac{d}{dx}\left[-\frac{\kappa}{2}\left(\partial_x\frac{\widetilde{\Gamma}}{\xi}\right)^2 \frac{\partial_x h}{\xi^3} - \frac{\kappa}{\xi^4}\left(\partial_x\widetilde{\Gamma}\partial_x h + \widetilde{\Gamma}\partial_{xx}h - 3\frac{\widetilde{\Gamma}}{\xi^2}(\partial_x h)^2\partial_{xx}h \right)\partial_x\frac{\widetilde{\Gamma}}{\xi} \right]$$

$$\quad -\frac{d^2}{dx^2}\left[\frac{\kappa}{\xi^3}\left(\partial_x\frac{\widetilde{\Gamma}}{\xi}\right)\Gamma\partial_x h \right]$$

$$= -\frac{d}{dx}\left\{ \frac{\kappa}{\xi^3}\left[-\frac{1}{2}(\partial_x\Gamma)^2\,\partial_x h - \left(\partial_x\Gamma\partial_x h + \Gamma\partial_{xx}h - 2\frac{\Gamma}{\xi^2}(\partial_x h)^2\partial_{xx}h \right)\partial_x\Gamma \right.\right.$$

$$\left.\left. -\left(3\frac{\Gamma}{\xi^2}(\partial_x h)^2\partial_{xx}h - \partial_x\Gamma\partial_x h - \Gamma\partial_{xx}h \right)\partial_x\Gamma + \Gamma\partial_x h\partial_{xx}\Gamma \right]\right\}$$

$$= \frac{d}{dx}\left\{ \frac{\kappa}{\xi^3}\left[\frac{1}{2}(\partial_x\Gamma)^2\,\partial_x h + \frac{\Gamma}{\xi^2}(\partial_x h)^2(\partial_{xx}h)\partial_x\Gamma - \Gamma\partial_x h\partial_{xx}\Gamma \right]\right\}. \tag{A12}$$

2. Variations with respect to $\widetilde{\Gamma}$

$$\frac{\delta F_{\text{wet}}}{\delta\widetilde{\Gamma}} = \frac{1}{\xi}\partial_\Gamma f, \tag{A13}$$

$$\frac{\delta F_{\text{surf}}}{\delta\widetilde{\Gamma}} = \partial_\Gamma g, \tag{A14}$$

$$\frac{\delta F_{\text{grad}}}{\delta\widetilde{\Gamma}} = -\frac{\kappa}{\xi^4}(\partial_x\Gamma)(\partial_x h)(\partial_{xx}h) - \frac{d}{dx}\left[\frac{\kappa}{\xi^2}\partial_x\Gamma \right] \tag{A15}$$

$$= -\frac{\kappa}{\xi^4}(\partial_x\Gamma)(\partial_x h)(\partial_{xx}h) + \kappa\left[\frac{2}{\xi^4}(\partial_x h)(\partial_{xx}h)(\partial_x\Gamma) - \frac{1}{\xi^2}\partial_{xx}\Gamma \right] \tag{A16}$$

$$= \frac{\kappa}{\xi^4}(\partial_x\Gamma)(\partial_x h)(\partial_{xx}h) - \frac{\kappa}{\xi^2}\partial_{xx}\Gamma. \tag{A17}$$

3. Collecting the terms

The resulting expressions are

$$\frac{\delta F}{\delta h} = \partial_h f + \partial_h g - \frac{d}{dx}\left[\frac{1}{\xi}\left(g - \Gamma\partial_\Gamma g - \frac{\kappa}{2\xi^2}(\partial_x\Gamma)^2 + \frac{\kappa}{\xi^2}\Gamma\partial_{xx}\Gamma \right)\partial_x h - \frac{\kappa}{\xi^5}\Gamma(\partial_x h)^2(\partial_{xx}h)\partial_x\Gamma \right], \tag{A18}$$

$$\frac{\delta F}{\delta\widetilde{\Gamma}} = \frac{1}{\xi}\partial_\Gamma f + \partial_\Gamma g - \frac{\kappa}{\xi^2}\partial_{xx}\Gamma + \frac{\kappa}{\xi^4}(\partial_x\Gamma)(\partial_x h)\partial_{xx}h.$$

This seems the appropriate stage in the derivation to apply the long-wave approximation, i.e., to use $(\partial_x h)^2 \equiv \varepsilon \ll 1$. Therefore, $\xi \approx 1 + (1/2)\varepsilon^2$ and one obtains

$$\frac{\delta F}{\delta h} = \partial_h f + \partial_h g - \frac{d}{dx}\left[\left(g - \Gamma\partial_\Gamma g - \frac{\kappa}{2}(\partial_x\Gamma)^2 + \kappa\Gamma\partial_{xx}\Gamma \right)\partial_x h - \kappa\Gamma(\partial_x h)^2(\partial_{xx}h)\partial_x\Gamma \right], \tag{A19}$$

$$\frac{\delta F}{\delta\widetilde{\Gamma}} = \partial_\Gamma f + \partial_\Gamma g - \kappa\partial_{xx}\Gamma + \kappa(\partial_x\Gamma)(\partial_x h)\partial_{xx}h.$$

The respective last term is $O(\varepsilon^2)$ smaller than the other terms with prefactor κ and can therefore safely be dropped, yielding

$$
\begin{aligned}
\frac{\delta F}{\delta h} &= \partial_h f + \partial_h g - \frac{d}{dx}\left[\left(g - \Gamma\partial_\Gamma g - \frac{\kappa}{2}(\partial_x\Gamma)^2 + \kappa\Gamma\partial_{xx}\Gamma\right)\partial_x h\right], \\
\frac{\delta F}{\delta\widetilde{\Gamma}} &= \partial_\Gamma f + \partial_\Gamma g - \kappa\partial_{xx}\Gamma.
\end{aligned}
\tag{A20}
$$

Equations (25) in the main text are obtained by setting $\partial_h g = \partial_\Gamma f = 0$, whereas the results in Eqs. (14) are obtained by setting $\partial_h g = \partial_\Gamma f = 0$ together with $\kappa = 0$.

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