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Gradient Dynamics Description for Films of Mixtures and Suspensions: Dewetting Triggered by Coupled Film Height and Concentration Fluctuations

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A thermodynamically consistent gradient dynamics model for the evolution of thin layers of liquid mixtures, solutions, and suspensions on solid substrates is presented which is based on a film-height- and mean-concentration-dependent free energy functional. It is able to describe a large variety of structuring processes, including coupled dewetting and decomposition processes. As an example, the model is employed to investigate the dewetting of thin films of liquid mixtures and suspensions under the influence of effective long-range van der Waals forces that depend on solute concentration. The occurring fluxes are discussed, and it is shown that spinodal dewetting may be triggered through the *coupling* of film height and concentration fluctuations. Fully nonlinear calculations provide the time evolution and resulting steady film height and concentration profiles.

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Understanding the behavior of free surface layers and drops of simple and complex liquids becomes increasingly important because the drive towards further miniaturization of fluidic systems towards micro- [1] and eventually nanofluidic [2] devices depends on our ability to gain control of the various interfacial effects on small scales. Liquid layers frequently occur either naturally, e.g., as a tear film in the eye, or industrially, e.g., as protection or lubrication layers. They are also instrumental in many wet process stages of printing, (nano-)structuring, and coating technologies where films or drops of a liquid are applied to a surface with the aim of producing a homogeneous or structured layer of either the liquid or a solute. For reviews, see Refs. [3–6].

Their omnipresence in natural and industrial processes provides a strong incentive to investigate the creation, instabilities, rupture dynamics, and short- and long-time structure formations of free surface thin liquid films on solid substrates. These processes are well investigated experimentally [7,8] and theoretically [9,10] for films of simple liquids on smooth solid substrates. Continuum models describe the evolution of the film thickness profile $h(\mathbf{x},t)$ as a gradient dynamics $\partial_t h = \nabla\cdot\{Q(h)\nabla\delta F[h]/\delta h\}$ for the free energy $F[h] = \int d\mathbf{x}[\gamma\xi + f(h)]$ [11] that accounts for wettability through the local wetting energy $f(h)$ and for capillarity through the local surface energy $\gamma\xi$ [6]. Here, $\xi d\mathbf{x} = (1+\frac{1}{2}|\nabla h|^2)d\mathbf{x}$ is the long-wave (or small-gradient) approximation of the surface area element in Monge parametrization, γ is the liquid-gas interface tension, the variational derivative $\delta F[h]/\delta h = -\gamma\Delta h - \Pi(h)$ corresponds to the pressure where $\Pi(h) = -df/dh$ is the Derjaguin or disjoining pressure [12–14], $Q(h) = h^3/3\eta$ is the mobility function in the case of no slip at the substrate where η is the dynamic viscosity (for the case of slip, see, e.g., Ref. [15]), $\mathbf{x} = (x,y)^T$, and $\nabla = (\partial_x,\partial_y)^T$. The described model may be derived via a long-wave approximation from the Navier-Stokes and continuity equations with adequate boundary conditions at the free surface and the solid substrate [3,4,16].

The dynamics of films of simple liquids is rather well understood. However, the situation strongly differs for films of complex liquids as, for instance, colloidal (nano-)particle suspensions, mixtures, polymer and surfactant solutions, polymer blends, and liquid crystals. Practically, layers of such complex liquids occur far more widely than films of simple liquid, but a systematic understanding of the possible pathways of their evolution that result from the coupled processes of dewetting, decomposition, evaporation, and adsorption has not been reached. Free surface films of such liquids occur, for instance, as tear films [17], lung lining [18], in the production of organic solar cells [19], or semiconductor nanoparticle rings [20]. Layers of solutions and suspensions with volatile solvent are frequently employed in intermediate stages of the production of homogeneous or structured layers of the solute, e.g., as a nonlithographic technique for covering large areas with regular arrays of small-scale structures. Reviews of experiments, models, and applications can be found in Ref. [21] (surfactant solutions), Refs. [22,23] (deposition processes from solution), and Ref. [24] (polymer blends). Although in all these systems the interfacial effects of capillarity and wettability are still the main driving forces, they may now interact with the dynamics of inner degrees of freedom as, e.g., the diffusive transport of solutes or surfactants, phase separation, and other phase transitions, or the evaporation or condensation of solvent- and concentration-dependent wettability.

The present work provides a consistent framework for the theoretical description of many of the observed dynamical processes in films of liquid mixtures, solutions, and suspensions. After introducing the model, we discuss limiting cases and elucidate the physical meaning of the occurring fluxes. As an example, we apply the presented general framework to the case of a film of a liquid mixture where the wettability depends on the local concentration. This shows that dewetting may be triggered through the *coupling* of film height and concentration fluctuations.

We consider a thin nonvolatile liquid film of a mixture on a solid substrate (see Fig. 1) that without additional influx of energy relaxes towards some static equilibrium state, much as in many of the experiments reviewed in Ref. [24]. In the case without evaporation, the approach to equilibrium for this relaxational system is described by a gradient dynamics of the underlying free energy functional

$$F[h,\psi] = \int [\gamma\xi + f(h,\phi) + hg(\phi) + \Sigma]dA. \qquad (1)$$

It is an extension of the above introduced $F[h]$ that accounts for (i) a dependence of the wetting energy on local concentration, (ii) the bulk free energy of the mixture per substrate area $hg(\phi)$, and (iii) the energetic cost of strong gradients in the concentration (through $\Sigma = (\sigma/2)h|\nabla\phi|^2$, where σ is the interfacial stiffness).

The gradient dynamics has to be written in terms of the *conserved fields*, film thickness $h(\mathbf{x},t)$, and effective local solute layer thickness $\psi(\mathbf{x},t) = h(\mathbf{x},t)\phi(\mathbf{x},t)$. The nonconserved field ϕ is the dimensionless height-averaged per volume solute concentration. The general coupled evolution equations for two such conserved order parameter fields in the framework of linear nonequilibrium thermodynamics are

$$\begin{aligned}\partial_t h &= \nabla\cdot\left[Q_{hh}\nabla\frac{\delta F}{\delta h} + Q_{h\psi}\nabla\frac{\delta F}{\delta\psi}\right],\\ \partial_t\psi &= \nabla\cdot\left[Q_{\psi h}\nabla\frac{\delta F}{\delta h} + Q_{\psi\psi}\nabla\frac{\delta F}{\delta\psi}\right].\end{aligned} \qquad (2)$$

The mobility matrix

$$\mathbf{Q} = \begin{pmatrix} Q_{hh} & Q_{h\psi}\\ Q_{\psi h} & Q_{\psi\psi}\end{pmatrix} = \frac{1}{3\eta}\begin{pmatrix} h^3 & h^2\psi\\ h^2\psi & h\psi^2 + 3\eta\tilde{D}\psi\end{pmatrix} \qquad (3)$$

is symmetric and positive definite, corresponding to Onsager reciprocal relations and the condition for positive entropy production, respectively [25]. $\tilde{D}$ is the molecular mobility of the solute.

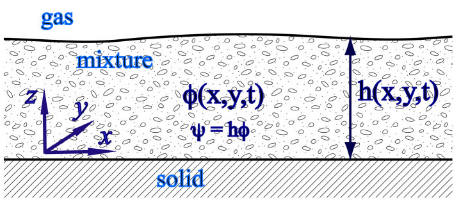

FIG. 1 (color online). Sketch of the considered geometry for a film of a liquid mixture whose components we call solvent and solute. The relevant *conserved* fields are the film height profile h and the effective local solute layer thickness $\psi = h\phi$, where ϕ is the *nonconserved* height-averaged solute concentration.

To perform the variations in Eqs. (2), one has to replace ϕ everywhere by ψ/h. The extended free energy (1) for a film of a mixture [11] results in convective and diffusive fluxes (for brevity, written in terms of h and ϕ)

$$\mathbf{J}_{\mathrm{conv}} = \frac{h^3}{3\eta}\left\{\gamma\nabla\Delta h - \nabla\partial_h f + \frac{\partial_\phi f}{h}\nabla\phi - \frac{\sigma}{h}[\nabla\cdot(h\nabla\phi)]\nabla\phi - \frac{\sigma}{2}\nabla|\nabla\phi|^2\right\}, \qquad (4)$$

$$\mathbf{J}_{\mathrm{diff}} = -\tilde{D}h\phi\nabla\left[\frac{\partial_\phi f}{h} + \partial_\phi g - \frac{\sigma}{h}\nabla\cdot(h\nabla\phi)\right], \qquad (5)$$

respectively. Employing the fluxes, we bring the gradient dynamics equations (2) into the form

$$\partial_t h = -\nabla\cdot\mathbf{J}_{\mathrm{conv}}, \qquad (6)$$

$$\partial_t(\phi h) = -\nabla\cdot(\phi\mathbf{J}_{\mathrm{conv}} + \mathbf{J}_{\mathrm{diff}}), \qquad (7)$$

which is common in the hydrodynamic literature [3,21,26].

Before discussing important limiting cases, we elucidate the physical meaning of the individual flux contributions. In the convective flux [Eq. (4)], the first term is due to Laplace pressure gradients [3]; the second term is the Derjaguin pressure contribution due to wettability; and the final two terms represent the Korteweg flux, i.e., a bulk concentration-gradient-driven flux (cf. Ref. [27] for a discussion of the related bulk model H). The third term is a flux driven by concentration gradients within the bulk of the film but only if the film is sufficiently thin such that its two interfaces "feel" each other. This novel flux is a direct consequence of the concentration dependence of the wetting energy $f(h,\phi)$ and has a similar magnitude as the Derjaguin pressure contribution [28].

The first term of the diffusive flux [Eq. (5)] is also uncommon in the literature, although it is a natural consequence of the gradient dynamics form (2). It represents the influence of the concentration-dependent wettability on diffusion. The second term is the flux due to gradients of the chemical potential $\mu = \partial_\phi g$ in the bulk of the film while the final term is a Korteweg contribution to diffusion that counters steep concentration gradients, e.g., for decomposing solvent-solute films.

The general evolution equations [(6) and (7) with (4) and (5)] recover several known models as limiting cases (this is used to determine $\mathbf{Q}$). Most importantly, (i) for a constant film height h, without wettability contribution ($f = 0$) and appropriately defined bulk free energy g, Eq. (7) becomes the Cahn-Hilliard equation that describes, e.g., the spinodal decomposition of a binary mixture [31]; (ii) as in (i) but with $\sigma = 0$ and a purely entropic (ideal gaslike)

$$g = g_{\mathrm{id}}(\phi) = \frac{k_B T}{a^3}\phi(\log\phi - 1), \qquad (8)$$

where a is a molecular length scale related to the solute, one recovers the standard diffusion equation with diffusion constant $\tilde{D}k_BT/a^3$ (see, e.g., Sec. IV of Ref. [32]); (iii) for $f = f(h)$, $\sigma = 0$, and $g = g_{\mathrm{id}}$, one recovers the conserved part of long-wave equations used, e.g., to study dewetting of and solute deposition from solutions and suspensions [26,33,34]; and (iv) again without wettability, but with Korteweg fluxes ($\sigma \neq 0$), and employing the double-well potential $g \sim (\phi^2 - 1)^2$ for the solvent-solute interaction, one obtains the thin film limit of model H [27] as derived recently via a long-wave asymptotic expansion [35,36].

Next, we present as an example the practically relevant case of a solute-dependent wettability, i.e., $f = f(h, \phi)$. For clarity, we only include entropic bulk terms for the solute-solvent interaction, i.e., $g = g_{\mathrm{id}}$ [Eq. (8)] and $\partial_\phi g = (k_BT/a^3)\log\phi$, implying absolute stability against bulk solute-solvent decomposition. For the wetting energy, we use the combination of long-range van der Waals interactions and an always stabilizing ($B > 0$) short-range contribution [14,37]:

$$f(h, \phi) = -\frac{A(\phi)}{2h^2} + \frac{B}{5h^5}. \tag{9}$$

Note that we combine a concentration-dependent Hamaker "constant" $A(\phi)$ and a constant B. One may as well introduce a concentration-dependent short-range contribution or use a different form for the short-range contribution [38]; however, these choices do not affect the main results. The Derjaguin pressure is $\Pi(h, \phi) = -\partial_h f$ while $\partial_\phi f$ could be called a Derjaguin chemical potential. $A(\phi)$ is determined employing homogenization techniques. For many experimentally employed mixtures, such as e.g., poly(methyl methacrylate)/polystrene (PMMA/PS), toluene/acetone, or PS/toluene on Si or SiO, a linear dependence is an excellent approximation over the entire concentration range [39]. Selecting the case where the pure solvent is wetting $A_0 \equiv A(\phi = 0) < 0$, we write $A(\phi) = |A_0|(-1 + \mathrm{Wc}\phi)$, where the nondimensional number Wc quantifies the strength of the concentration dependence of wettability. Experimentally, Wc may be changed by choosing a different solute. For the materials we are interested in, $|A_0|$ varies in the range $[10^{-22}, 10^{-19}]$ Nm and Wc lies in the range $[-10, 15]$. For example, a mixture of PS and PMMA on a silicon (Si) substrate (used, e.g., in Ref. [40]) yields $A_0 = -2.22 \times 10^{-19}$ and $\mathrm{Wc} = -0.11$, and for a solution of PS in toluene on silicon oxide (SiO), one obtains $A_0 = 1.74 \times 10^{-21}$ and $\mathrm{Wc} = 7.1$, while a mixture of toluene and acetone on SiO gives $\mathrm{Wc} = -9.0$.

Note that for $A_0 < 0$ and $\mathrm{Wc} < 0$, both a film of pure solvent and a film of pure solute are absolutely stable. With $g = g_{\mathrm{id}}$, the bulk solute-solvent mixture is stable as well. A film of mixture might then be expected to be stable for all $\mathrm{Wc} < 0$ and to become unstable for $\mathrm{Wc} > 0$ when $\mathrm{Wc}\phi > 1$ because then $A(\phi) > 0$. This expectation, however, assumes that the mixture in the film remains homogeneous, i.e., that concentration fluctuations are always damped. However, a linear stability analysis of flat homogeneous films with respect to fluctuations δh and $\delta\psi$ shows that the fluctuations in film height and concentration couple, rendering the system more unstable. Figure 2(a) shows that even for $\mathrm{Wc} < 0$, where all decoupled subsystems are stable, the film of a mixture can be linearly unstable in an extended experimentally accessible range of the parameter space.

Here, the dimensionless number $\mathrm{Ew} = k_bTl^3/|A_0|a^3$ is the ratio of entropic and wetting influences [41]. In other words, a film of stable solvent can be destabilized by a stable solute if the diffusion of the solute is sufficiently weak, i.e., if Ew is sufficiently small. For common mixtures, solutions, and nanoparticle suspensions, Ew can range from $O(10^{-4})$ to $O(10^4)$. The estimate is based on a typical precursor thickness of $l \approx 1$ nm [42] and a solute length scale a between 0.1 and 10 nm (this corresponds, e.g., to the size of molecules or (nano-)particles diffusing in the film) [39]. Also for $\mathrm{Wc} > 0$, the film becomes unstable at smaller Wc than expected under the assumption that the mixture stays homogeneous [dashed line in Fig. 2(a)]. Because h and ψ are both conserved, the instability is of long wavelength; i.e., at onset (at critical Wc or Ew), it has a zero wave number (cf. Ref. [6]). Therefore, for finite domains, the stability borders in Fig. 2(a) are slightly shifted.

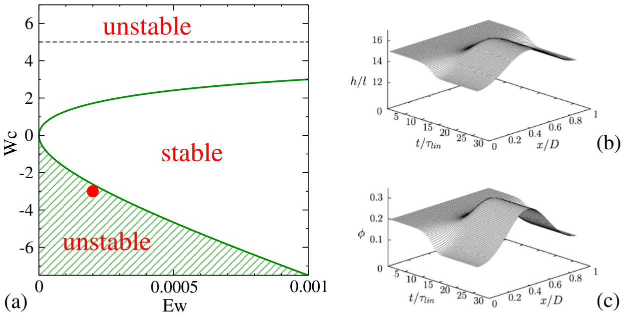

FIG. 2 (color online). Shown is in (a) the linear stability of flat homogeneous films (of thickness $h_0/l = 15$ and concentration $\phi_0 = 0.2$) with respect to coupled fluctuations in film height and concentration in the plane spanned by the ratio of entropic and wetting influences Ew and the strength of the concentration dependence of wettability Wc. For parameter values $\mathrm{Ew} = 0.002$ and $\mathrm{Wc} = -3$ marked by the red circle in (a), panels (b) and (c) show for the case of one spatial dimension (dimensionless domain size $D/L = 1500$) space-time plots of the fully nonlinear coupled short-time evolution of the height and concentration profiles, respectively. Time is given in units of the typical time τ_{lin} of the fastest linear instability mode. In all calculations, the nondimensional interfacial stiffness is fixed to $\sigma/(l\gamma) = 0.1$ while the nondimensional surface tension is set to one through the choice of the lateral length scale L [41].

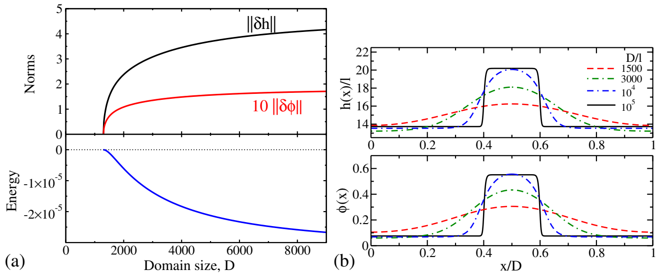

FIG. 3 (color online). (a) Norms (top) and energy per length (bottom) of the family of steady drops in dependence of the domain size D/L at $\mathrm{Ew} = 0.002$ and $\mathrm{Wc} = -3$ corresponding to the red circle in Fig. 2(a). (b) Thickness (top) and concentration (bottom) profiles at various domain sizes as given in the legend.

Starting from a homogeneous flat film, we illustrate in Figs. 2(b) and 2(c) the resulting spontaneous structure formation [43]. During the shown linear and nonlinear stages of the short-time evolution, the steady state shown in Fig. 3(b) is approached [43]. In a large domain, many such small droplets will undergo a long-time coarsening process (not shown) to reach pancakelike drops, as shown in Fig. 3(b) for $D/L = 10^5$. Inspecting the h and ϕ profiles and the energy in Fig. 3, the physical mechanism that drives the structuring becomes clear: Although the film cannot reduce its energy by modulating its thickness profile at homogeneous concentration, it is still able to do so by simulaneously modulating its thickness and concentration profiles. In the present example, the solute is enriched (depleted) in the thicker (thinner) part of the profile. The characteristics of the coexisting flat parts visible in Fig. 3(b) for $D/L = 10^5$ may also be obtained through an analysis of the binodals of the system, i.e., of the film height and concentration values at coexistence [39]. Note that the structuring results in extended flat regions of different heights that are still much larger than the vertical length scale; i.e., all regions may still accommodate a diffusing solute with $a > l$. Furthermore, one may include steric effects due to the solute size into the free energy.

The presented example illustrates that the above introduced thermodynamically consistent long-wave model allows one to predict a novel interface instability for thin films (below about 100 nm) of liquid mixtures and suspensions under the influence of long-range van der Waals forces that are concentration dependent. The resulting coupling of film height and concentration fluctuations always renders such films more unstable than the decoupled subsystems. The chosen numerical example shows that the destabilization can even occur if all decoupled subsystems are unconditionally stable. However, the presented gradient dynamics formulation has further far-reaching implications for the description of thin films of complex fluids: For so-called nanofluids (nanoparticle suspensions), often a structural Derjaguin pressure [44] is included into the hydrodynamic description [45,46]. However, Eqs. (5) show that this is incomplete. Instead, a structural wetting energy has to be introduced that results, in consequence, in additional contributions to the convective, diffusive (and evaporative) flux. An accounting for attractive solvent-solute interactions (beyond the entropic term considered in the example) allows one to investigate how the various decomposition and dewetting instability modes couple, resulting in a number of different instability types and evolution pathways somewhat similar to the ones described for two-layer films of immiscible liquids [47].

In summary, we have presented a general gradient dynamics model and a particular underlying free energy [11] which is able to describe a wide range of dynamical processes in thin films of liquid mixtures, solutions, and suspensions on solid substrates, including the dynamics of coupled dewetting and decomposition. We have argued that on the one hand, the model recovers known limiting cases, including the long-wave limit of model H. On the other hand, we have discussed the physical meaning of important contributions that are missing in the hydrodynamic literature and have shown that they are needed for a thermodynamically consistent description of, e.g., evolution pathways controlled by concentration-dependent wettability. As an example, we have investigated the dewetting of thin films of liquid mixtures and suspensions under the influence of long-range van der Waals forces that are concentration dependent.

The presented gradient dynamics form will allow for systematic future developments. Most importantly, the here presented model for a film of a mixture *without* enrichment or depletion boundary layers at the interfaces may be combined with models for films with an insoluble surfactant [32,48] to also describe systems where enrichment or depletion layers form at the interfaces, including instabilities and structuring processes, as observed in Ref. [30].

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