Gradient dynamics description for films of mixtures and suspensions - the case of dewetting triggered by coupled film height and concentration fluctuations

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Abstract

A gradient dynamics model based on an extended interface Hamiltonian is presented that is able to describe the dynamics of structuring processes in thin films of liquid mixtures, solutions and suspensions on solid substrates including coupled dewetting and decomposition. After discussing known limiting cases 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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The behaviour of free surface layers of simple and complex liquids is of decisive importance for many processes and systems as such films frequently occur either naturally, e.g., as 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. [1–4]. Their omnipresence in natural and industrial processes provides a strong incentive to investigate the creation, instabilities, rupture dynamics, and short- and long-time structure formation of free surface thin liquid films on solid substrates. These processes are well investigated experimentally [5, 6] and theoretically [7, 8] for films of simple liquids on smooth solid substrates. Continuum models describe the evolution of the film thickness profile \( h(x, t) \) as a gradient dynamics 
\[
\frac{\partial h}{\partial t} = \nabla \cdot [Q(h) \nabla \delta F[h]/\delta h]
\]
for the effective interface hamiltonian 
\[
F[h] = \int dV (\gamma \xi + f(h))
\]
that accounts for wettability through the local wetting energy \( f(h) \) and for capillarity through the local surface energy \( \gamma \xi \) [4]. Here, 
\[
\xi dx = \sqrt{1 + \frac{1}{2} |\nabla h|^2} dx
\]
is the surface area element in long-wave (or small-gradient) approximation, \( \gamma \) 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 [9–11], \( Q(h) = h^3/3\eta \) is the mobility function in the case of no-slip at the substrate where \( \eta \) is the dynamic viscosity (for the case of slip see, e.g., [12]), \( x = (x, y)^T \), 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 [1, 2, 13]. As a result, the qualitative behaviour of films of simple liquids is rather well understood although quantitative agreement of experiment and theory is still exceptional [8, 14].

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 [15], lung lining [16], in the production of organic solar cells [17], semiconductor nanoparticle rings [18], protein crystals [19], and fuel cells [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 non-lithographic technique for covering large areas with regular arrays of small-scale
FIG. 1: 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 \( \phi \) is the non-conserved height-averaged solute concentration.

structures. These may be concentric gold rings with potential uses as resonators in advanced optical communications systems [21] or ordered arrays of cyanine dye complex micro-domes employed in photo-functional surfaces [22]. Partial reviews of experiments and models can be found in [23] (surfactant solutions), [24, 25] (deposition processes from solution) and [26] (polymer blends). Although in all these systems the interfacial effects of capillarity and wettability are still 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, evaporation/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 known in the literature and elucidate the physical meaning of the occurring fluxes. Applying the framework to the case of a film of a liquid mixture where the wettability depends on the local concentration shows that dewetting may be triggered through the coupling of film height and concentration fluctuations.

We consider a thin film of a mixture of two non-volatile liquids 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 [26]. In the case without evaporation the approach to equilibrium for this relaxational system is described by a gradient dynamics for the conserved fields film thickness \( h(x, t) \) and effective local solute layer thickness \( \psi(x, t) = h(x, t)\phi(x, t) \). The non-conserved field \( \phi \) is the dimensionless height-averaged per volume solute concentration. The
general form of coupled evolution equations for two such conserved order parameter fields \( h \) and \( \psi \) in the framework of linear nonequilibrium thermodynamics is

\[
\begin{align*}
\partial_t h &= \nabla \cdot \left[ Q_{hh} \nabla \frac{\delta F}{\delta h} + Q_{h\psi} \nabla \frac{\delta F}{\delta \psi} \right], \\
\partial_t \psi &= \nabla \cdot \left[ Q_{\psi h} \nabla \frac{\delta F}{\delta h} + Q_{\psi\psi} \nabla \frac{\delta F}{\delta \psi} \right].
\end{align*}
\]

(1)

The mobility matrix

\[
Q = \begin{pmatrix}
Q_{hh} & Q_{h\psi} \\
Q_{\psi h} & Q_{\psi\psi}
\end{pmatrix} = \frac{1}{3\eta} \begin{pmatrix}
h^3 & h^2 \psi \\
h^2 \psi & h\psi^2 + 3\tilde{D} \psi
\end{pmatrix}
\]

(2)
is symmetric and positive definite corresponding to Onsager reciprocal relations and the condition for positive entropy production, respectively \[27\]. \( \tilde{D} \) is the molecular mobility of the solute. The underlying free energy functional

\[
F[h, \psi] = \int \left[ \gamma(\phi) \xi + f(h, \phi) + hg(\phi) + \Sigma \right] dA
\]

(3)
is obtained from the above introduced interface hamiltonian by (i) amending the capillarity and wettability contributions to now reflect a potential dependence on local concentration \[r.h.s. \text{ term one and two of Eq. (3)}\], (ii) adding the bulk free energy of the mixture per substrate area \( hg(\phi) \), and (iii) adding the final term \( \Sigma = \frac{\sigma}{2} h|\nabla \phi|^2 \) that represents the energetic cost of strong gradients in the concentration (\( \sigma \) is the interfacial stiffness). Note that to perform the variations in Eqs. (1) one has to replace \( \phi \) everywhere by \( \psi/h \). The extended interface hamiltonian (3) for a film of a mixture results in convective and diffusive fluxes (for brevity, written in terms of \( h \) and \( \phi \))

\[
\begin{align*}
J_{\text{conv}} &= \frac{h^3}{3\eta} \left\{ \nabla \left[ \xi \nabla (\gamma \nabla h) \right] + \frac{\gamma'}{h} \xi \nabla \phi - \nabla \partial_h f \\
&\quad - \frac{\sigma}{h} \nabla \cdot (h \nabla \phi) \right\}, \\
J_{\text{diff}} &= -\frac{\tilde{D} h \phi}{\eta} \nabla \left[ \frac{\gamma' \xi}{h} + \frac{\partial_h f}{h} + \frac{\partial_\phi f}{h} \right.
\]

\]

\[
\left. - \frac{\sigma}{h} \nabla \cdot (h \nabla \phi) \right],
\]

(4)

respectively. The dash stands for a derivative of \( g \) or \( \gamma \) w.r.t. \( \phi \). Employing the fluxes we bring the gradient dynamics equations (1) into the form

\[
\begin{align*}
\partial_t h &= -\nabla \cdot J_{\text{conv}}, \\
\partial_t (\phi h) &= -\nabla \cdot (\phi J_{\text{conv}} + J_{\text{diff}}),
\end{align*}
\]

(6)

(7)

which is common in the hydrodynamic literature \[1, 23, 28\].
Before discussing some 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 \( \gamma(\phi) \) is often replaced by a constant reference value \( \gamma_0 \) \([1]\)); the second term represents a Marangoni flux, i.e., a surface tension-gradient driven flux (one may approximate \( \xi \approx 1 \)); the third term is the Derjaguin pressure contribution due to wettability; and the fourth and fifth term represent the Korteweg flux, i.e., a bulk concentration-gradient driven flux (cf. \([29]\) for a discussion of such fluxes in the bulk model-H \([30]\), i.e., Korteweg-Navier-Stokes equations coupled to the convective Cahn-Hilliard equation). The final term is neither a Marangoni nor a Korteweg flux, but may be seen as being related to both because it is 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 flux is a direct consequence of the concentration dependence of the wetting energy \( f(h, \phi) \). Most literature on film dynamics includes a concentration-dependent wettability only through the Derjaguin contribution forming our third term and therefore breaks the overall gradient dynamics form (1). An exception is Ref. \([31]\) which proposes a gradient dynamics model for the coupled decomposition and dewetting of a thin film of a binary polymer blend in terms of constrained functional derivatives w.r.t. the conserved field \( h \) and the non-conserved field \( \phi \) \([32]\).

The first and the second term of the diffusive flux [Eq. (5)] are not common in the literature although they are natural consequences of the gradient dynamics form (1). They represent contributions of the Marangoni effect at the free surface and the concentration-dependent wettability to diffusion, respectively. The third term is the flux due to gradients of the chemical potential \( \mu = g' \) in the bulk of the film while the final term counters steep concentration gradients, e.g., for decomposing solvent-solute films. One may call it a Korteweg contribution to diffusion.

Several limiting cases of the presented evolution equations \([(6,7) \text{ with } (4,5)]\) are well known in the literature. We discuss the most important ones in the case of constant surface tension \( \gamma \equiv \gamma_0 \): (i) For constant film height \( h \), without wettability contribution \( (f = 0) \) and appropriately defined \( g \), Eq. (7) becomes the Cahn-Hilliard equation that describes, e.g., the spinodal decomposition of a binary mixture \([33,34]\); (ii) As in (i) but with \( \sigma = 0 \) and a purely entropic (ideal gas-like)

\[
g = g_{id}(\phi) = \frac{k_B T}{a^3} \phi (\log \phi - 1),
\]

where \( a \) is a molecular length scale related to the solute, one recovers the standard diffusion equation with diffusion constant \( \tilde{D} k_B T / a^3 \eta \) (see, e.g., section IV of \([35]\)); (iii) For \( f = f(h) \), \( \sigma = 0 \)
and \( g = g_{id} \) one recovers the conserved part of long-wave equations used, e.g., to study dewetting of and solute deposition from solutions and suspensions [28, 36] (see also [37] for the case of particle-laden films including gravity influences). Note, that adding a non-conserved (Allen-Cahn type) \( \sim \delta F/\delta h \) term to the first equation of (1) would account for the evaporation of a volatile solvent including the dependence of evaporation on osmotic pressure (a term missed in [28, 36]); (iv) Again without wettability, but with full incorporation of 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 [29, 30, 38] as derived recently via a long-wave asymptotic expansion [39, 40].

In the following we focus on the practically relevant example 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. \( g = g_{id} \) [Eq. (8)], implying that the system is by definition stable against bulk solute-solvent decomposition; we keep \( \gamma \) and \( \sigma \) constant. The fluxes are then given by Eqs. (4) and (5) with \( \gamma' = 0 \) and \( g' = (k_B T/a^3) \log \phi \). For the wetting energy we use the combination of long-range van der Waals interactions and an always stabilising (\( B > 0 \)) short range contribution [11, 41]:

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

The Derjaguin pressure is \( \Pi(h, \phi) = -\partial_h f \) while \( \partial_\phi f \) could be called a Derjaguin chemical potential. The concentration-dependent Hamaker 'constant' is determined employing homogenization techniques (see [42]). For many experimentally employed mixtures as e.g., PMMA/PS, toluene/acetone or PS/toluene on Si or SiO a linear dependence is an excellent approximation over the entire concentration range [43]. Selecting the case where the pure solvent is wetting \( A_0 \equiv A(\phi = 0) < 0 \), we write \( A(\phi) = |A_0|(-1 + Wc \phi) \) where the nondimensional number \( Wc \) quantifies the strength of the concentration-dependence of wettability [43]. Note that for \( A_0 < 0 \) and \( Wc < 0 \), both, a film of pure solvent and a film of pure solute, are absolutely stable. With \( g = g_{id} \) the bulk solute-solvent mixture is stable as well. A film of mixture might then be expected to be stable for all \( Wc < 0 \) and to become unstable for \( Wc > 0 \) when \( Wc \phi > 1 \) 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 \( \delta h \) and \( \delta \psi \) shows that the fluctuations in film height and concentration couple, rendering the system more unstable. Fig. 2(a) shows that even for \( Wc < 0 \) where all decoupled subsystems are stable, the film of a mixture can be linearly unstable in an extended experimentally accessible range of
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 $E_w$ and the strength of the concentration-dependence of wettability $W_c$. For parameter values $E_w = 0.002$ and $W_c = -3$ 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 profile, respectively. Time is given in units of the typical time $\tau_{\text{lin}}$ of the fastest linear instability mode.

The parameter space.

Here the dimensionless number $E_w = k_b T l^3 / |A_0| a^3$ is the ratio of entropic and wetting influences [44]. 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 $E_w$ is sufficiently small. For common mixtures, solutions and nanoparticle suspensions $E_w$ can range from $O(10^{-7})$ to $O(10^4)$ [42, 43]. Also for $W_c > 0$ the film becomes unstable at smaller $W_c$ than expected under the assumption that the mixture stays homogeneous (dashed line in Fig. 2(a)). Because $h$ and $\psi$ are both conserved, the instability is of long wavelength, i.e., at onset (at critical $W_c$ or $E_w$) it has zero wavenumber (cf. [4]). Therefore, for finite domains the stability borders in Fig. 2(a) are slightly shifted.

Starting from a homogeneous flat film, we illustrate in Fig. 2(b,c) the resulting spontaneous structure formation. During the shown linear and nonlinear stages of the short-time evolution, the steady state shown in Fig. 3(b) is approached. In a large domain many such small droplets
FIG. 3: (Color online) (a) Norms and (b) energy per length of the family of steady drops in dependence of the domain size $D/L$ at $E_w = 0.002$, $W_c = -3$ corresponding to the red square in Fig. 2(a). (c) Thickness (top) and concentration (bottom) profiles at various domain sizes as given in the legend.

will undergo a long-time coarsening process (not shown) to reach pancake-like drops as shown in Fig. 3(b) for $D/L = 10^5$. Inspecting the $h$ and $\phi$ profiles and the energy in Fig. 3 the physical mechanism that drives the structuring becomes clear: Although the film can not reduce its energy by modulating its thickness profile at homogeneous concentration, it is still able to do so by simultaneously 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 [42].

We have presented a general gradient dynamics model and a particular underlying extended interface hamiltonian (the thermodynamic free energy) that 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 are needed for a thermodynamically consistent description of, e.g., evolution pathways controlled by concentration-dependent wettability. To illustrate this, 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. Discussing the occurring fluxes we have highlighted a term that is neither a Marangoni (surface
tension-driven) nor a Korteweg (bulk concentration-driven) flux, but is driven by concentration gradients within films that are sufficiently thin (below about 100nm) such that its two interfaces 'feel' each other. It is a direct consequence of a concentration dependence of the wetting energy. Furthermore, we have shown that the resulting coupling of film height and concentration fluctuations always renders such films more unstable than the decoupled subsystems. This may result in coupling-induced spinodal patterning as we have further illustrated by nonlinear considerations.

Beyond the shown example, the presented gradient dynamics model has direct consequences for a number of systems. For instance, when including a structural Derjaguin pressure [45] in the description of nano-particle suspensions [46, 47] all the wetting energy-related terms of the convective, diffusive (and evaporative) fluxes that have been discussed above, need to be accounted for. Another example are systems were additionally to a concentration-dependent wetting energy also attractive solvent-solute interactions are present. Then the various decomposition and dewetting instability modes couple, resulting in a number of different instability types and evolution pathways somewhat not unlikely the ones described for two-layer films of immiscible liquids [48]. It is also straightforward to incorporate additional effects as gravity or electrical fields as well as solvent evaporation including its dependence on osmotic pressure.

The gradient dynamics form (1) with mobilities (2) and underlying energy (3) 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 surfactants [35, 49] to also describe systems where enrichment or depletion layers form at the interfaces, including instabilities and structuring processes as observed in [50]. Another advantage of the presented form is that amendments of the mobilities (e.g., to include slippage effects [12]) and of the energy functional (e.g., to include elastic energies for liquid crystals [51, 52]) may be introduced within a consistent framework. We believe that this will allow us to improve our understanding of various dynamic phenomena in free surface films and drops of complex liquids - a knowledge that becomes increasingly important because the drive towards further miniaturisation of fluidic systems towards micro- [53] and eventually nano-fluidic [54] devices depends on our ability to gain control of the various interfacial effects on small scales.

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[1] A. Oron, S. H. Davis, and S. G. Bankoff, Rev. Mod. Phys. 69, 931 (1997).
[2] R. V. Craster and O. K. Matar, Rev. Mod. Phys. 81, 1131 (2009).
[3] D. Bonn, J. Eggers, J. Indekeu, J. Meunier, and E. Rolley, Rev. Mod. Phys. 81, 739 (2009).
[4] U. Thiele, J. Phys.: Condens. Matter 22, 084019 (2010).
[5] G. Reiter, Phys. Rev. Lett. 68, 75 (1992).
[6] R. Seemann, S. Herminghaus, and K. Jacobs, J. Phys.: Condens. Matter 13, 4925 (2001).
[7] U. Thiele, M. G. Velarde, and K. Neuffer, Phys. Rev. Lett. 87, 016104 (2001).
[8] J. Becker, G. Grün, R. Seemann, H. Mantz, K. Jacobs, K. R. Mecke, and R. Blossey, Nat. Mater. 2, 59 (2003).
[9] P.-G. de Gennes, Rev. Mod. Phys. 57, 827 (1985).
[10] V. M. Starov and M. G. Velarde, J. Phys.-Condes. Matter 21, 464121 (2009).
[11] J. N. Israelachvili, Intermolecular and Surface Forces (Academic Press, London, 2011), 3rd ed.
[12] A. Münch, B. Wagner, and T. P. Witelski, J. Eng. Math. 53, 359 (2005).
[13] U. Thiele, in Thin Films of Soft Matter, edited by S. Kalliadasis and U. Thiele (Springer, Wien, 2007), pp. 25–93.
[14] R. Fetzer, K. Jacobs, A. Münch, B. Wagner, and T. P. Witelski, Phys. Rev. Lett. 95, 127801 (2005).
[15] A. Sharma and E. Ruckenstein, Amer. J. Optom. Physiol. Opt. 62, 246 (1985).
[16] J. Grotberg, Phys. Fluids 23, 021301 (2011).
[17] J. Heier, J. Groenewold, F. A. Castro, F. Nüesch, and R. Hany, in Organic Optoelectronics and Photonics III, Proc. of SPIE Vol. 6999 (2008), p. 69991J.
[18] S. Maenosono, C. D. Dushkin, S. Saita, and Y. Yamaguchi, Langmuir 15, 957 (1999).
[19] N. D. Denkov, O. D. Velev, P. A. Kratchevsky, I. B. Ivanov, H. Yoshimura, and K. Nagayama, Langmuir 8, 3183 (1992).
[20] T. Hutzenlaub, N. Paust, R. Zengerle, and C. Ziegler, J. Power Sources 196, 8048 (2011).
[21] S. W. Hong, J. Xu, and Z. Q. Lin, Nano Lett. 6, 2949 (2006).
[22] Y. Hashimoto and O. Karthaus, J. Colloid Interface Sci. 311, 289 (2007).
[23] O. K. Matar and R. V. Craster, Soft Matter 5, 3801 (2009).
[24] L. Frastia, A. J. Archer, and U. Thiele, Soft Matter 8, 11363 (2012).
[25] W. Han and Z. Lin, Angew. Chem. Int. Ed. 51, 1534 (2012).
[26] M. Geoghegan and G. Krausch, Prog. Polym. Sci. 28, 261 (2003).
[27] S. R. de Groot and P. Mazur, Non-equilibrium Thermodynamics (Dover publications, New York, 1984), ISBN 0-486-64741-2.
[28] L. Frastia, A. J. Archer, and U. Thiele, Phys. Rev. Lett. 106, 077801 (2011).
[29] D. M. Anderson, G. B. McFadden, and A. A. Wheeler, Ann. Rev. Fluid Mech. 30, 139 (1998).
[30] P. C. Hohenberg and B. I. Halperin, Rev. Mod. Phys. 49, 435 (1977).
[31] N. Clarke, Macromolecules 38, 6775 (2005).
[32] The resulting system of integro-differential evolution equations does not correspond to a limit of our Eqs. (1)-(3). The model of [31] is used in [50] to discuss the lateral instability of an enrichment layer on a film of a polymer blend. Their model and the here presented one do, however, not account for the vertical structure of the film.
[33] J. W. Cahn, J. Chem. Phys. 42, 93 (1965).
[34] J. S. Langer, in Solids far from Equilibrium, edited by C. Godreche (Cambridge University Press, 1992), pp. 297–363.
[35] U. Thiele, A. J. Archer, and M. Plapp, Phys. Fluids 24, 102107 (2012).
[36] M. R. E. Warner, R. V. Craster, and O. K. Matar, J. Colloid Interface Sci. 267, 92 (2003).
[37] B. P. Cook, A. L. Bertozzi, and A. E. Hosoi, SIAM J. Appl. Math. 68, 760 (2007).
[38] U. Thiele, S. Madruga, and L. Frastia, Phys. Fluids 19, 122106 (2007).
[39] L. Ó. Náraigh and J. L. Thiffeault, Nonlinearity 23, 1559 (2010).
[40] A small discrepancy in the mobilities arises because the free energy and the mobility, on which the Cahn-Hilliard Equation is based, are approximated independently of each other.
[41] L. M. Pismen, Colloid Surf. A-Physicochem. Eng. Asp. 206, 11 (2002).
[42] D. Todorova, Ph.D. thesis, Loughborough University (2013).
[43] Experimentally, the dimensionless number \( W_c \) 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 \( W_c \) lies in the range \([-10, 15]\). For example, a mixture of polystyrene (PS) and poly(methyl methacrylate) (PMMA) on a silicon (Si) substrate (used, e.g., in [55]) yields \( A_0 = -2.22 \times 10^{-19} \) and \( W_c = -0.11 \) and for a solution of PS in toluene on silicon oxide (SiO) one obtains \( A_0 = 1.74 \times 10^{-21} \) and \( W_c = 7.1 \). If one chooses \( l \sim 10^{-9} \) m and considers values for the solute length scale \( a \) between 0.1 nm and 100 nm (corresponding to the size of diffusing molecules of (nano-)-particles), at room temperature one obtains
a range of $Ew$ from $10^{-7}$ to $10^4$.

[44] For the analysis, Eqs. (1)-(3) are nondimensionalised employing scales $l = (B/|A_0|)^{1/3}$, $L = \sqrt{l(\gamma/|A_0|)}$, and $\tau = l\eta/\kappa$ for vertical and horizontal length scales and time, respectively, where the energy scale is $\kappa = |A_0|/l^2$. In the case of a partially wetting solvent, $l$ corresponds to its precursor film height.

[45] B. V. Deryagin and N. V. Churaev, J. Colloid Interf. Sci. 49, 249 (1974).

[46] D. T. Wasan and A. D. Nikolov, Nature 423, 156 (2003).

[47] R. V. Craster, O. K. Matar, and K. Seifiane, Langmuir 25, 3601 (2009).

[48] A. Pototsky, M. Bestehorn, D. Merkt, and U. Thiele, J. Chem. Phys. 122, 224711 (2005).

[49] M. H. Köpf, S. V. Gurevich, R. Friedrich, and L. F. Chi, Langmuir 26, 10444 (2010).

[50] K. R. Thomas, N. Clarke, R. Poetes, M. Morariu, and U. Steiner, Soft Matter 6, 3517 (2010).

[51] S. Mechkov, A. Cazabat, and G. Oshanin, J. Phys.-Condes. Matter 21, 464131 (2009).

[52] T.-S. Lin, L. J. Cummings, A. J. Archer, L. Kondic, and U. Thiele (2013), http://arxiv.org/abs/1301.4110.

[53] T. M. Squires and S. R. Quake, Rev. Mod. Phys. 77, 977 (2005).

[54] D. Mijatovic, J. C. T. Eijkel, and A. van den Berg, Lab Chip 5, 492 (2005).

[55] S. Y. Heriot and R. A. L. Jones, Nat. Mater. 4, 782 (2005).