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A Variational approach to thin film hydrodynamics of binary mixtures

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Abstract

In order to model the dynamics of thin films of mixtures, solutions, and suspensions, a thermodynamically consistent formulation is needed such that various coexisting dissipative processes with cross couplings can be correctly described in the presence of capillarity, wettability, and mixing effects. In the present work, we apply Onsager's variational principle to the formulation of thin film hydrodynamics for binary fluid mixtures. We first derive the dynamic equations in two spatial dimensions, one along the substrate and the other normal to the substrate. Then, using long-wave asymptotics, we derive the thin film equations in one spatial dimension along the substrate. This enables us to establish the connection between the present variational approach and the gradient dynamics formulation for thin films. It is shown that for the mobility matrix in the gradient dynamics description, Onsager's reciprocal symmetry is automatically preserved by the variational derivation. Furthermore, using local hydrodynamic variables, our variational approach is capable of introducing diffusive dissipation beyond the limit of dilute solute. Supplemented with a Flory–Huggins-type mixing free energy, our variational approach leads to a thin film model that treats solvent and solute in a symmetric manner. Our approach can be further generalized to include more complicated free energy and additional dissipative processes.

Keywords: liquid thin films, modeling, liquid–solid interfaces, binary mixtures, capillarity, wettability

1. Introduction

As free surface films of simple and complex liquids are ubiquitous entities in nature and technology, they are studied and applied in many fields of science and engineering. If these films are 'thin', i.e. there exists a disparity of the length scales along the free surface and perpendicular to it, one can take advantage of this disparity and model the physico-chemical hydrodynamics of the films in a unified way, namely, employing a long-wave approximation (also called lubrication model or thin-film model) [1].

In particular, the behavior of simple liquids in this regime is interface-dominated, i.e. controlled by the effects of capillarity and wettability. This is well described by the various long-wave thin film evolution equations that account for the various physical settings that mostly involve single liquid layers [1–4]. It is well known that these evolution equations can be written as a gradient dynamics governed by a free energy functional [4, 5] that is of a similar form as the interface Hamiltonian introduced in statistical physics in the context of wetting transitions [6].

Recently, an increasing number of theoretical and experimental studies have focused on the dynamics of thin

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films of complex liquids [3, 7–9], e.g. polymer solutions [10–14], colloidal suspensions [14–17], mixtures (of simple liquids or of polymers) [7, 18–22], liquids covered by surfactants at the liquid-air interface [23–27], and even liquid films covered by self-propelled surfactants [28, 29]. Closely related systems are thin layered films consisting of non-miscible liquids [3, 30–34]. In these complex liquids, diffusive transport, phase separation, and phase transitions, which naturally arise from the coexistence of two or more components, participate in the film evolution and interact with and influence the effects of capillarity and wettability. Physically, this leads to the cross-coupling between the various transport processes involved in thin film hydrodynamics and, in consequence, intricate instabilities and nonlinear behaviors not found in the decoupled systems.

Steps toward a more unified description of such systems in the form of a gradient dynamics of a number of coupled fields with a conserved dynamics were presented in the past years. Thin-film models presented in a gradient dynamics form include models for the evolution of two-layer films [31, 35–37], of films covered by an insoluble surfactant [27] and of films of non-surface active liquid mixtures, solutions, and suspensions [22, 38]. Compared to thin-film models in 'hydrodynamic formulation' where additional effects, e.g. concentration-dependent wettability, are often added in an ad hoc manner, the gradient dynamics corresponds to a 'thermodynamic formulation' that automatically ensures thermodynamic consistency. This consistency is inherent in the gradient dynamics formulation if correct conserved fields are chosen, and allows for straightforward generalizations through the introduction of more complicated free energy functionals. For instance, in the case of a nonvolatile film of a mixture, solution or suspension, the basic fields are the conserved film height and the conserved effective solute height fields [22]. Note that in the case of a thin film of a mixture, there exists an alternative gradient dynamics approach [18, 19] constructed based on the evolution of the conserved film height and the non-conserved height-averaged concentration field. The resulting model consists of integro-differential equations where the integrals result from the use of constrained variations. The status of this model is still under discussion (see, e.g. the remarks in the final part of [9]).

A further advantage of formulating the evolution equations as a general gradient dynamics is that one may readily adapt results obtained in the analysis of other kinetic equations for coupled conserved fields (e.g. [20, 35, 39]), for coupled conserved and non-conserved fields (model C in the classification of [40], analyzed in [41]), and for a conserved field coupled to a field with a combined conserved and non-conserved dynamics [42, 43]. In such a way it has, for example, been shown that the coupling of fluctuations of different fields may always trigger new instabilities that do not occur when the fields are decoupled. For the case of a film of a mixture or a surfactant covered film, this implies that spinodal dewetting may be caused by the coupling of film height and concentration fluctuations.

In the following we focus entirely on the case of films of mixtures, solutions, and suspensions as treated in [22].

Written in terms of the conserved fields, i.e. film thickness and effective solute layer thickness, the gradient dynamics expresses the corresponding fluxes in the linear response regime with a symmetric and positive definite mobility matrix. However, the mobility matrix is not derived from anything more basic or fundamental within the gradient dynamics description itself. In fact, it is determined from a comparison with previously known hydrodynamic long-wave models as limiting cases normally without ad hoc additions [22]. However, even if those models contained thermodynamic inconsistencies through ad hoc additions, their leading terms would still be correct and could be used for comparison. Since the hydrodynamic long-wave equations for mixtures were derived in the limit of a dilute solute (as evidenced by the explicit form taken by the diffusion term), the mobility matrix in the gradient dynamics description is inevitably only valid in the same limit. In particular, it has been shown that the gradient dynamics description can recover the long-wave limit [20] of model H [40] apart from a small difference in mobility. This indicates that the transport coefficients in model H itself might be oversimplified. It is therefore imperative to formulate a modeling approach that on the one hand can ensure thermodynamic consistency as in the gradient dynamics description, and on the other hand is able to describe the dissipative dynamics using local hydrodynamic variables that are more fundamental than those conserved fields in the gradient dynamics description. Such a modeling approach would open up the possibilities of introducing a diffusive dissipation beyond the limit of dilute solute, of deriving a more general mobility matrix for the long-wave gradient dynamics description and, in consequence, of arriving at a description where solvent and solute are treated in a symmetric manner—a symmetry that may be broken later on by introducing molecules of different sizes, with different interactions with the substrate, etc.

The coexistence of different dissipative processes is commonly seen in soft matter with multiple components (e.g. solutions and mixtures) and/or internal degrees of freedom (liquid crystals) [44]. To describe coupled irreversible processes in the linear response regime, Onsager formulated a variational principle that is fundamental to macroscopic thermodynamics [45, 46]. This principle is based upon a general class of reciprocal relations and opens up a straightforward and unified way of deriving dynamic equations for soft matter [44, 47, 48].

Based on Onsager's variational principle, the purpose of this work is to present a variational approach to the modeling of thin film hydrodynamics of binary mixtures. This is achieved by introducing a free energy functional that takes into account the effects of capillarity, wettability, and binary mixing, and a dissipation functional that takes into account viscous dissipation and diffusive dissipation. By writing both functionals in the long-wave limit, we directly derive the long-wave evolution equations for the conserved fields, i.e. film thickness and effective solute layer thickness, in the gradient dynamics form. Since the dissipation functional is expressed using local hydrodynamic variables, we are able to introduce a diffusive dissipation beyond the limit of dilute

solute. Supplemented with a Flory–Huggins-type free energy functional [49], this results in a gradient dynamics description with a more general mobility matrix. The advantage of our variational approach is reflected through the following. (i) The solute-solvent symmetry in binary mixtures, once introduced in the free energy functional (say, of Flory–Huggins type) and the dissipation functional, will inevitably be manifested in the final evolution equations. (ii) The Onsager reciprocal symmetry of the mobility matrix will always be preserved as long as the variational procedure is correctly followed, and thermodynamic consistency is therefore ensured. (iii) A proper linear transformation from one set to another set of conserved fields can be performed with the reciprocal symmetry preserved [50]. (iv) Formulated at a level that is more fundamental than the gradient dynamics, the present approach can be used for further generalization to include more coupled dissipative processes, e.g. to describe free surfaces covered by soluble or insoluble surfactants [27].

The paper is organized as follows. In section 2, we present a brief review of Onsager's variational principle [44–48]. In section 3, there are two simple applications to demonstrate the basic physics and techniques for carrying out the present study. In section 4, we present a variational approach to thin film hydrodynamics of binary mixtures. We first derive the modeling equations in two spatial dimensions, one along the substrate and the other normal to the substrate. Then, using the asymptotic behavior of thin films, we derive the thin film equations in one spatial dimension along the substrate. The connection with the gradient dynamics description is also established. In section 5, we show how to construct a model for thin film hydrodynamics in a way symmetric with respect to solvent and solute. The paper is concluded in section 6 with a few remarks.

2. Onsager's variational principle

For a closed system, consider the fluctuations of a set of (coarse grained) variables α_i $(i = 1, \cdots, n)$ measured relative to their most probable (equilibrium) values. The entropy of the system S has a maximum S_e at equilibrium so that $\Delta S = S - S_e$ can be written in the quadratic form

$$\Delta S = -\frac{1}{2}\sum_{i,j=1}^{n} \beta_{ij}\alpha_i\alpha_j$$

where the coefficient matrix β is symmetric and positive definite. The probability density at $\{\alpha_i\}$ is given by

$$f(\alpha_1, \cdots, \alpha_n) = f(0, \cdots, 0)\mathrm{e}^{\Delta S/k_\mathrm{B}}$$

where k_B is the Boltzmann constant. The thermodynamic force conjugate to α_i is defined by

$$X_i = \frac{\partial \Delta S}{\partial \alpha_i} = -\sum_{j=1}^{n} \beta_{ij}\alpha_j,$$

which is a linear combination of α_j $(j = 1, \cdots, n)$ not far from equilibrium.

In the linear response regime, the time evolution of the (macroscopic) state is described by the linear equations

$$\frac{\mathrm{d}}{\mathrm{d}t}\alpha_i(t) = \sum_{j=1}^{n} L_{ij}X_j(t),$$

in which the phenomenological kinetic coefficients L_{ij} satisfy the reciprocal relations $L_{ij} = L_{ji}$, which can be derived from microscopic reversibility [45, 46]. Based on this reciprocal symmetry, Onsager formulated a variational principle governing the time evolution of the state.

For isothermal systems with temperature being constant in space and time, Onsager's variational principle may be outlined as follows [44, 47, 48]. Let the rates of change of the variables α_i $(i = 1, \cdots, n)$ be denoted by $\dot{\alpha}_i$. An action function (also called Rayleighian [48]), hereafter denoted by $\mathcal{A}$, can be constructed for minimization with respect to $\dot{\alpha}_i$ $(i = 1, \cdots, n)$. There are two physically distinct parts in $\mathcal{A}$ which can be written as

$$\mathcal{A} = \frac{1}{2}\sum_{i,j=1}^{n} \zeta_{ij}\dot{\alpha}_i\dot{\alpha}_j + \sum_{i=1}^{n}\frac{\partial F}{\partial \alpha_i}\dot{\alpha}_i,$$

where the first term on the right-hand side is called the dissipation function, hereafter denoted by Φ, which is defined to be half the rate of free energy dissipation, and the second term is the rate of change of the free energy $F = F(\alpha_1, \cdots, \alpha_n)$, hereafter denoted by $\dot{F}$. Note that Φ is quadratic in the rates, with the friction coefficient matrix ζ being symmetric and positive definite. Minimizing $\mathcal{A}$ with respect to $\dot{\alpha}_i$, we obtain

$$\sum_{j=1}^{n} \zeta_{ij}\dot{\alpha}_j = -\frac{\partial F}{\partial \alpha_i}$$

for the time evolution of the state. It follows that the rate of free energy dissipation $\dot{F} = \sum_{i=1}^{n}(\partial F/\partial \alpha_i)\,\dot{\alpha}_i$ equals -2Φ.

3. Two simple applications of Onsager's variational principle

In this section, we go through two simple applications of Onsager's variational principle. The techniques involved in these applications are essential to a variational approach to the modeling of thin film hydrodynamics of binary mixtures, which is presented in section 4.

3.1. Thin film hydrodynamics of one-component liquids

Consider a thin film of a one-component simple liquid on a solid substrate [1, 3]. The model described below includes the capillarity associated with the liquid–gas interface, the wettability of the liquid on the solid surface, and the free energy dissipation due to shear viscosity. For simplicity, the film thickness profile $h = h(x, t)$ is described in one spatial dimension (with h measured in the z direction, see figure 1). The free energy functional is given by

$$F[h] = \int \mathrm{d}x \left\{\gamma\left[1 + \frac{1}{2}(\partial_x h)^2\right] + f(h)\right\}, \qquad (1)$$

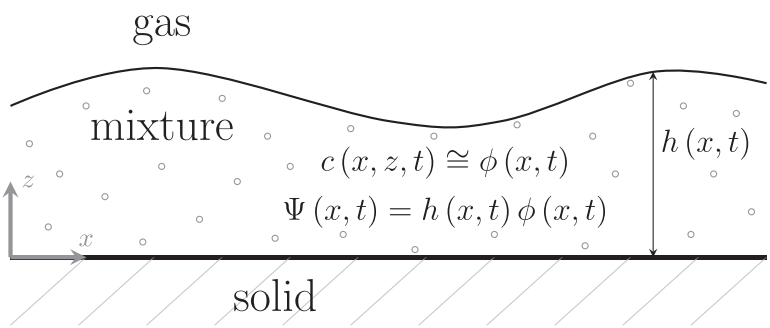

Figure 1. Schematic illustration for a film of binary mixture on a smooth solid substrate. The definitions of the relevant order parameter fields are given as well.

where γ is the liquid–gas interfacial tension, $[1+\frac{1}{2}(\partial_x h)^2]\mathrm{d}x$ is the long-wave approximation of the surface arc length element $\mathrm{d}s = [1+(\partial_x h)^2]^{1/2}\mathrm{d}x$, and $f(h)$ is the wetting (or binding) energy locally dependent on h. In the following, ∂_t, ∂_x and ∂_z denote the partial derivatives with respect to time t and the coordinates x and z. Note that $F[h]$ corresponds to the interface Hamiltonian discussed in statistical physics [6]. The rate of change of the free energy is found to be

$$\dot{F} = \int \mathrm{d}x \frac{\delta F}{\delta h}\partial_t h = \int \mathrm{d}x \left[-\gamma\partial_x^2 h + f'(h)\right]\partial_t h, \tag{2}$$

where an integration by parts is involved and $f'(h) = \mathrm{d}f/\mathrm{d}h$. Here the boundary terms are dropped as we will not touch the modeling of the three-phase contact line. The variation of $\dot{F}$ with respect to the rate $\partial_t h$ is of the form

$$\delta\dot{F} = \int \mathrm{d}x \left[-\gamma\partial_x^2 h + f'(h)\right]\delta(\partial_t h). \tag{3}$$

The dissipation functional associated with the shear viscosity is given by

$$\Phi_v = \int \mathrm{d}x \int_0^h \mathrm{d}z \left[\frac{\eta}{2}(\partial_z u)^2\right], \tag{4}$$

where η is the shear viscosity and u is the x component of fluid velocity $\mathbf{v}(x,z,t) = u(x,z,t)\hat{\mathbf{x}} + w(x,z,t)\hat{\mathbf{z}}$ in the 2D xz space. Due to the slow variation of h with x, the rate of viscous dissipation is represented by $\eta(\partial_z u)^2$ in the long-wave limit. The variation of Φ_v with respect to the rate u is of the form

$$\delta\Phi_v = -\int \mathrm{d}x \int_0^h \mathrm{d}z\,(\eta\partial_z^2 u)\delta u + \int \mathrm{d}x \left[(\eta\partial_z u)\delta u\right]|_{z=h}, \tag{5}$$

in which the no-slip boundary condition $u = 0$ is used at the solid surface $z = 0$. To impose the incompressibility condition $\partial_x u + \partial_z w = 0$, there is one more term

$$C = \int \mathrm{d}x \int_0^h \mathrm{d}z \left[-p(\partial_x u + \partial_z w)\right] \tag{6}$$

to be included in Onsager's action $\mathcal{A}$, with p being a local Lagrange multiplier which is physically the local pressure. The variation of C with respect to the rates u and w is of the form

$$\delta C = \int \mathrm{d}x \int_0^h \mathrm{d}z \left[\delta u\partial_x p + \delta w\partial_z p\right] - \int \mathrm{d}s\; p(x,h,t)\delta v_n, \tag{7}$$

where v_n is the outward normal velocity at $z = h$, given by $v_n = [1+(\partial_x h)^2]^{-1/2}\partial_t h$. Using $\mathrm{d}s = [1+(\partial_x h)^2]^{1/2}\mathrm{d}x$, we express δC as

$$\delta C = \int \mathrm{d}x \int_0^h \mathrm{d}z \left[\delta u\partial_x p + \delta w\partial_z p\right] - \int \mathrm{d}x p(x,h,t)\delta(\partial_t h). \tag{8}$$

From $\delta\dot{F}$, $\delta\Phi_v$, and δC expressed above, we can obtain $\delta\mathcal{A} = \delta\dot{F} + \delta\Phi_v + \delta C$ as a linear combination of δu, δw, and $\delta(\partial_t h)$. Minimizing $\mathcal{A}$ with respect to $\partial_t h$ leads to

$$p(x,h,t) = -\gamma\partial_x^2 h + f'(h) \tag{9}$$

which gives the pressure at $z = h$. Minimizing $\mathcal{A}$ with respect to u gives

$$\eta\partial_z^2 u - \partial_x p = 0, \tag{10}$$

which describes the force balance in the tangential direction. Minimizing $\mathcal{A}$ with respect to w gives

$$\partial_z p = 0, \tag{11}$$

which describes the hydrostatic equilibrium in the vertical direction. Finally, minimizing $\mathcal{A}$ with respect to u at $z = h$ gives

$$\eta\partial_z u = 0, \tag{12}$$

which is the boundary condition for the tangential stress at the free surface. Supplemented with the no-slip condition $u = 0$ at the solid surface, the above equations can be used to determine a parabolic profile for $u(x,z,t)$ in the form

$$u(x,z,t) = \frac{1}{\eta}\partial_x\left[-\gamma\partial_x^2 h + f'(h)\right]\left(\frac{z^2}{2} - zh\right), \tag{13}$$

from which the flux $J_h = \int_0^h \mathrm{d}z\, u$ is found to be

$$J_h = \frac{h^3}{3\eta}\partial_x\left[\gamma\partial_x^2 h - f'(h)\right]. \tag{14}$$

In the form of the conservation law $\partial_t h = -\partial_x J_h$ for h, we obtain the thin film evolution equation

$$\partial_t h = -\partial_x \left\{ \frac{h^3}{3\eta} \partial_x \left[\gamma \partial_x^2 h - f'(h) \right] \right\}. \tag{15}$$

It is worth pointing out that in this approach, volume conservation is imposed via the incompressibility condition $\partial_x u + \partial_z w = 0$ and the conservation law for h in the form of $\partial_t h = -\partial_x J_h$, which can be derived from the flux definition $J_h = \int_0^h \mathrm{d}z\, u$, the incompressibility condition, and the kinematic boundary conditions $w = 0$ at the solid surface $z = 0$ and $w = \partial_t h + u\partial_x h$ at the free surface of the film $z = h$ [1]. An important observation [4, 5] is that equation (15) can be brought into the form of the gradient dynamics for the conserved field h:

$$\partial_t h = \partial_x \left(\frac{h^3}{3\eta} \partial_x \frac{\delta F}{\delta h} \right), \tag{16}$$

where $h^3/3\eta$ is the mobility coefficient and the variational derivative $\delta F/\delta h$ is given by $\delta F/\delta h = -\gamma \partial_x^2 h + f'(h)$.

3.2. Diffusion of dilute solute

Consider a binary fluid mixture in which one component is called the solvent and the other component is called the solute [44, 48]. It is assumed that the volumes of the pure solvent and the pure solute are additive. Let $n_{\max}$ denote the maximum number density of solute particles in the pure solute and c denote the volume fraction of the solute in the binary mixture with $0 \leqslant c \leqslant 1$. The number density of solute particles in the binary mixture is given by $n_{\max} c$. For simplicity, the model is still described in the 2D xz space, with $c = c(x, z, t)$. Here we restrict our discussion to the dilute limit of $c \to 0$. The free energy functional arising from the entropy of the solute distribution is

$$F[c] = \int\int \mathrm{d}x\mathrm{d}z\, g(c) = n_{\max} k_{\mathrm{B}} T \int\int \mathrm{d}x\mathrm{d}z\, c(\log c - 1), \tag{17}$$

where $g(c)$ is the free energy density and T is the temperature. The rate of change of the free energy is given by

$$\dot{F} = \int\int \mathrm{d}x\mathrm{d}z\, \mu_c \partial_t c, \tag{18}$$

where the chemical potential μ_c is defined by $\mu_c = \delta F/\delta c = g'$ and equals $n_{\max} k_{\mathrm{B}} T \log c$. Using the conservation law for the diffusive transport of the solute, $\partial_t c = -\nabla \cdot \mathbf{j}$, with $\mathbf{j}$ being the diffusive flux, we can express $\dot{F}$ as

$$\dot{F} = \int\int \mathrm{d}x\mathrm{d}z\, (\nabla \mu_c) \cdot \mathbf{j}, \tag{19}$$

in which an integration by parts is involved. The variation of $\dot{F}$ with respect to the rate $\mathbf{j}$ is of the form

$$\delta \dot{F} = \int\int \mathrm{d}x\mathrm{d}z\, (\nabla \mu_c) \cdot \delta \mathbf{j}. \tag{20}$$

In the limit of dilute solute, the dissipation functional associated with the diffusive transport is given by

$$\Phi_d = \frac{1}{2} \int\int \mathrm{d}x\mathrm{d}z\, \frac{n_{\max} \zeta \mathbf{j}^2}{c}, \tag{21}$$

in which ζ is the friction/drag coefficient for the diffusive motion of a solute particle. This can be seen as follows. Physically, the rate of dissipation for one particle is $\zeta \mathbf{v}_d^2$, in which $\mathbf{v}_d$ is the mean velocity. As $n_{\max} c$ is the number density of solute particles, the density of the rate of dissipation is $n_{\max} c(\zeta \mathbf{v}_d^2)$. Furthermore, the diffusive flux $\mathbf{j}$ related to $\mathbf{v}_d$ via $\mathbf{j} = c\mathbf{v}_d$, implying that the density of the rate of dissipation is $n_{\max} \zeta \mathbf{j}^2/c$, which leads to equation (21) for Φ_d. The variation of Φ_d with respect to the rate $\mathbf{j}$ is of the form

$$\delta \Phi_d = \int\int \mathrm{d}x\mathrm{d}z\, \frac{n_{\max} \zeta \mathbf{j} \cdot \delta \mathbf{j}}{c}. \tag{22}$$

Employing $\delta \dot{F}$ and $\delta \Phi_d$ expressed above and minimizing $\mathcal{A} = \dot{F} + \Phi_d$ with respect to $\mathbf{j}$, we obtain the constitutive equation

$$\mathbf{j} = -\frac{c}{n_{\max} \zeta} \nabla \mu_c = -\frac{k_{\mathrm{B}} T}{\zeta} \nabla c. \tag{23}$$

As we consider the dilute limit here, it corresponds to Fick's law, i.e. the diffusion coefficient D is a constant independent of c, given by $D = k_{\mathrm{B}} T/\zeta$ according to the Einstein relation. It is worth emphasizing that $\mathbf{j} = -(k_{\mathrm{B}} T/\zeta)\nabla c$ is derived with F and Φ_d both expressed in the limit of dilute solute. Note that in equation (23), $-c\nabla \mu_c$ can be written as $-\nabla \Pi(c)$, where $\Pi(c)$ is the osmotic pressure $\Pi(c) = cg' - g$, given by $c\mu_c - n_{\max} k_{\mathrm{B}} T c(\log c - 1) = n_{\max} k_{\mathrm{B}} T c$ [48]. As the chemical potential μ_c is defined by the variational derivative $\delta F/\delta c$, the conservation law for c can be written as

$$\partial_t c = \nabla \cdot \left(\frac{c}{n_{\max} \zeta} \nabla \frac{\delta F}{\delta c} \right) \tag{24}$$

in the gradient dynamics form, with $c/n_{\max} \zeta$ being the mobility coefficient.

4. Thin film hydrodynamics of binary mixtures

In this section, we present a variational approach to the modeling of thin film hydrodynamics of a binary mixture [1, 3, 22, 38]. To be consistent with the discussion above, we still call one component the solvent and the other the solute. We consider the 'simplest' mixture [44] by making the following assumptions. (i) The pure solvent and the pure solute have equal molecular volume and equal molecular mass. (ii) The volumes of the pure solvent and the pure solute are additive. Under these two assumptions, we have the following: (a) The mass fraction is equivalent to the volume fraction. (b) The mixture is incompressible with a mass density that is constant in space and time. (c) The mass-averaged velocity is equivalent to the volume-averaged velocity.

4.1. Transport equations and conservation laws

Consider a thin film of a binary mixture on a solid substrate in the 2D xz space. Following section 3, we use $h = h(x,t)$ to denote the film thickness profile, $\mathbf{v}(x,z,t) = u(x,z,t)\hat{\mathbf{x}} + w(x,z,t)\hat{\mathbf{z}}$ to denote the velocity field, and $c(x,z,t)$ to denote the volume fraction of the solute with $0 \leqslant c \leqslant 1$. As the mass fraction and the volume fraction are equivalent, hereafter we call c the relative concentration. The mass density of the mixture ρ is a constant and the incompressibility condition for $\mathbf{v}$ is $\partial_x u + \partial_z w = 0$. The transport equation for c reads

$$\partial_t c + u\partial_x c + w\partial_z c = -\partial_x j_x - \partial_z j_z, \tag{25}$$

where j_x and j_z are the two components of the diffusive flux $\mathbf{j} = j_x\hat{\mathbf{x}} + j_z\hat{\mathbf{z}}$.

As to the kinematic boundary conditions, we have $u = 0$ and $w = 0$ at the solid surface $z = 0$, $w = \partial_t h + u\partial_x h$ at the free surface of the film $z = h$ [1], $j_z = 0$ at $z = 0$, and $j_n = 0$ at $z = h$. Here the subscript n denotes the outward normal component. Note that $j_n = 0$ means $\mathbf{j}$ is locally tangent to the free surface, i.e. $j_z = (\partial_x h) j_x$.

The conservation law for h reads

$$\partial_t h + \partial_x J_h = 0, \tag{26}$$

where the flux J_h is given by $J_h(x,t) = \int_0^{h(x,t)} \mathrm{d}z\, u(x,z,t)$. Note that equation (26) can be derived from the incompressibility condition and the kinematic boundary conditions for w at the solid surface $z = 0$ and the free surface of the film $z = h$ [1].

The effective solute layer thickness Ψ is locally defined by $\Psi(x,t) = \int_0^{h(x,t)} \mathrm{d}z\, c(x,z,t)$ [22]. The conservation law for Ψ reads

$$\partial_t \Psi + \partial_x J_\Psi = 0, \tag{27}$$

where the flux J_Ψ is given by $J_\Psi(x,t) = \int_0^{h(x,t)} \mathrm{d}z\, (uc + j_x)(x,z,t)$. Note that equation (27) is consistent with the boundary conditions for $\mathbf{v}$ and $\mathbf{j}$. If the variation of c along the z direction is negligibly small, i.e. $c(x,z,t) \simeq \phi(x,t)$, then equation (27) for $\Psi(x,t) = h(x,t)\phi(x,t)$ leads to

$$\partial_t \phi + \frac{J_h}{h}\partial_x \phi + \frac{1}{h}\partial_x \int_0^h \mathrm{d}z\, j_x = 0, \tag{28}$$

which is the balance equation for $\phi(x,t)$. It will be shown that $c(x,z,t) \simeq \phi(x,t)$ can be justified via a long-wave asymptotic expansion. Below ϕ is used only if $c(x,z,t)$ is approximately independent of z.

4.2. A variational approach in two-dimensional space

The free energy is a functional of the film thickness profile h and the solute distribution c, given by

$$F[h,c] = \gamma \int \mathrm{d}x \left[1 + \frac{1}{2}(\partial_x h)^2\right] + \int \mathrm{d}x \int_0^h \mathrm{d}z \left[g(c) + W(z,c)\right], \tag{29}$$

in which $g(c)$ is the free energy density due to mixing and $W(z,c)$ is the potential energy density due to long-range (van der Waals) liquid–solid interactions. It is noted that $F[h,c]$ includes all the free energy contributions in equations (1) and (17). The chemical potential, defined via $\mu_c = \delta F/\delta c$, is given by

$$\mu_c(z,c) = \partial_c g(c) + \partial_c W(z,c), \tag{30}$$

which locally depends on z and c. The rate of change of F is found to be

$$\dot{F} = \gamma \int \mathrm{d}x \left(-\partial_x^2 h\right)\partial_t h + \int \mathrm{d}x \int_0^h \mathrm{d}z\, \mu_c \partial_t c + \int \mathrm{d}x\, (g+W)\,|_{z=h}\partial_t h, \tag{31}$$

in which $\partial_t c$ can be replaced with $-u\partial_x c - w\partial_z c - \partial_x j_x - \partial_z j_z$ according to equation (25). The variation of $\dot{F}$ with respect to the rates $\partial_t h$, $\mathbf{v}$, and $\mathbf{j}$ is of the form

$$\delta\dot{F} = \int \mathrm{d}x \left[-\gamma\partial_x^2 h + (g+W)\,|_{z=h}\right]\delta(\partial_t h) - \int \mathrm{d}x \int_0^h \mathrm{d}z\, \mu_c\,(\delta u\partial_x c + \delta w\partial_z c) + \int \mathrm{d}x \int_0^h \mathrm{d}z\, (\nabla\mu_c)\cdot\delta\mathbf{j}, \tag{32}$$

in which an integration by parts, supplemented with the boundary conditions for $\mathbf{j}$, is involved. This comes from $-\int \mathrm{d}x \int_0^h \mathrm{d}z\, \mu_c \nabla\cdot\mathbf{j} = \int \mathrm{d}x \int_0^h \mathrm{d}z\, (\nabla\mu_c)\cdot\mathbf{j}$ with $j_z = 0$ at $z = 0$ and $j_n = 0$ at $z = h$, and the corresponding variation with respect to $\mathbf{j}$ becomes $\int \mathrm{d}x \int_0^h \mathrm{d}z\, (\nabla\mu_c)\cdot\delta\mathbf{j}$ in equation (32). The dissipation functional associated with viscous momentum transport and diffusive transport is given by

$$\Phi = \int \mathrm{d}x \int_0^h \mathrm{d}z \left[\frac{\eta}{2}(\partial_z u)^2\right] + \int\int \mathrm{d}x\mathrm{d}z\, \frac{\mathbf{j}^2}{2M(c)}, \tag{33}$$

in which $M(c)$ is the c-dependent mobility associated with diffusion. The variation of Φ with respect to the rates u and $\mathbf{j}$ is of the form

$$\delta\Phi = -\int \mathrm{d}x \int_0^h \mathrm{d}z\, (\eta\partial_z^2 u)\delta u + \int \mathrm{d}x \left[(\eta\partial_z u)\delta u\right]|_{z=h} + \int\int \mathrm{d}x\mathrm{d}z\, \frac{\mathbf{j}\cdot\delta\mathbf{j}}{M(c)}. \tag{34}$$

The incompressibility condition $\partial_x u + \partial_z w = 0$ is to be imposed by adding C, already expressed in equation (6), into Onsager's action $\mathcal{A}$. The local Lagrange multiplier p in C acts as the local pressure. The variation of C with respect to the rate $\mathbf{v}$ is given by equation (8). Note that in the above derivation, the limits 0 and h in the z-integrals are explicitly written down if necessary for the performed integration by parts.

Using the expressions for $\delta\dot{F}$, $\delta\Phi$, and δC, we obtain the variation of Onsager's action $\delta\mathcal{A} = \delta\dot{F} + \delta\Phi + \delta C$ as a linear combination of δu, δw, $\delta\mathbf{j}$, and $\delta(\partial_t h)$. Minimizing $\mathcal{A}$ with respect to $\partial_t h$, we have

$$p(x,h,t) = -\gamma\partial_x^2 h + (g+W)\,|_{z=h} \tag{35}$$

for the pressure at $z = h$. Minimizing $\mathcal{A}$ with respect to u, we have

$$\mu_c \partial_x c + \eta \partial_z^2 u - \partial_x p = 0 \tag{36}$$

for the force balance in the tangential direction. Minimizing $\mathcal{A}$ with respect to w, we have

$$\mu_c \partial_z c - \partial_z p = 0 \tag{37}$$

for the hydrostatic equilibrium in the vertical direction. Minimizing $\mathcal{A}$ with respect to u at $z = h$, we have

$$\eta \partial_z u = 0, \tag{38}$$

for the tangential stress at the free surface. Finally, minimizing $\mathcal{A}$ with respect to $\mathbf{j}$, we have

$$\mathbf{j} = -M(c)\nabla \mu_c \tag{39}$$

for the diffusive flux.

To proceed toward a long-wave theory, we note that the liquid–solid interaction energy density $W(z, c)$ is related to the wetting energy (per unit area) f through

$$\int_0^h \mathrm{d}z\, W(z, \phi) = f(h, \phi), \tag{40}$$

in which ϕ represents the z-independent value of c in $W(z, c)$. We emphasize that $f(h, \phi)$ is introduced only if $c(x, z) = \phi(x)$ is satisfied, a point to be elaborated below. Based on equation (40), an approximation for W can be introduced, and the hydrodynamics governed by equations (35)–(37) and (39) can be formulated as a long-wave theory in one spatial dimension.

4.3. Long-wave asymptotics for thin films

The liquid–solid interaction energy density $W = W(z, c)$ explicitly depends on z through the first argument z and implicitly depends on z through the second argument $c = c(x, z)$. If it is assumed that c does not vary with z, i.e. $c(x, z) = \phi(x)$, then $W(z, c)$ becomes $W(z, \phi)$ whose z-integral defines $f(h, \phi)$ according to equation (40). Furthermore, $W(z, \phi)$ can be approximated by its average over the film thickness $h^{-1}\int_0^h \mathrm{d}z\, W(z, \phi)$:

$$\bar{W}(h, \phi) = \frac{f(h, \phi)}{h}. \tag{41}$$

This removes the explicit dependence on z from W, which is now given by $W = \bar{W}(h, \phi)$ with $h = h(x)$ and $\phi = \phi(x)$, and therefore paves the way for a variational approach in terms of fields that are defined in one spatial dimension (x). Note that the approximation of $W(z, \phi)$ by $\bar{W}(h, \phi)$ is to be applied away from the free surface $z = h$. At the free surface, $W|_{z=h} = W(h, \phi)$ is given by $\partial_h f(h, \phi)$ according to equation (40). Typically, the wetting energy $f(h, \phi)$ is not simply proportional to h [22], and consequently $h^{-1} f(h, \phi) \neq \partial_h f(h, \phi)$.

In order to justify the assumption of $c(x, z) = \phi(x)$ and the subsequent introduction of $f(h, \phi)$, we need to study the long-wave asymptotics for thin films. We show that if the explicit dependence on z is removed from $W(z, c)$, then the long-wave asymptotics leads to $c(x, z) = \phi(x)$, which in turn leads to the introduction of $f(h, \phi)$ via equation (40). With the explicit dependence on z removed from $W(z, c)$ and $c(x, z)$ given by $\phi(x)$, W becomes represented by $\bar{W}(h, \phi)$ defined in equation (41). Here we point out that $f(h, \phi)$ and $\bar{W}(h, \phi)$ are both quantities suitable for a description in 1D space. This means the basic approximation made is that the explicit dependence on z is removed from $W(z, c)$. Starting from this approximation, below we present the long-wave asymptotics.

With the explicit dependence on z removed from $W(z, c)$, the chemical potential μ_c defined in equation (30) only depends on c. As a result, the diffusive flux in equation (39) can be written as $\mathbf{j} = -D(c)\nabla c$, with $D(c) = M(c)d\mu_c/dc$ being the collective diffusion coefficient [44]. To simplify the presentation of the long-wave asymptotics below, we use a diffusion coefficient D independent of c. Following the steps below, it can readily be seen that the long-wave asymptotics is not affected by letting D depend on c. With $\mathbf{j} = -D\nabla c$, equation (25) becomes

$$\partial_t c + u\partial_x c + w\partial_z c = D\partial_x^2 c + D\partial_z^2 c. \tag{42}$$

In the long-wave limit of thin film hydrodynamics, the characteristic or mean film thickness H is much smaller than the length scale L for variations in the x direction, i.e. $\epsilon = H/L \ll 1$. It is natural to scale x by L and z by $H = \epsilon L$ with the scaled coordinates given by $\bar{x} = x/L$ and $\bar{z} = z/\epsilon L$. Then, $\partial/\partial\bar{x}$ and $\partial/\partial\bar{z}$ are both $O(1)$. If the characteristic (tangential) velocity of the problem is U, then the dimensionless velocity in the x direction is $\bar{u} = u/U$ and the dimensionless velocity in the z direction is $\bar{w} = w/\epsilon U$, with the incompressibility condition given by $\partial\bar{u}/\partial\bar{x} + \partial\bar{w}/\partial\bar{z} = 0$, which implies that $\bar{u}$ and $\bar{w}$ are both $O(1)$. The time t is to be scaled by L/U with the dimensionless time given by $\bar{t} = Ut/L$. Using $\bar{x}$, $\bar{z}$, $\bar{u}$, $\bar{w}$, and $\bar{t}$, we can rewrite equation (42) as

$$\partial_{\bar{t}} c + \bar{u}\partial_{\bar{x}} c + \bar{w}\partial_{\bar{z}} c = \bar{D}\partial_{\bar{x}}^2 c + \epsilon^{-2}\bar{D}\partial_{\bar{z}}^2 c, \tag{43}$$

with the dimensionless parameter $\bar{D}$ given by $\bar{D} = D/UL$.

For $\epsilon = H/L \ll 1$, it is expected that the variation of $c(x, z, t)$ is negligibly small along the z direction. This can be justified as follows. Let's write $c(x, z, t)$ as

$$c(x, z, t) = \phi(x, t) + \epsilon^2\theta(x, z, t), \tag{44}$$

with $\phi(x, t)$ being a constant in the z direction, and write $\bar{u}(x, z, t)$ as

$$\bar{u}(x, z, t) = \bar{u}_h(x, t) + [\bar{u}(x, z, t) - \bar{u}_h(x, t)], \tag{45}$$

with $\bar{u}_h(x, t)$ defined as $\bar{u}_h(x, t) = J_h(x, t)/hU$. Substituting equations (44) and (45) into equation (43), we have

$$\begin{aligned}&\partial_{\bar{t}}\phi + \epsilon^2\partial_{\bar{t}}\theta + [\bar{u}_h + (\bar{u} - \bar{u}_h)]\partial_{\bar{x}}\phi + \epsilon^2\bar{u}\partial_{\bar{x}}\theta + \epsilon^2\bar{w}\partial_{\bar{z}}\theta \\ &\quad = \bar{D}\partial_{\bar{x}}^2\phi + \epsilon^2\bar{D}\partial_{\bar{x}}^2\theta + \bar{D}\partial_{\bar{z}}^2\theta,\end{aligned} \tag{46}$$

which include $O(1)$ terms and $O(\epsilon^2)$ terms. To the leading order, we have

$$\partial_{\bar{t}}\phi + \bar{u}_h\partial_{\bar{x}}\phi + (\bar{u} - \bar{u}_h)\partial_{\bar{x}}\phi = \bar{D}\partial_{\bar{x}}^2\phi + \bar{D}\partial_{\bar{z}}^2\theta \tag{47}$$

formed by all the $O(1)$ terms. Rewritten in the original dimensional variables with $u_h(x,t) = J_h(x,t)/h$, equation (47) becomes

$$\partial_t\phi + u_h\partial_x\phi + (u-u_h)\partial_x\phi = D\partial_x^2\phi + \epsilon^2 D\partial_z^2\theta, \tag{48}$$

which can be divided into two equations:

$$\partial_t\phi + u_h\partial_x\phi = D\partial_x^2\phi + \frac{\partial_x h}{h}D\partial_x\phi \tag{49}$$

and

$$(u-u_h)\partial_x\phi = \epsilon^2 D\partial_z^2\theta - \frac{\partial_x h}{h}D\partial_x\phi. \tag{50}$$

It is interesting to note that equation (49) can be derived by substituting $j_x = -D\partial_x\phi$ into equation (28) for $c(x,z,t) \simeq \phi(x,t)$. It is also interesting to note that the $\int_0^h \mathrm{d}z\cdots$ integral of equation (50) is identically zero. On the left-hand side, this follows from the definition of u_h: $u_h(x,t) = J_h(x,t)/h$, and on the right-hand side, this follows from $-D\partial_z(\epsilon^2\theta)|_{z=h} = \partial_x h(-D\partial_x\phi)$ according to the boundary condition $j_z = (\partial_x h)j_x$ at the free surface, with $j_z = -D\partial_z(\epsilon^2\theta)$ and $j_x = -D\partial_x\phi$.

4.4. A variational approach in 1D space

Based on the asymptotic expansion $c(x,z,t) = \phi(x,t) + \epsilon^2\theta(x,z,t)$, the thin film equations for $h(x,t)$ and $\phi(x,t)$ can be formulated in one spatial dimension.

We start from the free energy. The c-dependent part, represented by the second term in the right-hand side of equation (29), becomes $\int \mathrm{d}x\,[hg(\phi) + f(h,\phi)]$, and the total free energy is a functional of h and ϕ, given by

$$F[h,\phi] = \gamma\int \mathrm{d}x\left[1+\frac{1}{2}(\partial_x h)^2\right] + \int \mathrm{d}x\,[hg(\phi)+f(h,\phi)]. \tag{51}$$

The chemical potential, now defined via $\mu_\phi = h^{-1}\delta F/\delta\phi$, is given by

$$\mu_\phi = \partial_\phi g(\phi) + \frac{1}{h}\partial_\phi f(h,\phi). \tag{52}$$

The rate of change of $F[h,\phi]$ can be written as

$$\dot F = \gamma\int \mathrm{d}x\left(-\partial_x^2 h\right)\partial_t h + \int \mathrm{d}x h\mu_\phi\partial_t\phi + \int \mathrm{d}x(g+\partial_h f)\partial_t h, \tag{53}$$

in which $\partial_t\phi$ can be replaced with $-h^{-1}\int_0^h \mathrm{d}z\,u\partial_x\phi - h^{-1}\partial_x J_x$ according to equation (28). Here J_x is the z-integrated tangential diffusive flux, defined by $J_x = \int_0^h \mathrm{d}z\,j_x$. The variation of $\dot F$ with respect to the rates $\partial_t h$, u, and J_x is of the form

$$\delta\dot F = \int \mathrm{d}x\left[-\gamma\partial_x^2 h + (g+\partial_h f)\right]\delta(\partial_t h) - \int \mathrm{d}x\int_0^h \mathrm{d}z\,\mu_\phi\partial_x\phi\delta u + \int \mathrm{d}x\,\partial_x\mu_\phi\delta J_x. \tag{54}$$

It will be shown that the only dependence (of u) on z can be explicitly obtained.

According to the asymptotic expansion $c(x,z,t) = \phi(x,t) + \epsilon^2\theta(x,z,t)$, if $j_x \simeq -\tilde M(\phi)\partial_x\phi$ is $O(1)$, then $j_z \simeq -\epsilon^2\tilde M(\phi)\partial_z\theta$ is $O(\epsilon)$. Note that this is consistent with the boundary condition $j_z = (\partial_x h)j_x$ at the free surface (with $\partial_x h \sim \epsilon$). Substituting $J_x = hj_x$ and $j_z = 0$ into equation (33), we have the dissipation functional

$$\Phi = \int \mathrm{d}x\int_0^h \mathrm{d}z\left[\frac{\eta}{2}(\partial_z u)^2\right] + \int \mathrm{d}x\frac{J_x^2}{2hM(\phi)}. \tag{55}$$

The variation of Φ with respect to the rates u and J_x is of the form

$$\delta\Phi = -\int \mathrm{d}x\int_0^h \mathrm{d}z\,(\eta\partial_z^2 u)\delta u + \int \mathrm{d}x\left[(\eta\partial_z u)\delta u\right]|_{z=h} + \int \mathrm{d}x\frac{J_x\delta J_x}{hM(\phi)}. \tag{56}$$

The incompressibility condition $\partial_x u + \partial_z w = 0$ is still to be imposed by adding C into Onsager's action $\mathcal{A}$. The expressions for C and its variation are given by equations (6) and (8).

The governing equations for thin film evolution can be obtained by minimizing Onsager's action $\mathcal{A} = \dot F + \Phi + C$ with respect to all the involved rates. Minimizing $\mathcal{A}$ with respect to $\partial_t h$, we have

$$p(x,h,t) = -\gamma\partial_x^2 h + (g+\partial_h f) \tag{57}$$

for the pressure at $z = h$. Minimizing $\mathcal{A}$ with respect to u, we have

$$\mu_\phi\partial_x\phi + \eta\partial_z^2 u - \partial_x p = 0 \tag{58}$$

for the force balance in the tangential direction. Minimizing $\mathcal{A}$ with respect to w, we have

$$-\partial_z p = 0 \tag{59}$$

for the hydrostatic equilibrium in the vertical direction. Minimizing $\mathcal{A}$ with respect to u at $z = h$, we have

$$\eta\partial_z u = 0, \tag{60}$$

for the tangential stress at the free surface. Finally, minimizing $\mathcal{A}$ with respect to J_x, we have

$$J_x = -hM(\phi)\partial_x\mu_\phi \tag{61}$$

for the integrated tangential diffusive flux. It is noted that $p(x,z,t)$ is a constant in the z direction, and therefore a parabolic profile for $u(x,z,t)$ can be obtained from equations (58) (60) in the form

$$u(x,z,t) = \frac{1}{\eta}\left\{\partial_x\left[-\gamma\partial_x^2 h + (g+\partial_h f)\right] - \mu_\phi\partial_x\phi\right\}\times\left(\frac{z^2}{2} - zh\right), \tag{62}$$

from which the flux J_h is found to be

$$J_h = \frac{h^3}{3\eta}\left\{\partial_x\left[\gamma\partial_x^2 h - (g+\partial_h f)\right] + \mu_\phi\partial_x\phi\right\}. \tag{63}$$

Using $\partial_\phi g \partial_x \phi = \partial_x g$, we have

$$J_h = \frac{h^3}{3\eta}\left[\partial_x\left(\gamma\partial_x^2 h\right) - \partial_x\left(\partial_h f\right) + \frac{1}{h}\partial_\phi f\,\partial_x\phi\right] \tag{64}$$

for the flux associated with the conserved field h. Substituting equation (52) into (61), we have

$$J_x = -hM(\phi)\partial_x\left(\partial_\phi g + \frac{1}{h}\partial_\phi f\right). \tag{65}$$

The flux associated with the conserved field $\Psi = \int_0^h \mathrm{d}z\, c$, given by $J_\Psi = \int_0^h \mathrm{d}z\,(uc + j_x)$, now takes the form of $J_\Psi = J_h\phi + J_x$ for $c(x,z,t) = \phi(x,t)$ and can be readily written down. Given the explicit expressions for J_h and J_Ψ, the thin film equations for $h(x,t)$ and $\Psi(x,t) = h(x,t)\phi(x,t)$ are obtained from the conservation laws in equations (26) and (27). Finally, we would like to point out that our variational derivation of the thin film equations can be readily generalized to two spatial dimensions.

4.5. Gradient dynamics

It is straightforward to derive the gradient dynamics description [22, 38] from the above variational approach. The rate of free energy dissipation can be expressed in terms of the conserved fields h and Ψ as

$$\dot{F} = \int \mathrm{d}x\left(\frac{\delta F}{\delta h}\partial_t h + \frac{\delta F}{\delta \Psi}\partial_t \Psi\right). \tag{66}$$

Using the conservation laws (26) and (27) for h and Ψ, respectively, followed by integration by parts, we obtain

$$\dot{F} = \int \mathrm{d}x\left(J_h\partial_x\frac{\delta F}{\delta h} + J_\Psi\partial_x\frac{\delta F}{\delta \Psi}\right), \tag{67}$$

in which J_h and J_Ψ are the rates or fluxes induced by the forces $\partial_x(\delta F/\delta h)$ and $\partial_x(\delta F/\delta\Psi)$. These two forces vanish at equilibrium because h and Ψ are conserved fields and therefore $\delta F/\delta h$ and $\delta F/\delta\Psi$ must be homogeneous in equilibrium. Introducing the mobility matrix $\mathbf{Q}$ in the linear response regime, we have

$$\begin{bmatrix} J_h \\ J_\Psi \end{bmatrix} = -\begin{bmatrix} Q_{hh} & Q_{h\Psi} \\ Q_{\Psi h} & Q_{\Psi\Psi} \end{bmatrix}\begin{bmatrix} \partial_x\dfrac{\delta F}{\delta h} \\ \partial_x\dfrac{\delta F}{\delta \Psi} \end{bmatrix}, \tag{68}$$

which lead to the coupled evolution equations

$$\begin{bmatrix} \partial_t h \\ \partial_t \Psi \end{bmatrix} = \partial_x\left(\begin{bmatrix} Q_{hh} & Q_{h\Psi} \\ Q_{\Psi h} & Q_{\Psi\Psi} \end{bmatrix}\begin{bmatrix} \partial_x\dfrac{\delta F}{\delta h} \\ \partial_x\dfrac{\delta F}{\delta \Psi} \end{bmatrix}\right). \tag{69}$$

It follows that $\dot{F}$ can be written as

$$\dot{F} = -\int \mathrm{d}x\begin{bmatrix} \partial_x\dfrac{\delta F}{\delta h} & \partial_x\dfrac{\delta F}{\delta \Psi} \end{bmatrix}\mathbf{Q}\begin{bmatrix} \partial_x\dfrac{\delta F}{\delta h} \\ \partial_x\dfrac{\delta F}{\delta \Psi} \end{bmatrix} \tag{70}$$

and

$$\dot{F} = -\int \mathrm{d}x\begin{bmatrix} J_h & J_\Psi \end{bmatrix}\mathbf{Q}^{-1}\begin{bmatrix} J_h \\ J_\Psi \end{bmatrix}. \tag{71}$$

The matrix $\mathbf{Q}$ must be positive definite according to the second law of thermodynamics. Furthermore, since the model is derived using Onsager's variational principle, $\mathbf{Q}$ must satisfy the reciprocal symmetry: $Q_{h\Psi} = Q_{\Psi h}$.

We are ready to give the explicit expressions for all the entries of $\mathbf{Q}$. With ϕ replaced by Ψ/h in equation (51) for F, we have

$$\frac{\delta F}{\delta h} = -\gamma\partial_x^2 h + g - \partial_\phi g\frac{\Psi}{h} + \partial_h f - \partial_\phi f\frac{\Psi}{h^2} \tag{72}$$

and

$$\frac{\delta F}{\delta \Psi} = \partial_\phi g + \frac{1}{h}\partial_\phi f = \mu_\phi. \tag{73}$$

It follows that J_h in equation (64) can be expressed as

$$J_h = -\frac{h^3}{3\eta}\partial_x\frac{\delta F}{\delta h} - \frac{h^2\Psi}{3\eta}\partial_x\frac{\delta F}{\delta \Psi}, \tag{74}$$

which gives $Q_{hh} = h^3/3\eta$ and $Q_{h\Psi} = h^2\Psi/3\eta$. From $J_\Psi = J_h\phi + J_x$ and equation (65) for J_x, we obtain

$$J_\Psi = -\frac{h^2\Psi}{3\eta}\partial_x\frac{\delta F}{\delta h} - \left(\frac{h\Psi^2}{3\eta} + hM\right)\partial_x\frac{\delta F}{\delta \Psi}, \tag{75}$$

which gives $Q_{\Psi h} = h^2\Psi/3\eta$ and $Q_{\Psi\Psi} = h\Psi^2/3\eta + hM$. It is readily seen that the reciprocal relation $Q_{h\Psi} = Q_{\Psi h}$ is satisfied.

Finally, we would like to point out that with Ψ chosen as a conserved field, the corresponding flux $J_\Psi = J_h\phi + J_x$ combines the contributions of both convection (J_h) and diffusion (J_x). This combination is an acceptable transformation [50] and results in a non-diagonal matrix $\mathbf{Q}^{-1}$ in equation (71), where $\dot{F}$ is quadratic in the fluxes J_h and J_Ψ. It is interesting to note that the off-diagonal entries $Q_{h\Psi}$ and $Q_{\Psi h}$ are nonzero even if diffusion is absent ($M = 0$). This means that here the cross-coupling is not of dynamic origin (as the dissipation functional (33) or (55) does not couple the fluid mixture velocity and the diffusive flux) but rather arises from the choice of Ψ as a conserved field whose corresponding flux J_Ψ contains contributions from both convection and diffusion.

5. Toward a symmetric formulation

A thin film model for a non-surface-active mixture, which is valid in the entire concentration range and allows for a consistent inclusion of evaporation, is best constructed in a symmetric way with respect to solvent and solute. In order to do so, we introduce the effective layer thicknesses ψ_1 for the solvent and ψ_2 for the solute whose sum gives the film height $h = \psi_1 + \psi_2$. The final gradient dynamics can be expressed as evolution equations for ψ_1 and ψ_2, or as evolution equations for h and one of the ψ_i. Other choices are possible as well. In addition, the mass densities are denoted by ρ_i for $i = 1, 2$ as above, while the height-averaged concentrations are $\phi_i = \psi_i/h$ with $\phi_1 + \phi_2 = 1$.

5.1. Bulk transport equations and diffusive flux

Let us start from the continuity equations of the two miscible components, with the solvent labeled by the subscript '1' and the solute labeled by the subscript '2'. They read

$$\frac{\partial \rho_1}{\partial t} + \nabla \cdot (\rho_1 \mathbf{v}_1) = 0 \tag{76}$$

and

$$\frac{\partial \rho_2}{\partial t} + \nabla \cdot (\rho_2 \mathbf{v}_2) = 0, \tag{77}$$

in which $\mathbf{v}_i$ $(i = 1, 2)$ is the velocity of a particular species. The mass density ρ and velocity $\mathbf{v}$ of the solution are defined by $\rho = \rho_1 + \rho_2$ and $\rho\mathbf{v} = \rho_1\mathbf{v}_1 + \rho_2\mathbf{v}_2$. Physically, $\mathbf{v}$ is the mass-averaged velocity which is a field variable that enters into the hydrodynamic momentum equation. The local relative concentration of the solute is defined by $c = \rho_2/\rho$ and that of the solvent is given by $1 - c$. It follows that $\mathbf{v}$ equals $(1 - c)\mathbf{v}_1 + c\mathbf{v}_2$.

Adding equations (76) and (77) gives the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \tag{78}$$

for ρ. For the simplest mixture considered here, ρ is constant in space and time, and consequently $\mathbf{v}$ satisfies the incompressibility condition $\nabla \cdot \mathbf{v} = 0$. Defining $\mathbf{j}_1 = \rho_1(\mathbf{v}_1 - \mathbf{v})$ and $\mathbf{j}_2 = \rho_2(\mathbf{v}_2 - \mathbf{v})$ to measure diffusion, we have $\mathbf{j}_1 + \mathbf{j}_2 = 0$, meaning that diffusion can be measured by $\mathbf{j}_2$ (or $\mathbf{j}_1$) alone. We emphasize that the diffusion discussed here is defined relative to the motion of the center of mass of a fluid element. For mixtures diffusing on a substrate, diffusion may also be defined with respect to the substrate or to a resting background medium as often done in dynamical density functional theory [43]. How the gradient dynamics formulations resulting from the two distinct choices are related will be briefly discussed in section 5.4.

Rewriting equation (77) as

$$\frac{\partial}{\partial t}(\rho c) + \nabla \cdot (\rho c \mathbf{v} + \mathbf{j}_2) = 0 \tag{79}$$

and using $\rho = \text{const.}$ and $\nabla \cdot \mathbf{v} = 0$, we obtain

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = -\nabla \cdot \mathbf{j}, \tag{80}$$

in which $\mathbf{j}$ is the diffusive flux associated with c, defined by $\mathbf{j} = \mathbf{j}_2/\rho$. We note that $\mathbf{j}$ may be expressed either as $\mathbf{j} = c(\mathbf{v}_2 - \mathbf{v})$ or as $\mathbf{j} = c(1 - c)(\mathbf{v}_2 - \mathbf{v}_1)$, which reveals its physical nature.

5.2. Dissipation functional

From $\mathbf{j} = c(1 - c)(\mathbf{v}_2 - \mathbf{v}_1)$, a dissipation functional can be constructed to describe the diffusive transport in a way that is symmetric with respect to solvent and solute.

A solution consists of two interpenetrating components whose relative motion generates diffusion. In the regime of linear response, the rate of dissipation is quadratic in the relative velocity $\mathbf{v}_2 - \mathbf{v}_1$ between the two components. In order to propose an expression for the density of the rate of dissipation, we need to measure the number of frictional contacts between the two components. Neglecting any short-range order, this number is proportional to $c(1 - c)$, which is the probability for forming a solute-solvent pair at a particular spatial point. Therefore, the density of the rate of dissipation is proportional to $c(1 - c)(\mathbf{v}_2 - \mathbf{v}_1)^2$. In the limit of dilute solute $(c \to 0)$, this density should take the form of $n_{\max} c\zeta(\mathbf{v}_2 - \mathbf{v}_1)^2$, in which $n_{\max}$ is the particle number density of the solution, $n_{\max}c$ is that of the solute, and ζ is the drag coefficient of a solute particle (see section 3.2). In the other limit $(1 - c \to 0)$, the density of the rate of dissipation should take the form of $n_{\max}(1 - c)\zeta(\mathbf{v}_2 - \mathbf{v}_1)^2$, in which the same drag coefficient is used for a solvent particle surrounded by the solute. Here the similarity in molecular sizes between solvent and solute is assumed. Based on the above observations, it is natural to adopt $n_{\max}c(1 - c)\zeta(\mathbf{v}_2 - \mathbf{v}_1)^2$ as the simplest expression for the density of the rate of dissipation, which is symmetric with respect to $c = 1/2$ in the entire range of c.

By definition, the dissipation functional is half the rate of free energy dissipation. Expressed in terms of the diffusive flux $\mathbf{j}$, the dissipation functional associated with diffusion takes the form of

$$\Phi_d^{\text{sym}} = \frac{1}{2}\int\int \mathrm{d}x\mathrm{d}z\, \frac{n_{\max}\zeta \mathbf{j}^2}{c(1 - c)}, \tag{81}$$

which is symmetric with respect to the relative concentrations of solvent and solute. It can be readily used for the diffusive part of Φ in equations (33) and (55), with

$$M(c) = \frac{c(1 - c)}{n_{\max}\zeta}. \tag{82}$$

To achieve a symmetric formulation for thin film hydrodynamics, the free energy functional also needs to be symmetric. This can be realized by using the Flory–Huggins free energy of mixing for $g(c)$ [44, 49]:

$$g(c) = n_{\max}k_{\mathrm{B}}T\big\{c(\log c - 1) + (1 - c)[\log(1 - c) - 1] + \chi c(1 - c)\big\}, \tag{83}$$

which enters into the expression for $F[h, c]$ in equation (29) (and subsequently the expression for $F[h, \phi]$ in equation (51)). Physically, it is understood that a symmetric formulation is possible only if the similarity in molecular sizes between solvent and solute is assumed, an assumption made for both the diffusive dissipation functional Φ_d^{sym} and the symmetric free energy density of mixing $g(c)$. Note, however, that once a consistent symmetric formulation is established, asymmetries between the components may be re-introduced in a controlled manner.

With the help of equations (81) and (83), thin film hydrodynamics can be formulated for concentrated solutions following the variational approach presented in section 4. It is physically expected that high concentration will lead to nonlinear diffusion and strong coupling between flow and diffusion, both of which have been incorporated in the present formulation.

Finally, we would like to point out that our variational approach is developed to derive the local dynamics expressed

in terms of fluid velocity and solute concentration. Starting from the local dynamic equations, the gradient dynamics expressed in terms of conserved fields can be formulated in a straightforward way, as demonstrated in section 4.5. Based on the results in sections 4.5 and 5.2, in the next section we give a complete symmetric formulation for the gradient dynamics of a film of a mixture.

5.3. Symmetric gradient dynamics model for mixture films

5.3.1. Free energy. The free energy functional is of the form given in equation (51). The local bulk free energy density g is of the Flory–Huggins type as expressed in equation (83), i.e. it consists of the two entropic terms

$$g_1(\phi_1) = n_{\max} k_B T\, \phi_1\, (\log \phi_1 - 1) \tag{84}$$

and

$$g_2(\phi_2) = n_{\max} k_B T\, \phi_2\, (\log \phi_2 - 1)\,, \tag{85}$$

responsible for the diffusion of solvent and solute, and the interaction term

$$g_{12}(\phi_1) = n_{\max} k_B T \chi \phi_1 \phi_2. \tag{86}$$

The maximum number density is chosen to be identical for solvent and solute. Written in the conserved fields, i.e. the solvent height ψ_1 and the solute height ψ_2, one has

$$g = g_1 + g_2 + g_{12} = n_{\max} k_B T \left[\frac{\psi_1}{\psi_1+\psi_2}\left(\log\frac{\psi_1}{\psi_1+\psi_2} - 1\right) + \frac{\psi_2}{\psi_1+\psi_2}\left(\log\frac{\psi_2}{\psi_1+\psi_2} - 1\right) + \chi \frac{\psi_1\psi_2}{(\psi_1+\psi_2)^2}\right]. \tag{87}$$

Introducing the g of equation (87) into equation (51), we obtain for the free energy functional in terms of ψ_1 and ψ_2 the expression

$$F[\psi_1,\psi_2] = \int \left\{ \frac{\gamma}{2}[\nabla(\psi_1+\psi_2)]^2 + f(\psi_1+\psi_2) + n_{\max} k_B T \times \left[\psi_1(\log\psi_1 - 1) + \psi_2(\log\psi_2 - 1) - (\psi_1+\psi_2) \times \log(\psi_1+\psi_2) + \chi \frac{\psi_1\psi_2}{(\psi_1+\psi_2)} \right] \right\} \mathrm{d}x. \tag{88}$$

where γ is the liquid–gas interfacial tension, and $f(\psi_1+\psi_2)$ is the wetting energy that is assumed to locally depend on h.

The variational derivatives of F are

$$\frac{\delta F}{\delta \psi_1} = -\gamma\, \partial_{xx}(\psi_1+\psi_2) + \partial_{\psi_1} f + n_{\max} k_B T \left[\log\psi_1 - \log(\psi_1+\psi_2) - 1 + \chi \frac{\psi_2^2}{(\psi_1+\psi_2)^2}\right],$$
$$\frac{\delta F}{\delta \psi_2} = -\gamma\, \partial_{xx}(\psi_1+\psi_2) + \partial_{\psi_2} f + n_{\max} k_B T \left[\log\psi_2 - \log(\psi_1+\psi_2) - 1 + \chi \frac{\psi_1^2}{(\psi_1+\psi_2)^2}\right]. \tag{89}$$

Here we assume $f = f(\psi_1+\psi_2)$ for the wetting energy, and hence $\partial_{\psi_1} f = \partial_{\psi_2} f = f'$.

5.3.2. Purely diffusive case. We can now construct the matrix of mobility functions (i.e. the mobility matrix) using the results derived in section 4.5. We start from the case of transport by diffusion only. This corresponds to the limit of infinite viscosity ($\eta \to \infty$). According to equations (74) and (75), the mobility matrix defined through equation (68) is given by

$$\mathbf{Q} = \begin{pmatrix} Q_{hh} & Q_{h\Psi} \\ Q_{\Psi h} & Q_{\Psi\Psi} \end{pmatrix} = \begin{pmatrix} h^3/3\eta & h^2\Psi/3\eta \\ h^2\Psi/3\eta & h\Psi^2/3\eta + hM \end{pmatrix}, \tag{90}$$

which, in the limit of $\eta \to \infty$, becomes

$$\mathbf{Q}^{\mathrm{DIFF}} = \begin{pmatrix} Q^{\mathrm{DIFF}}_{hh} & Q^{\mathrm{DIFF}}_{h\Psi} \\ Q^{\mathrm{DIFF}}_{\Psi h} & Q^{\mathrm{DIFF}}_{\Psi\Psi} \end{pmatrix} = hM \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}. \tag{91}$$

For the moment, the mobility M is kept general. The symmetric expression proposed in section 5.2 will be further incorporated below.

As adopted in section 5, the solvent is labeled by the subscript '1' and the solute labeled by the subscript '2'. Through the relations $\psi_1 = h - \Psi$ and $\psi_2 = \Psi$, we have the transformation from $\mathbf{Q}^{\mathrm{DIFF}}$ for h and Ψ into $\mathbf{Q}^{\mathrm{diff}}$ for ψ_1 and ψ_2 in the form of

$$\mathbf{Q}^{\mathrm{diff}} = \mathbf{R}\mathbf{Q}^{\mathrm{DIFF}}\mathbf{R}^T, \tag{92}$$

where $\mathbf{R} = \begin{pmatrix} 1 & -1 \\ 0 & 1 \end{pmatrix}$ is defined by the transformation $\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \mathbf{R}\begin{pmatrix} h \\ \Psi \end{pmatrix}$, and superscript T indicates the transposed matrix. This leads to

$$\mathbf{Q}^{\mathrm{diff}} = \begin{pmatrix} Q^{\mathrm{diff}}_{\psi_1\psi_1} & Q^{\mathrm{diff}}_{\psi_1\psi_2} \\ Q^{\mathrm{diff}}_{\psi_2\psi_1} & Q^{\mathrm{diff}}_{\psi_2\psi_2} \end{pmatrix} = (\psi_1+\psi_2)M \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}. \tag{93}$$

The conservation laws for ψ_1 and ψ_2 can be written in matrix form as

$$\partial_t \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = -\partial_x \begin{pmatrix} J_{\psi_1} \\ J_{\psi_2} \end{pmatrix} = \partial_x \left[\begin{pmatrix} Q^{\mathrm{diff}}_{\psi_1\psi_1} & Q^{\mathrm{diff}}_{\psi_1\psi_2} \\ Q^{\mathrm{diff}}_{\psi_2\psi_1} & Q^{\mathrm{diff}}_{\psi_2\psi_2} \end{pmatrix} \begin{pmatrix} \partial_x \frac{\delta F}{\delta \psi_1} \\ \partial_x \frac{\delta F}{\delta \psi_2} \end{pmatrix} \right], \tag{94}$$

where the mobility matrix $\mathbf{Q}^{\mathrm{diff}}$ is explicitly involved. From the structure of $\mathbf{Q}^{\mathrm{diff}}$, we immediately have $J_{\psi_1} + J_{\psi_2} = 0$ for the fluxes J_{ψ_1} and J_{ψ_2}, which are defined through the conservation laws $\partial_t \psi_i + \partial_x J_{\psi_i} = 0$ (for $i = 1, 2$). As a result, we have $\partial_t h = \partial_t(\psi_1+\psi_2) = -\partial_x(J_{\psi_1} + J_{\psi_2}) = 0$. This means that the time evolution of h is frozen because no flow can be activated for $\eta \to \infty$. We would like to emphasize again that the diffusion discussed here is defined *relative to the motion of the center of mass of a fluid element*. Although the infinitely large viscosity freezes the motion of the center of mass and thus the time evolution of h, diffusion of the components still occurs in the binary mixture. Next we derive the purely diffusive fluxes J_{ψ_1} and J_{ψ_2}.

Using equation (93) for $\mathbf{Q}^{\mathrm{diff}}$, we obtain

$$J_{\psi_1} = -(\psi_1+\psi_2)M\partial_x\left(\frac{\delta F}{\delta\psi_1} - \frac{\delta F}{\delta\psi_2}\right). \tag{95}$$

According to equation (89), the above expression does not contain contributions from capillarity and wettability, but only contributions from the entropic and interaction parts of the mixing free energy. Substituting equation (89) into (95) yields

$$J_{\psi_1} = -(\psi_1+\psi_2)Mn_{\max}k_{\mathrm{B}}T\left(\frac{\partial_x\psi_1}{\psi_1}-\frac{\partial_x\psi_2}{\psi_2} +2\chi\frac{\psi_1\partial_x\psi_2-\psi_2\partial_x\psi_1}{(\psi_1+\psi_2)^2}\right), \tag{96}$$

Now we employ the symmetric M given in equation (82). Using $c=\psi_2/(\psi_1+\psi_2)$ for the relative concentration of the solute and the diffusion coefficient $D=k_{\mathrm{B}}T/\zeta$ in the dilute limit, we have

$$M=\frac{\psi_1\psi_2}{(\psi_1+\psi_2)^2}\frac{D}{n_{\max}k_{\mathrm{B}}T}. \tag{97}$$

Substituting equation (97) into (96), we obtain

$$\begin{aligned} J_{\psi_1} &= -D\frac{\psi_1\psi_2}{\psi_1+\psi_2}\left[\frac{\partial_x\psi_1}{\psi_1}-\frac{\partial_x\psi_2}{\psi_2}+2\chi\frac{\psi_1\partial_x\psi_2-\psi_2\partial_x\psi_1}{(\psi_1+\psi_2)^2}\right] \\ &= -D(\psi_1+\psi_2)\left[1-2\chi\frac{\psi_1\psi_2}{(\psi_1+\psi_2)^2}\right]\partial_x\left(\frac{\psi_1}{\psi_1+\psi_2}\right), \end{aligned} \tag{98}$$

which can be written as $J_{\psi_1}=-h\widetilde{D}\partial_x\phi_1$ with the non-Fickian diffusion coefficient $\widetilde{D}=D(1-2\chi\phi_1\phi_2)$. In a similar way we obtain $J_{\psi_2}=-h\widetilde{D}\partial_x\phi_2$. It is readily seen that the condition $J_{\psi_1}+J_{\psi_2}=0$ is satisfied for $\eta\to\infty$ because of $\phi_1+\phi_2=1$.

Substituting $\partial_t h=0$, $\psi_i=h\phi_i$ and $J_{\psi_i}=-h\widetilde{D}\partial_x\phi_i$ into $\partial_t\psi_i=-\partial_x J_{\psi_i}$ for $i=1,2$, we obtain

$$\partial_t\phi_i=\partial_x(\widetilde{D}\partial_x\phi_i)+\frac{\partial_x h}{h}\widetilde{D}\partial_x\phi_i. \tag{99}$$

For $\chi=0$, i.e. for constant $\widetilde{D}=D$, this is of the same form as equation (49) with $u_h=0$ (no convection).

5.3.3. Purely convective case. Now we turn to the case of transport by convection only. This corresponds to the limit of zero diffusive mobility ($M=0$). From $\mathbf{Q}$ in equation (90), we then obtain

$$\mathbf{Q}^{\mathrm{CONV}}=\begin{pmatrix} Q_{hh}^{\mathrm{CONV}} & Q_{h\Psi}^{\mathrm{CONV}} \\ Q_{\Psi h}^{\mathrm{CONV}} & Q_{\Psi\Psi}^{\mathrm{CONV}}\end{pmatrix}=\frac{h}{3\eta}\begin{pmatrix} h^2 & h\Psi \\ h\Psi & \Psi^2\end{pmatrix}. \tag{100}$$

Through the transformation from $\mathbf{Q}^{\mathrm{CONV}}$ for h and Ψ into $\mathbf{Q}^{\mathrm{conv}}$ for ψ_1 and ψ_2 in the form of

$$\mathbf{Q}^{\mathrm{conv}}=\mathbf{R}\mathbf{Q}^{\mathrm{CONV}}\mathbf{R}^T, \tag{101}$$

we obtain

$$\mathbf{Q}^{\mathrm{conv}}=\frac{\psi_1+\psi_2}{3\eta}\begin{pmatrix}\psi_1^2 & \psi_1\psi_2 \\ \psi_1\psi_2 & \psi_2^2\end{pmatrix}. \tag{102}$$

The conservation laws for ψ_1 and ψ_2 in matrix form can be written as

$$\partial_t\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}=-\partial_x\begin{pmatrix}J_{\psi_1}\\ J_{\psi_2}\end{pmatrix}=\partial_x\left[\begin{pmatrix} Q_{\psi_1\psi_1}^{\mathrm{conv}} & Q_{\psi_1\psi_2}^{\mathrm{conv}} \\ Q_{\psi_2\psi_1}^{\mathrm{conv}} & Q_{\psi_2\psi_2}^{\mathrm{conv}}\end{pmatrix}\times\begin{pmatrix}\partial_x\dfrac{\delta F}{\delta\psi_1}\\ \partial_x\dfrac{\delta F}{\delta\psi_2}\end{pmatrix}\right], \tag{103}$$

where the mobility matrix $\mathbf{Q}^{\mathrm{conv}}$ is explicitly involved. Below we derive the fluxes J_{ψ_1} and J_{ψ_2} contributed by convection only.

Using equation (102) for $\mathbf{Q}^{\mathrm{conv}}$, we obtain

$$J_{\psi_1}=-\frac{\psi_1+\psi_2}{3\eta}\psi_1\left(\psi_1\partial_x\frac{\delta F}{\delta\psi_1}+\psi_2\partial_x\frac{\delta F}{\delta\psi_2}\right). \tag{104}$$

Substituting equation (89) into (104), we obtain

$$J_{\psi_1}=-\frac{1}{3\eta}\psi_1(\psi_1+\psi_2)^2\partial_x\left[-\gamma\partial_x^2(\psi_1+\psi_2)+f'(\psi_1+\psi_2)\right], \tag{105}$$

and find that it does not contain contributions from the entropic and interaction parts of the mixing free energy, but only contributions from capillarity and wettability in equation (89).

Equation (105) can be written as $J_{\psi_1}=-\psi_1(h^2/3\eta)\partial_x\left[-\gamma\partial_x^2 h+f'(h)\right]$. In a similar way we obtain $J_{\psi_2}=-\psi_2(h^2/3\eta)\partial_x\left[-\gamma\partial_x^2 h+f'(h)\right]$. It follows that the evolution equations for ψ_1 and ψ_2 are given by

$$\begin{aligned}\partial_t\psi_1 &= -\partial_x\left\{\frac{1}{3\eta}\psi_1(\psi_1+\psi_2)^2\partial_x\left[\gamma\partial_x^2(\psi_1+\psi_2)-f'(\psi_1+\psi_2)\right]\right\}, \\ \partial_t\psi_2 &= -\partial_x\left\{\frac{1}{3\eta}\psi_2(\psi_1+\psi_2)^2\partial_x\left[\gamma\partial_x^2(\psi_1+\psi_2)-f'(\psi_1+\psi_2)\right]\right\}.\end{aligned} \tag{106}$$

The sum of these two equations is

$$\partial_t h=-\partial_x\left\{\frac{h^3}{3\eta}\partial_x\left[\gamma\partial_x^2 h-f'(h)\right]\right\}, \tag{107}$$

as expected for the transport by convection only (see equation (15) for one-component liquids).

5.3.4. General dynamics. It is interesting to note that in the completely symmetric case discussed above, the diffusive mobility matrix $\mathbf{Q}^{\mathrm{diff}}$ results in the fluxes J_{ψ_1} and J_{ψ_2} that only pick up contributions from the mixing free energy while the convective mobility matrix $\mathbf{Q}^{\mathrm{conv}}$ results in the fluxes J_{ψ_1} and J_{ψ_2} that only pick up contributions not related to the mixing free energy. Cross-contributions naturally appear if the symmetry is broken. Finally, we point out that equations (94) and (103) represent kinetic equations of linear nonequilibrium thermodynamics. Using the fact that $\mathbf{Q}^{\mathrm{diff}}$ and $\mathbf{Q}^{\mathrm{conv}}$ are additive and collecting the above obtained expressions, we give the general evolution equations for ψ_1 and ψ_2 in gradient dynamics form. In matrix form they can be written as

$$\partial_t\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}=-\partial_x\begin{pmatrix}J_{\psi_1}\\ J_{\psi_2}\end{pmatrix}=\partial_x\left[\left(\mathbf{Q}^{\mathrm{diff}}+\mathbf{Q}^{\mathrm{conv}}\right)\times\begin{pmatrix}\partial_x\dfrac{\delta F}{\delta\psi_1}\\ \partial_x\dfrac{\delta F}{\delta\psi_2}\end{pmatrix}\right], \tag{108}$$

or in expanded form as

$$\partial_t \psi_1 = -\partial_x \left\{ \frac{1}{3\eta} \psi_1 (\psi_1+\psi_2)^2 \partial_x \left[\gamma \partial_x^2 (\psi_1+\psi_2) - f'(\psi_1+\psi_2) \right] \right.$$
$$\left. -D(\psi_1+\psi_2) \left(1 - 2\chi \frac{\psi_1\psi_2}{(\psi_1+\psi_2)^2} \right) \partial_x \left(\frac{\psi_1}{\psi_1+\psi_2} \right) \right\},$$
$$\partial_t \psi_2 = -\partial_x \left\{ \frac{1}{3\eta} \psi_2 (\psi_1+\psi_2)^2 \partial_x \left[\gamma \partial_x^2 (\psi_1+\psi_2) - f'(\psi_1+\psi_2) \right] \right.$$
$$\left. -D(\psi_1+\psi_2) \left(1 - 2\chi \frac{\psi_1\psi_2}{(\psi_1+\psi_2)^2} \right) \partial_x \left(\frac{\psi_2}{\psi_1+\psi_2} \right) \right\}. \quad (109)$$

The basic symmetric formulation (108) may now be easily extended by including additional effects in the free energy functional $F[\psi_1, \psi_2]$. Then evolution equations either in terms of ψ_1 and ψ_2 or in terms of h and Ψ can be readily obtained. Such additional effects could be (i) a concentration-dependent wetting energy $f(\psi_1, \psi_2)$ (which is no longer a function of only $\psi_1 + \psi_2$), (ii) a more complicated mixing free energy density $g(\phi_1, \phi_2)$ to replace the simple Flory–Huggins one, or (iii) gradient terms in the concentration fields. Note that phase-transition limited evaporation may be included by adding nonconserved terms proportional to $\delta F/\delta\psi_i - \mu_i^g$ to the equation for ψ_i in (108). Here μ_i^g is the chemical potential of the component i in the gas phase. To model coating processes, one may also add terms that account for driving forces, e.g. the influence of a moving substrate that is drawn out of a bath. Such extensions are discussed in more details in the context of previous gradient dynamics models with non-symmetric diffusive mobilities [22, 38, 51].

5.4. Mobilities in other reference frames

In the above discussion, diffusion has been defined as occurring relative to the motion of the center of mass of a fluid element. Below we discuss how one may determine diffusive and convective mobilities when diffusion is defined as occurring relative to a resting substrate or background medium as often done in dynamical density functional theory (DDFT) [43].

Our starting point is the symmetric formulation with diffusion defined relative to the center of mass motion (see section 5.3.2). We have the diffusive mobility matrix for the fields (ψ_1, ψ_2)

$$\mathbf{Q}^{\text{diff}} = (\psi_1+\psi_2) M \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} = \frac{\psi_1\psi_2}{(\psi_1+\psi_2)} \frac{D}{n_{\max} k_B T} \times \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}. \quad (110)$$

We note that

$$\frac{\psi_1\psi_2}{(\psi_1+\psi_2)} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} + \frac{1}{(\psi_1+\psi_2)} \begin{pmatrix} \psi_1^2 & \psi_1\psi_2 \\ \psi_1\psi_2 & \psi_2^2 \end{pmatrix} = \begin{pmatrix} \psi_1 & 0 \\ 0 & \psi_2 \end{pmatrix}, \quad (111)$$

where the matrix on the right hand side is the diagonal matrix encountered, e.g. in DDFT where diffusion is defined with respect to the substrate. It is interesting to note that the second matrix on the left hand side may, up to a constant factor, be obtained from our convective mobility matrix in section 5.3.3 as $\mathbf{Q}^{\text{conv}}/(\psi_1+\psi_2)^2$ (from equation (102)).

Using $\psi_i = h\phi_i$, we find it instructive to write the mobility from equations (110) and (102) as

$$\mathbf{Q} = \mathbf{Q}^{\text{diff}} + \mathbf{Q}^{\text{conv}} = h\phi_1\phi_2 \frac{D}{n_{\max} k_B T} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} + \frac{h^3}{3\eta} \begin{pmatrix} \phi_1^2 & \phi_1\phi_2 \\ \phi_1\phi_2 & \phi_2^2 \end{pmatrix}. \quad (112)$$

A decomposition into the diffusive and convective mobilities with respect to a resting substrate gives

$$\mathbf{Q} = \widehat{\mathbf{Q}}^{\text{diff}} + \widehat{\mathbf{Q}}^{\text{conv}} = \frac{D\,h}{n_{\max} k_B T} \begin{pmatrix} \phi_1 & 0 \\ 0 & \phi_2 \end{pmatrix} + \left(\frac{h^3}{3\eta} - \frac{D\,h}{n_{\max} k_B T} \right) \begin{pmatrix} \phi_1^2 & \phi_1\phi_2 \\ \phi_1\phi_2 & \phi_2^2 \end{pmatrix}. \quad (113)$$

It is clearly seen that the first term in equation (113) corresponds to the diagonal mobility matrix employed in a DDFT for a layer of a binary nanoparticle-solvent mixture on a substrate [43]. There, however, no convective transport of the mixture with respect to the substrate is studied. The present discussion indicates that subtle issues arise when one tries to relate the results of studies that define diffusion with respect to the center of mass of a fluid element and those of studies that define diffusion with respect to the resting background.

6. Concluding remarks

In the present work we have employed Onsager's variational principle to first re-derive (i) the thin film (or long-wave) equation for a film of simple nonvolatile liquid on a smooth solid substrate and (ii) the standard diffusion equation. The concepts and procedures introduced in these two cases have then been applied to thin films of binary mixtures on solid surfaces. After deriving the evolution equations for film height and effective solute height in a general form, we have employed them to present a model that is symmetrically formulated with respect to solvent and solute, or more precisely, to the two components of the mixtures.

Our derivations start from free energy functionals and dissipation functionals which are expressed using variables that are more fundamental than the effective thicknesses that finally appear in the thin film equations. This approach has allowed us to examine the assumption(s) and approximation(s) that are implicitly made and applied in the thin film description of binary mixtures on solid surfaces. This has also provided a general scheme that may now be employed for further generalizations of the presented models by introducing more physical components, in addition to the capillarity, wettability, and miscibility aspects encoded in the free energy functionals and the viscous and diffusive transport processes encoded in the dissipation functionals.

It has been shown that the variational approach presented here naturally leads to a gradient dynamics description on the level of the independent conserved fields, namely the effective film heights. This gradient dynamics description is itself of the form of kinetic equations of linear

nonequilibrium thermodynamics with Onsager's reciprocal symmetry automatically satisfied by the mobility matrix. Note that the variational approach works properly only if fields are identified that can be varied independently. Therefore, for the presently studied film of binary mixture, the choice of height and height-averaged solute concentration is not advisable as it seems to result in kinetic equations that include constrained variations [18], where neither it is obvious whether Onsager's reciprocal symmetry is satisfied, nor it is clear how the diffusion equation emerges in the dilute limit (see [9, 38] for further discussion on this point).

Equations of the form (69) have also been derived and studied for the dynamics of thin two-layer films [31, 35–37] and of thin films covered by a layer of insoluble surfactant [27]. In the latter case, it is important to employ the surfactant concentration projected onto the substrate plane as the second field and *not* the surfactant concentration on the free surface of the film as it can not be varied independently of the film height. For instance, in the case of [27] only the right choice of the second field results in the correct definition of the density-dependent surface tension and, consequently, the correct linear Marangoni effect in the limit of low surfactant concentration. It should be interesting to consider the case of the surfactant covered film within the here presented formalism to pursue extensions of existing models toward the incorporation of surface viscosity and elasticity.

The symmetric formulation of the kinetic long-wave equations for the film of two-component mixture is valid at arbitrary concentrations of the two components. This allows one to avoid certain problems that literature models encounter at high solute concentrations. For instance, if a solution or suspension with a volatile solvent shall be considered, the presented gradient dynamics equations for conserved fields have to be augmented by evaporation term(s). If the evaporation dynamics is limited by the phase transition (and not by the diffusion in the gas phase), one may add a nonconserved term proportional to $\delta F/\delta h - \mu_{\rm gas}$, where $\mu_{\rm gas}$ is the chemical potential of the gas phase [4, 9]. In the present symmetric formulation, this term naturally contains an osmotic pressure contribution $(\phi g' - g)$ that results in an evaporation that ceases as $\phi \to 1$. Models in the gradient dynamics form for Langmuir–Blodgett transfer and dip-coating processes are reviewed in [51]. There the gradient dynamics equations for conserved fields (69) are augmented not only by terms accounting for evaporation but also by an advection term to model the transfer of material from a bath onto a moving plate. In this context, one should mention that there exist special cases in which systems permanently out of equilibrium may be modeled through adequate adaptations of gradient dynamics models that are, in general, relaxational. For instance, drops on an incline can be described by incorporating a proper long-wave potential energy into the free energy functional.

Finally we mention that the gradient dynamics form offers a thermodynamic point of view onto long-wave hydrodynamic models that brings them into the context of dynamical density functional theories (DDFT) [52, 53] for layers of colloidal fluids because for two-component systems they are of a similar form [43, 54]. Based on the discussion of relations between the diffusive mobility matrices measured with respect to different reference frames as presented in section 5.4 and, in general, the formal similarity of DDFT and thin-film hydrodynamics, it might be possible and worthwhile to develop a more unified view onto these models. That might facilitate the development of models that are based on proper energy functionals as obtained from statistical physics and dissipation functionals combining the various channels of dissipation.

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