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## (IN)COMPRESSIBILITY AND PARAMETER IDENTIFICATION IN PHASE FIELD MODELS FOR CAPILLARY FLOWS

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#### Dedicated to the memory of Professor Aleksandar Bakša.

ABSTRACT. Phase field (diffuse interface) models accommodate diffusive triple line motion with variable contact angle, thus allowing for the no-slip boundary condition without the stress singularities. We consider two commonly used classes of phase field models: the compositionally compressible (CC) model with compressibility limited to the fluid mix within the diffuse interface, and the incompressible (IC) model. First, we show that the CC model applied to fluids with dissimilar mass densities exhibits the computational instability leading to the breakup of the triple line. We provide a qualitative physical explanation of this instability and argue that the compositional compressibility within the diffuse interface is inconsistent with the global incompressible flow. Second, we derive the IC model as a systematic approximation to the CC model, based on a suitable choice of continuum velocity field. Third, we benchmark the IC model against sharp interface theory and experimental kinetics. The triple line kinetics is well represented by the triple line mobility parameter. Finally, we investigate the effects of the bulk phase field diffusional mobility parameter on the kinetics of the wetting process and find that within a wide range of magnitudes the bulk mobility does not affect the flow.

#### 1. Introduction

Flows controlled by capillary forces have long been a subject of interest [10,19, 20], as a fundamental physical problem, as well as related to industrial and natural processes, including: materials joining [25, 41, 42], painting [47] and coating [44], biological phenomena such as super-hydrophilic leafs in plant biology [37], and geology such as molten lava flows [39].

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Sharp interface models applied to capillary flows face two key problems. The first is the singularity of the solutions to fluid dynamics equations with no-slip boundary condition in the vicinity of the triple line [23, 24]. The remedies for this problem have been attempted by allowing a slip over a characteristic length within a sharp interface model [9,15], and even within the phase field models [49], but suffered from physical ambiguities and parameter uncertainties. The second problem is computational treatment of topological discontinuities (breakup and coalescence of domains) which often arise in capillary flows. Two solutions have emerged over the years: smoothed particle hydrodynamics [46] and the phase field (or diffuse interface) models. The latter treats the multiple materials in multiple domains as one material with phases distinguished by the value of the phase field variable. The interface are moved with the flow but locally adjust by diffusive mechanism.

The earliest recorded suggestion that an interface between two fluids is diffuse is probably the one by Poisson [48]. Gibbs [29] considered a similar idea, and van der Waals [57] proposed the first mathematical model. Following the formulations of Cahn and Hilliard [12] and Cahn [11], and the advances in computing power, the diffuse interface or phase field formulation has been widely used for modeling moving interfaces in both solids and fluids. Both types of applications have been recently reviewed; see Chen [16] for solids, and Anderson et al [4] and Kim [36] for fluids. In most applications, the phase field does not model the actual interface dimensions. Instead, the phase field model is viewed as a mathematical tool for computational treatment of changing topology. Its validity is based on its adherence to the corresponding sharp interface model and mapping of the phase field parameters to physical parameters [53, 59].

The phase field model allows for distinction between convective (slip) and diffusive motion of the triple line. While the convective motion is still subject to the no-slip boundary condition, the contact line moves by surface diffusion mechanism, driven by hydrodynamics and energy minimization. The mechanism is supported by molecular dynamics studies [38,56] and molecular kinetic theory [8,52]. Building on the Seppecher's analysis [51], the mathematical formulation of the problem has been developed by Jacqmin [34] and applied, using finite difference method, to analyze contact line dynamics in capillary flows. The Jacqmin's boundary condition was implemented into the finite element framework for incompressible (IC) flow by Yue and Feng [60,61] and Fu et al [27]. The current paper is to our knowledge the first finite element implementation of the Jacqmin's diffusive boundary condition for the compositionally compressible<sup>1</sup> (CC) model.

We consider the diffuse interface between two immiscible fluids, where the question of compositional compressibility of the thin interface layer becomes critical. While the thermodynamic consistency of the CC model [43] weights in its favor, the computational instabilities that arise when fluids have very different mass densities present an obstacle for its application. On the other hand, the IC model is

 $<sup>^{1}</sup>$ We believe that this name is more descriptive than quasi-incompressible used by Lowengrub and Truskinovsky [43].

much simpler, computationally stable and efficient. The assumptions and physical arguments given for the IC model can be less [22] or more rigorous [3]. Nevertheless, intuition dictates that the effect of compressibility in the thin interface layer (which is the main difference between the two models) is probably negligible. In this paper, we establish the mathematical connection between the two models and show that the IC model is the approximation to the thermodynamically rigorous CC model.

The interface between immiscible fluids is represented by a conserved phase field leading to the 4<sup>th</sup> order partial differential equation, known as the Cahn-Hilliard (CH) equation [12]. The problems in this class have been addressed in the past, with a variety of numerical methods, including the finite difference method [13, 14, 34], spectral, pseudo-spectral, and related methods [15, 40]. The drawbacks of such methods are seen in the difficulties in modeling irregular domains, nonlinear and history-dependent problems. The finite element (FE) formulations have been developed within the last decade. The mixed, discontinuous  $(C^0)$  Galerkin formulation has been first applied to a single, uncoupled Cahn-Hilliard equation by Kay and Welford [35]. The Galerkin continuous FE formulation ( $C^1$ ) for coupled Cahn–Hilliard/solid mechanics problem has been developed by Asle Zaeem and Mesarovic [6,7]. The coupling with the Navier-Stokes equations ( $C^0$ ) for the bulk multiphase flow with no solid boundaries has been implemented by Feng [26]. Hua et al [33] and Guo et al [30]. The triple line motion with equilibrium contact angle (instantaneous relaxation) has often been considered [21,28,58,63]. The dynamically variable contact angle with Jacquin's diffusive boundary condition has been implemented by Yue and Feng [60, 61] for the IC model.

The paper is organized as follows. In Section 2, we review the main features of the CC model enhanced with the Jaqmin's [34] diffusive boundary condition (mathematical details are relegated to Appendices A and B). In Section 3, we describe the computational instability of the CC model that arises when the two fluids have widely dissimilar mass densities. The instability is then explained by the simple mechanism whereby small change of volume of the interface requires massive displacement of the surrounding incompressible fluid. The problem can be resolved either by introduction of fluid elasticity, or by abandoning the compositional compressibility altogether. We pursue the latter option in Section 4, where we derive the IC model as a systematic approximation of the CC model. Parameter identification and dimensional analysis are discussed in Section 5. In Section 6, numerical results are compared to theory and experiments, and the effect of the purely computational parameter - the phase field mobility in the bulk, is discussed. The results are summarized in Section 7.

### 2. Compositionally compressible (CC) flow

We consider the isothermal flow of two immiscible fluids. The only mixing occurs in the thin interface layer, where a smooth transition in concentration of the components occurs. The key elements of the compositionally compressible (CC) model are:

(1) Adoption of the barycentric velocity as the continuum velocity field,

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- (2) Mass density as a function of the phase field variable, and,
- (3) The thermodynamic requirement for the dependence of chemical potential on pressure, which implies that the *specific*<sup>2</sup> free energy of a homogeneous fluid can only depend of  $\phi$ , so that the homogeneous free energy density is proportional to the mass density.

Consider an elementary volume V, containing two species<sup>3</sup>, with partial mass densities  $\rho^A$  and  $\rho^B$ , such that their sum is the total mass density  $\rho$ :

$$\rho^A = \frac{M^A}{V}; \quad \rho^B = \frac{M^B}{V}; \quad \rho = \frac{M}{V} = \frac{M^A + M^B}{V} = \rho^A + \rho^B.$$

The components velocities are  $\mathbf{u}_A$  and  $\mathbf{u}_B$ . Definition of the continuum velocity field  $\mathbf{u}(\mathbf{x})$  as the barycentric velocity:

(2.1) 
$$\rho \mathbf{u} = \rho^A \mathbf{u}_A + \rho^B \mathbf{u}_B,$$

preserves the total momentum of the mix and implies the standard mass balance:

(2.2) 
$$\frac{\bar{D}\rho}{Dt} = -\rho\nabla\cdot\mathbf{u},$$

where  $\overline{D}/Dt$  represents the material derivative. The phase variable is the mass fraction of A:

(2.3) 
$$\phi = \frac{\rho^A}{\rho},$$

so that the mass density is a function only of the phase variable (and not of pressure):

(2.4) 
$$\rho = \rho(\phi).$$

The definitions (2.1) and (2.3) imply<sup>4</sup> the diffusion law for the phase variable, with the diffusional flux proportional to the relative velocity of the component A:

(2.5) 
$$\rho \frac{D\phi}{Dt} = -\nabla \cdot \mathbf{q}; \quad \mathbf{q} = \rho^A (\mathbf{u}_A - \mathbf{u}).$$

Further, the functional dependence (2.4) forbids full incompressibility; if any diffusion is to occur, the mass density of a material element must change:

(2.6) 
$$\frac{D\rho}{Dt} = -\rho\nabla \cdot \mathbf{u} = \frac{d\rho}{d\phi}\frac{D\phi}{Dt} = -\frac{1}{\rho}\frac{d\rho}{d\phi}\nabla \cdot \mathbf{q} \neq 0.$$

While the choice of the barycentric velocity preserves the momentum of the mix, it fails to preserve the kinetic energy. Specifically, if the kinetic energy is

 $<sup>^{2}</sup>$ Specific energy = energy per unit mass; energy density = energy per unit volume.

<sup>&</sup>lt;sup>3</sup>Since we consider immiscible fluids, the distinction between species and phase is immaterial.
<sup>4</sup>The fact that the diffusion law (2.5) is the necessary consequence of the choice of the barycentric velocity as the material velocity, does not appear to be acknowledged in the literature. For example, Lowengrub and Truskinovsky [43] introduce (2.5) as an assumption, rather than a proven fact, while Abels [1] introduces a different assumption to prove (2.5). We give the proof of (2.5) in Appendix A.

written as

(2.7) 
$$\bar{\mathcal{K}} = \int_{V} \frac{1}{2} \rho \mathbf{u} \cdot \mathbf{u} dV$$

then the kinetic energy associated with the diffusional flux is neglected. From (2.1) and (2.5), this error is

$$\int_{V} \frac{q^2}{2\rho\phi(1-\phi)} dV.$$

However, this kinetic energy plays a role only in the thin interface layer between the two fluids. Elsewhere, the kinetic energy density in (2.7) is exact. Similarly, compositional compressibility is only relevant in the thin interface region. Elsewhere:

$$\mathbf{q} = \nabla \cdot \mathbf{q} = 0 \quad \Rightarrow \quad \frac{\overline{D}\rho}{Dt} = -\rho \nabla \cdot \mathbf{u} = 0.$$

We consider the following class of two-phase capillary flow problems. The volume of the computational cell V has the boundary  $\partial V$  with the unit outward normal **n**. A part of the boundary, S, is the interface with a rigid solid. The remainder, A, is the computational cell boundary within the fluid, chosen for convenience, and often with the computational efficiency constraint. We take:

$$\partial V = S \cup A.$$

At the solid boundary, we expect no normal diffusional flux. If the boundary A passes through a single phase, the normal diffusional flux vanishes. Finally, if it is necessary to cut the computational domain through the phase field interface, this is typically done so that the boundary is orthogonal to the interface. Since the diffusional flux is also orthogonal to the interface, the normal boundary flux is zero. Thus, we will assume that the normal flux vanishes everywhere along the boundary:

$$\mathbf{n} \cdot \mathbf{q} = 0 \quad \text{on } \partial V.$$

In Appendix B, we give derivation of the governing equations based on the principle of virtual power (PVP). Moreover, we show how the diffusive boundary condition [34] arises naturally from the linear dissipation assumption.

Let  $f(\phi)$  be the composition dependent specific free energy of a homogeneous fluid. It is a double-well potential with minima corresponding to the two phases (Figure 1). Then, the specific free energy for a non-homogeneous fluid, thermodynamically consistent with compositional compressibility, is written in the Cahn– Hilliard form:

$$\omega(\phi, \nabla \phi) = f(\phi) + \frac{1}{2}\kappa(\nabla \phi)^2.$$

The parameter  $\kappa$  and the parameters of the function  $f(\phi)$  (Figure 1) are related to the interface energy - a physical parameter, and to the width of the diffuse interface - a computational parameter, chosen with some latitude. More detailed discussion of model parameters will be given later in connection with the incompressible model.

For shorter writing, we introduce the symmetric-deviatoric gradient operator:

$$\Diamond \mathbf{u} = \mathbf{u} \nabla + \nabla \mathbf{u} - \frac{2}{3} (\nabla \cdot \mathbf{u}) \mathbf{I},$$



FIGURE 1. Free energy density of a homogeneous fluid as function of the phase variable. The relevant parameter is  $\Delta f$ , see discussion in Section 5.

where the dyads:  $(\mathbf{u}\nabla)_{ij} = \partial u_i / \partial x_j$ ;  $(\nabla \mathbf{u})_{ij} = \partial u_j / \partial x_i$ . The viscous deviatoric stress is then written as

$$oldsymbol{ au} = (\phi, 
abla \mathbf{u}) = \mu(\phi) \Diamond \mathbf{u}$$

Like mass density in (2.4), the viscosity  $\mu(\phi)$  and the solid-fluid interface energy  $\gamma(\phi)$  are interpolated between the values corresponding to the two fluids.

The governing equations, derived in Appendix B, consist of the Navier-Stokes equations (NS) modified to include the capillary stresses<sup>5</sup>, the compositional compressibility condition (CC), and the Cahn–Hilliard 4<sup>th</sup> order diffusion equation, which we write here as two 2<sup>nd</sup> order differential equations (CH1 and CH2) for the phase variable and the chemical potential M:

NS: 
$$\rho \frac{D\mathbf{u}}{Dt} = \rho \mathbf{g} + \nabla \cdot (\mu \Diamond \mathbf{u} - \kappa \rho \nabla \phi \nabla \phi - \pi \mathbf{I});$$
  
CC:  $\nabla \cdot \mathbf{u} = -\frac{1}{\rho^2} \frac{d\rho}{d\phi} \nabla \cdot (B \nabla M);$ 

(2.8)

CH1: 
$$\rho \frac{D \cdot \varphi}{Dt} = \nabla \cdot (B \nabla M);$$
  
CH2:  $M = \frac{df}{d\phi} - \frac{1}{\rho} \nabla \cdot (\kappa \rho \nabla \phi) - \frac{\pi}{\rho^2} \frac{d\rho}{d\phi}.$ 

 $\bar{D}\phi$ 

The field  $\pi(\mathbf{x})$  is identified with the non-capillary pressure. It arises as the Lagrange multiplier associated with the enforcement of the CC condition. The

<sup>&</sup>lt;sup>5</sup>The NS equation differs from the original Lowengrub and Truskinovsky [43] result in the treatment of volumetric dissipation. Note that compositional compressibility is not the standard (pressure) compressibility: there is no volume change in response to pressure, only in response to composition change. Moreover, the CC condition (2.6) implies that flux divergence  $\nabla \cdot \mathbf{q}$  and the velocity divergence  $\nabla \cdot \mathbf{u}$  are not independent rates. The equations (2.8) and (2.9) have been derived using the principle of virtual power (Appendix B), which requires careful definition of work (power) conjugate fields, so that the viscous dissipation is strictly deviatoric, while the diffusional dissipation is strictly volumetric. It is, of course, possible to consider volumetric dissipation (viscosity) as a result of some other mechanisms independent of diffusion [53].

diffusive boundary condition on the solid surface, derived in the Appendix B, is

(2.9) 
$$\frac{D\phi}{Dt} = -b\left(\kappa\rho\mathbf{n}\cdot\nabla\phi + \frac{d\gamma}{d\phi}\right) \quad \text{on } S.$$

Such boundary condition has been proposed by Jacqmin [34] motivated by the equilibrium contact angle condition. In the limit of sharp interface model, the vanishing of the term in parentheses is equivalent to the Young's equation. During the capillary flow, the boundary condition (2.9) allows for a variable dynamic contact angle [54]. The driving force for surface diffusion enabled triple line motion is local and is proportional to the deviation of the dynamic contact angle from the equilibrium contact angle. In Appendix B, we show that this boundary condition arises as a direct consequence of the linear non-negative dissipation on the solid boundary (i.e., dissipation accompanying the motion of the triple line). In our previous communication [27], we have shown that this assumption is consistent with experimental measurements of dynamic contact angle.

#### 3. Effect of interface layer compressibility on the large scale flow

When applied to the combination of fluids with vastly different mass densities (i.e., a liquid and a gas), the above equations exhibit computational instabilities at the triple line. The diffuse interface spreads in an unstable manner, as illustrated in Figure 2. The initial acceleration of the triple line is quickly followed by an unstable spreading of the interface in the triple line region, which eventually leads to computational failure. The instability is not limited to the triple line region. Prior to the triple line spreading, the shadow band of velocity divergence tracing the interface band at the distance comparable to the interface thickness (Figure 2(b)) appears. Similar shadow bands have been observed in multiphase flows without



FIGURE 2. Instability of the computational CC model with ratio of mass densities of liquid and gas of 811. Capillary rise between parallel walls. (a) Initial contours of the phase field. (b) Contours of the velocity divergence prior to computational failure. (c) Magnified instability region circled in (b). (d) Line contours corresponding to (c).

capillary walls [30]. We have performed calculations for a range of mesh densities and time steps, always leading to essentially identical results shown in Figure 2.

In investigating this instability our first suspicion was that the presence of  $\rho$  in (2.9) which varies by few orders of magnitude across the interface is the cause of instability. An alternative to the above formulation where the diffusive boundary condition is independent of mass density can be readily obtained by assuming a different specific energy<sup>6</sup>:

$$\omega(\phi, \nabla \phi) = f(\phi) + \frac{1}{2\rho} \kappa (\nabla \phi)^2.$$

The alternative CC model has somewhat different governing equations. The CC and CH1 equations remain the same, while in the NS equation the capillary stresses are now independent of mass density. The CH2 equation is substantially different:

NS: 
$$\rho(\phi) \frac{D\mathbf{u}}{Dt} = \rho \mathbf{g} + \nabla \cdot (\mu(\phi) \Diamond \mathbf{u} - \kappa \nabla \phi \nabla \phi - \pi \mathbf{I});$$
  
CH2: 
$$M = \frac{df}{d\phi} - \frac{\kappa}{2\rho^2} \frac{d\rho}{d\phi} (\nabla \phi)^2 - \frac{\kappa}{\rho} \nabla^2 \phi - \frac{\pi}{\rho^2} \frac{d\rho}{d\phi},$$

and the diffusive boundary condition is now independent of mass density:

$$\frac{D\phi}{Dt} = -b\Big(\kappa \mathbf{n}\cdot\nabla\phi + \frac{d\gamma}{d\phi}\Big) \quad \text{on } S.$$

The alternative formulation exhibits the same computational instability as the original one (Figure 2). The causes of this instability are not well understood at present. It bears emphasis that the existence theorems are only available for the IC model [2]. Here, we propose a physical explanation for this instability based on the analysis of the motion of the surrounding incompressible fluid caused by the compositional compressibility of the interface layer.

Consider a problem similar to the one studied by Guo et al [30] and illustrated in Figure 3, where an initially ellipsoidal drop of a dense incompressible fluid changes shape and becomes spherical. The computational domain includes the large volume of low density incompressible fluid and the volume of the CC interface with some average mass density. If the interface retains its original thickness, its total volume has decreased, so that a large volume of the surrounding incompressible fluid must be moved inwards<sup>7</sup>.

This is clearly not the physical reality. The local change of mass density will not be compensated by global motion of a large volume but rather by some local changes. On the level of the computational model, the solution will be prevented from evolving in this way, either by huge inertia of the surrounding fluid, or by the

<sup>&</sup>lt;sup>6</sup>Lowengrub and Truskinovsky [43] thermodynamic analysis is strictly applicable to the homogeneous fluid where the free energy density must have the form  $\rho f(\phi)$ . Nothing specific can be said about the Cahn–Hilliard non-homogeneous free energy density. It may equally be described with terms  $(\nabla \phi)^2$  or  $\rho(\nabla \phi)^2$ . The physical meaning and dimensions of the coefficient  $\kappa$  are, of course, different in the two cases.

 $<sup>^{7}</sup>$ This shrinking is characteristic of the CC model and is not related to the drop shrinking in the IC model analyzed by Yue et al [62].



FIGURE 3. Ellipsoidal interface evolves into a spherical one and consequently changes its volume. If the rest of the fluid is incompressible, such volume change requires large-scale motion of the surrounding fluid (indicated by arrows) and shrinking/expansion of the computational cell boundary.

boundary conditions (consider rigid boundaries or periodic boundary conditions). How can a local accommodation be accomplished?

First, the thickness of the interface may increase, so that the total volume of the interface remains constant. The large diffusional mobility B (see Section 5) ensures that the shape of the interface is determined by the equilibrium Cahn–Hilliard equation:  $\nabla^2 M \approx 0$ . This does not allow for significant thickening of the interface, so that this option may not be available. Second, the interface fluid may exhibit elasticity so that the elastic volume change counteracts the compositional volume change. This option is not available simply because fluid elasticity is not included in the model. Finally, the numerical model may locally compensate for the local volume change of the interface by changing the mass density in the close neighborhood, hence the ghost (shadow) velocity divergence. It is not clear whether such solution is a valid solution to the mathematical problem, or it emerges only as a numerical solution that minimizes the error norm.

While the CC formulation is locally thermodynamically consistent, there appears to be a global inconsistency between the compositional compressibility of the interface layer and incompressibility of the rest of the fluid. This can probably be resolved by introducing elasticity into the interface layer, but with a high mathematical and computational cost [55]. On the other hand, the IC model, previously considered as an ad hoc simple model, is derived below as a systematic approximation to the CC model. Such derivation allows (in principle) error estimates, although the discussion in this paper is limited to qualitative arguments about the size of the error.

#### 4. Incompressible flow as an approximation to CC flow

The functional dependence  $\rho(\phi)$  is a necessary component of a phase field model for materials with different mass densities. This alone disallows the exact incompressibility  $(\bar{D}\phi/\bar{D}t \neq 0 \Rightarrow \bar{D}\rho/\bar{D}t \neq 0)$ . Thus, an incompressible model can only be devised as an approximation to the compositionally compressible model. Consider  $\rho(\phi)$  such that

$$\frac{1}{\rho} = \frac{\phi}{\rho_{0A}} + \frac{1-\phi}{\rho_{0B}} \qquad \phi \in [0,1]$$

where  $\rho_{0A/B}$  are the densities of pure components. Then,

(4.1) 
$$\frac{1}{\rho^2} \frac{d\rho}{d\phi} = \frac{\rho_{0A} - \rho_{0B}}{\rho_{0A}\rho_{0B}} = \alpha = \text{const.}$$

Now we consider alternative continuum velocity field

$$\mathbf{v}(\mathbf{x}) = \mathbf{u}(\mathbf{x}) - \alpha \mathbf{q}(\mathbf{x}),$$

which, from (2.6) and (4.1), is divergence-free:

(4.2) 
$$\nabla \cdot \mathbf{v} = 0.$$

Note that, outside the thin interface region, the new velocity is identical to the old one:

$$\mathbf{v}(\mathbf{x}) = \mathbf{u}(\mathbf{x}) \qquad \text{for } \mathbf{x} \in V \setminus I$$

where V is the domain with size  $L^3$ , and I is the interface domain with size  $L^2h$ . The interface thickness h must be small compared to the smallest radius of interface expected curvature  $R_{\min}$ , which is typically small compared to the domain size:

$$(4.3) h \ll R_{\min} \ll L.$$

If instead of the barycentric velocity  $\mathbf{u}$ , we take  $\mathbf{v}$  to be the material velocity of the continuum, the error is only in the momentum and kinetic energy of the thin interface layer. In other words, only the inertia of the thin interface layer is affected. This appears to be a good approximation.

The new material velocity implies the new material derivative. For a scalar field  $Y(\mathbf{x})$  advected with the velocity field  $\mathbf{v}(\mathbf{x})$ :

(4.4) 
$$\frac{DY}{Dt} = \frac{\partial Y}{\partial t} + \mathbf{v} \cdot \nabla Y = \frac{\bar{D}Y}{Dt} + (\mathbf{v} - \mathbf{u}) \cdot \nabla Y.$$

We introduce the new phase field variable c, based on the linear interpolation of mass density:

(4.5) 
$$\rho = c\rho_{0A} + (1-c)\rho_{0B} \qquad c \in [0,1].$$

Then, it is easily shown (Appendix C) that the diffusion equation (2.5) can be replaced by

$$\frac{Dc}{Dt} = -\nabla \cdot \mathbf{J},$$

where the new flux vector is related to the old one as

$$\mathbf{J} = \frac{\rho}{\rho_{0A}\rho_{0B}}\mathbf{q}.$$

To complete the structure of the new (approximate) continuum, the mass density  $\rho$  should be convected with the new velocity **v**:

(4.6) 
$$\frac{D\rho}{Dt} = -\rho\nabla \cdot \mathbf{v} = 0.$$

Clearly, this new continuum has an intrinsic inconsistency. The dependence (4.5) is in direct contradiction to (4.6):

$$\frac{D\rho}{Dt} = \frac{d\rho}{dc}\frac{Dc}{Dt} \neq 0.$$

One way to formulate a mathematically consistent model is to:

- (a) Enforce the incompressibility condition (4.2) instead of the mass balance (4.6), and,
- (b) Assume that the power expanded on mass density change  $D\rho/Dt$  vanishes.

Then, the function  $\rho(c)$  appears in the governing equations as a parameter function. Such procedure produces the IC model in the form of the original model H [31, 32]. The derivation is given in Appendix D. It proceeds along the same steps as the one for the CC model (Appendix B) including: linear dissipation, energy balance and the principle of virtual power (PVP). An interesting technical point is the split of the rate of change of potential energy into the "chemical" and "densification" rates (D.4), where the latter is neglected following the discussion above.

For an IC fluid, the potential energy density need not depend on the mass density as in the CC case. The phase field form of the energy density is

$$\omega(c, \nabla c) = f(c) + \frac{1}{2}\kappa(\nabla c)^2$$

The remainder of the procedure is shown in Appendix D. The final governing equations take the following form

(4.7)  
NS: 
$$\rho \frac{D\mathbf{v}}{Dt} = \rho \mathbf{g} + \nabla \cdot \left[\mu(\mathbf{v}\nabla + \nabla \mathbf{v}) - \kappa \nabla c \nabla c\right] - \nabla \pi$$
  
IC:  $\nabla \cdot \mathbf{v} = 0,$   
CH1:  $\frac{Dc}{Dt} = \nabla \cdot (B\nabla\mathcal{M}),$   
CH2:  $\mathcal{M} = \frac{df}{dc} - \kappa \nabla^2 c.$ 

As before,  $\pi(\mathbf{x})$  is the non-capillary pressure, which arises as the Lagrange multiplier associated with the enforcement of the IC condition, so that the total pressure is given as

$$p = \pi + \frac{1}{3}\kappa(\nabla\phi)^2.$$

The diffusive boundary conditions ensuring a non-negative dissipation on the solid boundary is

(4.8) 
$$\frac{Dc}{Dt} = -b\left(\kappa \mathbf{n} \cdot \nabla c + \frac{d\gamma}{dc}\right) \qquad b > 0, \quad \text{on } S.$$

This completes the derivation of the IC model as a systematic approximation to the CC model. The two key steps are:

(1) Definition of the divergence-free velocity field which is equal to the barycentric velocity outside the thin interface region, and,

(2) The assumption of incompressibility allowing: adoption of the divergencefree velocity as the continuum velocity, and, energy density independent of mass density.

An alternative incompressible model based on volume averaged velocity field is given by Abels et al [3]. The present IC model has several versions, which are *mathematically equivalent*, but produce numerical differences. The main differences are in the order of derivatives of the main variables. This has an effect on the finite element computations, particularly if low order interpolation is used. One alternative is obtained by noting that

(4.9) 
$$\nabla \cdot (-\kappa \nabla c \nabla c) = \mathcal{M} \nabla c - \nabla \omega.$$

Next, we note that division of pressure into capillary and non-capillary parts is arbitrary and replace the variable  $\pi$  with

(4.10) 
$$\tilde{\pi} = \pi + \omega.$$

This yields the alternative NS equation in the form:

where the total pressure is now given as

$$p = \tilde{\pi} - f(c) - \frac{1}{6}\kappa(\nabla c)^2.$$

#### 5. Physical and computational parameter

By physical parameters, we mean the parameters in the standard fluid dynamics with sharp interfaces characterized by Gibbs [29] excess quantities. In addition to mass densities and viscosities of two fluids,  $\rho_0^{A/B}$  and  $\mu_0^{A/B}$ , these include the interface energies between the two fluids  $\Gamma$ , and between the solid and the two fluids:  $\gamma_{Bsol}$  and  $\gamma_{Asol}$ .

The interface width h is a computational parameter, chosen so that it is significantly smaller that the smallest expected radius of curvature. The equilibrium solution to the problem of flat infinite interface between fluids A and B gives the one-to-one relationship between  $(\Gamma, h)$  and the phase field parameters  $(\kappa, \Delta f)$ :

$$\kappa = \frac{3}{2}\Gamma h, \quad \Delta f = \frac{3}{4}\Gamma/h.$$

The interface width is expected to remain at all times very close to the equilibrium value [5, 6]. It is usually assumed that the exact shape of the free energy function has no measurable effect on either equilibrium or kinetics of the flow. The only relevant parameters are the relative values of minima and maxima. In this case (Figure 1), the only relevant parameter is  $\Delta f$ .

For the process driven by the capillary forces, the three characteristic times associated with the governing equations (4.7) and (4.8) are determined by dimensional analysis: the triple line mobility time  $t_b$ , the bulk mobility time  $t_B$ , and the viscosity time  $t_{\mu}$ :

(5.1) 
$$t_b = \frac{2}{3b\Gamma}, \quad t_B = \frac{2h^3}{3B\Gamma}, \quad t_\mu = \frac{2\mu_A^0 h}{3\Gamma}.$$

For immiscible fluids, the bulk mobility B has no physical significance; it is a computational parameter that enables diffusional rearrangements within the phase field interface layer. It should be large enough not to obstruct the motion, that is, the characteristic time for bulk mobility should be shorter than other two characteristic times:

$$t_B \leqslant t_b, \quad t_B \leqslant t_\mu.$$

The triple line moves by surface diffusion (uncorrelated motion of atoms) as opposed to slipping (correlated motion of atoms). The triple line mobility b determines the dissipation in the surface diffusion process. It could be, in principle, determined from molecular dynamics (MD) simulations, or from the combination of molecular statics (energy landscape) simulations and activation rate theory. The most practical solution appears to be matching of experimental kinetics in the regime where the capillary forces dominate [27].

#### 6. Computational results

6.1. Numerical method, boundary and initial conditions. The computations are performed with quadratic Lagrange interpolation for the velocity  $\mathbf{v}$ , the phase field variable c and the chemical potential  $\mathcal{M}$ . Linear Lagrange interpolation is used for the non-capillary pressure  $\tilde{\pi}$ . The alternative model (4.9) is used, with the Navier–Stokes equation (4.11) and the remaining governing equations given in (4.7). The commercial FE software COMSOL Multiphysics [17] with the parallel sparse direct solver is used. The time stepping is based on the backward differentiation formula. The initial conditions are common to all runs. The initial velocity and the diffusion potential are identically zero:

$$\mathbf{v}(\mathbf{x},0) = 0, \quad \mathcal{M}(\mathbf{x},0) = 0.$$

The initial configuration is always such that the denser fluid is on the bottom, so that the equilibrium solution (obtained from  $\mathcal{M} = 0$  and (4.7) CH2) is

$$c(x, y, 0) = \frac{1}{2} \left( 1 - \tanh \frac{2y}{h} \right).$$

The initial non-capillary pressure must be consistent with (4.10) and equilibrium under gravity:

(6.1) 
$$\tilde{\pi}(x,y,0) = \tilde{\pi}_0(x,y) = -g \int_{y_0}^y \rho(c(y)) dy, \quad \tilde{\pi}_0(x,0) = 0.$$

The types of boundary conditions used for different problems are:

- Wetting wall boundary condition: On the fluid-solid interface, no slip/penetration boundary condition for velocity ( $\mathbf{v} = 0$ ) and the diffusive boundary condition (4.8).
- Inlet and outlet boundary conditions apply at the ends of the computational cell in fluids. Both are characterized by the equilibrium pressure distribution (6.1) and the condition that the phase field interface is orthogonal to the boundary:

$$\mathbf{n} \cdot \nabla c = 0.$$

The inlet boundary condition requires the vanishing viscous stresses [64], while the outlet boundary condition [50] disallows normal gradient of velocity. Moreover, we assume the equilibrium pressure distribution at both fluid boundaries:

Inlet:  $\mathbf{n} \cdot [\mu(\nabla \mathbf{v} + \mathbf{v}\nabla)] = 0, \quad \tilde{\pi} = \tilde{\pi}_0(y),$ Outlet:  $\mathbf{n} \cdot \nabla \mathbf{v} = 0, \quad \tilde{\pi} = \tilde{\pi}_0(y)$ 

The fluid (inlet/outlet) boundaries are assumed to be sufficiently removed from the main region of interest. We have verified that the liquid coming through the inlet boundary acquires the expected laminar flow characteristics at short distance from the boundary.

• On all boundaries, we require vanishing normal diffusional flux:

 $\mathbf{n} \cdot \nabla \mathcal{M} = \mathbf{0}$ 

The justification is obvious for the solid boundary. On the fluid boundary, (6.3) is consistent with normality of the phase field interface (6.2) (diffusive flux is away orthogonal to the phase field level lines). In other words, we require that all matter is transported into the computational cell by flow  $(\mathbf{v})$ , and none by diffusion  $(\mathbf{q})$ .

For various runs, the macroscopic length scale L is estimated from equilibrium solutions. This also represents the order of magnitude of the interface radius of curvature. Then, the interface width h is selected to be  $h \ll L$ . In the runs presented below, the interface width varies between 0.09L for the meniscus between parallel plates, and 0.07L for the T-joint case. The adaptive mesh consisting of  $2^{nd}$ order triangular elements was finest at the interface. The element size is about 0.1h in all runs. The adaptive mesh density is determined based on the norm of the gradient of the phase field variable (COMSOL 2015). An example of mesh evolution is shown in the Figure 7 below.

**6.2. Equilibrium.** To benchmark our capillary flow computational formulation with IC flow, we consider the simple 2D geometry of the capillary rise between parallel plates. The physical parameters are shown in Table 1. The computational results are compared to the analytic solution for the sharp interface model. The computational interface shape matches perfectly the analytical shape (Figure 4(b)). Moreover, the pressure jump at the interface with curvature 1/R,

$$\Delta p = \Gamma/R,$$

is accurately represented by the computational phase field model (Figure 4(c)). The negative pressure represents interface tension [18].

**6.3. Effect of the phase field bulk diffusion mobility.** We investigate the effect of the bulk mobility parameter B on the diffuse interface kinetics. The triple line mobility b is obtained from experiments. Details of the extraction procedure are discussed in the next subsection, as well as in Fu et al [27]. The physical parameters (Table 1) and the selected interface width determine the physical characteristic times in (5.1), such that

$$\frac{t_b}{t_\mu} \approx \frac{2}{3} \times 10^3.$$

Parameter	Description	Value
$ ho_{ m Liquid}$	Liquid density	$960  [kg/m^3]$
$ ho_{ m Gas}$	Gas density	$1.184 \; [kg/m^3]$
$\mu_{ m Liquid}$	Liquid viscosity	0.0096 [Pa.s]
$\mu_{\rm Gas}$	Gas viscosity	$1.849 \times 10^{-5}$ [Pa.s]
Γ	Gas-liquid interface energy	$0.02089 \ [J/m^2]$
$ heta_{ m Eq}$	Equilibrium angle	30 [degree]
$L_{\text{Parallel plates}}$	Equilibrium meniscus height for parallel plates	$1.084851 \times 10^{-3} \text{ [m]}$
$L_{\mathrm{T-joint}}$	Equilibrium meniscus height for T-joint	$1.489358 \times 10^{-3}$ [m]

TABLE 1. Physical parameters (Liquid: Silicone oil, Gas: Air)



FIGURE 4. Numerical and analytical solutions of the capillary rise between parallel plates in equilibrium condition. The distance between the plates is 5 mm. (a) Phase field contours. (b) Meniscus shape defined as the line c = 1/2. (c) Pressure variation across the interface in the centerline x = 0.

Thus, the triple line mobility is the dominant physical process. Therefore, we investigate the effect of the relative magnitude of the bulk mobility B, characterized by  $t_B$  (5.1). The results are shown in Figure 5. In the early stages the kinetics are practically indistinguishable for 4 orders of magnitude change in B. The differences appear at later stages, closer to the equilibrium solution.

**6.4. Computational and experimental kinetics.** To benchmark the computational kinetics against the experimental one, we consider the T-joint experimental configuration shown in Figure 6 [27]. The fluid (Silicone oil) rests on the horizontal glass plate. The vertical glass plate is brought gradually into contact and the capillary rise follows. Computational results for one-half of the symmetric configuration are shown in Figure 7, together with the adaptive mesh.

In the early stages of this experiment, the triple line surges rapidly. Only a small quantity of liquid is moved initially, so that capillary forces dominate over viscous and inertial forces. We fit the triple line mobility to the initial tangent to



FIGURE 5. The effect of the bulk mobility on the kinetics of the interface in capillary rise between two parallel plates.  $t_{\mu} = 3.1 \times 10^{-5} s$ ;  $t_b = 2.0 \times 10^{-2} s$ .



FIGURE 6. Schematic of the T-joint configuration in experiment setup. Before (a) and after (b) the formation of capillary meniscus.

the triple line position history, and benchmark the results against the remainder of the experiments. The results are illustrated in Figure 8. The computational results match the experimental measurements very closely except in the final stages where the computational model underestimates the triple line velocity. Interestingly, the experimental and computational kinetics for water-air-glass system, which we reported earlier [27, Figure 16b], exhibit much better match in the later stages of the wetting process, including the final equilibrium. The nearly perfect match extends to the predicted and measured dynamic contact angle [27, Figure 17]. We speculate that the discrepancy between experimental and computational kinetics in the final stages of the wetting process observed in Figure 8 is the result of the polymeric nature of Silicone oil. Polymeric fluids often exhibit slip at the solid wall under various flow condition (e.g., Migler et al [45]), which may accelerate the triple line.



FIGURE 7. The evolution of the Silicone oil meniscus for the Tjoint formation at times t = 0 s, 1 s, and 30 s. Contour plots of the phase field (left) and the corresponding adaptive meshes (right).



FIGURE 8. Triple line motion history: computational prediction and experimental data. T-joint, Silicone oil and glass. Only the initial slope is fitted to get the triple line mobility parameter, b. (a) Linear scale. (b) Log-log scale. (Fu et al [27])

### 7. Summary

To develop a reliable computational model for capillary flows, we consider two types of phase field models, the compositionally compressible (CC) and the incompressible (IC) model. The motion of the triple line is assumed to take place by diffusion of fluid atoms on the solid surface. The diffusive boundary condition [34] is implemented into the finite element framework for both models.

The thermodynamically consistent CC model exhibits computational instability, initiated by appearance of ghost velocity divergence at some distance from the phase field interface, and further exacerbated by spreading of the triple line. The mathematical nature of this instability is not well understood at present and investigation of existence and uniqueness of solutions for the CC model is suggested for future research. Nevertheless, the physical explanation can be constructed based on the observation that a change of mass density in a small part of the computational domain requires movement of a large mass of surrounding incompressible (pure) phase. This problem does not appear when compositional compressibility of the fluid mix is abandoned and the fluids everywhere are considered fully incompressible.

The IC model was derived as approximation to the CC model. The key to the approximation is the alternative definition of the continuum velocity field, such that the new velocity field has vanishing divergence and matches the old velocity outside the interface layer.

A detailed benchmarking of the IC model is performed against the analytical solutions to the sharp interface problem and against experimental kinetics. The choice of physical and computational parameters is discussed. It is shown that the choice of the bulk diffusional mobility has little effect on the results. We find that the IC model very accurately represents both the capillary equilibrium and the capillary flow kinetics.

# Appendix A. Phase field diffusion as a consequence of the barycentric continuum velocity

The material rate of change of  $\rho^A$  can be written in two ways. From (2.3) and (2.4):

(A.1) 
$$\frac{\bar{D}\rho^A}{Dt} = \rho \frac{\bar{D}\phi}{Dt} + \phi \frac{\bar{D}\rho}{Dt}$$

On the other hand, using the balance for  $\rho^A$  and the total mass balance (2.2):

(A.2) 
$$\frac{\bar{D}\rho^{A}}{Dt} = \frac{\partial\rho^{A}}{\partial t} + \mathbf{u} \cdot \nabla\rho^{A} = -\nabla \cdot (\rho^{A}\mathbf{u}_{A}) + \mathbf{u} \cdot \nabla\rho^{A}$$
$$= -\nabla \cdot (\rho^{A}(\mathbf{u}_{A} - \mathbf{u})) - \rho^{A}\nabla \cdot \mathbf{u} = -\nabla \cdot (\rho^{A}(\mathbf{u}_{A} - \mathbf{u})) + \frac{\rho^{A}}{\rho}\frac{\bar{D}\rho}{Dt}.$$

Equating (A.1) and (A.2) yields:

(A.3) 
$$\rho \frac{D\phi}{Dt} = -\nabla \cdot \mathbf{q}, \quad \mathbf{q} = \rho^A (\mathbf{u}_A - \mathbf{u}).$$

= /

Thus, the diffusion law (A.3) is the direct consequence of:

- (i) the choice of the barycentric velocity as the material velocity, and,
- (ii) the functional dependence  $\rho(\phi)$ .

#### Appendix B. Energy balance and PVP for the CC model

The total potential energy is

$$\mathcal{P} = \int_{V} \rho[\omega(\phi, \nabla \phi) - \psi(\mathbf{x})] dV + \int_{\partial V} \gamma(\phi) d\partial V,$$

where  $\rho\psi(\mathbf{x})$  is the gravitational potential. The material rate of potential energy is:

(B.1) 
$$\frac{\bar{D}\mathcal{P}}{Dt} = \int_{V} \rho \Big\{ \frac{\partial \omega}{\partial \phi} \frac{\bar{D}\phi}{Dt} + \frac{\partial \omega}{\partial \nabla \phi} \cdot \frac{\bar{D}\nabla \phi}{Dt} - \nabla \psi \cdot \mathbf{u} \Big\} dV + \int_{S} \frac{d\gamma}{d\phi} \frac{\bar{D}\phi}{Dt} d\partial V.$$

The phase field variable is advected with the flow, so that

(B.2) 
$$\frac{\bar{D}\nabla\phi}{Dt} = \frac{\partial\nabla\phi}{\partial t} + \mathbf{u}\cdot\nabla\nabla\phi = \nabla\frac{\partial\phi}{\partial t} + \nabla(\mathbf{u}\cdot\nabla\phi) - \nabla\phi\cdot(\mathbf{u}\nabla) = \nabla\frac{\bar{D}\phi}{Dt} - \nabla\phi\cdot(\mathbf{u}\nabla).$$

Upon substituting (B.2) into (B.1), and after standard manipulation, we obtain

$$\frac{\bar{D}\mathcal{P}}{Dt} = \int_{V} \left\{ -\kappa \rho (\nabla \phi \nabla \phi) : (\mathbf{u}\nabla) - \rho \nabla \psi \cdot \mathbf{u} + \rho M_{0} \frac{\bar{D}\phi}{Dt} \right\} dV + \int_{S} \chi_{0} \frac{\bar{D}\phi}{Dt} d\partial V,$$

where

(B.3) 
$$M_0 = \frac{df}{d\phi} - \frac{1}{\rho} \nabla \cdot (\kappa \rho \nabla \phi), \quad \chi_0 = \kappa \rho \mathbf{n} \cdot \nabla \phi + \frac{d\gamma}{d\phi}.$$

Dissipation in the phase field fluid arises from viscosity and diffusional flux. Viscous dissipation density is the work rate of viscous stresses, with phase-dependent viscosity  $\mu(\phi)$ . The viscous stress tensor  $\tau$  is symmetric and deviatoric (traceless) and will therefore expand no power on volumetric and skew-symmetric portions of the velocity gradient:

$$\boldsymbol{\tau} = 2\mu(\phi) \left[\frac{1}{2}(\mathbf{u}\nabla + \nabla\mathbf{u}) - \frac{1}{3}(\nabla\cdot\mathbf{u})\mathbf{I}\right] = \mu(\phi) \Diamond \mathbf{u}$$

Diffusional dissipation in the bulk is expressed as the power expanded the rate of change of the phase. With the vanishing normal flux on the boundary:

(B.4) 
$$-\int_{V} \rho M \frac{\bar{D}\phi}{Dt} dV = \int_{V} M \nabla \cdot \mathbf{q} dV = -\int_{V} (\nabla M) \cdot \mathbf{q} dV$$

The motion of the triple line along the solid boundary is also dissipative. We assume the form analogous to (B.4):

$$\int_{\partial V} \chi \frac{\bar{D}\phi}{Dt} d\partial V, \quad \chi = 0 \text{ on } A.$$

For isothermal processes, the  $2^{nd}$  law of thermodynamics requires a non-negative total dissipation rate:

$$\mathcal{D} = \int_{V} \left[ \boldsymbol{\tau} : (\mathbf{u}\nabla) - \rho M \frac{\bar{D}\phi}{Dt} \right] dV + \int_{\partial V} \chi \frac{\bar{D}\phi}{Dt} d\partial V \ge 0,$$

which is satisfied if

(B.5) 
$$\mathbf{q} = -B\nabla M$$
,  $(B > 0)$  in  $V$ ,  $\frac{D\phi}{Dt} = b\chi$ ,  $(b > 0)$  on  $S$ .

The energy balance is then written as

$$\int_{\partial V} \mathbf{t} \cdot \mathbf{u} d\partial V = \frac{\bar{D}\mathcal{P}}{Dt} + \frac{\bar{D}\mathcal{K}}{Dt} + \mathcal{D},$$
$$\frac{\bar{D}\mathcal{K}}{Dt} = \int_{V} \rho \frac{\bar{D}\mathbf{u}}{Dt} \cdot \mathbf{u} dV.$$

Upon substitution of all the components:

(B.6) 
$$\int_{V} \left( \rho \nabla \psi - \rho \frac{D \mathbf{u}}{D t} \right) \cdot \mathbf{u} dV + \int_{\partial V} \mathbf{t} \cdot \mathbf{u} d\partial V$$
$$= \int_{V} \left\{ [\boldsymbol{\tau} - \kappa \rho (\nabla \phi \nabla \phi] : (\mathbf{u} \nabla) - \rho (M - M_0) \frac{\bar{D} \phi}{D t} \right\} dV$$
$$+ \int_{S} (\chi + \chi_0) \frac{\bar{D} \phi}{D t} d\partial V.$$

Upon interpreting the inertial forces as external body forces, the left-hand side of (B.6) represents power expenditure of external forces on  $\mathbf{u}$ , while the righthand side represents power expenditure of generalized internal forces on  $\mathbf{u}\nabla$  and  $\bar{D}\phi/Dt$ . Consider small variations  $\delta \mathbf{u}$  and  $\delta(\bar{D}\phi/Dt)$ . The statement of PVP can be formulated as follows: The power of external forces expanded on virtual velocities and fluxes equals the power of internal generalized forces (stresses) on the virtual internal kinematic gradients (deformation rates). Formally, the limit when variations approach zero is taken to preserve only the first order infinitesimals. Otherwise, the variations are arbitrary except for the requirement that they be kinematically allowable, i.e., vanish wherever an essential boundary condition is prescribed. The compositional compressibility constraint is introduced with the Lagrange multiplier  $\pi$ :

$$\int_{V} \pi \Big( \nabla \cdot \delta \mathbf{u} + \frac{\rho'}{\rho} \delta \frac{\bar{D}\phi}{Dt} \Big) dV = 0,$$

The statement of the PVP is:

$$\begin{split} \int_{V} \left( \rho \mathbf{g} - \rho \frac{\bar{D} \mathbf{u}}{Dt} \right) \delta \mathbf{u} dV &+ \int_{\partial V} \mathbf{t} \cdot \delta \mathbf{u} d\partial V \\ &= \int_{V} \left\{ \mathbf{\Sigma} : (\delta \mathbf{u} \nabla) - \rho \left( M - M_{0} + \frac{\pi}{\rho^{2}} \frac{d\rho}{d\phi} \right) \delta \frac{\bar{D} \phi}{Dt} \right\} dV \\ &+ \int_{S} (\chi + \chi_{0}) \delta \frac{\bar{D} \phi}{Dt} d\partial V. \end{split}$$

where  $\Sigma = \tau - \kappa \rho \nabla \phi \nabla \phi - \pi \mathbf{I}$ , and  $\mathbf{g} = \nabla \psi$ . This yields two independent variational statements:

(B.7) 
$$\int_{V} \left( \rho \frac{D\mathbf{u}}{Dt} - \rho \mathbf{g} - \nabla \cdot \mathbf{\Sigma} \right) \cdot \delta \mathbf{u} dV = \int_{\partial V} (\mathbf{t} - \mathbf{n} \cdot \mathbf{\Sigma}) \cdot \delta \mathbf{u} d\partial V,$$
$$\int_{V} \rho \left( M - M_0 + \frac{\pi}{\rho^2} \frac{d\rho}{d\phi} \right) \delta \frac{\bar{D}\phi}{Dt} dV = \int_{S} (\chi + \chi_0) \delta \frac{\bar{D}\phi}{Dt} d\partial V.$$

The  $1^{\rm st}$  variational statement yields the Cauchy equation of motion with standard boundary conditions:

$$\rho \frac{D\mathbf{u}}{Dt} = \rho \mathbf{g} + \nabla \cdot \boldsymbol{\Sigma} \quad \text{in } V, \qquad \mathbf{u} = \mathbf{u}^0 \, \underline{\vee} \, \mathbf{n} \cdot \boldsymbol{\Sigma} = \mathbf{t}^0 \quad \text{on } \partial V.$$

The  $2^{nd}$  variational statement in (B.7) implies

(B.8) 
$$M = M_0 - \frac{\pi}{\rho^2} \frac{d\rho}{d\phi}, \quad \chi = -\chi_0.$$

After substituting (B.3) into (B.8), and with (B.5) and (2.5) describing the diffusion, this completes the derivation of governing equations (2.8)–(2.9).

# Appendix C. Relationship between the two definitions of diffusional flux

From (4.4):

(C.1) 
$$\frac{D\rho}{Dt} = \frac{D\rho}{Dt} - \alpha \mathbf{q} \cdot \nabla \rho = -\rho \nabla \cdot (\mathbf{v} + \alpha \mathbf{q}) - \alpha \mathbf{q} \cdot \nabla \rho = -\alpha \nabla \cdot (\rho \mathbf{q}).$$

On the other hand, using the linear interpolation (4.3):

(C.2) 
$$\frac{D\rho}{Dt} = \frac{d\rho}{dc}\frac{Dc}{Dt} = (\rho_{0A} - \rho_{0B})\frac{Dc}{Dt} = -\frac{\rho_{0A} - \rho_{0B}}{\rho_{0A}\rho_{0B}}\nabla \cdot (\rho\mathbf{q}).$$

Upon equating (C.1) and (C.2):

$$\frac{Dc}{Dt} = -\nabla \cdot \left(\frac{\rho}{\rho_{0A}\rho_{0B}}\mathbf{q}\right) = -\nabla \cdot \mathbf{J}.$$

### Appendix D. Energy balance and PVP for the IC model

We write the total potential energy as

$$\mathcal{P} = \int_{V} \rho \Big[ \frac{\omega(c, \nabla c)}{\rho} - \psi(\mathbf{x}) \Big] dV + \int_{\partial V} \gamma(c) d\partial V.$$

The material rate of change of the potential energy is

(D.1) 
$$\frac{D\mathcal{P}}{Dt} = \int_{V} \left\{ \rho \left[ \frac{D}{Dt} \left( \frac{\omega}{\rho} \right) - \nabla \psi \cdot \mathbf{v} \right] \right\} dV + \int_{\partial V} \frac{d\gamma}{dc} \frac{Dc}{Dt} d\partial V.$$

Noting that c is advected with  $\mathbf{v}$ , the first term in (D.1) is:

(D.2) 
$$\int_{V} \rho \frac{D(\omega/\rho)}{Dt} dV = \int_{V} \left\{ \left[ \rho \frac{\partial(\omega/\rho)}{\partial c} - \nabla \cdot \left( \rho \frac{\partial(\omega/\rho)}{\partial \nabla c} \right) \right] \frac{Dc}{Dt} - \rho \left[ \frac{\partial(\omega/\rho)}{\partial \nabla c} \nabla c \right] : (\mathbf{v}\nabla) \right\} dV + \int_{\partial V} \rho \mathbf{n} \cdot \frac{\partial(\omega/\rho)}{\partial \nabla c} \frac{Dc}{Dt} d\partial V.$$

Then, consider the first two terms on the right hand side of (D.2):

$$\int_{V} \left[ \rho \frac{\partial(\omega/\rho)}{\partial c} - \nabla \cdot \left( \rho \frac{\partial(\omega/\rho)}{\partial \nabla c} \right) \right] \frac{Dc}{Dt} dV = \int_{V} \left( \frac{df}{dc} - \kappa \nabla^{2} c \right) \frac{Dc}{Dt} dV - \int_{V} \frac{\omega}{\rho} \frac{D\rho}{Dt} dV.$$

The 2<sup>nd</sup> term is the change in potential energy arising from the change in density, which is neglected, consistent with the assumption of incompressibility. The change in total potential energy is obtained as:

$$\frac{D\mathcal{P}}{Dt} = \int_{V} \left\{ \mathcal{M}_{0} \frac{Dc}{Dt} - \kappa (\nabla c \nabla c) : (\mathbf{v} \nabla) - \rho \mathbf{g} \cdot \mathbf{v} \right\} dV + \int_{\partial V} \chi_{0} \frac{Dc}{Dt} d\partial V,$$
$$\mathcal{M}_{0} = \frac{df}{dc} - \kappa \nabla^{2} c,$$
$$\chi_{0} = \frac{d\gamma}{dc} + \kappa \mathbf{n} \cdot \nabla c.$$

For incompressible fluids, the viscous stress tensor is

$$\mathbf{r} = \mu(\phi)(\mathbf{v}\nabla + \nabla\mathbf{v}).$$

Dissipation is defined in a manner analogous to the definitions in Appendix B:

$$\mathcal{D} = \int_{V_{\xi}} \left[ \boldsymbol{\tau} : (\mathbf{v}\nabla) - \mathcal{M}\frac{Dc}{Dt} \right] dV - \int_{\partial V_{\xi}} \chi \frac{Dc}{Dt} d\partial V \ge 0,$$
$$\mathbf{J} = -B\nabla\mathcal{M} \quad (B > 0) \text{in } V,$$
$$\frac{Dc}{Dt} = b\chi \quad (b > 0) \text{on } S.$$

The remainder of the derivation (energy balance and the PVP) is identical to the derivation in Appendix B, except that the condition enforced by the Lagrange multiplier  $\pi$ , is now:

$$\int_{V} \pi \delta \nabla \cdot \mathbf{v} dV = 0.$$

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## (НЕ)СТИШЉИВОСТ И ОДРЕЂИВАЊЕ ПАРАМЕТАРА У МОДЕЛИМА ФАЗНОГ ПОЉА ЗА КАПИЛАРНА ТЕЧЕЊА

РЕЗИМЕ. Модели фазног поља (разуђене међуповрши) су прилагођени дифузном кретању тројне линије са променљивим контактним углом, те тако дозвољавају примену неклизајућег граничног услова без сингуларитета напона. Разматрамо две често коришћене класе модела фазног поља: саставно стишљив (CC) модел, у коме је стишљивост ограничена на мешавину флуида унутар разуђене међуповрши и нестишљив (НС) модел. Прво, показујемо да СС модел примењен на комбинацију флуида различитих густина производи рачунску нестабилност, која се испољава кроз цепање тројне линије. Нудимо квалитативно физичко објашњење ове нестабилности, којим исходи да је саставна стишљивост разуђене међуповрши противречна глобалном нестишљивим течењу. Друго, изводимо НС модел као систематску апроксимацију СС модела, засновану на одговарајућем избору поља брзина континуума. Треће, поредимо резултате НС модела са теоријским решењима класичне теорије са дисконтинуитетима, као и са експерименталном кинетиком. У моделу фазног поља кинетика тројне линије је прецизно представљена параметром покретљивости тројне линије. Коначно, истражујемо утицај параметра запреминске покретљивости фазног поља на кинетику процеса квашења и налазимо да је тај утицај занемарљив унутар великог распона вредности овог параметра.

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