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Phase-Field Models of Cahn-Hilliard Fluids and Extra Fluxes

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Abstract

A class of models of Cahn-Hilliard fluids are developed by considering two incompressible non-reacting phases. The concentration of one of the phases, satisfying the classical diffusion equation, is regarded as the order parameter. The balance of energy and the entropy inequality are taken as for a single constituent but, owing to the non-simple character of the continuum, extra fluxes of energy and entropy are allowed to occur. Known models in the literature are recovered as particular cases.

Keywords: Cahn-Hilliard fluid, extra fluxes, phase-field models

1 Introduction

The transition between different phases, or constituents of a mixture, is often modelled by phase-field schemes where the sharp interface is replaced by a narrow layer across which the phases may mix. In the layer, diffusion and motion of the mixture occur and the mixture is described by an additional field, that of an order parameter. This is the essence of phase-field models [4]. Quite often, the order parameter is the concentration of a constituent or the mass density of the mixture.

Owing to the jump of mass density across the transition layer, the modelling allows for non-uniform densities and, mathematically, for a dependence of energy also on the mass density gradients. This idea traces back to van der Waals [16] and is at the basis of the Cahn-Hilliard model [6] for a purely diffusional problem. Improvements of the model have been set up to account for phase segregation where the (two) constituents of the mixture form separated or homogeneous domains. In this regard a realistic description has to involve the coupling of the equations of fluid dynamics with the occurrence of diffusion. This view is at the basis of [13] where the dependence of the energy upon concentration gradients plays a central role for both balance equations and constitutive properties.

Within the framework of continuum mechanics, the dependence of constitutive functions on appropriate gradients has to be compatible with thermodynamics. This in turn implies that a non-simple scheme is adopted in which the occurrence of additional fluxes of energy or entropy is allowed. Hence questions arise about the possible equivalence of different schemes and, otherwise, which scheme is more appropriate.

The purpose of this paper is twofold. The first fold is to set up a description of two-phase fluids following the guidelines of continuum mechanics. The concentration is governed by the classical balance equations for mixtures. The diffusion flux and the other constitutive functions are required to be compatible with thermodynamics. For generality, the continuum is allowed to be non-isothermal. For definiteness, the two phases are regarded as incompressible fluids so that the mixture is quasi-incompressible, which means that the densities are uniquely determined by the concentration. The thermodynamic framework is quite general in that extra-energy and extra-entropy fluxes are allowed to occur. The second fold is to show that there are similar, but inequivalent, models appeared in the literature which are associated with appropriate selections of the extra fluxes.

2 Mixture of incompressible constituents

We restrict attention to a binary mixture of two incompressible non-reacting fluids. Denote by ρ_{10}, ρ_{20} the two intrinsic constant densities of constituents 1 and 2. If ϕ is the volume fraction of constituent 1 we can write the total mass density ρ of the mixture as $\rho = \rho_1 + \rho_2$ where ρ_1 and ρ_2 are the peculiar mass densities, $\rho_1 = \rho_{10}\phi$, $\rho_2 = \rho_{20}(1-\phi)$. The concentration c of constituent 1 is defined by $c = \rho_1/\rho$; c and ϕ are related to each other by

$$c = \frac{\phi\rho_{10}}{\rho_{20} + (\rho_{10} - \rho_{20})\phi}, \qquad \phi = \frac{c\rho_{20}}{\rho_{10} + (\rho_{20} - \rho_{10})c}.$$

Hence, $c \in [0,1]$ is equivalent to $\phi \in [0,1]$ in that $c = 0,1 \Leftrightarrow \phi = 0,1$ and $dc/d\phi > 0$. Both c and ϕ are possible order parameters; we use the concentration c. The function $\rho(c)$,

$$\rho = \frac{\rho_{10}\rho_{20}}{\rho_{10} + (\rho_{20} - \rho_{10})c}, \tag{2.1}$$

is invertible in that the derivative ρ_c is nonzero and bounded. Indeed,

$$\rho_c = \tau \rho^2, \qquad \tau = \frac{1}{\rho_{20}} - \frac{1}{\rho_{10}}.$$

We now state the balance equations in a local form. The balance of mass for the mixture as a whole provides the classical continuity equation

$$\dot{\rho} = -\rho \nabla \cdot \mathbf{v}, \tag{2.2}$$

where $\dot{} = \partial_t + \mathbf{v} \cdot \nabla$. Since ρ and c are related by (2.1), it follows from (2.2) that $\dot{c}$ is determined by $\nabla \cdot \mathbf{v}$ through $\dot{c} = -(\rho/\rho_c)\nabla \cdot \mathbf{v}$.

The concentration c enters also the balance of mass for constituent 1. Let $\mathbf{v}_1, \mathbf{v}_2$ be the velocities of the constituents and $\mathbf{v} = c\mathbf{v}_1 + (1-c)\mathbf{v}_2$ the baricentric velocity. Also let $\mathbf{u}$ be the diffusion velocity and $\mathbf{j}$ the mass flux, $\mathbf{u} = \mathbf{v}_1 - \mathbf{v}$, $\mathbf{j} = \rho c \mathbf{u}$. The balance of mass for constituent 1 provides

$$\rho \dot{c} = -\nabla \cdot \mathbf{j}. \tag{2.3}$$

Hence $\dot{c}, \nabla \cdot \mathbf{v}$, and $\nabla \cdot \mathbf{j}$ are mutually related by

$$\rho \dot{c} = -\frac{1}{\tau} \nabla \cdot \mathbf{v} = -\nabla \cdot \mathbf{j}. \tag{2.4}$$

The balance of linear momentum for the mixture is given the standard form

$$\rho \dot{\mathbf{v}} = \nabla \cdot \mathbf{T} + \rho \mathbf{f}, \tag{2.5}$$

where $\mathbf{T}$ is the stress tensor and $\mathbf{f}$ is the body force density. The stress $\mathbf{T}$ is taken to be symmetric, as it follows from the balance of angular momentum.

Consistent with (2.5), we let the balance of energy be given by

$$\rho \dot{e} = \mathbf{T} \cdot \mathbf{L} - \nabla \cdot \mathbf{q} - \nabla \cdot \mathbf{w} + r + \zeta, \tag{2.6}$$

where e is the energy density, $\mathbf{L}$ the velocity gradient, $\mathbf{q}$ the heat flux and r the heat supply (per unit volume). Here $\mathbf{w}$ is a possible extra-energy flux vector and ζ an extra-energy supply. As we see in §5, both $\mathbf{w}$ and ζ arise naturally in modelling materials with internal structures (microforces).

The second law of thermodynamics is taken as the statement that the Clausius-Duhem inequality holds for any set of functions which satisfy the balance equations. Also because of possible nonlocal effects, the entropy flux is likely to be different from $\mathbf{q}/\theta$, θ being the absolute temperature. Hence, letting η be the entropy density and $\mathbf{k}$ the extra-entropy flux vector, we write the Clausius-Duhem inequality in the form

$$\rho \dot{\eta} \geq -\nabla \cdot (\mathbf{q}/\theta) - \nabla \cdot \mathbf{k} + \frac{r}{\theta}. \tag{2.7}$$

Substitution of $r - \nabla \cdot \mathbf{q}$ from (2.6) and use of the free energy $\psi = e - \theta\eta$ provide

$$-\rho(\dot{\psi} + \eta\dot{\theta}) + \mathbf{T} \cdot \mathbf{L} - \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta + \theta\nabla \cdot \mathbf{k} - \nabla \cdot \mathbf{w} + \zeta \geq 0. \tag{2.8}$$

The flux vectors $\mathbf{w}, \mathbf{k}$ occur in (2.8) in the form $\theta\nabla \cdot \mathbf{k} - \nabla \cdot \mathbf{w} + \zeta$. This indicates that thermodynamics places restrictions on $\theta\nabla \cdot \mathbf{k} - \nabla \cdot \mathbf{w} + \zeta$ but not separately on $\mathbf{k}, \mathbf{w}$ and ζ. That a simultaneous occurrence of the fluxes of extra energy and extra entropy leads to some degree of arbitrariness has already been noticed [10]. The arbitrariness is usually avoided by requiring that one of the two fluxes vanish. Sometimes $\mathbf{k} = 0$, as in [8], but very often $\mathbf{w} = 0, \zeta = 0$. It seems more reasonable to regard $\mathbf{w}$ as known, possibly zero, simply because the balance of energy is given by an equality between physically well-defined quantities (energy rate and powers). The recourse to $\mathbf{w}$ is reasonable when the model of the continuum is endowed with an internal structure. As an example of material with internal structure we mention [11] where any given atomic arrangement is assumed to be maintained by a system of microforces entering a further balance equation. In such a case $\mathbf{k} = 0$ whereas $\mathbf{w}$ and ζ are non-zero.

3 Thermodynamic restrictions

Let $\mathbf{D} = \mathrm{sym}\mathbf{L}$. Denote by a superposed $\circ$ the deviatoric part. Since $\mathrm{tr}\,\mathbf{D} = \mathrm{tr}\,\mathbf{L} = \nabla \cdot \mathbf{v}$ then $\overset{\circ}{\mathbf{D}} = \mathbf{D} - (1/3)(\nabla \cdot \mathbf{v})\mathbf{1}$, $\overset{\circ}{\mathbf{L}} = \mathbf{L} - (1/3)(\nabla \cdot \mathbf{v})\mathbf{1}$. We assume that $\mathbf{j}, \mathbf{T}, \mathbf{q}, \mathbf{k}$ are determined by the set of variables

$$\Gamma = (\theta, c, \nabla\theta, \nabla c, ..., \overset{\circ}{\mathbf{D}})$$

through appropriate constitutive functions, the dots denoting higher-order gradients of θ and c. Also we let e and ψ be C^2-functions of $\Gamma_0 = (\theta, c, \nabla\theta, \nabla c)$.

For any C^1-function f, on $\Omega \times \mathbb{R}$, the identity

$$\dot{\overline{\nabla f}} = \nabla \dot{f} - \mathbf{L}^T \nabla f \tag{3.1}$$

holds. Hence, time differentiation of ψ and substitution in (2.8) gives

$$\begin{aligned} -\rho[(\psi_\theta + \eta)\dot{\theta} + \psi_c \dot{c} + \psi_{\nabla\theta} \cdot (\nabla\dot{\theta} - \mathbf{L}^T\nabla\theta) + \psi_{\nabla c} \cdot (\nabla\dot{c} - \mathbf{L}^T\nabla c)] \\ + \mathbf{T} \cdot \mathbf{L} - \frac{1}{\theta}\mathbf{q} \cdot \nabla\theta + \theta\nabla \cdot \mathbf{k} - \nabla \cdot \mathbf{w} + \zeta \geq 0. \end{aligned} \tag{3.2}$$

By (2.6), the arbitrariness of the heat supply field $r(\mathbf{x}, t)$, on $\Omega \times \mathbb{R}$, allows us to say that $\dot{\theta}$ and $\nabla\dot{\theta}$, at a point $\mathbf{x}$ and time t, may be chosen as an arbitrary scalar and an arbitrary vector. The same argument does not apply to $\dot{c}$ and

$\nabla\dot{c}$ because $\nabla\cdot\mathbf{v}$, $\dot{c}$ and $\nabla\cdot\mathbf{j}$ are related to each other by (2.4). Now, inequality (3.2) holds for any value of $\nabla\dot{\theta}$ and $\dot{\theta}$ only if

$$\psi_{\nabla\theta} = 0, \qquad \eta = -\psi_\theta. \tag{3.3}$$

The remaining inequality is divided by θ to obtain

$$\frac{1}{\theta}[\mathbf{T} + \rho\nabla c \otimes \psi_{\nabla c}]\cdot\mathbf{L} - \frac{\rho}{\theta}\psi_c\dot{c} - \frac{\rho}{\theta}\psi_{\nabla c}\cdot\nabla\dot{c} - \frac{1}{\theta^2}\mathbf{q}\cdot\nabla\theta + \nabla\cdot\mathbf{k} + \frac{1}{\theta}(\zeta - \nabla\cdot\mathbf{w}) \geq 0. \tag{3.4}$$

Let

$$\delta_c\psi := \rho\psi_c - \theta\nabla\cdot(\frac{\rho}{\theta}\psi_{\nabla c}).$$

Upon some rearrangements, inequality (3.4) becomes

$$\frac{1}{\theta}[\mathbf{T} + \rho\nabla c \otimes \psi_{\nabla c}]\cdot\mathbf{L} - \frac{1}{\theta}\delta_c\psi\,\dot{c} - \frac{1}{\theta^2}\mathbf{q}\cdot\nabla\theta + \nabla\cdot(\mathbf{k} - \frac{\rho}{\theta}\psi_{\nabla c}\dot{c}) + \frac{1}{\theta}(\zeta - \nabla\cdot\mathbf{w}) \geq 0.$$

In view of (2.3) we can replace $\dot{c}$ to get

$$\frac{1}{\theta}[\mathbf{T} + \rho\nabla c \otimes \psi_{\nabla c}]\cdot\mathbf{L} + \frac{1}{\rho\theta}\delta_c\psi\nabla\cdot\mathbf{j} - \frac{1}{\theta^2}\mathbf{q}\cdot\nabla\theta + \nabla\cdot(\mathbf{k} + \frac{1}{\theta}\psi_{\nabla c}\nabla\cdot\mathbf{j}) + \frac{1}{\theta}(\zeta - \nabla\cdot\mathbf{w}) \geq 0. \tag{3.5}$$

A possible dependence of $\mathbf{T}$ on $\mathbf{L}$ is made explicit by letting

$$\mathbf{T} = -p\mathbf{1} + \mathbf{T}_0 + \nu\,\mathring{\mathbf{D}} + \lambda(\nabla\cdot\mathbf{v})\mathbf{1} + \alpha(\mathring{\mathbf{D}}\cdot\mathring{\mathbf{D}})\,\mathring{\mathbf{D}}, \tag{3.6}$$

where $\mathbf{T}_0$ is a tensor independent of $\mathbf{D}$. By (3.6), the effective shear viscosity modulus is $\nu + \alpha\,\mathring{\mathbf{D}}\cdot\mathring{\mathbf{D}}$.

Substitution of (3.6) in (3.5), use of (2.3) and some rearrangements yield

$$\begin{aligned}&(\mathring{\mathbf{T}}_0 + \rho\,\overset{\circ}{\overline{\nabla c\otimes\psi_{\nabla c}}})\cdot\mathring{\mathbf{L}} + (\mathrm{tr}\,\mathbf{T}_0 + \rho\nabla c\cdot\psi_{\nabla c})\nabla\cdot\mathbf{v} + \alpha(\mathring{\mathbf{D}}\cdot\mathring{\mathbf{D}})^2 + \nu\,\mathring{\mathbf{D}}\cdot\mathring{\mathbf{D}}\\ &+\lambda(\nabla\cdot\mathbf{v})^2 - \theta\mathbf{j}\cdot\nabla\frac{\mu}{\theta} - \frac{1}{\theta}\mathbf{q}\cdot\nabla\theta + \theta\nabla\cdot(\mathbf{k} + \frac{1}{\theta}\psi_{\nabla c}\nabla\cdot\mathbf{j} + \frac{\mu}{\theta}\mathbf{j}) + \zeta - \nabla\cdot\mathbf{w} \geq 0,\end{aligned}$$

where

$$\mu := \frac{1}{\rho}\delta_c\psi - \tau p. \tag{3.7}$$

The inequality holds if

$$\mathbf{T}_0 + \rho\nabla c\otimes\psi_{\nabla c} = 0, \qquad \alpha, \nu, \lambda \geq 0, \tag{3.8}$$

$$-\theta\mathbf{j}\cdot\nabla\frac{\mu}{\theta}-\frac{1}{\theta}\mathbf{q}\cdot\nabla\theta+\theta\nabla\cdot(\mathbf{k}+\frac{1}{\theta}\psi_{\nabla c}\nabla\cdot\mathbf{j}+\frac{\mu}{\theta}\mathbf{j})+\zeta-\nabla\cdot\mathbf{w}\geq 0. \tag{3.9}$$

In turn, inequality (3.9) holds if

$$\mathbf{k}=-\frac{1}{\theta}\psi_{\nabla c}\nabla\cdot\mathbf{j}-\frac{\mu}{\theta}\mathbf{j}, \qquad \mathbf{j}\cdot\nabla\frac{\mu}{\theta}+\frac{1}{\theta}\mathbf{q}\cdot\nabla\theta-(\zeta-\nabla\cdot\mathbf{w})\leq 0, \tag{3.10}$$

or if

$$\mathbf{k}=-\frac{1}{\theta}\psi_{\nabla c}\nabla\cdot\mathbf{j}-\frac{\mu}{\theta}\mathbf{j}+\frac{1}{\theta}\mathbf{w}, \qquad \mathbf{j}\cdot\nabla\frac{\mu}{\theta}+\frac{1}{\theta}(\mathbf{q}+\mathbf{w})\cdot\nabla\theta-\zeta\leq 0. \tag{3.11}$$

In addition, since $\mathbf{T}$ (and hence $\mathbf{T}_0$) is symmetric then ψ is subject to

$$\nabla c\otimes\psi_{\nabla c}=\psi_{\nabla c}\otimes\nabla c.$$

Hence it follows that

$$\psi_{\nabla c}=\chi(\theta,c,\nabla c)\nabla c,$$

which occurs if ψ depends on ∇c through $|\nabla c|$. If χ is independent of ∇c then ψ takes the additive form

$$\psi=\psi_0(\theta,c)+\frac{1}{2}\chi(\theta,c)|\nabla c|^2.$$

Some remarks are in order. No restriction is placed on p. It is reasonable to regard p as a function of c and θ. By (3.8), eq. (3.6) becomes

$$\mathbf{T}=-p\mathbf{1}-\chi\nabla c\otimes\nabla c+\nu\overset{\circ}{\mathbf{D}}+\lambda(\nabla\cdot\mathbf{v})\mathbf{1}+\alpha(\overset{\circ}{\mathbf{D}}\cdot\overset{\circ}{\mathbf{D}})\overset{\circ}{\mathbf{D}}. \tag{3.12}$$

In [13], the Cauchy stress tensor, say $\mathbf{T}$, is defined by

$$\mathbf{T}=-\rho^2\psi_\rho\mathbf{1}-\rho\nabla c\otimes\psi_{\nabla c}.$$

That $\mathbf{T}$ has to be defined rather than be derived as a thermodynamic restriction is consistent with the fact that, in quasi-incompressible mixtures, ρ is a function of c. Here, however, p is an arbitrary function, not generated by the free energy ψ.

It is natural to view μ as the chemical potential. By (3.7), μ consists of three contributions. First, $\delta_c\psi/\rho$ originates from the free-energy potential ψ and is then the strict analogue of the classical chemical potential which is defined as the variational derivative of ψ relative to the order parameter (see, e.g., [11]). Here, however, ψ enters the variational derivative in the rescaled form ψ/θ as is the case in other approaches (see, e.g., [4, 1]). Second, $-\tau p$ is the characteristic term associated with the quasi-incompressibility as is made evident by the factor ρ_c. It is of interest that $(\delta_c\psi)/\rho - \tau p$ coincides with the chemical potential in [13] (see (4.13)) when the temperature θ is uniform.

The results (3.3), (3.8), (3.9) hold if the set of variables Γ is allowed to contain also $\dot{c}, \nabla\dot{c}$. This feature is of interest to recover the results of [11].

By (3.11) we can take $\mathbf{j} = -\kappa\nabla(\mu/\theta)$, $\kappa \geq 0$. Select the free energy $\psi = \Psi(\theta, c) + \frac{1}{2}\chi|\nabla c|^2 + \tau P(c)$, P being the integral of p. Hence, by (2.3),

$$\rho\dot{c} = \nabla \cdot \{\kappa\nabla\frac{1}{\rho\theta}\delta_c[\Psi(\theta, c) + \frac{1}{2}\chi|\nabla c|^2]\}.$$

If $\rho, \theta, \kappa, \chi$ are constants then we find the standard form of the Cahn-Hilliard equation

$$\dot{c} = \kappa_0\Delta[\Psi_c(c) - \chi_0\Delta c]. \tag{3.13}$$

4 Relation to other approaches

Based on a variational analysis, Lowengrub and Truskinovsky [13] assume that the rate of work A done on the boundary $\partial\mathcal{P}$ of a material domain $\mathcal{P}$ is given by

$$A = \int_{\partial\mathcal{P}} [(\mathbf{T}\mathbf{n}) \cdot \mathbf{v} + \mathbf{t} \cdot \mathbf{n}\,\dot{c}]da$$

where $\mathbf{t} = \rho\psi_{\nabla c}$. As a consequence, the balance of energy becomes (see their (3.20))

$$\rho\dot{e} = \mathbf{T} \cdot \mathbf{L} + \nabla \cdot (\mathbf{t}\dot{c}) + r.$$

Gurtin [11] (see also [15]) takes the view that any given arrangement is maintained by a system of microforces,

$$\nabla \cdot \boldsymbol{\xi} + \pi + \gamma = 0,$$

where $\boldsymbol{\xi}$ is a vector stress, π is a scalar internal force and γ is a scalar body force. Hence, the power of microforces is given the form

$$A = \int_{\partial\mathcal{P}} \boldsymbol{\xi} \cdot \mathbf{n}\,\dot{c}\,da + \int_{\mathcal{P}} \gamma\dot{c}dv.$$

Next $\boldsymbol{\xi}$ too is shown to be related to the free energy, say $\boldsymbol{\xi} = \rho\psi_{\nabla c}$.

Though the approaches of [13] and [11] are different, they involve the same term $\nabla \cdot (\rho\psi_{\nabla c}\dot{c})$ as the power associated with the variation of c.

Here, instead, the balance of energy is allowed to be unaffected by the variation of the concentration and hence the balance law is taken in the classical form (2.6). Meanwhile the temperature field is allowed to be also space dependent and, owing to the non-simple character of the mixture, a nonzero extra-entropy flux $\mathbf{k}$ is allowed to occur. It looks advantageous that the energy balance equation is free from the additional term $\nabla \cdot (\rho\psi_{\nabla c}\dot{c})$.

4.1 Gibbs' equation and the second law

Here we address two purposes. First, the occurrence of $\dot{c}$ in the balance of energy, through $\mathbf{w}$, is not standard in classical thermodynamics. Rather, the second law is often stated in the form of Gibbs' equation as (see, e.g., [7])

$$\theta\dot{\eta} = \dot{e} + p\dot{v} - \sum_l \mu_l \dot{c}_l, \tag{4.1}$$

where $v = 1/\rho$ is the specific volume. Since no $\dot{c}$ term occurs in our approach (if $\mathbf{w} = 0, \zeta = 0$) it is natural to check whether $\dot{c}$-terms occur in the Gibbs equation though they do not appear in the energy balance. Second, we look for the possible forms of the entropy inequality compatible with

$$\psi = \psi(\theta, c, \nabla c), \qquad \eta = -\psi_\theta, \tag{4.2}$$

the stress tensor (3.12) and the balance of energy (2.6).

By (4.2), $\dot{\psi} = -\eta\dot{\theta} + \psi_c\dot{c} + \psi_{\nabla c}\cdot\dot{\overline{\nabla c}}$ and hence, by (3.1),

$$\frac{\rho}{\theta}(\dot{\psi} + \eta\dot{\theta}) = \frac{1}{\theta}\delta_c\psi\dot{c} + \nabla\cdot(\frac{\rho}{\theta}\psi_{\nabla c}\dot{c}) - \frac{\rho}{\theta}(\nabla c\otimes\psi_{\nabla c})\cdot\mathbf{L}.$$

Also, because $\dot{\psi} + \eta\dot{\theta} = \dot{e} - \theta\dot{\eta}$, by means of (3.7) we obtain

$$\rho\dot{\eta} = \frac{\rho}{\theta}\dot{e} - \frac{1}{\theta}[\rho\mu + \frac{\rho_c p}{\rho} - \frac{\rho_c}{3\rho}\nabla c\cdot\psi_{\nabla c} - \nabla\cdot(\frac{\rho}{\theta}\psi_{\nabla c}\dot{c}) + \frac{\rho}{\theta}(\nabla c\otimes\psi_{\nabla c})\cdot\mathbf{L}. \tag{4.3}$$

Substitution of $\dot{e}$ from (2.6) gives

$$\begin{aligned}\rho\dot{\eta} + \nabla\cdot\frac{\mathbf{q}}{\theta} - \frac{r}{\theta} &= -\nabla\cdot(\frac{\rho}{\theta}\psi_{\nabla c}\dot{c}) + \nabla\cdot(\frac{\mu}{\theta}\mathbf{j}) + \frac{1}{\theta}(\zeta - \nabla\cdot\mathbf{w}) + \frac{1}{\theta}\mathbf{T}\cdot\mathbf{L}\\ &-\frac{1}{\theta^2}\mathbf{q}\cdot\nabla\theta - \mathbf{j}\cdot\nabla\frac{\mu}{\theta} + \frac{1}{\theta}(p - \frac{1}{3}\nabla c\cdot\psi_{\nabla c})\nabla\cdot\mathbf{v} + \frac{\rho}{\theta}(\nabla c\otimes\psi_{\nabla c})\cdot\mathbf{L}.\end{aligned}$$

Moreover, substitution of $\mathbf{T}$ from (3.12) provides

$$\rho\dot{\eta} + \nabla\cdot\frac{\mathbf{q}}{\theta} - \frac{r}{\theta} + \nabla\cdot(\frac{\rho}{\theta}\psi_{\nabla c}\dot{c} - \frac{\mu}{\theta}\mathbf{j}) = -\frac{1}{\theta^2}\mathbf{q}\cdot\nabla\theta - \mathbf{j}\cdot\nabla\frac{\mu}{\theta} + \frac{1}{\theta}(\zeta - \nabla\cdot\mathbf{w} + \sigma), \tag{4.4}$$

where

$$\sigma = \nu\,\overset{\circ}{\mathbf{D}}\cdot\overset{\circ}{\mathbf{D}} + \alpha(\overset{\circ}{\mathbf{D}}\cdot\overset{\circ}{\mathbf{D}})^2 + \lambda(\nabla\cdot\mathbf{v})^2.$$

It is apparent from (4.4) that (2.7) holds with

$$\mathbf{k} = \frac{\rho}{\theta}\psi_{\nabla c}\dot{c} - \frac{\mu}{\theta}\mathbf{j}$$

if $\zeta = 0, \mathbf{w} = 0$. Otherwise, nonzero values of ζ and $\mathbf{w}$ affects the value of the extra-entropy flux $\mathbf{k}$. This is now exemplified by means of other approaches.

To check the possible consistency of other approaches with (4.4) we need to distinguish between different definitions of the chemical potential. By (3.7), μ is defined as

$$\rho\mu = \theta[\frac{\rho}{\theta}\psi_c - \nabla \cdot (\frac{\rho}{\theta}\psi_{\nabla c})] + \cdots ,$$

where ψ occurs in the rescaled form ψ/θ. The rescaled free energy occurs also in [1, 4]. In other cases, e.g. in [11, 13], the temperature θ does not enter explicitly and the chemical potential, call it μ_0, is defined by $\rho\mu_0 = \rho\psi_c - \nabla \cdot (\rho\psi_{\nabla c}) + \cdots$. Hence

$$\mu = \mu_0 + \frac{1}{\theta}\psi_{\nabla c} \cdot \nabla\theta.$$

The classical form (4.1) is based on the assumption that $\nabla c = 0$ or that ψ and η are unaffected by ∇c. In such a case (4.3) simplifies to

$$\rho\dot{\eta} = \frac{\rho}{\theta}\dot{e} - \frac{1}{\theta}[\rho\mu + \frac{\rho_c p}{\rho}]\dot{c}.$$

Since $\dot{v} = -\dot{\rho}/\rho^2 = -\tau\dot{c}$ then Gibbs' equation (4.1) is recovered provided only that we let $l = 1, 2$ and $\mu = \mu_1 - \mu_2$.

4.2 Two models with a non-zero extra-energy flux

A model of Cahn-Hilliard fluid is given in [9] where

$$\mathbf{w} = \psi_{\nabla c}\nabla \cdot \mathbf{j} + \mu_0\mathbf{j},$$

whereas $\zeta = 0$ and $\mathbf{k} = 0$. This conclusion follows at once from (4.4). For, letting $\zeta = 0, \mathbf{w} = \psi_{\nabla c}\nabla \cdot \mathbf{j} + \mu_0\mathbf{j}$ we have

$$\begin{aligned}&\frac{1}{\theta}(\zeta - \nabla \cdot \mathbf{w}) - \mathbf{j} \cdot \nabla\frac{\mu}{\theta} + \nabla \cdot (\frac{\mu}{\theta}\mathbf{j}) - \nabla \cdot (\frac{\rho}{\theta}\psi_{\nabla c}\dot{c})\\ &= -\frac{1}{\theta}\nabla \cdot (\mu_0\mathbf{j}) + \frac{\mu}{\theta}\nabla \cdot \mathbf{j} - \frac{1}{\theta^2}\nabla \cdot \mathbf{j}\,\nabla\theta \cdot \psi_{\nabla c} = -\frac{1}{\theta}\mathbf{j} \cdot \nabla\mu_0.\end{aligned}$$

This means that (4.4) reduces to

$$\rho\dot{\eta} + \nabla \cdot \frac{\mathbf{q}}{\theta} - \frac{r}{\theta} = -\frac{1}{\theta^2}\mathbf{q} \cdot \nabla\theta - \mathbf{j} \cdot \nabla\mu_0 + \frac{\sigma}{\theta},$$

where the extra-entropy flux is zero ($\mathbf{k} = 0$) and the dissipation term for $\mathbf{j}$ involves μ_0. The result of [9] is thus recovered. It is worth mentioning that [9] gives a model where $\mathbf{T}$ contains a term $\dot{g}\,\overset{\circ}{\mathbf{D}}$, $g = g(c)$. The same term can be shown to hold here with $\mathbf{w} = 0$ and $\mathbf{k}$ given by (3.10) or (3.11).

Another model for the Cahn-Hilliard fluid is given in [13] where

$$\mathbf{w} = \psi_{\nabla c} \nabla \cdot \mathbf{j}.$$

Because

$$-\frac{1}{\theta}\nabla \cdot \mathbf{w} - \mathbf{j} \cdot \nabla \frac{\mu}{\theta} + \nabla \cdot (\frac{\mu}{\theta}\mathbf{j}) - \nabla \cdot (\frac{\rho}{\theta}\psi_{\nabla c}\dot{c}) = \nabla \cdot (\frac{\mu_0}{\theta}\mathbf{j}) - \mathbf{j} \cdot \nabla \frac{\mu_0}{\theta},$$

eq. (4.4) becomes

$$\rho\dot{\eta} + \nabla \cdot \frac{\mathbf{q}}{\theta} - \frac{r}{\theta} - \nabla \cdot (\frac{\mu_0}{\theta}\mathbf{j}) = -\mathbf{j} \cdot \nabla \frac{\mu_0}{\theta} + \frac{\zeta + \sigma}{\theta}.$$

This implies that

$$\mathbf{k} = \frac{\mu_0}{\theta}\mathbf{j},$$

which provides (3.24a) of [13] and $\zeta \geq 0$. Indeed, $\zeta = 0$ in [13]. The seemingly different sign in [13] is due to the fact that $\mathbf{J}$ of [13] is opposite to $\mathbf{j}$, $\mathbf{J} = -\mathbf{j}$.

4.3 Demixing term

If $\mathbf{w} = 0$, $\zeta = 0$, by (3.11) the mass diffusion flux $\mathbf{j}$ is required to satisfy

$$\mathbf{j} \cdot \nabla \frac{\mu}{\theta} + \frac{1}{\theta^2}\mathbf{q} \cdot \nabla \theta \leq 0.$$

This shows that in uniform temperature fields ($\nabla\theta = 0$) we have $\mathbf{j} \cdot \nabla\mu \leq 0$, which means that $\mathbf{j}$ is opposite to $\nabla\mu$. This in turn means that the two species are pulled in opposite directions by the chemical potential gradient.

In the physical literature (see, e.g., [2, 12]) this view is modelled by regarding $-\varphi\nabla\mu$ as the force, per unit volume, produced by local chemical-potential variations, φ being an order parameter. For definiteness we may say that $\varphi = 2c - 1 \in [-1, 1]$. It is worth looking at [12] where a motivation is given for regarding $-\varphi\nabla\mu$ as the force that demix the phases.

As is often the case, the free energy ψ is taken in the form $\psi(\varphi, \nabla\varphi) = f(\varphi) + \frac{1}{2}\chi|\nabla\varphi|^2$, χ being a constant and f a double-well potential whose wells define the two phases. Hence, μ is defined as the variational derivative of ψ,

$$\mu = f'(\varphi) - \chi\Delta\varphi. \tag{4.5}$$

In addition to the viscosity term and the pressure contribution, a chemical stress tensor $\mathbf{T}^{\text{chem}}$ is taken to occur. Moreover it is stated that

$$\varphi \nabla \mu = -\nabla \cdot \mathbf{T}^{\text{chem}} \tag{4.6}$$

provided that $\mathbf{T}^{\text{chem}} := -\{\varphi f' - f - \chi[\varphi \Delta \varphi + \frac{1}{2}|\nabla \varphi|^2\}\mathbf{1} - \chi \nabla \varphi \otimes \nabla \varphi$. This follows at once in that $\varphi \nabla \mu = \varphi[f'' \nabla \varphi - \chi \Delta \nabla \varphi]$ and the same result arises for $-\nabla \cdot \mathbf{T}^{\text{chem}}$.

The validity of (4.6) is related to the classical (Ginzburg-Landau) form (4.5) of μ. However, irrespective of the fact that we can prove (4.6) for more general forms of the chemical potential for corresponding tensors $\mathbf{T}^{\text{chem}}$, this does not mean that $\varphi \nabla \mu$ is the correct force term to be inserted in the equation of motion. Rather, depending on the form of the chemical potential, upon substitution in $\mathbf{j} = -\kappa \nabla \mu$, the divergence $\nabla \cdot \mathbf{j}$ provides $-\rho \dot{c}(\varphi)$. Meanwhile, the stress tensor, as well as other constitutive functions, has to be compatible with thermodynamics. Here the stress tensor (3.12) is compatible with thermodynamics and does not involve any chemical stress tensor.

4.4 Balance of molar concentration

The Cahn-Hilliard equation is often associated with an order parameter [6, 5]. The derivation [11] starts with the mass balance $\dot{\rho} = -\nabla \cdot \mathbf{h}$, the mass flux $\mathbf{h}$ being related to μ through $\mathbf{h} = -\kappa \nabla \mu$. Next μ is defined as the variational derivative of ψ, $\mu = \psi_\rho - \nabla \cdot \psi_{\nabla \rho}$. The constitutive assumption $\psi = f(\rho) + (\alpha/2)|\nabla \rho|^2$ completes the derivation. So ρ is an order parameter which, however, is required to satisfy a balance of mass equation. As shown by (3.13), the concentration satisfies the Cahn-Hilliard equation.

In [3] the analogue of the mass (balance) is the composition or molar concentration. Let n_1, n_2 be the number of moles per unit volume and M_1, M_2 the molecular weight so that $\rho_\alpha = n_\alpha M_\alpha$, $\alpha = 1, 2$. Let $n = n_1 + n_2$. The composition X (of phase 1) is defined as n_1/n. If $M_1 \neq M_2$ then $X \neq c$. The number of moles is a conserved quantity and this is said to lead to the balance law (see (4) of [3])

$$\dot{X} + \nabla \cdot \mathbf{j}_X = 0. \tag{4.7}$$

Some objections can be raised against eq (4.7). 1) The number of moles is a conserved quantity but the composition is not. 2) The densities n_α satisfy the continuity equations, $\partial_t n_\alpha + \nabla \cdot (n_\alpha \mathbf{v}_\alpha) = 0$, $\alpha = 1, 2$. Let $\mathbf{V}$ denote the mean velocity $(n_1 \mathbf{v}_1 + n_2 \mathbf{v}_2)/n$. Summation over α gives $\partial_t n + \nabla \cdot (n\mathbf{V}) = 0$. Hence, letting $\mathbf{U}_1 = \mathbf{v}_1 - \mathbf{V}$ we find that

$$n\dot{X} + \nabla \cdot \mathbf{j}_X = 0, \tag{4.8}$$

where $\grave{X} = \partial_t X + \mathbf{V} \cdot \nabla X$, $\mathbf{j}_X = nX\mathbf{U}_1$. 3) Since $\mathbf{V} \neq \mathbf{v}$ then $\grave{X} \neq \dot{X}$.

It seems that the balance of composition should be in the form (4.8). However, since the balance of energy and the Clausius-Duhem inequality involve the total time derivative, e.g. $\dot{\psi} = \partial_t \psi + \mathbf{v} \cdot \nabla \psi$, then the composition X is not a convenient variable whereas such is c.

5 Models based on microforces

Evolution equations for two-phase, isothermal, systems are derived in [11] by means of the mass balance and of the balance of appropriate microforces. Here we re-visit the derivation by following the lines of continua with extra-fluxes.

5.1 Microforces in undeformable isothermal bodies

Let the body be undeformable and isothermal. A microforce system is characterized by a vector stress $\boldsymbol{\xi}$ and scalar body forces π, γ that represent, respectively, internal and external forces. At any point they are in equilibrium,

$$\nabla \cdot \boldsymbol{\xi} + \pi + \gamma = 0. \tag{5.1}$$

The power of the (external) forces is $(\boldsymbol{\xi} \cdot \mathbf{n})\dot{c}$ per unit area and $\gamma \dot{c}$ per unit volume. The balance of energy then reduces to

$$\rho \dot{e} = \nabla \cdot (\boldsymbol{\xi} \dot{c}) + \gamma \dot{c} + r,$$

which means that

$$\mathbf{w} = -\boldsymbol{\xi} \dot{c}, \qquad \zeta = \gamma \dot{c}.$$

Hence the entropy inequality (2.8) simplifies to

$$-\rho \dot{\psi} + \theta \nabla \cdot \mathbf{k} + \zeta - \nabla \cdot \mathbf{w} \geq 0. \tag{5.2}$$

Because θ is constant then a single flux $\mathbf{w} - \theta \mathbf{k}$ occurs and, without any loss of generality, we may set $\mathbf{k} = 0$. If θ is not constant then also $-\rho \eta \dot{\theta} - \mathbf{q} \cdot \nabla \theta / \theta$ has to occur in (5.2). Let $\psi = \psi(c, \nabla c)$, $\boldsymbol{\xi} = \boldsymbol{\xi}(c, \nabla c, \dot{c}, \nabla \dot{c})$, $\pi = \pi(c, \nabla c, \dot{c}, \nabla \dot{c})$. By means of (5.1), inequality (5.2) provides

$$-(\pi + \rho \psi_c)\dot{c} + (\boldsymbol{\xi} - \rho \psi_{\nabla c}) \cdot \nabla \dot{c} \geq 0. \tag{5.3}$$

We split $\pi, \boldsymbol{\xi}$ into a reversible and a dissipative part,

$$\pi = \pi_{\rm rev}(c, \nabla c) + \pi_{\rm dis}(c, \nabla c, \dot{c}, \nabla \dot{c}), \qquad \boldsymbol{\xi} = \boldsymbol{\xi}_{\rm rev}(c, \nabla c) + \boldsymbol{\xi}_{\rm dis}(c, \nabla c, \dot{c}, \nabla \dot{c}).$$

Hence (5.3) implies that $\pi_{\rm rev} = -\rho\psi_c$, $\boldsymbol{\xi}_{\rm rev} = \rho\psi_{\nabla c}$, and

$$-\pi_{\rm dis}\dot{c} + \boldsymbol{\xi}_{\rm dis} \cdot \nabla\dot{c} \geq 0. \tag{5.4}$$

Inequality (5.4) holds if

$$\pi_{\rm dis} = -\beta\dot{c} - \mathbf{b} \cdot \nabla\dot{c}, \qquad \boldsymbol{\xi}_{\rm dis} = \mathbf{a}\dot{c} + \mathbf{A}\nabla\dot{c},$$

where the scalar β, the vectors $\mathbf{b}, \mathbf{a}$, and the tensor $\mathbf{A}$ are functions of $c, \nabla c, \dot{c}, \nabla\dot{c}$ such that

$$\beta\dot{c}^2 + \dot{c}(\mathbf{b} + \mathbf{a}) \cdot \nabla\dot{c} + \nabla\dot{c} \cdot \mathbf{A}\nabla\dot{c} \geq 0.$$

Equation (5.1) then becomes

$$(\beta - \nabla \cdot \mathbf{a})\dot{c} + (\mathbf{b} - \mathbf{a}) \cdot \nabla\dot{c} = \nabla \cdot [\rho\psi_{\nabla c} + \mathbf{A}\nabla\dot{c}] - \rho\psi_c + \gamma. \tag{5.5}$$

Let now $\beta, \mathbf{a}, \mathbf{b}$, and $\mathbf{A}$ be constant and the material be isotropic, so that $\mathbf{a}, \mathbf{b} = 0$ and $\mathbf{A} = \kappa\mathbf{1}$. If, further, $\gamma = 0$ and $\psi = \hat{\psi}(c) + \chi|\nabla c|^2/2$ then (5.5) simplifies to

$$\beta\dot{c} = \nabla \cdot (\chi\rho\nabla c) + \kappa\Delta\dot{c} - \rho\hat{\psi}_c. \tag{5.6}$$

5.2 Microforces in diffusive species

The order parameter is identified with the density of a diffusing species of atoms. Here, though, we keep using the concentration c as the order parameter and hence the balance equation (2.3) still applies. The microforces $\boldsymbol{\xi}, \pi, \gamma$ are allowed to occur and to satisfy the equilibrium condition (5.1). Borrowing from [11] we let $\rho\dot{e} = \gamma\dot{c} + \nabla \cdot (\boldsymbol{\xi}\dot{c} - \mu\mathbf{j})$, which amounts to assuming that $\zeta = \gamma\dot{c}$, $\mathbf{w} = \mu\mathbf{j} - \boldsymbol{\xi}\dot{c}$. Hence we let $\mathbf{k} = 0$ and (2.8) becomes

$$-\rho\dot{\psi} + \gamma\dot{c} - \nabla \cdot (\mu\mathbf{j} - \boldsymbol{\xi}\dot{c}) \geq 0.$$

In view of (5.1), some rearrangements give

$$\rho\dot{\psi} + (\pi - \rho\mu)\dot{c} - \boldsymbol{\xi} \cdot \nabla\dot{c} + \mathbf{j} \cdot \nabla\mu \leq 0, \tag{5.7}$$

which is formally equal to (3.6) of [11] except for the occurrence of c as the order parameter and ρ as the non-constant mass density.

Let $\psi, \mathbf{j}, \boldsymbol{\xi}, \pi$ be functions of $\Gamma = (c, \nabla c, \dot{c}, \mu, \nabla\mu)$. It is assumed that fields c, μ can be found such that $\ddot{c}, \dot{\mu}$, and $(\nabla\mu)^{\cdot}$ have arbitrarily prescribed values at some chosen point and time. This allows us to see that, as a consequence of

(5.7), the free energy is a function of $c, \nabla c$ only, $\psi = \psi(c, \nabla c)$ and $\boldsymbol{\xi} = \rho\psi_{\nabla c}$. Hence (5.7) reduces to

$$(\rho\psi_c + \pi - \rho\mu)\dot{c} + \mathbf{j} \cdot \nabla\mu \leq 0. \tag{5.8}$$

Let

$$\pi = \pi_{\mathrm{rev}} + \pi_{\mathrm{dis}}, \qquad \pi_{\mathrm{rev}}(c, \nabla\mu) := -\rho\psi_c + \rho\mu$$

and hence

$$\pi_{\mathrm{dis}} = \pi + \rho\psi_c - \rho\mu. \tag{5.9}$$

By (5.8) it follows that there a scalar β, vectors $\mathbf{a}, \mathbf{b}$, and a tensor $\mathbf{A}$ such that

$$\pi_{\mathrm{dis}} = -\beta\dot{c} - \mathbf{b} \cdot \nabla\mu, \qquad \mathbf{j} = -\mathbf{a}\dot{c} - \mathbf{A}\nabla\mu, \tag{5.10}$$

and

$$\beta\dot{c}^2 + \dot{c}(\mathbf{a} + \mathbf{b}) \cdot \nabla\mu + \nabla\mu \cdot \mathbf{A}\nabla\mu \geq 0.$$

Again let $\psi = \hat{\psi}(c) + \frac{1}{2}\chi|\nabla c|^2$. By means of (5.9), $(5.10)_1$, and (5.1) we obtain

$$\rho\mu - \mathbf{b} \cdot \nabla\mu = \rho\hat{\psi}_c - \nabla \cdot (\chi\rho\nabla c) + \beta\dot{c} - \gamma. \tag{5.11}$$

Substitution of $\mathbf{j}$ from $(5.10)_2$ into (2.3) gives

$$\rho\dot{c} = \nabla \cdot (\mathbf{a}\dot{c} + \mathbf{A}\nabla\mu). \tag{5.12}$$

For a quasi-incompressible mixture, ρ is a function of c and hence eqs (5.11)-(5.12) constitute a system of equations in the unknowns c, μ. Apart from the occurrence of ρ, they are named Cahn-Hilliard-Gurtin equations [14].

6 Conclusions

Models of Cahn-Hilliard fluids describe space variation of the concentration. Constitutive functions then depend on the concentration gradients, and possibly on the temperature gradients, of various orders. Owing to the dependence on the gradients, extra-energy and -entropy fluxes $\mathbf{w}, \mathbf{k}$, as well as an extra-energy supply, are likely to occur in the energy equation and in the entropy inequality. After the general scheme of thermodynamic restrictions, section §4 shows that the simplest model arises by letting $\mathbf{k} = (\rho/\theta)\psi_{\nabla c}\dot{c} - (\mu/\theta)\mathbf{j}$ whereas $\mathbf{w} = 0, \zeta = 0$. Other models appeared in the literature are shown to be associated with different selections of $\mathbf{k}, \mathbf{w}, \zeta$. Models based on microforces naturally correspond to $\mathbf{k} = 0$ and nonzero $\mathbf{w}$ and ζ.

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