Paolo Podio-Guidugli

Models of Phase Segregation and Diffusion of Atomic Species on a Lattice

Abstract Two mathematical models for phase segregation and diffusion of an order parameter are derived, within one and the same continuum mechanical framework. These models are, respectively, of the Allen-Cahn type and of the Cahn-Hilliard type. Our framework is similar to that used in [1], in that a postulated *balance of microforces* plays a central role in both deductive paths, but differs from it, mainly in three ways: *imbalance of entropy* replaces for a dissipation inequality, whose form depends on the case, restricting the growth of free energy; *balance of energy* replaces for the mass balance introduced in [1] to arrive at (a generalization of) the C-H equation; and *chemical potential* is given the same role played by coldness in the deduction of the heat equation. When appropriate constitutive prescriptions are made, different in the cases of segregation and diffusion but consistent with the entropy imbalance, it is found that standard A-C and C-H processes are solutions of constant chemical potential of the corresponding generalized equations; in particular, the stationary solutions are the same.

1 Introduction

Two mathematematical models for phase segregation and phase diffusion are here derived, along lines different from those proposed by Gurtin in [1],

P. Podio-Guidugli
Dipartimento di Ingegneria Civile, Università di Roma TorVergata
Via del Politecnico, 1 - I-00133 Roma, Italy
Tel.: +39 (0)6-7259 7051
Fax: +39 (0)6-7259 7052
E-mail: ppg@uniroma2.it

the paper which motivated this work, to derive generalized versions of the Allen-Cahn and Cahn-Hilliard equations.

The standard A-C equation reads:

$$\beta\dot{\rho} = \alpha\Delta\rho - f'(\rho), \tag{1}$$

while the standard C-H equation is:

$$\dot{\rho} = \kappa\Delta(f'(\rho) - \alpha\Delta\rho); \tag{2}$$

all material constants α, β, and κ are positive; ρ is a scalar *order parameter*, interpreted as a phase descriptor; and f is a double-well potential that accounts for a *two-phase material system*.[1]

The derivations of these two equations offered in [1] are far from standard: they are based on a notion of *contact and distance microforces consistent with their own balance* and on a *dissipation inequality restricting the free-energy growth*. Such a dissipation inequality is a 'purely mechanical' counterpart of the Second Law of thermodynamics, regarded as appropriate to physical contexts such as those the A-C and C-H equations aim to describe.[2] In addition - but only to derive the second of these equations - an *order-parameter balance* is postulated and a *free-energy inflow proportional to the order-parameter inflow via the chemical potential* is made to enter the dissipation inequality.

I find Gurtin's method of derivation illuminating, but I prefer a variant of it that, while retaining Gurtin's balance of microforce, is based on a *microenergy balance* and a *microentropy growth imbalance*, with *microenergy and microentropy inflows deemed proportional via the chemical potential*. This I do to adapt to material systems susceptible to phase segregation and diffusion the standard format leading to the heat equation. That format, which I review in Section 2, is based on an energy equation and an entropy growth inequality, where *energy and entropy inflows are taken proportional via the coldness*, i.e., via the inverse of the absolute temperature.[3]

Two systems of evolution PDEs for material systems of the A-C and C-H types are derived in Section 3. Both systems can be specialized to obtain the generalized versions of equations (1) and (2) arrived at in [1]. I do not regard this as an especially important result. What in my opinion has more relevance is the clarification here achieved, through the systematic use of an energy balance and an entropy imbalance, of the formal role (hence, in a sense, of the generic physical nature) of the chemical potential in theories of phase

---

[1] (1) is also known as the *Ginzburg-Landau equation*, which is the way Gurtin refers to it in his cited paper; in order to facilitate comparisons, our notation and terminology (with the pointed-out exception) are kept as close as possible to those used there.

[2] One may contend that the qualifier 'purely mechanical' should not be attached to a macroscopic statement taking into account collectively as 'dissipation' those individual energy transfers that would become patent at a microscopic scale. Indeed, no dissipation is envisaged at the molecular dynamics scale: whatever happens is 'purely mechanical'.

[3] Apparently, the term 'coldness' was coined by Truesdell [2]. That, for thermodynamic consistency, the energy influx should be proportional to the mass influx of individual constituents of a fluid mixture was shown by Gurtin and Vargas in [3].

segregation and diffusion. In fact, in the intermediate stages of the standard derivations of the C-H equation, as well as in Gurtin's derivation, the chemical potential plays a pivotal role; yet, no trace of that field is found in the final product. The mathematical models I propose, in both of which the chemical potential enters in an essential manner, predict that *standard Allen-Cahn and Cahn-Hilliard processes take place at constant chemical potential*, that is, in a manner of speaking suggested by the analogy *chemical potential ∼ coldness*, they are *microscopically orderly* (Subsection 3.1); in particular, no essential differences with respect to the standard A-C and C-H theories emerge in statics. As to the two coupled PDEs, for the order parameter and the chemical potential, here suggested as a generalized alternative to the C-H equation, a mathematical study of the well-posedness issues is on its way.

2 The Heat Equation

In this section, our method of derivation is exemplified in the simple case when the target is (a generalization of) the heat equation, describing temperature evolution in rigid conductors.

A basic role is played by the *energy balance*

$$\dot{\varepsilon} = -\operatorname{div} \boldsymbol{q} + r, \tag{1}$$

and by the *entropy imbalance*

$$\dot{\eta} \geq -\operatorname{div}\left(\vartheta^{-1}\boldsymbol{q}\right) + \vartheta^{-1}r. \tag{2}$$

Here we have used standard notation: ε is *internal energy*, with associated *influx* $\boldsymbol{q}$ and *source* r; and η is *entropy*, with *influx* $\vartheta^{-1}\boldsymbol{q}$ and *source* $\vartheta^{-1}r$, where $\vartheta > 0$ is absolute *temperature*. We refer to the (influx, source) pair associated with an extensive field as to its *inflow*, and note that the inflows of entropy and internal energy are here deemed proportional, through the *coldness* ϑ^{-1}.

Next, as is customary, we introduce the *free energy*

$$\psi = \varepsilon - \eta\vartheta, \tag{3}$$

and, with the help of the energy balance, we formulate the entropy imbalance as the following 'reduced' *dissipation inequality*:

$$\dot{\psi} \leq -\eta\dot{\vartheta} - \vartheta^{-1}\boldsymbol{q} \cdot \nabla\vartheta, \tag{4}$$

restricting the free-energy growth.[4] With the constitutive assumptions

$$\psi = \widehat{\psi}(\vartheta, \nabla\vartheta), \quad \eta = \widehat{\eta}(\vartheta, \nabla\vartheta), \quad \boldsymbol{q} = \widehat{\boldsymbol{q}}(\vartheta, \nabla\vartheta), \tag{5}$$

the dissipation inequality (4) takes the form

$$(\partial_\vartheta\psi + \eta)\dot{\vartheta} + \partial_{\nabla\vartheta}\psi \cdot \nabla\dot{\vartheta} + \vartheta^{-1}\boldsymbol{q} \cdot \nabla\vartheta \leq 0. \tag{6}$$

---

[4] As is well-known, the modifier 'reduced' alludes to the fact that the source term has been eliminated from the entropy inequality, thanks to the energy balance.

We now require, *à la* Coleman-Noll, that (6) be satisfied whatever the local continuation of any conceivable process, that is, in the present case, whatever $(\dot{\vartheta}, \nabla\dot{\vartheta})$ at whatever state $(\vartheta, \nabla\vartheta)$. This requirement is satisfied if and only if

$$\widehat{\psi} \text{ is independent of } \nabla\vartheta, \quad \widehat{\eta}(\vartheta) = -\partial_\vartheta \widehat{\psi}(\vartheta), \tag{7}$$

and, moreover,

$$\widehat{\boldsymbol{q}}(\vartheta, \nabla\vartheta) \cdot \nabla\vartheta \leq 0 \quad \text{for all } \vartheta \text{ and } \nabla\vartheta. \tag{8}$$

By an argument given in Appendix B of [1], which is by now standard, it can be shown that (8) is equivalent to the following representation for the energy influx:

$$\widehat{\boldsymbol{q}}(\vartheta, \nabla\vartheta) = -\widehat{\boldsymbol{C}}(\vartheta, \nabla\vartheta)\nabla\vartheta, \tag{9}$$

where $\widehat{\boldsymbol{C}}$ is a mapping delivering the *conductivity tensor* $\boldsymbol{C}$ in a manner consistent with the inequality

$$\nabla\vartheta \cdot \widehat{\boldsymbol{C}}(\vartheta, \nabla\vartheta)\nabla\vartheta \geq 0 \quad \text{for all } \vartheta \text{ and } \nabla\vartheta. \tag{10}$$

With (7)-(9), the energy balance takes the form

$$\vartheta(\widehat{\eta}(\vartheta))\dot{} = \operatorname{div}\left(\widehat{\boldsymbol{C}}(\vartheta, \nabla\vartheta)\nabla\vartheta\right) + r; \tag{11}$$

moreover, with (11), the entropy imbalance (2) reduces to (8). Equation (11) generalizes the classical *heat equation*:

$$\lambda\dot{\vartheta} = \chi\Delta\vartheta + r,$$

which obtains upon choosing

$$\widehat{\eta}(\vartheta) = \lambda\log\vartheta + \text{a constant}, \quad \text{with} \quad \lambda > 0 \text{ the } \textit{latent heat},$$

and

$$\widehat{\boldsymbol{C}}(\vartheta, \nabla\vartheta) = \chi\boldsymbol{1}, \text{ a multiple of the identity, with } \chi > 0 \text{ the } \textit{conductivity}.$$

Remarks.
1. It follows from (7) that

$$\dot{\psi} = -\eta\dot{\vartheta}. \tag{12}$$

Consequently, in view also of (3), the time rates of entropy and energy are proportional via the coldness:

$$\dot{\eta} = \vartheta^{-1}\dot{\varepsilon}, \tag{13}$$

just as their inflows. As to the heat-conduction processes accounted for by the present theory, we note that those which are *isentropic* involve *no changes in internal energy*; and that those which are *isothermal* involve *no changes in free energy*.

2. In classical thermomechanics [2], as long as diffusion phenomena are ignored, the *internal dissipation* δ is defined to be

$$\delta := \vartheta\dot{\eta} - (-\operatorname{div}\boldsymbol{q} + r). \tag{14}$$

In view of definition (3) of the free energy, the internal dissipation is also expressible by the following alternative formula:

$$\delta = \dot{\varepsilon} + \operatorname{div}\boldsymbol{q} - r - \eta\dot{\vartheta} - \dot{\psi}. \tag{15}$$

In the purely thermal case, with the use of the energy balance (1), (15) yields:

$$\delta = \delta_{th} := -\eta\dot{\vartheta} - \dot{\psi}; \tag{16}$$

hence, in view of (12), $\delta \equiv 0$: there are no dissipative processes. More generally, when the energy balance includes the *internal working w*:

$$\dot{\varepsilon} = e + w, \quad e := -\operatorname{div}\boldsymbol{q} + r, \tag{17}$$

the internal dissipation is given the form

$$\delta = w - \eta\dot{\vartheta} - \dot{\psi}. \tag{18}$$

The inequalities

$$\delta \geq 0 \tag{19}$$

and

$$-\boldsymbol{q} \cdot \nabla\vartheta \geq 0 \tag{20}$$

(cf. (8)) are often called, respectively, the *Planck inequality* and the *Fourier inequality*, after Truesdell [2]; together, as is well known, they imply the *Clausius-Duhem inequality* (2), provided that internal energy is balanced according to (17).

If attention is restricted to isothermal processes, (18) and (19) yield

$$w - \dot{\psi} \geq 0. \tag{21}$$

In [1], when he derives his generalization of the Allen-Cahn equation,[5] Gurtin bases his discussion of admissible constitutive responses on a 'purely mechanical' dissipation inequality, his (2.3), which – the contingent form of w apart – can be given precisely this form. However, this does not mean that he in any manner, explicit or implicit, restricts his attention to isothermal processes: he simply ignores thermal variables altogether. This is legitimate, of course: nobody would insist that, to legitimately study elasticity, there is any need to specify in what more general thermomechanical theory we imagine to embed elasticity itself: for one, there are infinitely many such theories one can think of, so that any embedding is intrisically arbitrary; for two, elasticity, as a mathematical model, stands on its own feet as is: to assess to what collection of experimental facts its predictions apply is a separate issue. However, to establish elasticity's position with respect to, say, thermoelasticity, causes

---

[5] Or rather, we recall, the Ginzburg-Landau equation, in the terminology of [1].

no harm to anybody. And, in such a case, (21) would be the dissipation inequality appropriate to elasticity regarded as the isothermal sub-theory of thermoelasticity (see Appendix A of [1]).

To postulate (21) seems to us consistent with assuming that no changes in temperature (a macroscopic measure of *microscopic agitation*) or of chemical potential (as we shall see, a macroscopic measure of *microscopic organization*) are expected to accompany the microscopic phenomena that the Allen-Cahn equation aims to describe. We find such an assumption reasonable as a first approximation, yet unnecessary.

3 Models of Phase Segregation and Diffusion

We hereafter construct the title mathematical models along the same lines we used in the previous section to obtain a generalized version of the heat equation.

3.1 Common developments

The Allen-Cahn equation describes the evolution of the atomic arrangement within the unit cell of a lattice, in a two-phase material; such an arrangement is characterized macroscopically by a scalar order parameter ρ, interpreted as the volumetric density of one of the two phases (substitutional atoms and vacancies, say) of the material under study [1]. "[T]he Cahn-Hilliard equation, a conservation law, describes the transport of atoms between unit cells" [1].

Gurtin [1] begins his deduction of generalized versions of both the A-C equation and the C-H equation by assuming that any given arrangement is maintained by a system of *microforces*. He writes the *microforce balance* as follows:

$$\operatorname{div} \xi + \pi + \gamma = 0, \tag{22}$$

where ξ, the *microstress vector*, accounts for the interactions between atoms, while the scalar *internal microforce* π accounts for the atom-lattice interactions; and where the scalar *external microforce* γ represent a distance force exerted on the atom-lattice system by agencies external to it.[6] The modifier 'micro' is meant to suggest that the forces in question – as well as the energies and the entropy to be introduced later on – are different in nature from the standard forces associated with ordinary deformation processes. Just as in the classical theory of rigid conductors dealt with in the previous section, standard forces and energies are here ignored. The tacit assumption, whose applicability must be verified *a posteriori*, is that segregation and diffusion processes can be efficiently described, at least as a first approximation, irrespectively of possibly concomitant deformation processes.[7]

---

[6] Alternatively, ξ could be thought of as accounting for the *short-range* interactions between atoms, and π for both the *long-range* interactions between atoms and the atom-lattice interactions.

[7] A version of the C-H theory for deformable continua is found in Section 4 of [1].

We begin our deduction by writing the *microenergy balance* directly in the reduced form one arrives at with the use of (22), namely,

$$\dot{\varepsilon} = \bar{e} + w, \quad \bar{e} := -\operatorname{div}\bar{\boldsymbol{h}} + \overline{m}, \quad w := -\pi\dot{\rho} + \xi \cdot \nabla\dot{\rho}, \tag{23}$$

where $\bar{e}$ is an inflow of *microenergy* ε, consisting in an influx $\bar{\boldsymbol{h}}$ and a source $\overline{m}$, and where w is the *internal microworking*. Our equation (23) results from localization of the microenergy balance for an arbitrary control volume V:

$$\int_V \dot{\varepsilon} = -\int_{\partial V} \bar{\boldsymbol{h}} \cdot \boldsymbol{n} + \int_V \overline{m} + \int_{\partial V} (\xi \cdot \boldsymbol{n})\dot{\rho} + \int_V \gamma\dot{\rho},$$

with the use of (22). Note that $(\dot{\rho}\xi, \dot{\rho}\gamma)$ can be thought of as the additional energy inflow associated to the kinetics described by $\dot{\rho}$.

We next postulate the *microentropy imbalance*:

$$\dot{\eta} \geq -\operatorname{div}(\mu\bar{\boldsymbol{h}}) + \mu\,\overline{m}, \tag{24}$$

where η is the *microentropy* and $\mu > 0$ the *chemical potential.*

Comparison of (17) and (2) with, respectively, (23) and (24) shows that in the latter two relations *the chemical potential is given the same role as the coldness* in the former two: in short,

$$orderliness\ \mu \ \sim \ coldness\ \vartheta^{-1}.$$

If we consistently define, by analogy with (3), the *free microenergy* as

$$\psi = \varepsilon - \eta\,\mu^{-1}, \tag{25}$$

combination of (23), (24) and (25) yields the reduced dissipation inequality

$$\dot{\psi} \leq -\eta(\mu^{-1})\dot{} + \mu^{-1}\bar{\boldsymbol{h}} \cdot \nabla\mu - \pi\dot{\rho} + \xi \cdot \nabla\dot{\rho}. \tag{26}$$

We shall base our discussion of admissible material response upon consistency with this inequality in whatever conceivable process.

Remark. It would be tempting to interpret the order parameter as an arrangement's 'probability', but no normalization constraint such as

$$\int_\Omega \rho = 1 \tag{27}$$

enters the A-C theory (here Ω denotes the region occupied by the body of interest). Instead, the C-H equation (2) implies that

$$\int_\Omega \dot{\rho} = \left(\int_\Omega \rho\right)\dot{} = \int_{\partial\Omega} \kappa\,\partial_{\boldsymbol{n}}\mu, \quad \partial_{\boldsymbol{n}}\mu := \nabla\mu \cdot \boldsymbol{n}, \tag{28}$$

where

$$\mu := f'(\rho) - \alpha\Delta\rho; \tag{29}$$

if, as is customary, a homogeneous Neumann boundary condition is stipulated for the chemical potential μ, then the total of the order parameter ρ is conserved.[8] Were condition (27) regarded as a part of the theory, then it would be natural to consider formally an augmented free microenergy functional

$$\Psi_a\{\rho,\mu\} = \int_\Omega (\psi - \mu\rho), \quad \Psi\{\rho\} = \int_\Omega \psi, \tag{30}$$

and to characterize equilibrium by setting the variational derivative of Ψ_a equal to null:

$$\delta_\rho \Psi_a = \delta_\rho \Psi - \mu = 0. \tag{31}$$

This would establish the role of the chemical potential μ as the *reaction field* maintaining the normalization constraint at equilibrium, whatever the boundary conditions.

3.2 Phase segregation and the Allen-Cahn equation

Our key constitutive assumption is that all of ψ, η, ξ, π, and $\bar{h}$, depend on the list of variables $(\rho, \nabla\rho, \dot\rho, \mu)$, with the form of the constitutive mappings restricted by the requirement that the dissipation inequality (26) be satisfied identically for whatever local continuation of any given process, namely, whatever $(\nabla\dot\rho, \ddot\rho, \dot\mu, \nabla\mu)$ at whatever state $(\rho, \nabla\rho, \dot\rho, \mu)$. This is the case if and only if

$$\widehat{\psi} \text{ is independent of } \dot\rho, \quad \widehat{\eta}(\rho,\nabla\rho,\mu) = \mu^2 \partial_\mu \widehat{\psi}(\rho,\nabla\rho,\mu),$$
$$\widehat{\xi}(\rho,\nabla\rho,\mu) = \partial_{\nabla\rho}\widehat{\psi}(\rho,\nabla\rho,\mu), \quad \bar{h}(\rho,\nabla\rho,\dot\rho,\mu) \equiv 0, \tag{32}$$

and, moreover,

$$\widehat{\pi}_{dis}(\rho,\nabla\rho,\dot\rho,\mu)\,\dot\rho \leq 0, \tag{33}$$

where

$$\widehat{\pi}_{dis}(\rho,\nabla\rho,\dot\rho,\mu) := \widehat{\pi}(\rho,\nabla\rho,\dot\rho,\mu) + \partial_\rho\widehat{\psi}(\rho,\nabla\rho,\mu). \tag{34}$$

Inequality (33) is equivalent to the following representation result for the dissipative part of the internal microforce:

$$\widehat{\pi}_{dis}(\rho,\nabla\rho,\dot\rho,\mu) := -\widehat{\beta}(\rho,\nabla\rho,\dot\rho,\mu)\dot\rho, \quad \widehat{\beta}(\rho,\nabla\rho,\dot\rho,\mu) \geq 0. \tag{35}$$

Consequently, the constitutive mapping delivering the internal microforce is the sum of an energetic and a dissipative contribution, namely,

$$\widehat{\pi}(\rho,\nabla\rho,\dot\rho,\mu) = -\partial_\rho\widehat{\psi}(\rho,\nabla\rho,\mu) - \widehat{\beta}(\rho,\nabla\rho,\dot\rho,\mu)\dot\rho. \tag{36}$$

With the use of $(32)_{1,3}$, $(23)_3$, and (36), the microforce balance (22) takes the form

$$\widehat{\beta}(\rho,\nabla\rho,\dot\rho,\mu)\dot\rho = \text{div}\left(\partial_{\nabla\rho}\widehat{\psi}(\rho,\nabla\rho,\mu)\right) - \partial_\rho\widehat{\psi}(\rho,\nabla\rho,\mu) + \gamma. \tag{37}$$

---

[8] For a study of Neumann boundary conditions in the case of the generalized C-H model due to Gurtin, see [4].

Furthermore, with the use of $(32)_{2,4}$ and (25), equation (23) can be written as follows:

$$\mu^{-1}\big(\widehat{\eta}(\rho, \nabla\rho, \mu)\big)^{\cdot} = \widehat{\beta}(\rho, \nabla\rho, \dot{\rho}, \mu)\dot{\rho}^2 + \overline{m}, \tag{38}$$

an expression of the microenergy balance which, in view of (35), is consistent with

$$\dot{\eta} \geq \mu\,\overline{m}, \tag{39}$$

the form taken by the microentropy imbalance (24).

The microforce balance (37) *is our generalized version of the Allen-Cahn equation.* We note that, if the chemical potential μ is not regarded as a parameter, then (37) should be considered coupled with the microenergy balance (38). We also note that, for $\widehat{\psi}$ and $\widehat{\pi}$ independent of the chemical potential, inequality (26) reduces to the dissipation inequality postulated in [1], namely,

$$\dot{\psi} \leq \xi \cdot \nabla\dot{\rho} - \pi\dot{\rho} \tag{40}$$

(recall Remark 2 in Section 2); and that equation (37) reduces to the generalized form of the A-C equation derived in [1] (cf., respectively, inequality (2.2) in Section 2.1 and equation (2.12) in Section 2.3). The standard A-C equation (1) follows on choosing, in addition, $\gamma = 0$, $\widehat{\beta}$ constant-valued, and

$$\widehat{\psi}(\rho, \nabla\rho) = f(\rho) + \frac{1}{2}\alpha|\nabla\rho|^2, \tag{41}$$

with α a positive constant and f a double-well potential inducing phase segregation. More generally, *the same generalized A-C equation as in [1] obtains within our present framework whenever (i) the material response is chosen independent of the gradient of the chemical potential and (ii) attention is restricted to processes during which the chemical potential is kept constant in time.* In particular, in statics, and provided that $\overline{m}$ is set everywhere to null, the predictions of our mathematical model and Gurtin's are the same.

Remark. Our model has, with respect to the standard A-C model, the same position as thermoelasticity with respect to elasticity, with chemical potential playing the role of coldness: just as purely elastic processes can be regarded as isothermal thermomechanical processes, the A-C processes are those during which the chemical potential is kept constant, both in time and in space. We point out that such double constancy is required for a scalar field over the region occupied by a deformable material body to be *constant in time in a properly invariant manner*. To see that this is the case, let $\phi = \hat{\phi}(t, y)$ be a scalar field depending on the current place $y = \hat{y}(x, t)$ of a material point occupying the referential place x, so that

$$\dot{\phi} = \partial_t\phi + \partial_y\phi \cdot \boldsymbol{v}, \quad \nabla\phi = (\partial_y\phi)\nabla y,$$

with $\boldsymbol{v}$ the motion velocity and the deformation gradient ∇y an invertible tensor. In a galilean change in observer with relative velocity $\boldsymbol{a}$,

$$\boldsymbol{v} \mapsto \boldsymbol{v}^+ = \boldsymbol{v} + \boldsymbol{a}.$$

Hence,

$$\dot{\phi}^+ = \dot{\phi} \quad \text{for all vector } \boldsymbol{a} \quad \Leftrightarrow \quad \nabla\phi = 0. \tag{42}$$

In particular, for ϕ to be constant in time in a properly invariant manner, both $\partial_t\phi$ and $\nabla\phi$ must vanish.

3.3 Phase diffusion and the Cahn-Hilliard equation: Step 1

This time, our basic constitutive assumption is that all of ψ, η, ξ, π, and $\bar{\boldsymbol{h}}$, depend on the list of variables $(\rho, \nabla\rho, \mu, \nabla\mu)$, with the form of the constitutive mappings restricted by the requirement that the dissipation inequality (26) be satisfied identically for whatever the local continuation $(\dot{\rho}, \nabla\dot{\rho}, \dot{\mu}, \nabla\dot{\mu})$ of any given process. This is tantamount to requiring that

$$\widehat{\psi} \text{ is independent of } \nabla\mu, \quad \widehat{\pi}(\rho, \nabla\rho, \mu) = -\partial_\rho\widehat{\psi}(\rho, \nabla\rho, \mu),$$
$$\widehat{\eta}(\rho, \nabla\rho, \mu) = \mu^2\partial_\mu\widehat{\psi}(\rho, \nabla\rho, \mu), \quad \widehat{\xi}(\rho, \nabla\rho, \mu) = \partial_{\nabla\rho}\widehat{\psi}(\rho, \nabla\rho, \mu); \tag{43}$$

and that, moreover,

$$\bar{\boldsymbol{h}} \cdot \nabla\mu \geq 0, \tag{44}$$

or rather, equivalently, that

$$\bar{\boldsymbol{h}}(\rho, \nabla\rho, \mu, \nabla\mu) = \widehat{\boldsymbol{H}}(\rho, \nabla\rho, \mu, \nabla\mu)\nabla\mu, \quad \nabla\mu \cdot \widehat{\boldsymbol{H}}(\rho, \nabla\rho, \mu, \nabla\mu)\nabla\mu \geq 0. \tag{45}$$

In view of $(43)_{1,2}$, we write the microforce balance (22) as

$$-\text{div}\left(\partial_{\nabla\rho}\widehat{\psi}(\rho, \nabla\rho, \mu)\right) + \partial_\rho\widehat{\psi}(\rho, \nabla\rho, \mu) - \gamma = 0. \tag{46}$$

Moreover, with the use of (43), $(23)_3$, and (25), we give the microenergy balance (23) the form

$$\mu^{-1}\dot{\eta} = -\text{div}\,\bar{\boldsymbol{h}} + \overline{m}, \tag{47}$$

or more explicitly, in view also of $(45)_1$,

$$\mu^{-1}(\widehat{\eta}(\rho, \nabla\rho, \mu))\dot{} = -\text{div}\left(\widehat{\boldsymbol{H}}(\rho, \nabla\rho, \mu, \nabla\mu)\nabla\mu\right) + \overline{m}. \tag{48}$$

Remark. A relevant difference in the physics underlying our mathematical models of phase segregation and diffusion is that the relative dissipative mechanisms are different, dissipation being ascribed to work-conjugation of the microforce π_{dis} and the order parameter rate $\dot{\rho}$ in the former case (where, consequently, dissipative terms enter the microforce balance); to work conjugation of the microenergy influx $\bar{\boldsymbol{h}}$ and the gradient $\nabla\mu$ of the chemical potential, the field driving diffusion, in the latter.

3.4 Phase diffusion and the Cahn-Hilliard equation: Step 2

With a view toward reconstructing a model of Cahn-Hilliard type from (46) and (48), we need to further specialize our constitutive choices of a free-energy mapping $\widehat{\psi}$ and an influx-tensor mapping $\widehat{\boldsymbol{H}}$. As to the former, we take

$$\widehat{\psi}(\rho, \nabla\rho, \mu) = -\mu\rho + \widetilde{\psi}(\rho, \nabla\rho), \tag{49}$$

whence, with the use also of the second and fourth of (43),

$$\partial_\rho \widehat{\psi}(\rho, \nabla\rho, \mu) = -\mu + \partial_\rho \widetilde{\psi}(\rho, \nabla\rho) = -\widehat{\pi}(\rho, \nabla\rho, \mu), \tag{50}$$

$$\partial_{\nabla\rho} \widehat{\psi}(\rho, \nabla\rho, \mu) = \partial_{\nabla\rho} \widetilde{\psi}(\rho, \nabla\rho) = \widehat{\xi}(\rho, \nabla\rho, \mu), \tag{51}$$

$$\partial_\mu \widehat{\psi}(\rho, \nabla\rho, \mu) = -\rho \tag{52}$$

(note that *the microstress vector turns out to be independent of the chemical potential*).

With the first of (50) and of (51), the microforce balance (46) reads:

$$\mu = \partial_\rho \widetilde{\psi}(\rho, \nabla\rho) - \operatorname{div} \partial_{\nabla\rho} \widetilde{\psi}(\rho, \nabla\rho) - \gamma.^9 \tag{53}$$

From (52) and the third of (43) it follows that

$$\widehat{\eta}(\rho, \nabla\rho, \mu) = -\mu^2 \rho, \tag{54}$$

so that, in particular, the *microentropy is independent of the order-parameter gradient*. With (54) we can give the microenergy balance (48) the following form

$$-\mu^{-1}(\mu^2 \rho)^{\cdot} = -\operatorname{div}\left(\widehat{\boldsymbol{H}}(\rho, \nabla\rho, \mu, \nabla\mu)\nabla\mu\right) + \overline{m}. \tag{55}$$

Our general replacement for the Cahn-Hilliard diffusion equation is the system consisting of the microforce balance (53) *and the energy balance* (55). Equation (53) is identical to equation (3.15) of [1], although it has been derived in a slightly different manner. Instead, equation (55) is similar, but not identical to the generalized C-H equation deduced in [1], because it expresses a different balance. We discuss this issue in the next subsection, where we motivate the differences and try and make them as small as possible.

3.5 Relationship with Gurtin's diffusion model

When in Section 3 of [1] he deals with the C-H equation, Gurtin, in line with a view point developed by materials scientists [5], postulates the following *balance law for the order parameter*:

$$\dot{\rho} = -\operatorname{div}\boldsymbol{h} + m, \tag{56}$$

---

[9] Just as we did in the remark ending Subsection 3.1, in standard derivations of the Cahn-Hilliard equation it is customary *to define* the chemical potential to be the variational derivative of the free energy, which is precisely what this form of the microforce balance requires, for γ null (cf. equation (1.10) of [1] and our equation (31)).

with $(\boldsymbol{h}, m)$ the inflow of ρ. He then derives a representation for the order parameter influx:

$$\boldsymbol{h} = -\boldsymbol{M}\nabla\mu, \quad \text{with} \quad \boldsymbol{M} = \widehat{\boldsymbol{M}}(\rho, \nabla\rho, \mu, \nabla\mu), \tag{57}$$

and with

$$\nabla\mu \cdot \widehat{\boldsymbol{M}}(\rho, \nabla\rho, \mu, \nabla\mu)\nabla\mu \geq 0.^{10} \tag{58}$$

Combination of (56) and (57) yields the order-parameter balance

$$\dot{\rho} = \operatorname{div}\left(\widehat{\boldsymbol{M}}(\rho, \nabla\rho, \mu, \nabla\mu)\nabla\mu\right) + m. \tag{59}$$

Finally, substituting (53) into this last relation, Gurtin arrives at his *generalized Cahn-Hilliard equation*:

$$\dot{\rho} = \operatorname{div}\left(\widehat{\boldsymbol{M}}(\rho, \nabla\rho, \mu, \nabla\mu)\nabla\left(\partial_\rho\widetilde{\psi}(\rho, \nabla\rho) - \operatorname{div}\partial_{\nabla\rho}\widetilde{\psi}(\rho, \nabla\rho) - \gamma\right)\right) + m \tag{60}$$

(cf. equation (3.17) of [1]).

Gurtin also notes that a derivation of the standard C-H equation requires that the influx $\boldsymbol{h}$ be constitutively given in terms of a constant and isotropic *mobility tensor*

$$\boldsymbol{M} = \kappa\boldsymbol{1}, \quad \kappa > 0, \tag{61}$$

whence

$$\boldsymbol{h} = -\kappa\nabla\mu \tag{62}$$

(cf. equation (1.9) of [1]). With (62), the order-parameter balance (56) takes the form

$$\dot{\rho} = \kappa\Delta\mu + m, \tag{63}$$

and (60) becomes:

$$\dot{\rho} = \kappa\Delta\left(\partial_\rho\widetilde{\psi}(\rho, \nabla\rho) - \operatorname{div}\partial_{\nabla\rho}\widetilde{\psi}(\rho, \nabla\rho) - \gamma\right) + m. \tag{64}$$

The standard C-H equation (2) follows from (64), on choosing for $\widetilde{\psi}$ the same form specified in (41) for $\widehat{\psi}$ and on setting null both γ and m.

Suppose now that we choose $\widehat{\boldsymbol{H}}$ in (55) as follows:

$$\widehat{\boldsymbol{H}}(\rho, \nabla\rho, \mu, \nabla\mu) = \mu\widehat{\boldsymbol{M}}(\rho, \nabla\rho, \mu, \nabla\mu), \tag{65}$$

so that

$$\bar{\boldsymbol{h}} = \boldsymbol{H}\nabla\mu = -\mu\boldsymbol{h}. \tag{66}$$

---

[10] A kinetic (i.e., evolution) equation resulting from combination of (56) (with $m = 0$) and $(57)_1$ has been proposed by Truskinovsky in Appendix 1 of [6], where he also shows how to derive from it the standard Cahn-Hilliard equation, under the assumption that the chemical potential is the variational derivative of the internal energy. In the same paper, another kinetic equation is proposed (in our notations, $\dot{\rho} = -\beta^{-1}\mu$, with β a positive material constant), which, granted the same characterization of the chemical potential, yields a generalization of the Allen-Cahn equation (1).

In so doing, we have taken the microenergy influx proportional to the order-parameter influx via the chemical potential. If, as we also do, the microenergy source is assumed to be such that

$$\overline{m} = -\mu\, m, \tag{67}$$

then *the order-parameter inflow determines the microenergy inflow just as it determines the free-energy inflow in* [1]. Substitution of $(43)_3$, (66) and (67) into (47) yields:

$$-\mu^{-1}(\mu^2\rho)\dot{} = \mathrm{div}\,(\mu\boldsymbol{h}) - \mu\, m, \tag{68}$$

Comparison of the microenergy balance (68) with the order-parameter balance (56) shows that, *if the chemical potential is a space-time constant*, the two statements are equivalent. Thus, provided we restrict attention to the appropriate process class, our model yields the same predictions as the generalized C-H equation (60) of [1].

Remarks.
1. For $m = 0$, and for homogeneous Neumann boundary conditions

$$(\boldsymbol{M}\nabla\mu) \cdot \boldsymbol{n} = 0, \tag{69}$$

the balance (59) implies that the total of the order-parameter is conserved, just as in the case of the standard C-H equation. The same result cannot be expected to hold in general in a theory like ours, which does not postulate an order-parameter balance, and relies instead on the balance of microenergy. However, integration over a material region Ω of (48) gives:

$$\left(\int_\Omega \eta\right)\dot{} = -\int_{\partial\Omega} \mu\,(\boldsymbol{H}\nabla\mu) \cdot \boldsymbol{n} + \int_\Omega \nabla\mu \cdot \boldsymbol{H}\nabla\mu + \int_\Omega \overline{m}. \tag{70}$$

Thus, if the boundary condition

$$\mu(\boldsymbol{H}\nabla\mu) \cdot \boldsymbol{n} = 0 \quad \text{over } \partial\Omega \tag{71}$$

prevails, then the third of (45) and (54) imply that *in an unforced process* $(\overline{m} = 0)$ *the total microentropy cannot decrease*:

$$\left(\int_\Omega \eta\right)\dot{} \geq 0. \tag{72}$$

This conclusion indicates what boundary conditions on the chemical potential are physically plausible within our generalization of the Cahn-Hilliard theory.

2. For $\overline{m} = 0$ and $\boldsymbol{H} = \kappa\mu\boldsymbol{1}$, the microenergy balance (48) reads:

$$\mu^{-1}\dot{\eta} = \kappa(\mu\Delta\mu + |\nabla\mu|^2) = \frac{1}{2}\kappa\,\Delta\mu^2. \tag{73}$$

Moreover, the boundary condition (71) becomes

$$\mu^2\partial_{\boldsymbol{n}}\mu = 0 \quad (\;\Leftrightarrow\; \mu^2\partial_{\boldsymbol{n}}\mu^2 = 0) \quad \text{over } \partial\Omega. \tag{74}$$

Thus, if

$$\dot{\eta} = 0,$$

we see that, under circumstances that are typical of the standard Cahn-Hilliard processes regulated by (2), the balance of microenergy implies that *the microentropy is constant in time if and only if the chemical potential is a space-time constant*. When this is the case, the microforce balance (46) can be seen as the Euler-Lagrange equation of the free microenergy functional

$$\Psi\{\rho\} = \int_\Omega (\widehat{\psi}(\rho, \nabla\rho, \mu) - \gamma\rho) \quad \text{for } \widehat{\psi} \text{ as in (49).}$$

References

1. Gurtin, M.E.: Generalized Ginzburg-Landau and Cahn-Hilliard equations based on a microforce balance. *Physica D* **92** 178-192 (1996)
2. Truesdell, C. : Internal dissipation, Lecture 2 in *Rational Thermodynamics*, Springer-Verlag (1984).
3. Gurtin, M.E. and Vargas, A.S.: On the classical theory of reacting fluid mixtures. *Arch. Rational Mech. Anal.* **43** 179-197 (1971)
4. Miranville, A.: Consistent models of Cahn-Hilliard-Gurtin equations with Neumann boundary conditions. *Physica D* **158** 233-257 (2001)
5. Larché, F.C. and Cahn, J.W.: The interactions of composition and stress in crystalline solids. *Acta Metallurgica* **33** 331-357 (1985)
6. Truskinovsky, L.: Kinks versus shocks. Pp. 185-229 of *Shock Induced Transitions and Phase Structures in General Media*, J.E. Dunn, R. Fosdick, and M. Slemrod Ed.s, Springer- Verlag (1993).