

Generalized Ginzburg–Landau and Cahn–Hilliard equations based on a microforce balance

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Abstract

A unified framework for equations of Ginzburg–Landau and Cahn–Hilliard type is developed using, as a basis, a balance law for microforces in conjunction with constitutive equations consistent with a mechanical version of the second law.

1. Introduction

The Ginzburg–Landau equation¹

$$\beta \rho \dot{=} \alpha \Delta \rho - f'(\rho) \quad (\Delta = \text{Laplacian}) \quad (1.1)$$

and the Cahn–Hilliard equation²

$$\rho \dot{=} \kappa \Delta [f'(\rho) - \alpha \Delta \rho] \quad (1.2)$$

($\alpha > 0, \beta > 0, \kappa > 0$) are central to materials science, as they characterize important qualitative features of two-phase systems. Each of these equations governs the evolution of an order-parameter³ $\rho = \rho(x, t)$: the Ginzburg–Landau equation describes the ordering of atoms within unit cells on a lattice, while the Cahn–

Hilliard equation, a conservation law, describes the transport of atoms between unit cells.

Both the Ginzburg–Landau and Cahn–Hilliard equations are based on a free energy

$$\hat{\psi}(\rho, \nabla \rho) = f(\rho) + \frac{1}{2} \alpha |\nabla \rho|^2 \quad (1.3)$$

with $f(\rho)$, the “coarse-grain” free energy, a double-well potential whose wells define the phases, and both equations lead to a diffuse phase-interface within which ρ undergoes large variations.

The standard derivation of the Ginzburg–Landau equation begins with the constitutive equation (1.3) for the free energy and is based on considering the total free energy

$$\Psi(\rho) = \int_B \hat{\psi}(\rho, \nabla \rho) \, dv \quad (1.4)$$

of the region of space B occupied by the material. The formal variation $\delta \Psi(\rho)$ with respect to fields ρ that vanish on ∂B is given by

¹ This equation, which is attributed by Chan [1] to Landau and Khalatnikov [2], is also referred to as the Allen–Cahn equation [3].

² Cahn [4].

³ The term order-parameter is used to denote a field whose values describe the phase of the system under consideration.

$$\begin{aligned}\delta\Psi(\rho) &= \int_B [f'(\rho) \delta\rho + \alpha \nabla\rho \cdot \delta\nabla\rho] dv \\ &= \int_B [f'(\rho) - \alpha \Delta\rho] \delta\rho dv\end{aligned}\quad (1.5)$$

and yields the expression

$$\frac{\delta\Psi}{\delta\rho} = f'(\rho) - \alpha \Delta\rho \quad (1.6)$$

for the variational derivative (the coefficient of $\delta\rho$). Equilibrium is characterized by the vanishing of $\delta\Psi/\delta\rho$; the hypothesis underlying the standard derivation is that relaxation toward equilibrium be governed by a parameter $\beta > 0$ through a relation

$$\beta \rho' = -\frac{\delta\Psi}{\delta\rho}; \quad (1.7)$$

a consequence of (1.6) and (1.7) is the Ginzburg–Landau equation.

The Cahn–Hilliard equation is derived analogously. The starting point is the mass balance

$$\rho' = -\operatorname{div} \mathbf{h} \quad (1.8)$$

with the mass flux \mathbf{h} related to the chemical potential μ through the constitutive equation

$$\mathbf{h} = -\kappa \nabla\mu. \quad (1.9)$$

Again the free energy is presumed to have the form (1.3), which, because of the presence of density gradients, is incompatible with the standard definition of μ as the partial derivative of ψ with respect to ρ ; instead μ is defined as the variational derivative

$$\mu = \frac{\delta\Psi}{\delta\rho}; \quad (1.10)$$

this yields the Cahn–Hilliard equation

$$\rho' = \kappa \Delta \frac{\delta\Psi}{\delta\rho}. \quad (1.11)$$

Although these derivations of the Ginzburg–Landau and Cahn–Hilliard equations are simple,

elegant, and physically sound, I have three objections:

- the derivations limit the manner in which rate terms enter the equations;
- the derivations require a-priori specification of the constitutive equations;
- it is not clear how these derivations are to be generalized in the presence of processes such as deformation and heat transfer.⁴

The major advances in nonlinear continuum mechanics over the past thirty years are based on the separation of basic balance laws (such as those for mass and force), which are general and hold for large classes of materials, from constitutive equations (such as those for elastic solids and viscous fluids), which delineate specific classes of material behavior. In the derivations presented above there is no such separation, and it is not clear whether or not there is an underlying balance law that can form a basis for more general theories.

My view is that while derivations of the form (1.3)–(1.11) are useful and important, they should not be regarded as basic, but rather as precursors of more complete theories. While variational derivations often point the way toward a correct statement of basic laws, to me such derivations obscure the fundamental nature of balance laws in any general framework that includes dissipation.

What distinguishes the development presented here from other macroscopic theories of order-parameters is: (i) the separation of balance laws from constitutive equations; and (ii) the introduction of a new balance law for microforces. Here I continue an approach, begun in collaboration with Fried [8, 9], which is based on

⁴ In their discussions of the phase-field theory of solidification, Penrose and Fife [5] and Schofield and Oxtoby [6] replace balance of energy, a physical law that has been a basis for continuum physics for over a century, with a mixed variational relation of the form (1.11) involving internal energy and entropy. See also Hohenberg and Halperin [7].

the belief that fundamental physical laws involving energy should account for the working (expenditure of power) associated with each operative kinematical process. In the Ginzburg–Landau and Cahn–Hilliard theories the kinematics is that associated with the order-parameter ρ , and it seems plausible that there should be “microforces” whose working accompanies changes in ρ .⁵ Fried and I describe this working through terms of the form (force)($\dot{\rho}$), so that microforces are scalar rather than vector quantities. Specifically, the microforce system is characterized by a vector stress ξ together with scalar body forces π and γ that represent, respectively, *internal* and *external* forces distributed over the volume of B . To describe the precise manner in which these fields expend power it is useful to consider the body as a lattice or network together with atoms that move, microscopically, relative to the lattice.⁶ Here it is important to focus attention not on individual atoms but on configurations (i.e., arrangements or densities) of atoms as characterized by the order parameter ρ . Given an arbitrary control volume R (subregion of B), with \mathbf{n} the outward unit normal to ∂R , each of

$$\int_{\partial R} (\xi \cdot \mathbf{n}) \dot{\rho} \, da, \quad \int_R \pi \dot{\rho} \, dv, \quad \int_R \gamma \dot{\rho} \, dv$$

represents an expenditure of power on the atomic configurations within R :

- $(\xi \cdot \mathbf{n}) \dot{\rho}$ describes power expended across ∂R by configurations exterior to R , but neighboring ∂R ;
- $\pi \dot{\rho}$ represents power expended on the atoms of R by the lattice; for example, in the ordering of atoms within – or the transport of atoms

- between – unit cells of the lattice;
- $\gamma \dot{\rho}$ describes power expended on the atoms of R by sources external to the body.⁷

What is most important, this system of forces is presumed consistent with the *microforce balance*⁸

$$\int_{\partial R} \xi \cdot \mathbf{n} \, da + \int_R (\pi + \gamma) \, dv = 0 \quad (1.12)$$

for each control volume R .

To fix ideas I begin with the Ginzburg–Landau system as discussed in [8]. The treatment of [8] is based on the microforce balance (1.12), suitable constitutive equations, and a mechanical version of the second law which asserts that the free energy of R increase at a rate not greater than the working, $\mathcal{W}(R)$, of all forces *external* to R . Here

$$\mathcal{W}(R) = \int_{\partial R} (\xi \cdot \mathbf{n}) \dot{\rho} \, da + \int_R \gamma \dot{\rho} \, dv, \quad (1.13)$$

and the second law takes the form of a *dissipation inequality*

$$\left\{ \int_R \psi \, dv \right\}' \leq \int_{\partial R} (\xi \cdot \mathbf{n}) \dot{\rho} \, da + \int_R \gamma \dot{\rho} \, dv, \quad (1.14)$$

⁷ Cf. Hohenberg and Halperin [7], who introduce a source term in the Ginzburg–Landau equation that corresponds to γ .

⁸ The following two arguments might serve as partial motivation for the microforce balance: (1) At equilibrium, if the total free-energy has the form (1.4), then the requirement $\delta\Psi(\rho)=0$ for all $\delta\rho$ that vanish on ∂B yields the Euler–Lagrange equation $\operatorname{div} \xi + \pi = 0$ with $\xi = \partial_\rho \psi(\rho, \nabla\rho)$, $\pi = -\partial_\rho \psi(\rho, \nabla\rho)$. This represents a statical version of the microforce balance (1.12) with ξ and π given constitutive representations and $\gamma = 0$. In dynamics with general forms of dissipation there is no such variational principle; the use of a microforce balance is an attempt to extend to dynamics an essential feature of statical theories. (2) Standard forces in continua are associated with macroscopic length scales, while microforces describe forces associated with microscopic configurations of atoms. The need for a separate microforce balance seems a necessary consequence of the disparate length scales involved.

⁵ If the sole macroscopic manifestation of atomistic kinematics is the order-parameter ρ , then it seems reasonable that interatomic forces may be characterized macroscopically by fields that perform work when ρ undergoes changes.

⁶ Cf. Larché and Cahn [10], §2.

where ψ represents the free energy, per unit volume. (In Appendix A the dissipation inequality is derived from more fundamental versions of the first two laws under the assumption of isothermal conditions.) This inequality is for the material – lattice plus atoms – in R , and therefore does not include the working of π , which, being a force exerted by the lattice on the atoms, acts internally to the material in R ; on the other hand, (1.12) represents a force balance for the atomic configurations and therefore includes the action of π .

I introduce constitutive equations for ψ , the stress ξ , and the internal force π ; no constitutive relation is specified for the external force γ ; instead γ is presumed to be arbitrarily assignable, just as the standard body forces and heat supply are left assignable in the classical theories of mechanics and heat conduction.⁹ Specifically, ψ , ξ , and π are allowed to depend on the order parameter ρ and – to model capillarity and transition kinetics – also on $\nabla\rho$ and ρ' :¹⁰

$$\begin{aligned}\psi &= \hat{\psi}(\rho, \nabla\rho, \rho'), & \xi &= \hat{\xi}(\rho, \nabla\rho, \rho'), \\ \pi &= \hat{\pi}(\rho, \nabla\rho, \rho').\end{aligned}\quad (1.15)$$

Here one might argue that ρ' should not appear

in the constitutive equation for the free energy, but rather than omit it by fiat, I choose instead to show that a dependence on ρ' is incompatible with the second law.¹¹ Precisely, the dissipation inequality is used to show that ψ and ξ are independent of ρ' , and that

$$\xi = \partial_\rho \hat{\psi}(\rho, \nabla\rho), \quad \pi = -\partial_\rho \hat{\psi}(\rho, \nabla\rho) - \beta\rho', \quad (1.16)$$

where $\partial_\rho \hat{\psi}$ and $\partial_\rho \hat{\psi}$ denote the partial derivatives of $\hat{\psi}$ with respect to $\rho = \nabla\rho$ and ρ , and where $\beta = \beta(\rho, \nabla\rho, \rho') \geq 0$ is a constitutive modulus. The microforce balance $\text{div } \xi + \pi + \gamma = 0$ and the reduced constitutive equations (1.16) then yield a general nonlinear PDE, which for an energy of the form (1.3), constant β , and $\gamma = 0$ reduces to the Ginzburg–Landau equation.

The resulting PDE depends crucially on the particular form chosen for the constitutive equations. In Section 2.4 I show that the inclusion of $\nabla\rho'$ in the list of constitutive variables leads, for an energy of the form (1.3) and linear kinetics, to an equation

$$\beta\rho' = \alpha \Delta\rho + \kappa \Delta\rho' - f'(\rho) \quad (1.17)$$

containing the additional kinetic term $\kappa \Delta\rho'$ ($\kappa > 0$).

The Cahn–Hilliard theory is developed in Section 3 beginning with balance laws for mass and microforce in conjunction with a dissipation inequality of the form (1.14) augmented by terms associated with mass transport.¹² Within

⁹ The constitutive theories I discuss utilize the Coleman–Noll procedure [12], a procedure based on the premise that the second law be satisfied in all conceivable processes, irrespective of the difficulties involved in producing such processes in the laboratory. The rational application of the Coleman–Noll procedure requires external fields that ensure satisfaction of the underlying balance laws in all processes. This may seem artificial, but it is no more artificial than theories based on virtual work or minimum “energy”, as these require arbitrary variations of the fields, even though such variations are generally inconsistent with the resulting balance laws. The method of Coleman and Noll has the same goal as variational procedures: *to ensure a properly invariant theory consistent with basic physical laws under the widest possible set of circumstances.*

¹⁰ Here and throughout only *homogeneous* constitutive behavior is considered; thus, e.g., the first of (2.7) signifies $\psi(x, t) = \hat{\psi}(\rho(x, t), \nabla\rho(x, t), \rho'(x, t))$, so that $\hat{\psi}$ represents a constitutive response function for the free energy, while $\psi = \psi(x, t)$ represents the actual free energy as a field over the body.

¹¹ Truesdell, in discussing the formulation of *general* constitutive theories, adopts the view that “a quantity present as an independent variable in one constitutive equation should be so present in all, unless . . . its presence contradicts some law of physics or rule of invariance” (Truesdell and Noll [11], §96). Truesdell and Noll assert: “This . . . reflects on the scale of gross phenomena the fact that all observed effects result from a common structure such as the motions of molecules.”

¹² In [13] I gave a derivation of the Cahn–Hilliard equation based on this form of the second law, but I did not introduce a microforce balance and, consequently, the argument is far more complicated.

this framework I discuss the Cahn–Hilliard equation as well as various generalizations, including the equation¹³

$$\rho' = \kappa \Delta[f'(\rho) - \alpha \Delta\rho + \beta \rho'] \quad (1.18)$$

($\beta > 0$).

In Section 4 the Cahn–Hilliard theory is extended to allow for deformation.¹⁴ The basic balances are the standard force and moment balances associated with the gross deformation of the body in conjunction with balance laws for mass and microforce.

Notation. I consider a body B that occupies a fixed region in three-dimensional Euclidean space \mathbb{R}^3 . R will always designate a control volume (fixed subregion of B) and \mathbf{n} will always denote the outward unit normal to ∂R .

Vectors (elements of \mathbb{R}^3 viewed as 3×1 matrices) are denoted by lower-case boldface letters. Tensors (linear transformations of \mathbb{R}^3 into \mathbb{R}^3 viewed as 3×3 matrices) are denoted by upper-case boldface letters. $\mathbf{1}$ denotes the unit tensor; \mathbf{A}^T and $\text{tr } \mathbf{A}$ denote the transpose and trace of \mathbf{A} ; the inner product of \mathbf{A} and \mathbf{B} is defined by $\mathbf{A} \cdot \mathbf{B} = \text{tr}(\mathbf{A}^T \mathbf{B})$.

The gradient, divergence, Laplacian, and time derivative of a field $\varphi = \varphi(\mathbf{x}, t)$ are denoted, respectively, by $\nabla\varphi$, $\text{div } \varphi$, $\Delta\varphi$, and φ' . The derivative of a function f of a scalar variable (not time) is denoted by a prime: f' . For a vector field $\mathbf{u}(\mathbf{x})$, $\nabla\mathbf{u}(\mathbf{x})$ is the tensor with components $\partial u_i / \partial x_j$ ($i = \text{row index}$, $j = \text{column index}$). The divergence of a tensor field $\mathbf{A}(\mathbf{x})$ is the vector field with components $\Sigma_j \partial A_{ij} / \partial x_j$ ($i = \text{row index}$).

The partial derivative of a function $\Phi(a, b, c, \dots, d)$ (of n scalar, vector, or tensor variables)

with respect to b , say, is written $\partial_b \Phi(a, b, c, \dots, d)$.

2. Generalized Ginzburg–Landau equations

2.1. Basic laws: balance of forces and the dissipation inequality

I consider, as primitive physical quantities, the fields

- ρ order parameter,
- ψ free energy,
- ξ microstress,
- π internal microforce,
- γ external microforce,

defined on the body B for all time, and base the theory on the microforce balance (1.12) in conjunction with the dissipation inequality (1.14). The global laws (1.12) and (1.14) are to be satisfied for all time and all control volumes R , and are hence together equivalent to the *local microforce balance*

$$\text{div } \xi + \pi + \gamma = 0 \quad (2.1)$$

in conjunction with the *local dissipation inequality*

$$\psi' + \pi\rho' - \xi \cdot \nabla\rho' \leq 0. \quad (2.2)$$

The field

$$\mathcal{D} = -\psi' - \pi\rho' + \xi \cdot \nabla\rho' \geq 0 \quad (2.3)$$

represents dissipation, as its integral over R is the right side of (1.14) minus the left; a trivial but important consequence of this observation is the Lyapunov relation

$$\left\{ \int_B \psi \, dv \right\}' = - \int_B \mathcal{D} \, dv \leq 0 \quad (2.4)$$

for the body B whenever $\gamma \equiv 0$ and $(\xi \cdot \mathbf{n})\rho' = 0$ on ∂B .

¹³ Cf. the *linear* models of Aifantes [14], Stephenson [15], Durning [16], Jäckle and Frisch [17, 18], Binder, Frisch, and Jäckle [19]. Eq. (1.18) with $\alpha = 0$ is analyzed by Novick-Cohen and Pego [20].

¹⁴ Onuki [21, 22] and Nishimori and Onuki [23, 24] introduce and discuss a small-strain theory of elasticity with Cahn–Hilliard diffusion (cf. Cahn [4, 25], Larché and Cahn [26]).

2.2. Constitutive equations. Restrictions imposed by the second law

I consider constitutive equations giving the free energy ψ , the stress ξ , and the internal force π when the order parameter ρ and its derivatives $\nabla\rho$ and ρ' are known:

$$\begin{aligned}\psi &= \hat{\psi}(\rho, \nabla\rho, \rho'), \quad \xi = \hat{\xi}(\rho, \nabla\rho, \rho'), \\ \pi &= \hat{\pi}(\rho, \nabla\rho, \rho').\end{aligned}\quad (2.5)$$

Given an order-parameter field ρ , the constitutive equations (2.5) can be used to compute the fields ψ , ξ , and π ; the microforce balance (2.1) can then be used to determine the external force γ that must be supplied to support this *constitutive process*. The second law remains to be satisfied, a requirement that I use to obtain restrictions on constitutive equations. Specifically, *I require that the local dissipation inequality (2.2) hold for all such constitutive processes.*

To avoid notation such as $\partial_{\nabla\rho}\hat{\psi}(\rho, \nabla\rho, \rho')$ for the partial derivative with respect to $\nabla\rho$, it is convenient to write

$$p = \nabla\rho, \quad q = \rho'. \quad (2.6)$$

Then, granted (2.5), (2.2) is equivalent to the inequality

$$\begin{aligned}[\partial_p\hat{\psi}(\rho, \nabla\rho, \rho') + \hat{\pi}(\rho, \nabla\rho, \rho')]\rho' \\ + [\partial_p\hat{\psi}(\rho, \nabla\rho, \rho') - \hat{\xi}(\rho, \nabla\rho, \rho')]\cdot\nabla\rho' \\ + [\partial_q\hat{\psi}(\rho, \nabla\rho, \rho')]\rho'' \leq 0.\end{aligned}\quad (2.7)$$

It is possible to find a field ρ such that ρ , ρ' , ρ'' , $\nabla\rho$, and $\partial\rho'$ have arbitrarily prescribed values at some chosen point and time. Thus, since ρ'' and $\nabla\rho'$ appear linearly in (2.7), it follows that $\partial_q\hat{\psi}(\rho, \nabla\rho, \rho') = 0$, $\partial_p\hat{\psi}(\rho, \nabla\rho, \rho') = \hat{\xi}(\rho, \nabla\rho, \rho')$, for otherwise ρ'' and $\nabla\rho'$ could be chosen to violate (2.7).

The free energy and stress are therefore independent of ρ' and related through

$$\hat{\xi}(\rho, \nabla\rho) = \partial_p\hat{\psi}(\rho, \nabla\rho), \quad (2.8)$$

and the following inequality holds for all ρ , $\nabla\rho$, and ρ' :

$$\begin{aligned}\pi_{\text{dis}}(\rho, \nabla\rho, \rho')\rho' &\leq 0, \\ \pi_{\text{dis}}(\rho, \nabla\rho, \rho') &= \hat{\pi}(\rho, \nabla\rho, \rho') + \partial_p\hat{\psi}(\rho, \nabla\rho).\end{aligned}\quad (2.9)$$

Granted smoothness, the most general form of π_{dis} consistent with (2.9) is

$$\begin{aligned}\pi_{\text{dis}}(\rho, \nabla\rho, \rho') &= -\beta(\rho, \nabla\rho, \rho')\rho', \\ \beta(\rho, \nabla\rho, \rho') &\geq 0\end{aligned}\quad (2.10)$$

with $\beta(\rho, \nabla\rho, \rho')$ a constitutive modulus (cf. Appendix B). Thus $\pi = -\partial_p\hat{\psi} + \pi_{\text{dis}}$ and there are two contributions to the internal force: a contribution $-\partial_p\hat{\psi}$ that arises from changes in the free energy and a dissipative contribution $\pi_{\text{dis}} = -\beta\rho'$. In fact, the dissipation is given by

$$\mathcal{D} = -\pi_{\text{dis}}(\rho, \nabla\rho, \rho')\rho' = \beta(\rho, \nabla\rho, \rho')(\rho')^2. \quad (2.11)$$

Note that the constitutive relations are completely specified by a prescription of the response function $\hat{\psi}(\rho, \nabla\rho)$ for the free energy and a “kinetic modulus” $\beta(\rho, \nabla\rho, \rho') \geq 0$, for then (2.8)–(2.10) generate constitutive relations that are compatible with the dissipation inequality (2.2) in all constitutive processes.

2.3. The generalized Ginzburg–Landau equation

Using (2.8)–(2.10) in the force balance (2.1) yields

$$\begin{aligned}\beta(\rho, \nabla\rho, \rho')\rho' &= \text{div}[\partial_p\hat{\psi}(\rho, \nabla\rho)] \\ &\quad - \partial_p\hat{\psi}(\rho, \nabla\rho) + \gamma.\end{aligned}\quad (2.12)$$

This is the most general PDE based on the force balance (2.1) and constitutive relations (2.5) that are consistent with the second law in the form (2.2) (cf. [8]).

Choosing a constant, strictly positive kinetic-coefficient β in conjunction with a free energy of the form

$$\hat{\psi}(\rho, \nabla\rho) = f(\rho) + \frac{1}{2}\alpha|\nabla\rho|^2, \quad (2.13)$$

with $f(\rho)$ a “coarse-grain” free energy and α a

strictly positive constant, leads, for $\gamma = 0$, to the standard Ginzburg–Landau equation

$$\beta \rho' = \alpha \Delta \rho - f'(\rho). \quad (2.14)$$

2.4. Further generalization of the Ginzburg–Landau equation

A more general theory in which the stress ξ is dissipative is obtained by allowing for constitutive relations in which $\nabla \rho'$ enters the list of independent constitutive variables:

$$\begin{aligned} \psi &= \hat{\psi}(\rho, \nabla \rho, \rho', \nabla \rho'), \quad \xi = \hat{\xi}(\rho, \nabla \rho, \rho', \nabla \rho'), \\ \pi &= \hat{\pi}(\rho, \nabla \rho, \rho', \nabla \rho'). \end{aligned} \quad (2.15)$$

Using the notation (2.6) augmented by $\mathbf{r} = \nabla \rho'$ and proceeding as before leads to the inequality (2.7) with the arguments $(\rho, \nabla \rho, \rho')$ replaced by $(\rho, \nabla \rho, \rho', \nabla \rho')$ and with the additional term $\partial_r \hat{\psi}(\rho, \nabla \rho, \rho', \nabla \rho') \cdot \nabla \rho'$ added to the left side; this leads to the conclusions $\partial_r \hat{\psi} = 0$ and $\partial_q \hat{\psi} = 0$, so that

$$\psi = \hat{\psi}(\rho, \nabla \rho). \quad (2.16)$$

Further, and what is most important, $\nabla \rho'$ no longer appears linearly in the inequality, and so it no longer follows that $\partial_p \hat{\psi} = \hat{\xi}$; instead, all that one may conclude is that, for all $\rho, \nabla \rho, \rho'$, and $\nabla \rho'$,

$$\begin{aligned} \pi_{\text{dis}}(\rho, \nabla \rho, \rho', \nabla \rho') \rho' - \xi_{\text{dis}}(\rho, \nabla \rho, \rho', \nabla \rho') \cdot \nabla \rho' \\ \leq 0, \end{aligned} \quad (2.17)$$

where

$$\begin{aligned} \pi_{\text{dis}}(\rho, \nabla \rho, \rho', \nabla \rho') &= \hat{\pi}(\rho, \nabla \rho', \nabla \rho') + \partial_p \hat{\psi}(\rho, \nabla \rho), \\ \xi_{\text{dis}}(\rho, \nabla \rho, \rho', \nabla \rho') &= \hat{\xi}(\rho, \nabla \rho, \rho', \nabla \rho') \\ &\quad - \partial_p \hat{\psi}(\rho, \nabla \rho). \end{aligned} \quad (2.18)$$

The most general solution of the inequality (2.17) is (cf. Appendix B)

$$\begin{aligned} \pi_{\text{dis}}(\rho, \nabla \rho, \rho', \nabla \rho') &= -\beta \rho' - \mathbf{b} \cdot \nabla \rho', \\ \xi_{\text{dis}}(\rho, \nabla \rho, \rho', \nabla \rho') &= \mathbf{a} \rho' + \mathbf{A} \nabla \rho', \end{aligned} \quad (2.19)$$

with

$$\beta = \beta(\rho, \nabla \rho, \rho', \nabla \rho') \quad (\text{a scalar}),$$

$$\mathbf{a} = \mathbf{a}(\rho, \nabla \rho, \rho', \nabla \rho') \quad (\text{a vector}),$$

$$\mathbf{b} = \mathbf{b}(\rho, \nabla \rho, \rho', \nabla \rho') \quad (\text{a vector}),$$

$$\mathbf{A} = \mathbf{A}(\rho, \nabla \rho, \rho', \nabla \rho') \quad (\text{a tensor}),$$

constitutive moduli that render the dissipation

$$\mathcal{D} = \beta(\rho')^2 + \rho'(\mathbf{b} + \mathbf{a}) \cdot \nabla \rho' + \nabla \rho' \cdot \mathbf{A} \nabla \rho' \quad (2.20)$$

nonnegative for all values of $(\rho, \nabla \rho, \rho', \nabla \rho')$.

The resulting PDE, obtained upon combining the constitutive relations and the force balance, is

$$\begin{aligned} (\beta - \text{div } \mathbf{a}) \rho' + \mathbf{c} \cdot \nabla \rho' &= \text{div}[\partial_p \hat{\psi}(\rho, \nabla \rho) + \mathbf{A} \nabla \rho'] \\ &\quad - \rho \hat{\psi}(\rho, \nabla \rho) + \gamma, \end{aligned} \quad (2.21)$$

with $\mathbf{c} = \mathbf{b} - \mathbf{a}$. If the free energy has the simple form (2.13), if $\beta, \mathbf{b}, \mathbf{a}$, and \mathbf{A} are constant, if the material is isotropic so that $\mathbf{c} = 0$ and $\mathbf{A} = \kappa \mathbf{1}$, and if $\gamma = 0$, then (2.21) reduces to

$$\beta \rho' = \alpha \Delta \rho + \kappa \Delta \rho' - f'(\rho). \quad (2.22)$$

3. Diffusion. Generalized Cahn–Hilliard equations

3.1. Basic laws

I now discuss a theory in which the order parameter is identified with the density ρ of a diffusing, essentially independent¹⁵ species of atoms. I base the theory on balance of mass, the microforce balance (1.12), and a generalization of the dissipation inequality that accommodates diffusion. I therefore consider, as primitive physical quantities, the fields

¹⁵ For example, if the diffusing atoms consist of a single interstitial species, or if the material is a binary substitutional alloy with atoms constrained to lie on lattice points. In the latter case ρ is the density of one of the species, say species α , the other species, β , being eliminated via the constraint, and μ is the chemical potential of α minus that of β .

- ρ density = order parameter,
 μ chemical potential,
 ψ free energy
 \mathbf{h} mass flux,
 m external mass supply,
 ξ microstress,
 π internal microforce,
 γ external microforce.

Balance of mass is the requirement that

$$\left\{ \int_R \rho \, dv \right\}' \leq - \int_{\partial R} \mathbf{h} \cdot \mathbf{n} \, da + \int_R m \, dv \quad (3.1)$$

for every control volume R .

Within the present context the second law is the assertion that the rate at which the free energy of R increases cannot exceed the working on R plus the rate at which free energy is carried into R by mass transport. The rate of working is given by

$$\mathcal{W}(R) = \int_{\partial R} (\xi \cdot \mathbf{n}) \rho' \, da + \int_R \gamma \rho' \, dv, \quad (3.2)$$

because the density ρ is considered as an order parameter, and the free energy carried into R by mass transport is characterized by the chemical potential through the contributions

$$- \int_{\partial R} \mu \mathbf{h} \cdot \mathbf{n} \, da + \int_R \mu m \, dv. \quad (3.3)$$

The appropriate form of the second law is therefore the *dissipation inequality* (cf. [13])

$$\left\{ \int_R \psi \, dv \right\}' \leq - \int_{\partial R} \mu \mathbf{h} \cdot \mathbf{n} \, da + \int_R \mu m \, dv + \int_{\partial R} (\xi \cdot \mathbf{n}) \rho' \, da + \int_R \gamma \rho' \, dv. \quad (3.4)$$

Since R is arbitrary, balance of mass yields

$$\rho' = -\operatorname{div} \mathbf{h} + m, \quad (3.5)$$

and combining (3.4), localized, with (2.1) and (3.5) yields the *local dissipation inequality*

$$\psi' + (\pi - \mu) \rho' - \xi \cdot \nabla \rho' + \mathbf{h} \cdot \nabla \mu \leq 0. \quad (3.6)$$

As before, I define the dissipation \mathcal{D} to be the negative of the left side of (3.6); the integral of \mathcal{D} over R is then the right side of (3.4) minus the left, so that, for $m = \gamma = 0$,

$$\left\{ \int_B \psi \, dv \right\}' = - \int_B \mathcal{D} \, dv \leq 0$$

$$\text{if } (\xi \cdot \mathbf{n}) \rho' = \mathbf{h} \cdot \mathbf{n} = 0 \text{ on } \partial B,$$

$$\left\{ \int_B (\psi - \mu_0 \rho) \, dv \right\}' = - \int_B \mathcal{D} \, dv \leq 0$$

$$\text{if } (\xi \cdot \mathbf{n}) \rho' = 0, \mu = \mu_0 = \text{const. on } \partial B. \quad (3.7)$$

3.2. Constitutive equations. Restrictions imposed by the second law

In standard theories of diffusion the chemical potential is given, constitutively, as a function of the density, but here I wish to consider systems sufficiently far from equilibrium that a relation of this type is no longer valid; instead I allow the chemical potential and its gradient to join the density and density gradient in the list of constitutive variables. Specifically, I consider constitutive equations of the form:

$$\begin{aligned} \psi &= \hat{\psi}(\rho, \nabla \rho, \mu, \nabla \mu), \quad \mathbf{h} = \hat{\mathbf{h}}(\rho, \nabla \rho, \mu, \nabla \mu), \\ \xi &= \hat{\xi}(\rho, \nabla \rho, \mu, \nabla \mu), \quad \pi = \hat{\pi}(\rho, \nabla \rho, \mu, \nabla \mu). \end{aligned} \quad (3.8)$$

It is convenient to introduce the notation

$$\mathbf{p} = \nabla \rho, \quad \mathbf{s} = \nabla \mu, \quad \mathbf{Z} = (\rho, \nabla \rho, \mu, \nabla \mu). \quad (3.9)$$

Given a constitutive process (in the sense of (3.8)), the force and mass balances (2.1) and (3.5) may be used to compute the external microforce γ and mass supply m needed to support the process. The requirement that all such constitutive processes be consistent with the second law in the form of the local dissipation inequality (3.6) is then equivalent to the requirement that the inequality

$$\begin{aligned} [\partial_\rho \hat{\psi}(\mathbf{Z}) + \hat{\pi}(\mathbf{Z}) - \mu] \rho' + [\partial_\rho \hat{\psi}(\mathbf{Z}) - \hat{\xi}(\mathbf{Z})] \cdot \nabla \rho' \\ + [\partial_\mu \hat{\psi}(\mathbf{Z})] \mu' + [\partial_s \hat{\psi}(\mathbf{Z})] \cdot \nabla \mu' + \hat{\mathbf{h}}(\mathbf{Z}) \cdot \nabla \mu \leq 0, \end{aligned} \quad (3.10)$$

hold for all fields ρ and μ . Thus, arguing as before, $\partial_\mu \hat{\psi} = 0$, $\partial_s \hat{\psi} = 0$, $\partial_\rho \hat{\psi} = \hat{\xi}$, and $\partial_\rho \hat{\psi} = \mu - \hat{\pi}$. Thus $\hat{\psi}$ and $\hat{\xi}$ are independent of μ and $\nabla\mu$; $\hat{\pi}$ is independent of $\nabla\mu$;

$$\begin{aligned}\hat{\pi}(\rho, \nabla\rho, \mu) &= \mu - \partial_\rho \hat{\psi}(\rho, \nabla\rho), \\ \hat{\xi}(\rho, \nabla\rho) &= \partial_\rho \hat{\psi}(\rho, \nabla\rho); \end{aligned} \quad (3.11)$$

and

$$\hat{h}(\mathbf{Z}) \cdot \nabla\mu \leq 0 \quad (3.12)$$

for all \mathbf{Z} , so that \hat{h} has the form (cf. Appendix B)

$$\hat{h}(\mathbf{Z}) = -A(\mathbf{Z}) \nabla\mu \quad (3.13)$$

with $A(\mathbf{Z})$, the *mobility tensor*, a constitutive quantity consistent with the inequality $s \cdot A(\mathbf{X})s \geq 0$ for all \mathbf{Z} . Further, diffusion is now the sole source of dissipation with

$$\mathcal{D} = \nabla\mu \cdot A(\mathbf{Z}) \nabla\mu. \quad (3.14)$$

Combining (3.11) and the force balance (2.1),

$$\mu = \partial_\rho \hat{\psi}(\rho, \nabla\rho) - \text{div}[\partial_\rho \hat{\psi}(\rho, \nabla\rho)] - \gamma, \quad (3.15)$$

an expression for the chemical potential that reduces to the classical relation $\mu = \partial_\rho \hat{\psi}$ when the free energy is independent of the density gradient and γ vanishes. Interestingly, the general relation (3.15) with $\gamma = 0$ gives the chemical potential as the variational derivative of the total free energy (1.4) with respect to density:

$$\mu = \frac{\delta\Psi}{\delta\rho}. \quad (3.16)$$

3.3. The generalized Cahn–Hilliard equation

Substituting (3.13) and (3.15) in the mass balance (3.5) yields the generalized Cahn–Hilliard equation

$$\begin{aligned}\rho' &= \text{div } A \nabla \{ \partial_\rho \hat{\psi}(\rho, \nabla\rho) - \text{div}[\partial_\rho \hat{\psi}(\rho, \nabla\rho)] - \gamma \} \\ &\quad + m \end{aligned} \quad (3.17)$$

with $A = A(\mathbf{Z})$. The standard Cahn–Hilliard equation follows upon choosing a constant mobility tensor of the form $A = \kappa \mathbf{1}$ in conjunction with the free energy (2.13) and $\gamma = m = 0$:

$$\rho' = \kappa \Delta [f'(\rho) - \alpha \Delta \rho]. \quad (3.18)$$

3.4. Inclusion of kinetics

A more general theory may be based on constitutive relations in which ρ' enters the list of independent constitutive variables:

$$\begin{aligned}\psi &= \hat{\psi}(\rho, \nabla\rho, \rho', \mu, \nabla\mu), \\ \mathbf{h} &= \hat{h}(\rho, \nabla\rho, \rho', \mu, \nabla\mu), \\ \xi &= \hat{\xi}(\rho, \nabla\rho, \rho', \mu, \nabla\mu), \\ \pi &= \hat{\pi}(\rho, \nabla\rho, \rho', \mu, \nabla\mu). \end{aligned} \quad (3.19)$$

In this case compatibility with the dissipation inequality yields the following conclusions: the free energy and microstress are independent of ρ' , μ , and $\nabla\mu$;

$$\hat{\xi}(\rho, \nabla\rho) = \partial_\rho \hat{\psi}(\rho, \nabla\rho); \quad (3.20)$$

the inequality

$$\begin{aligned}\pi_{\text{dis}}(\mathbf{Z}) \rho' + \hat{h}(\mathbf{Z}) \cdot \nabla\mu &\leq 0, \\ \pi_{\text{dis}}(\mathbf{Z}) &= \hat{\pi}(\mathbf{Z}) + \partial_\rho \hat{\psi}(\rho, \nabla\rho) - \mu \end{aligned} \quad (3.21)$$

is satisfied for all

$$\mathbf{Z} = (\rho, \nabla\rho, \rho', \mu, \nabla\mu). \quad (3.22)$$

The results of Appendix B applied to (3.21) yield the existence of constitutive moduli $\beta = \beta(\mathbf{Z})$ (a scalar), $\mathbf{b} = \mathbf{b}(\mathbf{Z})$ and $\mathbf{a} = \mathbf{a}(\mathbf{Z})$ (vectors), and $A = A(\mathbf{Z})$ (a tensor), such that

$$\begin{aligned}\pi_{\text{dis}}(\rho, \nabla\rho, \rho', \mu, \nabla\mu) &= -\beta \rho' - \mathbf{b} \cdot \nabla\mu, \\ \hat{h}(\rho, \nabla\rho, \rho', \mu, \nabla\mu) &= -\mathbf{a} \rho' - A \nabla\mu, \end{aligned} \quad (3.23)$$

and such that (3.21) is satisfied.

Combining the first of (3.23) with the force balance (2.1) yields a complicated expression for the chemical potential:

$$\begin{aligned}\mu - \mathbf{b} \cdot \nabla\mu &= \partial_\rho \hat{\psi}(\rho, \nabla\rho) - \text{div}[\partial_\rho \hat{\psi}(\rho, \nabla\rho)] \\ &\quad + \beta \rho' - \gamma. \end{aligned} \quad (3.24)$$

For an isotropic material $\mathbf{b} = \mathbf{0}$ and (3.24) reduces to

$$\begin{aligned}\mu &= \partial_\rho \hat{\psi}(\rho, \nabla \rho) - \operatorname{div}[\partial_\rho \hat{\psi}(\rho, \nabla \rho)] + \beta \rho' - \gamma \\ &= \frac{\delta \Psi}{\delta \rho} + \beta \rho' - \gamma,\end{aligned}\quad (3.25)$$

so that the chemical potential is represented only in part as a variational derivative.

The general PDE that follows from these constitutive equations is obtained upon substituting (3.24) and the second of (3.23) into the mass balance (3.5). Granted isotropy, constant values of the constitutive moduli in (3.23), a free energy in the form (2.13), and $\gamma = m = 0$, this PDE reduces to

$$\rho' = \kappa \Delta[f'(\rho) - \alpha \Delta \rho + \beta \rho'], \quad (3.26)$$

with corresponding dissipation $\mathcal{D} = \beta(\rho')^2 + \kappa |\nabla \mu|^2$.

The Cahn–Hilliard theory can be further generalized to accomodate memory effects, but that is beyond the scope of the present paper.

4. The Cahn–Hilliard equation for deformable continua

I now generalize the theory to allow for deformation, but I restrict attention to situations in which diffusion occurs on a time scale large compared to that associated with inertia, which I consequently neglect. As basic balances I consider the standard force and moment balances associated with the gross deformation of the body in conjunction with the balance laws for mass and microforce discussed in previous sections.

4.1. Basic laws

I consider a body B identified with the region of space it occupies in a fixed uniform reference configuration. Material points are then points $\mathbf{x} \in B$, while control volumes R are subsets of B .

Let \mathbf{y} be a motion of B . Then \mathbf{y} is a field that associates with each material point \mathbf{x} and time t a point

$$\mathbf{y}(\mathbf{x}, t) = \mathbf{x} + \mathbf{u}(\mathbf{x}, t). \quad (4.1)$$

The field \mathbf{u} is the displacement, while

$$\mathbf{F} = \mathbf{I} + \nabla \mathbf{u}, \quad (4.2)$$

subject to $\det \mathbf{F} > 0$, is the deformation gradient. Here and in what follows all derivatives are material (Lagrangian): ∇ and div are the gradient and divergence with respect to the material point \mathbf{x} , while $\dot{\mathbf{u}}$, for example, is the derivative of $\mathbf{u}(\mathbf{x}, t)$ with respect to t holding \mathbf{x} fixed.

Associated with each motion are the fields described in Section 3.1 as well as the classical fields

\mathbf{S} (Piola–Kirchhoff) stress tensor,

\mathbf{b} body force vector,

associated with the gross motion of the body. The underlying balances are the mass balance¹⁶ (3.1), the microforce balance (1.12), and the standard macrobalances for forces and moments:

$$\begin{aligned}\int_{\partial R} \mathbf{S} \mathbf{n} \, da + \int_R \mathbf{b} \, dv &= \mathbf{0}, \\ \int_{\partial R} \mathbf{y} \times \mathbf{S} \mathbf{n} \, da + \int_R \mathbf{y} \times \mathbf{b} \, dv &= \mathbf{0};\end{aligned}\quad (4.3)$$

together, (4.3) are equivalent to the local balances

$$\operatorname{div} \mathbf{S} = \mathbf{0}, \quad \mathbf{S} \mathbf{F}^T = \mathbf{F} \mathbf{S}^T. \quad (4.4)$$

There are now two distinct systems of forces: a microforce system consisting of a stress ξ , an internal force π , and an external force γ , subject to the balance (2.1), and a macroforce system consisting of a stress \mathbf{S} and a body force \mathbf{b} , subject to (4.4). The physical nature of these systems manifests itself in the manner in which the forces perform work: as before, ξ , π , and γ work against changes in the order parameter ρ ,

¹⁶I assume that the lattice deforms with the body via the motion \mathbf{y} , and that, as before, atoms diffuse relative to the lattice; cf. Larché and Cahn [10, 27]. As this diffusion is described in the reference configuration, \mathbf{h} is measured per unit undeformed area.

while the working of S and b is given by the standard relation

$$\int_{\partial R} \mathbf{S} \mathbf{n} \cdot \mathbf{u}' \, da + \int_R \mathbf{b} \cdot \mathbf{u}' \, da, \quad (4.5)$$

in which the material velocity \mathbf{u}' represents the kinetics. Thus and by (1.13), I base the theory on the *dissipation inequality*

$$\begin{aligned} \left\{ \int_R \psi \, dv \right\}' \leq & - \int_{\partial R} \mu \mathbf{h} \cdot \mathbf{n} \, da + \int_R \mu m \, dv \\ & + \int_{\partial R} (\xi \cdot \mathbf{n}) \rho' \, da + \int_R \gamma \rho' \, dv \\ & + \int_{\partial R} \mathbf{S} \mathbf{n} \cdot \mathbf{u}' \, da + \int_R \mathbf{b} \cdot \mathbf{u}' \, da. \end{aligned} \quad (4.6)$$

Combining (2.1), (3.5), (4.4), and (4.6) yields the *local dissipation inequality*

$$\psi' - \mathbf{S} \cdot \mathbf{F}' + (\pi - \mu) \rho' - \xi \cdot \nabla \rho' + \mathbf{h} \cdot \nabla \mu \leq 0. \quad (4.7)$$

Define the dissipation \mathcal{D} to be the negative of the left side of (4.7) and assume that $\gamma = m = 0$, $\mathbf{b} = \mathbf{0}$. Then the Lyapunov relations (3.7) follow provided the restriction $\mathbf{S} \mathbf{n} \cdot \mathbf{u}' = 0$ on ∂B is added. If instead $\mathbf{S} \mathbf{n} = S_0 \mathbf{n}$ on ∂B with S_0 constant, then (3.7) remains valid, but with ψ replaced by $\psi - S_0 \cdot \nabla \mathbf{u}$.

4.2. Constitutive equations. Restrictions imposed by the second law

I consider constitutive equations of the form

$$\begin{aligned} \psi &= \hat{\psi}(F, \rho, \nabla \rho, \mu, \nabla \mu), \\ S &= \hat{S}(F, \rho, \nabla \rho, \mu, \nabla \mu), \\ \mathbf{h} &= \hat{\mathbf{h}}(F, \rho, \nabla \rho, \mu, \nabla \mu), \\ \xi &= \hat{\xi}(F, \rho, \nabla \rho, \mu, \nabla \mu), \\ \pi &= \hat{\pi}(F, \rho, \nabla \rho, \mu, \nabla \mu), \end{aligned} \quad (4.8)$$

which accounts for deformation, but not for kinetics, as ρ' is not included in the list of constitutive variables. (The inclusion of ρ' as well as \mathbf{F}' presents no essential difficulty.)

I assume that \hat{S} is consistent with the second of (4.4). In addition, I require that constitutive response be invariant under changes in observer; precisely, I assume that (4.8) is invariant under the transformations

$$\begin{aligned} \psi &\rightarrow \psi, \quad S \rightarrow QS, \quad \mathbf{h} \rightarrow \mathbf{h}, \\ \xi &\rightarrow \xi, \quad \pi \rightarrow \pi, \\ (F, \rho, \nabla \rho, \mu, \nabla \mu) &\rightarrow (QF, \rho, \nabla \rho, \mu, \nabla \mu) \end{aligned} \quad (4.9)$$

for all orthogonal tensors Q . This leads to the following restrictions in which, for convenience, the variables $\rho, \nabla \rho, \mu$, and $\nabla \mu$ are suppressed:

$$\begin{aligned} \hat{\psi}(F) &= \hat{\psi}(C), \quad \hat{S}(F) = F \tilde{S}(C), \quad \hat{\mathbf{h}}(F) = \hat{\mathbf{h}}(C), \\ \hat{\xi}(F) &= \hat{\xi}(C), \quad \hat{\pi}(F) = \hat{\pi}(C), \end{aligned} \quad (4.10)$$

with $C = FF^T$ the right Cauchy–Green strain tensor (cf., e.g., [28]) I will make no further use of the restricted relations (4.10), as the general development is simpler using the deformation gradient F .

Let

$$\begin{aligned} p &= \nabla \rho, \quad s = \nabla \mu, \\ Z &= (F, \rho, \nabla \rho, \mu, \nabla \mu). \end{aligned} \quad (4.11)$$

Arguing as before, compatibility of the constitutive relations (4.8) with the dissipation inequality (4.7) leads to the following generalizations of the results established in Section 3b: $\hat{\psi}$, \hat{S} , and $\hat{\xi}$ are independent of μ and $\nabla \mu$; $\hat{\pi}$ is independent of $\nabla \mu$;

$$\begin{aligned} \hat{\pi}(F, \rho, \nabla \rho, \mu) &= \mu - \partial_\rho \hat{\psi}(F, \rho, \nabla \rho), \\ \hat{\xi}(F, \rho, \nabla \rho) &= \partial_\rho \hat{\psi}(F, \rho, \nabla \rho), \\ \hat{S}(F, \rho, \nabla \rho) &= \partial_F \hat{\psi}(F, \rho, \nabla \rho); \end{aligned} \quad (4.12)$$

$\hat{\mathbf{h}}$ has the form

$$\hat{\mathbf{h}}(Z) = -A(Z) \nabla \mu \quad (4.13)$$

with $A(Z)$ consistent with the inequality $s \cdot A(Z)s \geq 0$ for all Z ; diffusion is the sole source of dissipation with $\mathcal{D} = \nabla \mu \cdot A(Z) \nabla \mu$.

Combining (4.12) and the force balance (2.1) shows that the chemical potential is, once again,

for $\gamma = 0$ the variational derivative of the total energy with respect to density:

$$\begin{aligned}\mu &= \partial_\rho \hat{\psi}(\mathbf{F}, \rho, \nabla \rho) - \operatorname{div}[\partial_\rho \hat{\psi}(\mathbf{F}, \rho, \nabla \rho)] - \gamma \\ &= \frac{\delta \Psi}{\delta \rho} - \gamma.\end{aligned}\quad (4.14)$$

4.3. Partial differential equations

Assume, for convenience, that the *external fields vanish*: $\gamma = m = 0$, $\mathbf{b} = \mathbf{0}$. Then, combining the reduced constitutive relations with the mass and force balances leads to the general system

$$\begin{aligned}\rho^\cdot &= \operatorname{div}(\mathbf{A} \nabla \mu), \\ \operatorname{div} \mathbf{S} &= \mathbf{0}, \\ \mu &= \partial_\rho \hat{\psi}(\mathbf{F}, \rho, \nabla \rho) - \operatorname{div}[\partial_\rho \hat{\psi}(\mathbf{F}, \rho, \nabla \rho)], \\ \mathbf{S} &= \partial_{\mathbf{F}} \hat{\psi}(\mathbf{F}, \rho, \nabla \rho),\end{aligned}\quad (4.15)$$

with $\mathbf{A} = \mathbf{A}(\mathbf{Z})$. This system, supplemented by (4.10), is the most general properly invariant system consistent with the constitutive relations (4.8) and the second law in the form (4.6).

4.4. Linear elastic phases

To model situations in which the displacement gradient is small, I now reconsider the theory assuming, from the outset, that the deformation is infinitesimal. To set the theory within that framework I redefine \mathbf{F} to be $\nabla \mathbf{u}$ and replace the second of (4.4) by the requirement that \mathbf{S} be symmetric:

$$\mathbf{S} = \mathbf{S}^T; \quad (4.16)$$

the steps leading to (4.12) and (4.13) then remain unchanged. Further, invariance of the constitutive equations under infinitesimal rotations (replacement of $\nabla \mathbf{u}$ by $\nabla \mathbf{u} + \boldsymbol{\Omega}$ skew) implies that the constitutive functions can depend on $\nabla \mathbf{u}$ only through the infinitesimal strain

$$\mathbf{E} = \frac{1}{2}(\nabla \mathbf{u} + \nabla \mathbf{u}^T), \quad (4.17)$$

and this leads to the conclusion that \mathbf{F} in (4.12) can be replaced by \mathbf{E} .

I now assume that the external fields vanish.

Consistent with the assumption of infinitesimal deformations, I require that the free energy be at most quadratic in \mathbf{E} ; in fact, I now consider free energies of the form

$$\begin{aligned}\hat{\psi}(\mathbf{E}, \rho, \nabla \rho) &= W(\mathbf{E}, \rho) + f(\rho) + \frac{1}{2}\alpha |\nabla \rho|^2, \\ W(\mathbf{E}, \rho) &= \frac{1}{2} \boldsymbol{\mathcal{E}} \cdot \mathbf{C}(\rho) \boldsymbol{\mathcal{E}}, \quad \boldsymbol{\mathcal{E}} = \mathbf{E} - \bar{\mathbf{E}}(\rho),\end{aligned}\quad (4.18)$$

where $\mathbf{C}(\rho)$, a positive definite, symmetric linear transformation of symmetric tensors into symmetric tensors, is the elasticity tensor; $\bar{\mathbf{E}}(\rho)$, a symmetric tensor, is the stress-free strain when the density is ρ ; and $f(\rho)$ is a double-well potential that defines the two phases. This form of the free energy yields the relations

$$\begin{aligned}\mathbf{S} &= \partial_{\mathbf{E}} W(\mathbf{E}, \rho) = \mathbf{C}(\rho) \boldsymbol{\mathcal{E}}, \\ \mu &= f'(\rho) + \partial_\rho W(\mathbf{E}, \rho) - \alpha \Delta \rho \\ &= f'(\rho) + \frac{1}{2} \boldsymbol{\mathcal{E}} \cdot \mathbf{C}'(\rho) \boldsymbol{\mathcal{E}} - \mathbf{S} \cdot \bar{\mathbf{E}}'(\rho) - \alpha \Delta \rho\end{aligned}\quad (4.19)$$

for the stress and chemical potential. These constitutive relations augment the balances $\operatorname{div} \mathbf{S} = \mathbf{0}$, $\rho^\cdot = -\operatorname{div}(\mathbf{A} \nabla \mu)$, and, if the mobility tensor \mathbf{A} and the elasticity tensor \mathbf{C} are constant, the basic equations take the form

$$\begin{aligned}\rho^\cdot &= \mathbf{A} \cdot \nabla \nabla [f'(\rho) - \alpha \Delta \rho - \mathbf{S} \cdot \bar{\mathbf{E}}'(\rho)], \\ \operatorname{div}(\mathbf{C}[\mathbf{E} - \bar{\mathbf{E}}(\rho)]) &= \mathbf{0}\end{aligned}\quad (4.20)$$

with $\bar{\mathbf{E}}$ given by (4.17). For an isotropic material with $\bar{\mathbf{E}}(\rho)$ linear in $\rho - \rho_0$ ($\rho_0 = \text{const.}$),

$$\begin{aligned}\mathbf{C}\mathbf{D} &= 2a\mathbf{D} + b(\operatorname{tr} \mathbf{D})\mathbf{1}, \quad \bar{\mathbf{E}}(\rho) = e(\rho - \rho_0)\mathbf{1}, \\ \mathbf{A} &= \kappa \mathbf{1},\end{aligned}\quad (4.21)$$

and, defining $k = (2a + 3b)e$, $\lambda = 4ke/(2a + b)$, (4.20) reduce to

$$\begin{aligned}\rho^\cdot &= \kappa \Delta [f'(\rho) - \alpha \Delta \rho + \lambda \rho], \\ a \Delta \mathbf{u} + (a + b) \nabla \operatorname{div} \mathbf{u} - k \nabla \rho &= \mathbf{0}.\end{aligned}\quad (4.22)$$

In these special circumstances the equation for ρ is independent of the deformation (cf., e.g., [5, 22, 26]), although diffusion and deformation will generally be coupled through the boundary conditions.

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Appendix A. Mechanical version of the second law

The theories I discuss are based on a version of the second law of thermodynamics appropriate to a purely mechanical theory. To motivate this version of the second law, consider, for an arbitrary control volume R , the first two laws in the form of an energy balance

$$\left\{ \int_R \varepsilon \, dv \right\}' = - \int_{\partial R} \mathbf{q} \cdot \mathbf{n} \, da + \int_R r \, dv + \mathcal{W}(R) + \mathcal{M}(R) \quad (\text{A.1})$$

and an entropy-growth inequality¹⁷

$$\left\{ \int_R \eta \, dv \right\}' \geq - \int_{\partial R} (\mathbf{q}/\theta) \cdot \mathbf{n} \, da + \int_R (r/\theta) \, dv \quad (\text{A.2})$$

in which ε is the internal energy, η is the entropy, θ is the (absolute) temperature, \mathbf{q} is the heat flux, r is the heat supply, $\mathcal{W}(R)$ is the rate of working on R of *all* forces exterior to R , and $\mathcal{M}(R)$ is the rate at which energy is added to R by mass transport.

It is convenient to define the free energy ψ by

$$\psi = \varepsilon - \theta \eta. \quad (\text{A.3})$$

Assume isothermal conditions:

$$\theta = \text{constant}. \quad (\text{A.4})$$

Then multiplying the entropy inequality by θ and subtracting the resulting equation from the energy balance yields the *global dissipation inequality*

$$\left\{ \int_R \psi \, dv \right\}' \leq \mathcal{W}(R) + \mathcal{M}(R). \quad (\text{A.5})$$

The theories discussed here are based on this inequality, which asserts that *the rate at which the free energy increases cannot exceed the sum of the working and the energy inflow due to mass transport*. For the Ginzburg–Landau system there is no diffusion and the working is due entirely to microforces; in that case $\mathcal{W}(R)$ is given by (1.13) and $\mathcal{M}(R)$ vanishes. For the Cahn–Hilliard system $\mathcal{M}(R) \neq 0$, and if the body B is allowed to deform, then $\mathcal{W}(R)$ includes the working of the more standard forces that accompany the gross motion of B .

Appendix B. Solution of thermodynamical inequalities

The inequality (2.17) can be written succinctly in the form

$$\mathbf{F}(X, Y) \cdot Y \leq 0 \quad (\text{B.1})$$

with

$$\begin{aligned} X &= (\rho, \nabla \rho), \quad Y = (\rho', \nabla \rho'), \\ \mathbf{F}(X, Y) &= (\pi_{\text{dis}}(\rho, \nabla \rho, \rho', \nabla \rho'), \\ &\quad -\xi_{\text{dis}}(\rho, \nabla \rho, \rho', \nabla \rho')). \end{aligned}$$

I now give a general solution of (B.1) within a framework that yields (2.10), (2.19), (3.13), and (3.23) as special cases (cf. [30]).

The general problem can be stated as follows: given a smooth function \mathbf{F} from $\mathbb{R}^p \times \mathbb{R}^q$ into \mathbb{R}^q , find a general solution of the inequality (B.1) for all $X \in \mathbb{R}^p$ and $Y \in \mathbb{R}^q$. The variable X appears as a parameter and I may, without loss in generality, suppress it when convenient.

For $\lambda > 0$, $\mathbf{F}(\lambda Y) \cdot \lambda Y \leq 0$ and hence $\mathbf{F}(\lambda Y) \cdot Y \leq 0$. Thus, letting $\lambda \rightarrow 0$, $\mathbf{F}(0) \cdot Y \leq 0$ for all Y ,

¹⁷ The Clausius–Duhem inequality (cf. Truesdell and Toupin [29], §§256–258).

so that $F(\mathbf{0}) = \mathbf{0}$. Thus

$$F(Y) = \left\{ \int_0^1 \nabla F(sY) ds \right\} Y \quad (\text{B.2})$$

for all Y ; hence, writing $-B(Y)$ for the quantity $\{\cdots\}$, $F(Y) = -B(Y)Y$ for all Y . The general solution F of (B.1) is therefore

$$F(X, Y) = -B(X, Y)Y \quad (\text{B.3})$$

with $B(X, Y)$, for each (X, Y) , a linear transformation from \mathbb{R}^q into \mathbb{R}^q consistent with the inequality

$$Y \cdot B(X, Y)Y \geq 0. \quad (\text{B.4})$$

Because of the dependence of $B(X, Y)$ on Y , the inequality (B.4) is weaker than positive definiteness for $B(X, Y)$. However, when F is *quasilinear*, that is, when $F(X, Y)$ is linear in Y for each X , then

$$F(X, Y) = -B(X)Y \quad (\text{B.5})$$

for all (X, Y) , with $B(X)$ positive semi-definite.

More generally, the relation (B.5) holds to first order in Y :

$$F(X, Y) = -B(X)Y - o(|Y|) \quad \text{as } Y \rightarrow \mathbf{0} \quad (\text{B.6})$$

with $B(X)$ positive semi-definite; and, for X and Y both small,

$$F(X, Y) = -BY + o(|X| + |Y|) \quad \text{as } X, Y \rightarrow \mathbf{0} \quad (\text{B.7})$$

with B constant and positive semi-definite.

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