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GENERALIZED GINZBURG-LANDAU AND CAHN-HILLIARD EQUATIONS BASED ON A MICROFORCE BALANCE

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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 equation[1]

$$\beta\rho^{\cdot} = \alpha\Delta\rho - f'(\rho) \qquad (\Delta = \text{Laplacian}) \tag{1.1}$$

and the Cahn-Hilliard equation[2]

$$\rho^{\cdot} = \gamma\Delta[f'(\rho) - \alpha\Delta\rho] \tag{1.2}$$

($\alpha > 0$, $\beta > 0$, $\gamma > 0$) 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-parameter[3] $\rho = \rho(\mathbf{x},t)$: the Ginzburg-Landau equation describes the ordering of atoms within unit cells in 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

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

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[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.

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

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

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

$$\delta\Psi(\rho) = \int_B [f'(\rho)\delta\rho + \alpha\nabla\rho\cdot\delta\nabla\rho]\,dv = \int_B [f'(\rho) - \alpha\Delta\rho]\,\delta\rho\,dv \tag{1.5}$$

and yields the expression

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

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

$$\beta\rho^{\cdot} = -\delta\Psi/\delta\rho; \tag{1.7}$$

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

$$\rho^{\cdot} = -\operatorname{div}\mathbf{h} \tag{1.8}$$

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

$$\mathbf{h} = -\gamma\nabla\mu. \tag{1.9}$$

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 ψ with respect to ρ; instead μ is defined as the variational derivative

$$\mu = \delta\Psi/\delta\rho; \tag{1.10}$$

this yields

$$\rho^{\bullet} = \gamma\Delta[\delta\Psi/\delta\rho], \tag{1.11}$$

which is the Cahn-Hilliard equation.

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 the belief that fundamental physical laws involving energy should account for the working associated with each operative kinematical process. In the Ginzburg-Landau and Cahn-Hilliard theories the kinematics is that associ-

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[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].

ated with the order-parameter ρ, and it seems plausible that there should be "microforces" whose working accompanies changes in ρ. Fried and I characterize this working by terms of the form (force)$(\rho^{\cdot})$, so that (in this context) microforces are scalar rather than vector quantities. Precisely, we assume that these forces are described by a (vector) stress $\boldsymbol{\xi}$, which characterizes forces transmitted across surfaces, and a (scalar) body force π that represents internal forces distributed over the volume of the material. The basic hypothesis is the microforce balance

$$\int_{\partial R} \boldsymbol{\xi}\cdot\mathbf{n}\,da + \int_{R} \pi\,dv = 0 \tag{1.12}$$

for each control volume R (subregion of B) in conjunction with the expression

$$\mathcal{W}(R) = \int_{\partial R} \rho^{\cdot}\boldsymbol{\xi}\cdot\mathbf{n}\,da \tag{1.13}$$

for the working of the stress. Here $\mathbf{n}$ is the outward unit normal to ∂R.

To fix ideas I first review the Ginzburg-Landau system as derived in [8]. The treatment is based on the microforce balance, suitable constitutive equations, and a version of the second law (appropriate to a purely mechanical system) in the form of a *dissipation inequality* which asserts that the free energy increase at a rate not greater than the working:[5]

$$\{\int_{R} \psi\,dv\}^{\cdot} \le \int_{\partial R} \rho^{\cdot}\boldsymbol{\xi}\cdot\mathbf{n}\,da. \tag{1.14}$$

We consider constitutive equations in which the free energy ψ, the stress $\boldsymbol{\xi}$, and the internal force π depend on the order parameter ρ and—to model capillarity and transition kinetics—also on $\nabla\rho$ and $\rho^{\cdot}$:

$$\psi = \hat{\psi}(\rho,\nabla\rho,\rho^{\cdot}), \qquad \boldsymbol{\xi} = \hat{\boldsymbol{\xi}}(\rho,\nabla\rho,\rho^{\cdot}), \qquad \pi = \hat{\pi}(\rho,\nabla\rho,\rho^{\cdot}). \tag{1.15}$$

Here one might argue that $\rho^{\cdot}$ should not appear in the constitutive equation for the free energy, and we agree, but rather than omit it by fiat, we choose instead to show that a dependence on $\rho^{\cdot}$ is incompatible with the second law.[6]

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[5] Section 2 gives a thermodynamic justification of (1.14). An advantage of basing the theory on such an inequality is that Lyapunov relations for the resulting PDE's follow automatically.

[6] Truesdell, in discussing the formulation of *general* constitutive theories, adopts the view that "a quantity present as an independent variable in one constitutive equation

Precisely, we use the dissipation inequality, via the Coleman-Noll procedure [12], to show that ψ and $\boldsymbol{\xi}$ are independent of $\rho^{\bullet}$, and that

$$\boldsymbol{\xi} = \partial_{\mathbf{p}}\hat{\psi}(\rho,\nabla\rho), \qquad \pi = -\partial_{\rho}\hat{\psi}(\rho,\nabla\rho) - \beta\rho^{\bullet}, \tag{1.16}$$

where $\partial_{\mathbf{p}}\hat{\psi}$ and $\partial_{\rho}\hat{\psi}$ denote the partial derivatives of $\hat{\psi}$ with respect to $\mathbf{p} = \nabla\rho$ and ρ, and where $\beta = \beta(\rho,\nabla\rho,\rho^{\bullet}) \geq 0$ is a constitutive modulus. The microforce balance $\operatorname{div}\boldsymbol{\xi} + \pi = 0$ and the reduced constitutive equations (1.16) yield a general nonlinear PDE, which for an energy of the form (1.3) and constant β reduces to the Ginzburg-Landau equation. I show here that, more generally, the inclusion of $\nabla\rho^{\bullet}$ in the list of constitutive variables leads, under analogous assumptions, to an equation

$$\beta\rho^{\bullet} = \alpha\Delta\rho + \gamma\Delta\rho^{\bullet} - f'(\rho) \tag{1.17}$$

containing an additional kinetic term $\gamma\Delta\rho^{\bullet}$ ($\gamma > 0$).

The Cahn-Hilliard theory is developed in Section 4 beginning with balance laws for mass and microforce in conjunction with a dissipation inequality of the form (1.14) augmented by a term representing energy-transport by diffusion.[7] Within this framework I discuss the Cahn-Hilliard equation as well as various generalizations, including the equation[8]

$$\rho^{\bullet} = \gamma\Delta[f'(\rho) - \alpha\Delta\rho + \beta\rho^{\bullet}] \tag{1.18}$$

($\beta > 0$). In Section 5 the Cahn-Hilliard theory is further generalized to allow for deformation.[9]

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should be so present in all, unless........its presence contradicts some law of physics or rule of invariance" (Truesdell and Noll [10], §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." See also Weinberg [11], who, in a discussion of general relativity, comments that it is "not enough to to say that........is an unnecessary complication. Simplicity, like everything else, must be explained."

[7] 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 *configurational* force balance and, consequently, the argument is far more complicated.

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

[9] Onuki [21,22] and Nishimori and Onuki [23,24] introduce and discuss a small-strain theory of elasticity with Cahn-Hilliard diffusion. See also Cahn [4,25], Larché and Cahn [26].

Notation. 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; $\mathbf{a}\otimes\mathbf{b}$, the tensor product of $\mathbf{a}$ and $\mathbf{b}$, is defined by $(\mathbf{a}\otimes\mathbf{b})\mathbf{u}=(\mathbf{b}\cdot\mathbf{u})\mathbf{a}$ for all $\mathbf{u}$; $\mathbf{A}^{\mathsf{T}}$ and $\mathrm{tr}\mathbf{A}$ denote the transpose and trace of $\mathbf{A}$; the inner product of A and B is defined by $\mathbf{A}\cdot\mathbf{B}=\mathrm{tr}(\mathbf{A}^{\mathsf{T}}\mathbf{B})$.

The gradient, divergence, Laplacian, and time derivative of a field $\varphi=\varphi(\mathbf{x},t)$ are denoted, respectively, by $\nabla\varphi$, $\mathrm{div}\,\varphi$, $\Delta\varphi$, and $\varphi^{\boldsymbol{\cdot}}$. 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 = row index, j = 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 = row index).

The partial derivative of a function $\Phi(a,b,c,\ldots,d)$ (of n scalar, vector, or tensor variables) with respect to b, say, is written $\partial_b\Phi(a,b,c,\ldots,d)$.

2. ORDER PARAMETER. MICROFORCES

a. Order parameter. Surfaces of uniform state

I consider a body B that occupies a fixed region in three-dimensional euclidean space $\mathbb{R}^3$, with B comprised of material whose state at each $\mathbf{x}\in B$ and time t is characterized by a scalar *order-parameter* $\rho(\mathbf{x},t)$. The level sets of ρ at time t are sets of the form $\rho(\mathbf{x},t)=$constant and represent sets of uniform state. Assume, for the moment, that each level set $\mathcal{S}(t)$ describes a smoothly evolving surface; the fields

$$\mathbf{m} = -\nabla\rho/|\nabla\rho|, \qquad V = \rho^{\boldsymbol{\cdot}}/|\nabla\rho| \tag{2.1}$$

then define a unit normal and corresponding normal velocity on each level surface, while the tensor $\mathbf{1}-\mathbf{m}\otimes\mathbf{m}$ projects vector fields onto their components tangent to the level surfaces.

A velocity field $\mathbf{v}(\mathbf{x},t)$ for each level surface $\mathcal{S}(t)$ can be determined using local parametrizations $\mathbf{x}=\mathbf{r}(u,t)$ for $\mathcal{S}(t)$ by defining $\mathbf{v}(\mathbf{x},t)=(\partial/\partial t)\mathbf{r}(u,t)$. Fields $\mathbf{v}(\mathbf{x},t)$ determined in this manner satisfy

$$V = \mathbf{v}\cdot\mathbf{m}, \tag{2.2}$$

but their tangential components are arbitrary; in fact, such fields $\mathbf{v}$ have the form

$$\mathbf{v} = V\mathbf{m} + (\mathbf{1} - \mathbf{m}\otimes\mathbf{m})\mathbf{w}, \tag{2.3}$$

with $\mathbf{w}$ an arbitrary vector field, and conversely (at least locally in time granted sufficient regularity). Fields $\mathbf{v}$ of the form (2.3) will be referred to as *admissible velocity fields*.

b. The microforce balance. Rate of working

I assume that the evolution of ρ is accompanied by a system of forces characterized by a stress tensor $\mathbf{C}$ and an internal force $\mathbf{g}$. Given any control volume R with outward unit normal $\mathbf{n}$, $\mathbf{Cn}$ represents the force, per unit area, exerted on R across ∂R, while $\mathbf{g}$ represents internal forces, per unit volume, distributed over the interior of R. These forces are assumed consistent with the microforce balance

$$\int_{\partial R} \mathbf{Cn}\,da + \int_{R} \mathbf{g}\,dv = \mathbf{0} \tag{2.4}$$

for all R, or equivalently,

$$\operatorname{div}\mathbf{C} + \mathbf{g} = 0. \tag{2.5}$$

Essential to the theory is an expression for the rate at which the microforces perform work. The only kinematics available for such an expression is that associated with the evolution of the order parameter, and a basic supposition of the theory is that the microstress works to change the state of points of the body through an expenditure of power computed using the velocity $\mathbf{v}$ of surfaces of uniform state. Precisely, the *rate of working* $\mathfrak{W}(R)$ on a control volume R is taken to be

$$\mathfrak{W}(R) = \int_{\partial R} \mathbf{Cn}\cdot\mathbf{v}\,da, \tag{2.6}$$

with the stipulation that $\mathfrak{W}(R)$ be independent of the choice of admissible velocity field $\mathbf{v}$, so that $\mathfrak{W}(R)$ is independent of how the state surfaces are parametrized. The force $\mathbf{g}$ is not included in this working, as it acts internally.

By (2.3), invariance under changes in the admissible velocity field is equivalent to the requirement that

$$\int_{\partial R} \mathbf{Cn}\cdot(\mathbf{1}-\mathbf{m}\otimes\mathbf{m})\mathbf{w}\,da = \int_{\partial R} [(\mathbf{1}-\mathbf{m}\otimes\mathbf{m})\mathbf{Cn}]\cdot\mathbf{w}\,da = 0 \qquad (2.7)$$

for all vector fields $\mathbf{w}$ and all control volumes R; hence $(\mathbf{1}-\mathbf{m}\otimes\mathbf{m})\mathbf{C}=\mathbf{0}$, so that $\mathbf{C}=\mathbf{m}\otimes\mathbf{C}^{\mathsf{T}}\mathbf{m}$. Thus and by (2.1),

$$\mathbf{C} = -\nabla\rho\otimes\boldsymbol{\xi} \qquad (2.8)$$

with $\boldsymbol{\xi}=-|\nabla\rho|^{-2}\mathbf{C}^{\mathsf{T}}\nabla\rho$, and this leads to an intrinsic expression for the working:

$$\mathcal{W}(R) = \int_{\partial R} \rho^{\cdot}\boldsymbol{\xi}\cdot\mathbf{n}\,da. \qquad (2.9)$$

The field $\boldsymbol{\xi}$ will be referred to as the *reduced stress;* (2.9) shows that $\boldsymbol{\xi}$ works directly over changes in the order parameter ρ.

Next, substituting (2.8) into (2.5) yields

$$\nabla\rho\,\mathrm{div}\,\boldsymbol{\xi} + (\nabla\nabla\rho)\boldsymbol{\xi} - \mathbf{g} = \mathbf{0}, \qquad (2.10)$$

and taking the inner product of this relation with $\mathbf{m}$ and simplifying yields an expression for the force balance normal to surfaces of uniform state:

$$\mathrm{div}\,\boldsymbol{\xi} + \pi = 0, \qquad (2.11)$$

where

$$\pi = -|\nabla\rho|^{-2}\nabla\rho\cdot[\mathbf{g} - (\nabla\nabla\rho)\boldsymbol{\xi}] \qquad (2.12)$$

is the *reduced internal force*. The intrinsic velocity of an evolving surface is normal; tangential motion is irrelevant. For that reason the component of $\mathbf{g}$ tangent to surfaces of uniform state is taken to be indeterminate (not specified by a constitutive equation but rather as defined by the tangential balance), so that only the normal balance (2.11), or equivalently,

$$\int_{\partial R} \boldsymbol{\xi}\cdot\mathbf{n}\,da + \int_{R} \pi\,dv = 0, \qquad (2.13)$$

is relevant to the discussion.

The discussion given above was meant only to motivate the expressions (2.9) and (2.11) for the working and normal force balance. All further considerations will be based on (2.9) and (2.11), which are more generally applicable than the original expressions in terms of **C** and **g**, since they are valid even when the level sets of ρ are not surfaces.

c. The second law for mechanical theories. Dissipation inequality

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

$$\Big(\int_R \varepsilon\, dv\Big)^{\cdot} = -\int_{\partial R} \mathbf{q}\cdot\mathbf{n}\, da + \int_R r\, dv + \mathcal{W}(R) + \mathcal{M}(R) \tag{2.14}$$

and an entropy-growth inequality[10]

$$\Big\{\int_R \eta\, dv\Big\}^{\cdot} \geq -\int_{\partial R} (\mathbf{q}/\theta)\cdot\mathbf{n}\, da + \int_R (r/\theta)\, dv \tag{2.15}$$

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 diffusion across ∂R.

It is convenient to define the free energy ψ by

$$\psi = \varepsilon - \theta\eta. \tag{2.16}$$

Assume isothermal conditions:

$$\theta = \text{constant}. \tag{2.17}$$

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

$$\Big\{\int_R \psi\, dv\Big\}^{\cdot} \leq \mathcal{W}(R) + \mathcal{M}(R). \tag{2.18}$$

All subsequent considerations will be based on this inequality, which asserts that *the rate at which the energy increases cannot exceed the sum of the working and the energy inflow due to diffusion*. For the Ginzburg-Landau system there

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[10] The Clausius-Duhem inequality (cf. Truesdell and Toupin [26], §§256-258).

is no diffusion and the working is due entirely to microforces; in that case $\mathcal{W}(R)$ is given by (2.9) and $\mathcal{M}(R)$ vanishes. For the Cahn-Hilliard system $\mathcal{M}(R) = 0$, and if B is allowed to deform, then $\mathcal{W}(R)$ includes the working of the standard forces that accompany deformation.

d. Why the internal force π appears in the microforce balance but not in the working

The following discussion, which is naive, is meant only to present a conceptual interpretation of the action of microforces. Consider the cartoon shown in Figure 1 in which there are two basic elements: a lattice and a system of atomic configurations within the lattice. There is a stress ξ between adjacent atomic configurations, internal forces π exerted by the lattice on each configuration, and a stress ℓ exerted across adjacent portions of the lattice. A control volume R may be viewed in two ways: (i) as a control volume containing both atoms and lattice; and (ii) as a control volume containing only atoms. In writing the dissipation inequality (2.18) the viewpoint is (i) with the free energy interpreted as the free energy of the entire structure; hence π is not present in the working. But in the statement of the microforce balance the interpretation is (ii), as (ii) captures the action of the internal forces, while (i) does not, and (ii) does not require knowledge of the forces ℓ, which are indeterminate since the lattice is rigid.

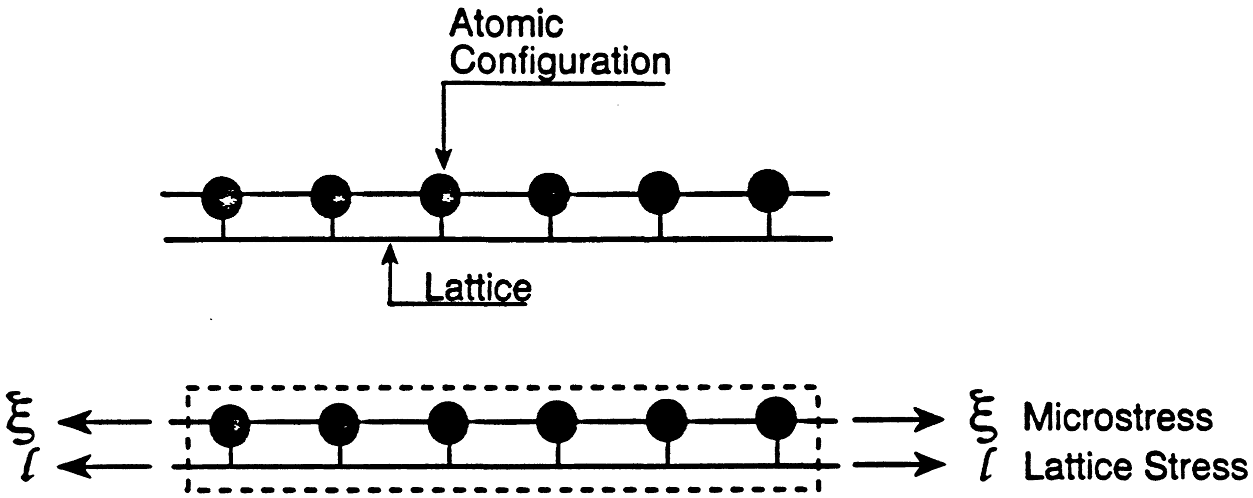
3. GENERALIZED GINZBURG-LANDAU EQUATIONS

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

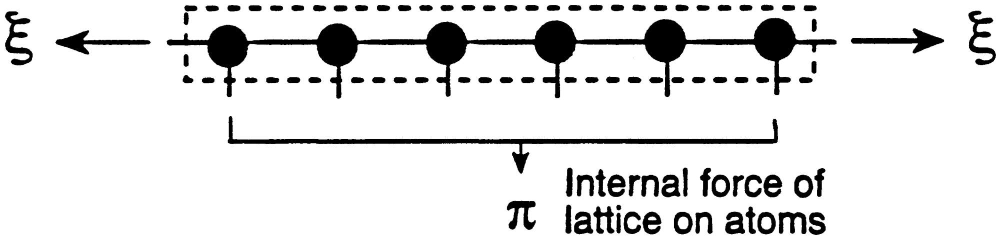
I begin with a theory based on the force balance (2.13) and a version of the second law—appropriate to a purely mechanical system—which asserts that *the rate at which the energy increases cannot exceed the working*. I consider, as primitive physical quantitites, the fields

ρ	order parameter,
ψ	free energy,
ξ	reduced microstress,
π	reduced internal force,

defined on the body B for all time, and write the second law in the form of a *dissipation inequality*



Control volume used for the dissipation inequality. The Lattice force ℓ performs no work as the lattice does not move.



Control volume used for the microforce balance.

Figure 1. Cartoon showing why the internal forces are present in the microforce balance but not in the working

$$\{\int_{R}\psi\,dv\}^{\cdot} \le \int_{\partial R}\rho^{\cdot}\boldsymbol{\xi}\cdot\mathbf{n}\,da \tag{3.1}$$

to be satisfied for all time and all control volumes R.

Since R is arbitrary, $\psi^{\cdot} \le \mathrm{div}(\rho^{\cdot}\boldsymbol{\xi})$, and this and the force balance (2.11) combine to form the *local dissipation inequality*

$$\psi^{\cdot} + \pi\rho^{\cdot} - \boldsymbol{\xi}\cdot\nabla\rho^{\cdot} \le 0. \tag{3.2}$$

The field

$$\mathcal{D} = -\psi^{\cdot} - \pi\rho^{\cdot} + \boldsymbol{\xi}\cdot\nabla\rho^{\cdot} \ge 0 \tag{3.3}$$

represents dissipation, as its integral over R is the right side of (3.1) minus the left; a trivial but important consequence of this observation is the Lyapunov relation

$$\{\int_{B}\psi\,dv\}^{\cdot} = -\int_{B}\mathcal{D}\,dv \le 0 \tag{3.4}$$

for the body B whenever $\rho^{\cdot}\boldsymbol{\xi}\cdot\mathbf{n}=0$ on ∂B.

b. Constitutive equations. Restrictions imposed by the second law

As constitutive equations I allow the free energy ψ, the stress $\boldsymbol{\xi}$, and the internal force π to depend on the order parameter ρ and—to model capillarity and transition kinetics—also on $\nabla\rho$ and $\rho^{\cdot}$:[11]

$$\psi = \hat{\psi}(\rho,\nabla\rho,\rho^{\cdot}), \qquad \boldsymbol{\xi} = \hat{\boldsymbol{\xi}}(\rho,\nabla\rho,\rho^{\cdot}), \qquad \pi = \hat{\pi}(\rho,\nabla\rho,\rho^{\cdot}). \tag{3.5}$$

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

$$\mathbf{p} = \nabla\rho, \qquad q = \rho^{\cdot}. \tag{3.6}$$

Not all constitutive relations of the form (3.5) are admissible, as without further restrictions (3.5) will violate the dissipation inequality (3.2). To deter-

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[11] Here and throughout only *homogeneous* constitutive behavior is considered; thus, e.g., the first of (2.7) signifies $\psi(\mathbf{x},t) = \hat{\psi}(\varphi(\mathbf{x},t),\nabla\varphi(\mathbf{x},t),\varphi^{\cdot}(\mathbf{x},t))$, so that $\hat{\psi}$ represents a constitutive response function for the free energy, while $\psi=\psi(\mathbf{x},t)$ represents the actual free energy as a field over the body.

mine these restrictions choose an arbitrary order-parameter field ρ, and use (3.5) to compute a *constitutive process* consisting of ρ and the fields ψ, ξ, and π; this constitutive process will satisfy (3.2) if and only if

$$[\partial_\rho \hat{\psi}(\rho,\nabla\rho,\dot{\rho}) + \hat{\pi}(\rho,\nabla\rho,\dot{\rho})]\dot{\rho} + [\partial_{\mathbf{p}} \hat{\psi}(\rho,\nabla\rho,\dot{\rho}) - \hat{\xi}(\rho,\nabla\rho,\dot{\rho})]\cdot\nabla\dot{\rho} + \partial_q \hat{\psi}((\rho,\nabla\rho,\dot{\rho}))\ddot{\rho} \le 0. \tag{3.7}$$

It is possible to find a field ρ such that ρ, $\dot{\rho}$, $\ddot{\rho}$, $\nabla\rho$, and $\nabla\dot{\rho}$ have arbitrarily prescribed values at some chosen point and time. Thus, since $\ddot{\rho}$ and $\nabla\dot{\rho}$ appear linearly in (3.7), it follows that $\partial_q \hat{\psi}(\rho,\nabla\rho,\dot{\rho}) = 0$, $\partial_{\mathbf{p}} \hat{\psi}(\rho,\nabla\rho,\dot{\rho}) = \hat{\xi}(\rho,\nabla\rho,\dot{\rho})$, for otherwise $\ddot{\rho}$ and $\nabla\dot{\rho}$ could be chosen to violate (3.7).

The free energy and stress are therefore independent of $\dot{\rho}$ and related through

$$\hat{\xi}(\rho,\nabla\rho) = \partial_{\mathbf{p}} \hat{\psi}(\rho,\nabla\rho), \tag{3.8}$$

and the following inequality holds for all ρ, $\nabla\rho$, and $\dot{\rho}$:

$$\pi_{\text{dis}}(\rho,\nabla\rho,\dot{\rho})\,\dot{\rho} \le 0, \qquad \pi_{\text{dis}}(\rho,\nabla\rho,\dot{\rho}) = \hat{\pi}(\rho,\nabla\rho,\dot{\rho}) + \partial_\rho \hat{\psi}(\rho,\nabla\rho). \tag{3.9}$$

Granted smoothness, the most general form of π_{dis} consistent with (3.9) is

$$\pi_{\text{dis}}(\rho,\nabla\rho,\dot{\rho}) = -\beta(\rho,\nabla\rho,\dot{\rho})\dot{\rho}, \qquad \beta(\rho,\nabla\rho,\dot{\rho}) \ge 0 \tag{3.10}$$

with $\beta(\rho,\nabla\rho,\dot{\rho})$ a constitutive modulus. (A verification of (3.10) will be given in Section 3e.) Thus $\pi = -\partial_\rho\hat{\psi} + \pi_{\text{dis}}$ and there are two contributions to the internal force: a contribution $-\partial_\rho\hat{\psi}$ that represents the internal force that would be present were $\dot{\rho} = 0$, and a dissipative contribution $\pi_{\text{dis}} = -\beta\dot{\rho}$. In fact, the dissipation is given by

$$\mathcal{D} = -\pi_{\text{dis}}(\rho,\nabla\rho,\dot{\rho})\,\dot{\rho} = \beta(\rho,\nabla\rho,\dot{\rho})(\dot{\rho})^2. \tag{3.11}$$

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" $\beta(\rho,\nabla\rho,\dot{\rho}) \ge 0$, for then (3.8) - (3.10) generate constitutive relations that are compatible with the dissipation inequality (3.2) in all constitutive processes.

c. The generalized Ginzburg-Landau equation

Using (3.8)-(3.10) in the force balance (2.11) yields

$$\beta(\rho,\nabla\rho,\dot{\rho})\dot{\rho} = \operatorname{div}[\partial_{\mathbf{p}}\hat{\psi}(\rho,\nabla\rho)] - \partial_{\rho}\hat{\psi}(\rho,\nabla\rho). \tag{3.12}$$

This is the most general PDE based on the force balance (2.11) and constitutive relations (3.5) that are consistent with the second law in the form (3.2).

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

$$\hat{\psi}(\rho,\nabla\rho) = f(\rho) + \tfrac{1}{2}\alpha|\nabla\rho|^2, \tag{3.13}$$

with $f(\rho)$ a "coarse-grain" free energy and α a strictly positive constant, leads to the standard Ginzburg-Landau equation:

$$\beta\dot{\rho} = \alpha\Delta\rho - f'(\rho). \tag{3.14}$$

d. Further generalization of the Ginzburg-Landau equation

A more general theory in which the stress $\boldsymbol{\xi}$ is dissipative is obtained by allowing for constitutive relations in which $\nabla\dot{\rho}$ enters the list of independent constitutive variables:

$$\psi = \hat{\psi}(\rho,\nabla\rho,\dot{\rho},\nabla\dot{\rho}), \qquad \boldsymbol{\xi} = \hat{\boldsymbol{\xi}}(\rho,\nabla\rho,\dot{\rho},\nabla\dot{\rho}), \qquad \pi = \hat{\pi}(\rho,\nabla\rho,\dot{\rho},\nabla\dot{\rho}). \tag{3.15}$$

Using the notation (3.6) augmented by $\mathbf{r} = \nabla\dot{\rho}$ and proceeding as before leads to the inequality (3.7) with the arguments $(\rho,\nabla\rho,\dot{\rho})$ replaced by $(\rho,\nabla\rho,\dot{\rho},\nabla\dot{\rho})$ and with the additional term $\partial_{\mathbf{r}}\hat{\psi}(\rho,\nabla\rho,\dot{\rho},\nabla\dot{\rho})\cdot\nabla\ddot{\rho}$ added to the left side; this leads to the conclusions $\partial_{\mathbf{r}}\hat{\psi} = \mathbf{0}$ and $\partial_q\hat{\psi} = 0$, so that

$$\psi = \hat{\psi}(\rho,\nabla\rho). \tag{3.16}$$

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

$$\pi_{\mathrm{dis}}(\rho,\nabla\rho,\dot{\rho},\nabla\dot{\rho})\,\dot{\rho} - \boldsymbol{\xi}_{\mathrm{dis}}(\rho,\nabla\rho,\dot{\rho},\nabla\dot{\rho})\cdot\nabla\dot{\rho} \le 0, \tag{3.17}$$

where

$$\begin{aligned}\pi_{\mathrm{dis}}(\rho,\nabla\rho,\dot\rho,\nabla\dot\rho) &= \hat\pi(\rho,\nabla\rho,\dot\rho,\nabla\dot\rho) + \partial_\rho\hat\psi(\rho,\nabla\rho),\\ \boldsymbol{\xi}_{\mathrm{dis}}(\rho,\nabla\rho,\dot\rho,\nabla\dot\rho) &= \hat{\boldsymbol{\xi}}(\rho,\nabla\rho,\dot\rho,\nabla\dot\rho) - \partial_{\mathbf{p}}\hat\psi(\rho,\nabla\rho).\end{aligned} \tag{3.18}$$

As I will show in Section 3e, the most general solution of the inequality (3.17) is

$$\begin{aligned}\pi_{\mathrm{dis}}(\rho,\nabla\rho,\dot\rho,\nabla\dot\rho) &= -\beta\dot\rho - \mathbf{b}\cdot\nabla\dot\rho,\\ \boldsymbol{\xi}_{\mathrm{dis}}(\rho,\nabla\rho,\dot\rho,\nabla\dot\rho) &= \mathbf{m}\dot\rho + \mathbf{M}\nabla\dot\rho,\end{aligned} \tag{3.19}$$

with

$\beta = \beta(\rho,\nabla\rho,\dot\rho,\nabla\dot\rho)$ (a scalar), $\mathbf{b} = \mathbf{b}(\rho,\nabla\rho,\dot\rho,\nabla\dot\rho)$ (a vector)
$\mathbf{m} = \mathbf{m}(\rho,\nabla\rho,\dot\rho,\nabla\dot\rho)$ (a vector), $\mathbf{M} = \mathbf{M}(\rho,\nabla\rho,\dot\rho,\nabla\dot\rho)$ (a tensor),

constitutive moduli that render the dissipation

$$\mathcal{D} = \beta(\dot\rho)^2 + \dot\rho(\mathbf{b}+\mathbf{m})\cdot\nabla\dot\rho + \nabla\dot\rho\cdot\mathbf{M}\nabla\dot\rho \tag{3.20}$$

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

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

$$(\beta - \operatorname{div}\mathbf{m})\dot\rho + \mathbf{c}\cdot\nabla\dot\rho = \operatorname{div}[\,\partial_{\mathbf{p}}\hat\psi(\rho,\nabla\rho) + \mathbf{M}\nabla\dot\rho\,] - \partial_\rho\hat\psi(\rho,\nabla\rho), \tag{3.21}$$

with $\mathbf{c} = \mathbf{b} - \mathbf{m}$. If the free energy has the simple form (3.13), if β, $\mathbf{b}$, $\mathbf{m}$, and M are constant, and if the material is isotropic so that $\mathbf{c} = \mathbf{0}$ and $\mathbf{M} = \gamma\mathbf{1}$, then (3.21) reduces to

$$\beta\dot\rho = \alpha\Delta\rho + \gamma\Delta\dot\rho - f'(\rho). \tag{3.22}$$

e. Solution of thermodynamical inequalities

The inequality (3.17) can be written succintly in the form

$$\mathbf{F}(\mathbf{X},\mathbf{Y})\cdot\mathbf{Y} \le 0 \tag{3.23}$$

with

$$\mathbf{X} = (\rho,\nabla\rho), \quad \mathbf{Y} = (\dot\rho,\nabla\dot\rho), \quad \mathbf{F}(\mathbf{X},\mathbf{Y}) = (\pi_{\mathrm{dis}}(\rho,\nabla\rho,\dot\rho,\nabla\dot\rho), -\boldsymbol{\xi}_{\mathrm{dis}}(\rho,\nabla\rho,\dot\rho,\nabla\dot\rho)).$$

I now give a general solution of (3.23) within a framework that yields (3.10) and (3.19) as special cases, but is sufficiently general for subsequent applications.

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 (3.23) for all $\mathbf{X} \in \mathbb{R}^p$ and $\mathbf{Y} \in \mathbb{R}^q$. The variable $\mathbf{X}$ appears as a parameter and I may, without loss in generality, suppress it when convenient.

For $\lambda > 0$, $\mathbf{F}(\lambda\mathbf{Y}) \cdot \lambda\mathbf{Y} \le 0$ and hence $\mathbf{F}(\lambda\mathbf{Y}) \cdot \mathbf{Y} \le 0$. Thus, letting $\lambda \to 0$, $\mathbf{F}(\mathbf{0}) \cdot \mathbf{Y} \le 0$ for all $\mathbf{Y}$, so that $\mathbf{F}(\mathbf{0}) = \mathbf{0}$. Thus

$$\mathbf{F}(\mathbf{Y}) = \Big\{ \int_0^1 \nabla\mathbf{F}(s\mathbf{Y})\,ds \Big\} \mathbf{Y} \tag{3.24}$$

for all $\mathbf{Y}$; hence, writing $-\mathbf{B}(\mathbf{Y})$ for the quantity $\{\ldots\}$, $\mathbf{F}(\mathbf{Y}) = -\mathbf{B}(\mathbf{Y})\mathbf{Y}$ for all $\mathbf{Y}$. The general solution $\mathbf{F}$ of (3.23) is therefore

$$\mathbf{F}(\mathbf{X},\mathbf{Y}) = -\mathbf{B}(\mathbf{X},\mathbf{Y})\mathbf{Y} \tag{3.25}$$

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

$$\mathbf{Y} \cdot \mathbf{B}(\mathbf{X},\mathbf{Y})\mathbf{Y} \ge 0. \tag{3.26}$$

Because of the dependence of $\mathbf{B}(\mathbf{X},\mathbf{Y})$ on $\mathbf{Y}$, the inequality (3.26) is weaker than positive definiteness for $\mathbf{B}(\mathbf{X},\mathbf{Y})$. However, when $\mathbf{F}$ is *quasilinear,* that is, when $\mathbf{F}(\mathbf{X},\mathbf{Y})$ is linear in $\mathbf{Y}$ for each $\mathbf{X}$, then

$$\mathbf{F}(\mathbf{X},\mathbf{Y}) = -\mathbf{B}(\mathbf{X})\mathbf{Y} \tag{3.27}$$

for all $(\mathbf{X},\mathbf{Y})$, with $\mathbf{B}(\mathbf{X})$ positive semi-definite.

More generally, the relation (3.27) holds to first order in $\mathbf{Y}$:

$$\mathbf{F}(\mathbf{X},\mathbf{Y}) = -\mathbf{B}(\mathbf{X})\mathbf{Y} + o(|\mathbf{Y}|) \qquad \text{as } \mathbf{Y} \to \mathbf{0} \tag{3.28}$$

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

$$\mathbf{F}(\mathbf{X},\mathbf{Y}) = -\mathbf{B}\mathbf{Y} + o(|\mathbf{X}| + |\mathbf{Y}|) \qquad \text{as } \mathbf{X},\mathbf{Y} \to \mathbf{0} \tag{3.29}$$

with $\mathbf{B}$ constant and positive semi-definite.

4. DIFFUSION. GENERALIZED CAHN-HILLIARD EQUATIONS

a. Basic laws

I now consider a theory in which the order parameter is identified with the density ρ of a diffusing, essentially independent[12] species of atoms. I base the theory on balance of mass, the force balance (2.13), and a generalization of the dissipation inequality that accomodates diffusion. I therefore consider, as primitive physical quantitites, the fields

ρ	density = order parameter,
μ	chemical potential,
$\mathbf{h}$	mass flux,
ψ	free energy,
$\boldsymbol{\xi}$	reduced microstress,
π	reduced internal force.

Balance of mass is the requirement that

$$\{\int_R \rho\,dv\}^\cdot \le -\int_{\partial R} \mathbf{h}\cdot\mathbf{n}\,da \tag{4.1}$$

for every control volume R.

Within the present context the second law is the assertion that the rate at which the energy of R increases cannot exceed the working on R plus the rate at which energy is transported to R by diffusion. Since the chemical potential measures energy per unit mass,

$$-\int_{\partial R} \mu\mathbf{h}\cdot\mathbf{n}\,da \tag{4.2}$$

represents the energy carried into R across ∂R by diffusion, and, since the density ρ is considered as an order parameter,

$$\mathcal{W}(R) = \int_{\partial R} \dot{\rho}\,\boldsymbol{\xi}\cdot\mathbf{n}\,da \tag{4.3}$$

represents the rate of working. The appropriate form of the second law is there-

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[12] 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.

fore the *dissipation inequality* (cf. [13])

$$\{\int_R \psi\, dv\}^{\cdot} \le -\int_{\partial R} \mu \mathbf{h}\cdot\mathbf{n}\, da + \int_{\partial R} \rho^{\cdot} \boldsymbol{\xi}\cdot\mathbf{n}\, da. \tag{4.4}$$

Since R is arbitrary, balance of mass yields

$$\rho^{\cdot} = -\operatorname{div}\mathbf{h}, \tag{4.5}$$

and combining (4.4), localized, with (2.11) and (4.5) yields the *local dissipation inequality*

$$\psi^{\cdot} + (\pi - \mu)\rho^{\cdot} - \boldsymbol{\xi}\cdot\nabla\rho^{\cdot} + \mathbf{h}\cdot\nabla\mu \le 0. \tag{4.6}$$

As before, I define the dissipation $\mathcal{D}$ to be the negative of the left side of (4.6); the integral of $\mathcal{D}$ over R is then the right side of (4.4) minus the left, so that

$$\begin{aligned} &\{\int_B \psi\, dv\}^{\cdot} = -\int_B \mathcal{D}\, dv \le 0 && \text{if } \rho^{\cdot}\boldsymbol{\xi}\cdot\mathbf{n} = \mathbf{h}\cdot\mathbf{n} = 0 \text{ on } \partial B, \\ &\{\int_B (\psi - \mu_0\rho)\, dv\}^{\cdot} = -\int_B \mathcal{D}\, dv \le 0 && \text{if } \rho^{\cdot}\boldsymbol{\xi}\cdot\mathbf{n} = 0,\ \mu = \mu_0 = \text{const. on } \partial B. \end{aligned} \tag{4.7}$$

b. 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. Precisely, I consider constitutive equations of the form:

$$\begin{aligned} \psi &= \hat{\psi}(\rho,\nabla\rho,\mu,\nabla\mu), & \mathbf{h} &= \hat{\mathbf{h}}(\rho,\nabla\rho,\mu,\nabla\mu), \\ \boldsymbol{\xi} &= \hat{\boldsymbol{\xi}}(\rho,\nabla\rho,\mu,\nabla\mu), & \pi &= \hat{\pi}(\rho,\nabla\rho,\mu,\nabla\mu). \end{aligned} \tag{4.8}$$

Let

$$\mathbf{p} = \nabla\rho, \qquad \mathbf{s} = \nabla\mu, \qquad \mathbf{Z} = (\rho,\nabla\rho,\mu,\nabla\mu). \tag{4.9}$$

As before, I require consistency of the constitutive relations with the local dissipation inequality. Thus, substituting (4.8) into (4.6),

$$[\partial_\rho \hat{\psi}(\mathbf{Z}) + \hat{\pi}(\mathbf{Z}) - \mu]\rho^{\cdot} + [\partial_{\mathbf{p}} \hat{\psi}(\mathbf{Z}) - \hat{\boldsymbol{\xi}}(\mathbf{Z})]\cdot\nabla\rho^{\cdot} + [\partial_\mu \hat{\psi}(\mathbf{Z})]\mu^{\cdot} + [\partial_{\mathbf{s}} \hat{\psi}(\mathbf{Z})]\cdot\nabla\mu^{\cdot} + \hat{\mathbf{h}}(\mathbf{Z})\cdot\nabla\mu \le 0, \tag{4.10}$$

so that $\partial_\mu \hat{\psi} = 0$, $\partial_{\mathbf{s}} \hat{\psi} = 0$, $\partial_{\mathbf{p}} \hat{\psi} = \hat{\boldsymbol{\xi}}$, and $\partial_\rho \hat{\psi} = \mu - \hat{\pi}$. Thus $\hat{\psi}$ and $\hat{\boldsymbol{\xi}}$ are independent of μ and $\nabla\mu$; $\hat{\pi}$ is independent of $\nabla\mu$;

$$\hat{\pi}(\rho,\nabla\rho,\mu) = \mu - \partial_\rho \hat{\psi}(\rho,\nabla\rho), \qquad \hat{\boldsymbol{\xi}}(\rho,\nabla\rho) = \partial_{\mathbf{p}} \hat{\psi}(\rho,\nabla\rho); \tag{4.11}$$

and

$$\hat{\mathbf{h}}(\mathbf{Z})\cdot\nabla\mu \le 0 \tag{4.12}$$

for all $\mathbf{Z}$, so that, by (3.25), $\hat{\mathbf{h}}$ has the form

$$\hat{\mathbf{h}}(\mathbf{Z}) = -\mathbf{M}(\mathbf{Z})\nabla\mu \tag{4.13}$$

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

$$\mathcal{D} = \nabla\mu\cdot\mathbf{M}(\mathbf{Z})\nabla\mu. \tag{4.14}$$

Combining (4.11) and the force balance (2.11),

$$\mu = \partial_\rho \hat{\psi}(\rho,\nabla\rho) - \operatorname{div}[\partial_{\mathbf{p}} \hat{\psi}(\rho,\nabla\rho)], \tag{4.15}$$

an expression for the chemical potential that reduces to the classical relation $\mu = \partial_\rho \hat{\psi}$ if the free energy is independent of the density gradient. Interestingly, the general relation (4.15) gives the chemical potential as the variational derivative of the total free energy (1.4) with respect to density:

$$\mu = \delta\Psi/\delta\rho. \tag{4.16}$$

c. The generalized Cahn-Hilliard equation

Substituting (4.13) and (4.15) in the mass balance (4.5) yields the generalized Cahn-Hilliard equation

$$\rho^{\cdot} = \operatorname{div}\mathbf{M}\nabla\{\partial_\rho \hat{\psi}(\rho,\nabla\rho) - \operatorname{div}[\partial_{\mathbf{p}} \hat{\psi}(\rho,\nabla\rho)]\} \tag{4.17}$$

with $\mathbf{M} = \mathbf{M}(\mathbf{Z})$. The standard Cahn-Hilliard equation follows upon choosing a constant mobility tensor of the form $\mathbf{M} = \gamma\mathbf{1}$ in conjunction with the free energy (3.13):

$$\rho^{\cdot} = \gamma\Delta[f'(\rho) - \alpha\Delta\rho]. \tag{4.18}$$

d. Inclusion of kinetics

A more general theory may be based on constitutive relations in which $\rho^{\cdot}$ enters the list of independent constitutive variables:

$$\begin{aligned} \psi &= \hat{\psi}(\rho,\nabla\rho,\rho^{\cdot},\mu,\nabla\mu), & \mathbf{h} &= \hat{\mathbf{h}}(\rho,\nabla\rho,\rho^{\cdot},\mu,\nabla\mu), \\ \boldsymbol{\xi} &= \hat{\boldsymbol{\xi}}(\rho,\nabla\rho,\rho^{\cdot},\mu,\nabla\mu), & \pi &= \hat{\pi}(\rho,\nabla\rho,\rho^{\cdot},\mu,\nabla\mu). \end{aligned} \tag{4.19}$$

In this case compatibility with the dissipation inequality yields the following conclusions: the free energy and stress are independent of $\rho^{\cdot}$, μ, and $\nabla\mu$;

$$\hat{\boldsymbol{\xi}}(\rho,\nabla\rho) = \partial_{\mathbf{p}}\hat{\psi}(\rho,\nabla\rho); \tag{4.20}$$

the inequality

$$\pi_{dis}(\mathbf{Z})\rho^{\cdot} + \hat{\mathbf{h}}(\mathbf{Z})\cdot\nabla\mu \le 0, \qquad \pi_{dis}(\mathbf{Z}) = \hat{\pi}(\mathbf{Z}) + \partial_\rho\hat{\psi}(\rho,\nabla\rho) - \mu \tag{4.21}$$

is satisfied for all

$$\mathbf{Z} = (\rho,\nabla\rho,\rho^{\cdot},\mu,\nabla\mu). \tag{4.22}$$

The results of Section 3e applied to (4.21) yield the existence of constitutive moduli $\beta = \beta(\mathbf{Z})$ (a scalar), $\mathbf{b} = \mathbf{b}(\mathbf{Z})$ and $\mathbf{m} = \mathbf{m}(\mathbf{Z})$ (vectors), and $\mathbf{M} = \mathbf{M}(\mathbf{Z})$ (a tensor), such that

$$\begin{aligned} \pi_{dis}(\rho,\nabla\rho,\rho^{\cdot},\mu,\nabla\mu) &= -\beta\rho^{\cdot} - \mathbf{b}\cdot\nabla\mu, \\ \hat{\mathbf{h}}(\rho,\nabla\rho,\rho^{\cdot},\mu,\nabla\mu) &= -\mathbf{m}\rho^{\cdot} - \mathbf{M}\nabla\mu, \end{aligned} \tag{4.23}$$

and such that (3.26) is satisfied.

Combining the first of (4.23) with the force balance (2.11) yields a complicated expression for the chemical potential:

$$\mu - \mathbf{b}\cdot\nabla\mu = \partial_\rho\hat{\psi}(\rho,\nabla\rho) - \operatorname{div}[\partial_{\mathbf{p}}\hat{\psi}(\rho,\nabla\rho)] + \beta\rho^{\cdot}. \tag{4.24}$$

For an isotropic material $\mathbf{b} = \mathbf{0}$ and (4.24) reduces to

$$\mu = \partial_\rho \hat{\psi}(\rho,\nabla\rho) - \operatorname{div}[\partial_{\mathbf{p}} \hat{\psi}(\rho,\nabla\rho)] + \beta\dot{\rho} = \delta\Psi/\delta\rho + \beta\dot{\rho}, \tag{4.25}$$

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

The general PDE that follows from these constitutive equation is obtained upon substituting (4.24) and the second of (4.23) into the mass balance (4.5). Granted isotropy, constant values of the constitutive moduli in (4.23), and a free energy in the form (3.13), this PDE reduces to

$$\dot{\rho} = \gamma\Delta[f'(\rho) - \alpha\Delta\rho + \beta\dot{\rho}], \tag{4.26}$$

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

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

5. 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.

a. 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

$$\mathbf{y}(\mathbf{x},t) = \mathbf{x} + \mathbf{u}(\mathbf{x},t). \tag{5.1}$$

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

$$\mathbf{F} = \mathbf{1} + \nabla\mathbf{u}, \tag{5.2}$$

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 $\mathbf{u}^{\cdot}$, 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 3a as well as a tensor field **S** that represents the (Piola-Kirchhoff) stress; these fields are presumed consistent with the mass balance (4.1), the microforce balance (2.13), and the standard balance laws

$$\int_{\partial R}\mathbf{S}\mathbf{n}\,da = \mathbf{0}, \qquad \int_{\partial R}\mathbf{y}\times\mathbf{S}\mathbf{n}\,da = \mathbf{0}, \tag{5.3}$$

or equivalently,

$$\operatorname{div}\mathbf{S} = \mathbf{0}, \qquad \mathbf{S}\mathbf{F}^{\mathsf{T}} = \mathbf{F}\mathbf{S}^{\mathsf{T}}. \tag{5.4}$$

There are now two distinct systems of forces: a microforce system consisting of a stress $\boldsymbol{\xi}$ and an internal force π subject to the balance (2.11), and a macroforce system defined by a stress S consistent with (5.4). The physical nature of these systems manifests itself in the manner in which the stresses perform work: $\boldsymbol{\xi}$ works against changes in the order parameter ρ through the expression (4.3), while the working of the macrostress **S** is given by the standard relation

$$\int_{\partial R}\mathbf{S}\mathbf{n}\cdot\mathbf{u}^{\cdot}\,da \tag{5.5}$$

in which the material velocity $\mathbf{u}^{\cdot}$ represents the kinetics. I therefore base the theory on the *dissipation inequality*

$$\Big\{\int_{R}\psi\,dv\Big\}^{\cdot} \le -\int_{\partial R}\mu\mathbf{h}\cdot\mathbf{n}\,da + \int_{\partial R}\rho^{\cdot}\boldsymbol{\xi}\cdot\mathbf{n}\,da + \int_{\partial R}\mathbf{S}\mathbf{n}\cdot\mathbf{u}^{\cdot}\,da. \tag{5.6}$$

Combining (2.11), (4.5), (5.4), and (5.6) yields the *local dissipation inequality*

$$\psi^{\cdot} - \mathbf{S}\cdot\mathbf{F}^{\cdot} + (\pi-\mu)\rho^{\cdot} - \boldsymbol{\xi}\cdot\nabla\rho^{\cdot} + \mathbf{h}\cdot\nabla\mu \le 0 \tag{5.7}$$

Defining the dissipation $\mathcal{D}$ to be the negative of the left side of (5.7) leads to the Lyapunov relations (4.7), provided the restriction $\mathbf{S}\mathbf{n}\cdot\mathbf{u}^{\cdot} = 0$ on ∂B is added. If instead $\mathbf{S}\mathbf{n} = \mathbf{S}_0\mathbf{n}$ on ∂B with $\mathbf{S}_0$ constant, then (4.7) remains valid, but with ψ replaced by $\psi - \mathbf{S}_0 \cdot \nabla \mathbf{u}$.

b. Constitutive equations. Restrictions imposed by the second law

I consider constitutive equations of the form

$$\begin{gathered}\psi = \hat{\psi}(\mathbf{F},\rho,\nabla\rho,\mu,\nabla\mu), \quad \mathbf{S} = \hat{\mathbf{S}}(\mathbf{F},\rho,\nabla\rho,\mu,\nabla\mu), \quad \mathbf{h} = \hat{\mathbf{h}}(\mathbf{F},\rho,\nabla\rho,\mu,\nabla\mu), \\ \boldsymbol{\xi} = \hat{\boldsymbol{\xi}}(\mathbf{F},\rho,\nabla\rho,\mu,\nabla\mu), \qquad \pi = \hat{\pi}(\mathbf{F},\rho,\nabla\rho,\mu,\nabla\mu),\end{gathered} \tag{5.8}$$

which accounts for deformation, but not for kinetics, as $\rho^{\cdot}$ is not included in the list of constitutive variables.[13]

I assume that $\hat{\mathbf{S}}$ is consistent with the second of (5.4). In addition, I require that constitutive response be invariant under changes in observer; precisely, I assume that (5.8) is invariant under the transformations

$$\begin{gathered}\psi \to \psi, \quad \mathbf{S} \to \mathbf{Q}\mathbf{S}, \quad \mathbf{h} \to \mathbf{h}, \quad \boldsymbol{\xi} \to \boldsymbol{\xi}, \quad \pi \to \pi, \\ (\mathbf{F},\rho,\nabla\rho,\mu,\nabla\mu) \to (\mathbf{Q}\mathbf{F},\rho,\nabla\rho,\mu,\nabla\mu)\end{gathered} \tag{5.9}$$

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

$$\begin{gathered}\hat{\psi}(\mathbf{F}) = \tilde{\psi}(\mathbf{C}), \quad \hat{\mathbf{S}}(\mathbf{F}) = \mathbf{F}\tilde{\mathbf{S}}(\mathbf{C}), \quad \hat{\mathbf{h}}(\mathbf{F}) = \tilde{\mathbf{h}}(\mathbf{C}), \\ \hat{\boldsymbol{\xi}}(\mathbf{F}) = \tilde{\boldsymbol{\xi}}(\mathbf{C}), \quad \hat{\pi}(\mathbf{F}) = \tilde{\pi}(\mathbf{C})\end{gathered} \tag{5.10}$$

with $\mathbf{C} = \mathbf{F}^{\mathsf{T}}\mathbf{F}$ the right Cauchy-Green strain tensor (cf., e.g., [28]). I will make no further use of the restricted relations (5.10), as the general development is simpler using the variable $\mathbf{F}$.

Let

$$\mathbf{p} = \nabla\rho, \qquad \mathbf{s} = \nabla\mu, \qquad \mathbf{Z} = (\mathbf{F},\rho,\nabla\rho,\mu,\nabla\mu). \tag{5.11}$$

Compatibility of the constitutive relations (5.8) with the dissipation inequality (5.7) leads to the following generalizations of the results established in Section 4b: $\hat{\psi}$, $\mathbf{S}$, and $\hat{\boldsymbol{\xi}}$ are independent of μ and $\nabla\mu$; $\hat{\pi}$ is independent of $\nabla\mu$;

$$\begin{gathered}\hat{\pi}(\mathbf{F},\rho,\nabla\rho,\mu) = \mu - \partial_\rho \hat{\psi}(\mathbf{F},\rho,\nabla\rho), \quad \hat{\boldsymbol{\xi}}(\mathbf{F},\rho,\nabla\rho) = \partial_{\mathbf{p}} \hat{\psi}(\mathbf{F},\rho,\nabla\rho), \\ \hat{\mathbf{S}}(\mathbf{F},\rho,\nabla\rho) = \partial_{\mathbf{F}} \hat{\psi}(\mathbf{F},\rho,\nabla\rho);\end{gathered} \tag{5.12}$$

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[13] The inclusion of $\rho^{\cdot}$ as well as $\mathbf{F}^{\cdot}$ presents no essential difficulty.

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

$$\hat{\mathbf{h}}(\mathbf{Z}) = -\mathbf{M}(\mathbf{Z})\nabla\mu \tag{5.13}$$

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

Combining (5.12) and the force balance (2.11) shows that the chemical potential is, once again, the variational derivative of the total energy with respect to density:

$$\mu = \partial_\rho \hat{\psi}(\mathbf{F},\rho,\nabla\rho) - \mathrm{div}[\partial_{\mathbf{p}} \hat{\psi}(\mathbf{F},\rho,\nabla\rho)] = \delta\Psi/\delta\rho. \tag{5.14}$$

c. Partial differential equations

Combining the reduced constitutive relations with the mass and force balance leads to the general system

$$\begin{aligned} &\rho^{\boldsymbol{\cdot}} = \mathrm{div}(\mathbf{M}\nabla\mu), && \mu = \partial_\rho \hat{\psi}(\mathbf{F},\rho,\nabla\rho) - \mathrm{div}[\partial_{\mathbf{p}} \hat{\psi}(\mathbf{F},\rho,\nabla\rho)], \\ &\mathrm{div}\mathbf{S} = \mathbf{0}, && \mathbf{S} = \partial_{\mathbf{F}} \hat{\psi}(\mathbf{F},\rho,\nabla\rho), \end{aligned} \tag{5.15}$$

with $\mathbf{M} = \mathbf{M}(\mathbf{Z})$. This system, supplemented by (5.10), is the most general properly invariant system consistent with the constitutive relations (5.8) and the second law in the form (5.6).

d. 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 (5.4) by the requirement that $\mathbf{S}$ be symmetric:

$$\mathbf{S} = \mathbf{S}^{\mathsf{T}}; \tag{5.16}$$

the steps leading to (5.12) and (5.13) then remain unchanged. Further, invariance of the constitutive equations under infinitesimal rotations (replacement of $\nabla\mathbf{u}$ by $\nabla\mathbf{u} + \mathbf{\Omega}$ with $\mathbf{\Omega}$ skew) implies that the constitutive functions can depend on $\nabla\mathbf{u}$ only through the infinitesimal strain

$$\mathbf{E} = \tfrac{1}{2}(\nabla\mathbf{u} + \nabla\mathbf{u}^{\mathsf{T}}), \tag{5.17}$$

and this leads to the conclusion that $\mathbf{F}$ in (5.12) can be replaced by $\mathbf{E}$.

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

$$\begin{aligned} &\hat{\psi}(E,\rho,\nabla\rho) = W(E,\rho) + \tfrac{1}{2}\alpha|\nabla\rho|^2, \\ &W(E,\rho) = \tfrac{1}{2}\mathbf{E}\cdot\mathbb{C}(\rho)\mathbf{E} + \mathbf{E}\cdot\bar{S}(\rho) + f(\rho), \end{aligned} \tag{5.18}$$

where $\mathbb{C}(\rho)$, a symmetric linear transformation of symmetric tensors into symmetric tensors, is the elasticity tensor; $\bar{\mathbf{S}}(\rho)$, a symmetric tensor, is a "compositional stress"; and $f(\rho)$ is a double-well potential that defines the two phases. This form of the free energy yields the relations

$$\begin{aligned} &S = \partial_{\mathbf{E}} W(E,\rho) = \mathbb{C}(\rho)E + \bar{S}(\rho), \\ &\mu = \partial_\rho W(E,\rho) - \alpha\Delta\rho = f'(\rho) + \tfrac{1}{2}\mathbf{E}\cdot\mathbb{C}'(\rho)\mathbf{E} + \mathbf{E}\cdot\bar{S}'(\rho) - \alpha\Delta\rho, \end{aligned} \tag{5.19}$$

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

$$\dot{\rho} = M\cdot\nabla\nabla[f'(\rho) - \alpha\Delta\rho + \mathbf{E}\cdot\bar{S}'(\rho)], \qquad \operatorname{div}[\,\mathbb{C}\mathbf{E} + \bar{S}(\rho)] = \mathbf{0} \tag{5.20}$$

with E given by (5.17). For an isotropic material with $\bar{S}(\rho)$ linear in $\rho - \rho_0$ (ρ_0 = const.)

$$\mathbb{C}\mathbf{E} = 2a\mathbf{E} + b(\operatorname{tr}\mathbf{E})\mathbf{1}, \quad \bar{S}(\rho) = k(\rho - \rho_0)\mathbf{1}, \quad M = \gamma\mathbf{1}, \tag{5.21}$$

and (5.20) reduce to

$$\dot{\rho} = \gamma\Delta[f'(\rho) - \alpha\Delta\rho + k\operatorname{div}\mathbf{u}], \qquad a\Delta\mathbf{u} + (a+b)\nabla\operatorname{div}\mathbf{u} + k\nabla\rho = 0. \tag{5.22}$$

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