NONISOTHERMAL PHASE SEPARATION BASED ON A MICROFORCE BALANCE

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Abstract. Our aim in this article is to derive models for nonisothermal phase separation. Starting from the two fundamental laws of thermodynamics, we consider the approach of Gurtin, based on a balance law for microforces, to derive nonisothermal Cahn-Hilliard type equations. These equations extend previous models derived by Alt and Pawlow based on an entropy principle to nonisotropic materials and to systems that are far from equilibrium. We also extend this approach to the Ginzburg-Landau (Allen-Cahn) equation, for which we recover, as particular cases, some models obtained by Frémond with a physically different approach.

1. Introduction. The Cahn-Hilliard equation for isothermal phase separation (see [6], [7] and [14])

$$\frac{\partial \rho}{\partial t} + \alpha \kappa \Delta^2 \rho - \kappa \Delta f'(\rho) = 0, \quad \alpha, \kappa > 0,$$

(1.1)

where $\rho$ is the order parameter, plays a fundamental role in materials science. It is a conservation law which describes important qualitative features of two-phase systems, namely the transport of atoms between unit cells. This phenomenon can be observed, for instance, when a binary alloy is cooled down sufficiently. One then observes a partial nucleation (i.e. the apparition of nucleides in the material) or a total nucleation (the so-called spinodal decomposition: the material quickly becomes inhomogeneous, forming a fine-grained structure, see [6]). In this model, which assumes that the process is caused by an instantaneous quench below a critical temperature, only diffusive phenomena are taken into account.

Now, in realistic physical systems, quenches are usually carried out over a finite period of time, so that phase separation can begin before the final quenching is reached. Furthermore, external thermal activation can be used to control the

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separation process and the resulting spatial structure. Thus, Alt and Pawłow proposed in [1] (see also [2]) a model for nonisothermal phase separation (see also [13] for a model for phase separation during continuous cooling: the model is merely the Cahn-Hilliard equation with temperature dependent coefficients; we should also mention previous models of nonisothermal phase transitions such as, e.g., the conserved and nonconserved models proposed by Caginalp, see [5]), which reads as follows:

\[
\frac{\partial \rho}{\partial t} = -\text{div} h \quad (\text{mass balance}), \tag{1.2}
\]

\[
\frac{\partial e}{\partial t} + \text{div} q = 0 \quad (\text{energy equation}), \tag{1.3}
\]

\[
h = -l_{11}\frac{\partial \mu}{\partial \theta} + l_{12}\nabla \frac{1}{\theta}, \tag{1.4}
\]

\[
q = l_{22}\nabla \frac{1}{\theta} - l_{21}\frac{\partial \mu}{\partial \theta}, \tag{1.5}
\]

\[
\frac{\mu}{\theta} = \partial_{\rho} \frac{\psi}{\partial \theta} - \text{div}(\partial_{\rho} \frac{\psi}{\partial \theta}), \tag{1.6}
\]

\[l_{11} > 0, \ l_{22} > 0, \ l_{11}l_{22} - l_{12}l_{21} > 0,\]

where \(h\) is the mass flux, \(e\) is the internal energy, \(q\) is the heat flux, \(\mu\) is the chemical potential, \(\theta\) is the absolute temperature and \(\psi = \psi(\rho, \nabla \rho, \theta)\) is the free energy, which is linked to the entropy \(s\) by the thermodynamical relation (Gibbs’ relation)

\[
\psi = e - \theta s. \tag{1.7}
\]

Here, (1.6) was proposed in [1] as a generalization of the corresponding relation in isothermal phase separation (corresponding to \(\theta = \text{Const.}\); (1.2), (1.3) and (1.6) give, for \(\theta = \text{Const.}\) and \(\psi(\rho, \nabla \rho) = \frac{\alpha}{2} |\nabla \rho|^2 + f(\rho)\) (the classical Ginzburg-Landau free energy), the (isothermal) Cahn-Hilliard equation) and the constitutive equations (1.4) and (1.5) are postulated (see also [14]; actually these constitutive equations arise as an implementation of the classical approach of Onsager, see [20, 21]). Furthermore, we have

\[
s = -\partial_{\theta} \psi, \tag{1.8}
\]

\[
e = \partial_{\rho} \frac{\psi}{\partial \theta}. \tag{1.9}
\]

Here and below, the notation \(\partial_X\) stands for the partial derivation with respect to the variable \(X\).

We can note that the derivation of the above model follows closely that of the isothermal one (see [1] and [14]). However, Alt and Pawłow obtained in [3], based on an entropy principle (in particular, no a priori specification is made on the entropy flux and the Gibbs’ relation (1.7) is a consequence of a weaker form of entropy inequality), more general models. In these models, the constitutive equation for the chemical potential is assumed to depend linearly on \(\nabla \frac{1}{\theta}\) and takes the more general form

\[
\frac{\mu}{\theta} = \partial_{\rho} \frac{\psi}{\partial \theta} - \text{div}(\partial_{\rho} \frac{\psi}{\partial \theta}) + l \cdot \nabla \frac{1}{\theta}, \tag{1.10}
\]
for a vector \( l = l(\rho, \nabla \rho, \frac{1}{2}) \). Furthermore, more general forms of the constitutive equations for the mass and heat fluxes are derived. It is important nevertheless to note here that the theory developed in [3] (and also in [1, 2]) is essentially a thermodynamical theory near constant equilibria (in particular, Alt and Pawlow also assume that the mass and heat fluxes depend linearly on \( \nabla \frac{\theta}{\rho} \) and \( \nabla \frac{1}{2} \), which can be interpreted as a thermodynamical theory near the equilibria \( \frac{\theta}{\rho} = \text{Const.} \) and \( \frac{1}{2} = \text{Const.} \). Moreover, this analysis is essentially restricted to the case of isotropic materials.

Now, according to Gurtin (see [14]), even though it is physically sound and important, the Cahn-Hilliard equation should be regarded as a precursor of more complete theories. In particular, he makes the following objections to the classical (isothermal) theory:
- It limits the manner in which rate terms enter the equations.
- It requires a priori specifications of the constitutive equations for the mass flux (and for the heat flux in the nonisothermal case; we note again that (1.4) and (1.5) are postulated). Gurtin further notes that such postulated constitutive equations may no longer be valid if the system is far from equilibrium.
- It is not clear how it can be generalized in the presence of processes such as deformations or heat transfers. Actually, Zhiqiang Bi and Sekerta proposed in [26] a generalization of the Cahn-Hilliard equation (they also developed a general thermodynamically consistent phase field model based on a proper entropy functional which is postulated) which accounts for heat transfers. However, this generalization follows the classical theory.
- There is no clear separation of basic balance laws (such as those for mass and forces) from constitutive equations (such as those for elastic solids and viscous fluids) which delineate specific classes of material behaviors. Such a separation is one of the major advances in nonlinear continuum mechanics over the past thirty years.
- It is not clear whether or not there is an underlying balance law which can form a basis for more complete theories.

Based on these observations, Gurtin proposed in [14] several generalizations of the (isothermal) Cahn-Hilliard equation. More precisely, a relevant feature which distinguishes his approach from other macroscopic theories of order parameters is the separation of balance laws from constitutive equations and the introduction of a new balance law for internal microforces, namely

\[
\text{div} \, \zeta + \pi = 0, \quad (1.11)
\]

where we have neglected the external actions and where \( \zeta \) (a vector) is the microstress and \( \pi \) (a scalar) corresponds to the internal microforces. Actually, at equilibrium, the requirement that the first variation of the total free energy vanishes yields the Euler-Lagrange equation \( \text{div} \, \zeta + \pi = 0 \), with \( \zeta = \partial \nabla \rho \psi \) and \( \pi = -\partial_{\rho} \psi \), which represents a statical version of the microforce balance (1.11), with \( \zeta \) and \( \pi \) being given constitutive representations. Such a variational principle is no longer available in dynamics with general forms of dissipation and the microforce balance (1.11) can then be seen as an attempt to extend to dynamics an essential feature of statical theories. Furthermore, we can note that relation (1.11) provides a balance for interactions at a microscopic level, whereas standard forces are associated with macroscopic length scales. These different length scales can also explain the need for a separate balance law for microforces. Finally, this point is motivated by
the belief that fundamental physical laws involving energy should account for the working associated with each operative kinematical process (that associated with the order parameter in the Cahn-Hilliard theory). It thus seems plausible that there should be microforces whose working accompanies changes in the order parameter; reasonably, such interatomic forces may be characterized macroscopically by fields which perform work when the order parameter undergoes changes. This working is expressed through terms of the form $\frac{\partial \rho}{\partial t}$ (although we might very well consider terms of the form $\nabla \frac{\partial \rho}{\partial t}$), so that the microforces are scalar rather than vector quantities (see [14]).

We should note that Gurtin’s approach is essentially a two-scale approach and that, in many systems, one can observe multiscale phenomena; clearly, such phenomena cannot be well modelled in even a good two-scale methodology. It would thus be interesting to develop a more general theory which would account for multiscale phenomena; unfortunately, this does not seem to be an easy task.

Of course, in order to have a full description of the dynamics of the phase separation process, relation (1.11) has to be complemented with the fundamental balance laws. Clearly, these laws, and especially the energy equality, have to be expressed in a form which takes into account the action of the internal microforces. Furthermore, we do not introduce (as was done in [1]) a system of constitutive equations for the mass and heat fluxes stating the explicit form of the physical quantities. Rather, still following Gurtin [14], we keep these quantities in an implicit form and just specify a list, which is taken as wide as possible, of independent constitutive variables upon which they are allowed to depend. It is only a posteriori that, following Coleman and Noll (see [8]), the admissible expressions for the physical parameters are deduced and this is done by solving a system of thermodynamical inequalities which arises as a direct consequence of the balance laws (and, in particular, of the second law). In particular, this kind of procedure allows us to describe what seems to be the most general class of free energies, of heat fluxes and of chemical potentials which are compatible with the fundamental laws in this nonisothermal setting.

Let us stress again that this is indeed a new and relevant feature of Gurtin’s approach; actually, it appears that, in former derivations, one first chose (possibly on the basis of experiments) the expression of the free energy and the other quantities and then proved a posteriori that these choices were compatible with the balance laws. For instance, this seems to be the approach used by Frémond in [13], based on different, yet very similar to ours, considerations. Actually, in [13], a dynamical variant of (1.11), accounting for the balance of the so-called “microscopic movements”, is considered. Such microscopic movements are assumed to give rise to the macroscopic effects leading to the phase transition, even within a rigid body framework. Then, using the analogue of (1.11) and the energy equation, Frémond shows that suitable (classes of) free energies lead to the “thermodynamical consistency” of the derivation. We have to note that, despite its different physical basis, Frémond’s approach gives rise to the same types of equations as those derived within our approach in several concrete cases.

Due to the nonisothermal character of the phenomenon that we consider, it is worth noting that the fundamental relation stating that our models comply with thermodynamics is the entropy growth (Clausius-Duhem) inequality (inequality (2.7) below). Actually, while in the approaches of Alt and Pawlow in [3] and of Frémond (but also in other former derivations), the validity of (2.7) is essentially
a theorem, here, following Coleman and Noll, \((2.7)\) is one of the fundamental laws which are taken as a starting point of our procedure. We should emphasize that, contrary to the approaches of Alt and Pawlow in [3] and of Frémond, we specify here the expression of the entropy flux (equal to \(\frac{q}{\theta}\)). We should also note that, in the original work [14] of Gurtin, \((2.7)\) was actually replaced by a dissipation inequality for the free energy, consequence of the first two laws of thermodynamics under isothermal conditions (see [14], Appendix A). This is of course not suitable when one considers the dependence on the temperature, since it is no longer physically correct to assume that the free energy decreases along solution trajectories. Instead, we obtain here a more complicated dissipation inequality (see \((2.10)\) below), accounting for nonisothermal effects.

Our main purpose in this article is to extend the approach of Gurtin to the nonisothermal case to derive nonisothermal Cahn-Hilliard models. In particular, these models generalize those derived by Alt and Pawlow to nonisotropic materials and to system that are far from equilibrium (see Section 3). We also consider in Section 4 the Ginzburg-Landau (Allen-Cahn) equation. This equation, which describes the ordering of atoms within unit cells on a lattice, was also derived and generalized in [14] based on the above considerations. In that case, we recover some of the models of Frémond. We thus obtain a very wide class of nonisothermal Cahn-Hilliard and Ginzburg-Landau systems; moreover, we give examples of the resulting equations when considering various concrete choices of the free energy coming from the literature and compatible with this derivation.

We note that all the systems of partial differential equations that we obtain present a highly nonlinear character, so that performing a rigorous mathematical analysis appears in most cases to be an indeed challenging task. Moreover, up to our knowledge, almost no contribution seems to be available in the literature for this kind of equations, with the exception of a few works devoted to the analysis of Frémond type models [4,11,16,17,18,25]. We studied in [19] the well-posedness of a (simplified) Ginzburg-Landau system derived in Section 4 and we shall address the mathematical analysis of other models in subsequent works. Another even more challenging task would be to make suitable and reasonable tests against experiments for the models derived in this article.

2. Derivation of the nonisothermal Cahn-Hilliard model. In order to derive our model, we consider the two fundamental laws of thermodynamics (see [14], Appendix A; see also [8]):

- First law (energy equation):

\[
\frac{d}{dt} \int_{\mathcal{R}} e \, dx = - \int_{\partial \mathcal{R}} q \cdot \nu d\sigma + W(\mathcal{R}) + M(\mathcal{R}),
\]

where \(\mathcal{R}\) is an arbitrary control volume, \(\nu\) is the unit outer normal vector to \(\partial \mathcal{R}\), \(W(\mathcal{R})\) is the rate of working of all forces exterior to \(\mathcal{R}\) and \(M(\mathcal{R})\) is the rate at which free energy is added to \(\mathcal{R}\) by mass transport (we assume here that there is no heat supply). We have (see [14])

\[
W(\mathcal{R}) = \int_{\partial \mathcal{R}} (\zeta \cdot \nu) \frac{\partial \rho}{\partial t} d\sigma,
\]

\[
M(\mathcal{R}) = \int_{\partial \mathcal{R}} \mu h \cdot \nu d\sigma,
\]
so that (2.1) can be rewritten as
\[
\frac{d}{dt} \int_{\mathcal{R}} e \, dx = - \int_{\partial \mathcal{R}} q \cdot v \, d\sigma + \int_{\partial \mathcal{R}} (\zeta \cdot v) \frac{\partial \rho}{\partial t} \, d\sigma - \int_{\partial \mathcal{R}} \mu h \cdot \nu d\sigma. \tag{2.4}
\]
Using Green’s formula to treat the surface integrals, we find
\[
\frac{d}{dt} \int_{\mathcal{R}} e \, dx = \int_{\mathcal{R}} (- \text{div} \, q + \frac{\partial \rho}{\partial t} \text{div} \, \zeta + \zeta \cdot \nabla \frac{\partial \rho}{\partial t} - \mu \text{div} \, h - h \cdot \nabla \mu) \, dx, \tag{2.5}
\]
which yields, using the mass balance (1.2) and the microforce balance (1.11) and noting that the control volume \( \mathcal{R} \) is arbitrary,
\[
\frac{\partial e}{\partial t} = - \text{div} \, q + (\mu - \pi) \frac{\partial \rho}{\partial t} + \zeta \cdot \nabla \frac{\partial \rho}{\partial t} - h \cdot \nabla \mu. \tag{2.6}
\]

- Second law (entropy-growth inequality): \( \frac{d}{dt} \int_{\mathcal{R}} s \, dx \geq - \int_{\partial \mathcal{R}} (\frac{\rho}{\theta}) \cdot \nu d\sigma, \) \( \tag{2.7} \)
  which yields, noting that the control volume \( \mathcal{R} \) is arbitrary,
\[
\frac{\partial s}{\partial t} \geq - \text{div} \, \left( \frac{\rho}{\theta} \right). \tag{2.8}
\]

We now multiply (2.6) by \( \frac{1}{\theta} \) to obtain
\[
\frac{\partial \tilde{\psi}}{\partial t} - \mu \frac{\partial \tilde{\psi}}{\partial t} = - \text{div} \, \left( \frac{\rho}{\theta} \right) + q \cdot \nabla \frac{1}{\theta} + \left( \frac{\mu}{\theta} - \pi \right) \frac{\partial \rho}{\partial t} + \zeta \cdot \nabla \frac{\partial \rho}{\partial t} - h \cdot \nabla \mu. \tag{2.9}
\]
Since we know from thermodynamics that \( \frac{\partial \tilde{\psi}}{\partial t} = \tilde{\psi} - s \) (Gibbs’ relation), we then deduce from (2.8) and (2.9) that
\[
\frac{\partial \tilde{\psi}}{\partial t} - \mu \frac{\partial \tilde{\psi}}{\partial t} \leq q \cdot \nabla \frac{1}{\theta} + \left( \frac{\mu}{\theta} - \pi \right) \frac{\partial \rho}{\partial t} + \zeta \cdot \nabla \frac{\partial \rho}{\partial t} - h \cdot \nabla \mu. \tag{2.10}
\]

It is reasonable, in view of the form of equations (1.2) – (1.6) and following [14] (see also [3]), to consider \( Z = (\rho, \nabla \rho, \frac{\rho}{\theta}, \nabla \frac{\rho}{\theta}, \frac{1}{\theta}, \nabla \frac{1}{\theta}) \) as independent constitutive variables (in the derivation of (1.2) – (1.6), we would have had \( Z = (\rho, \nabla \rho, \frac{1}{\theta}, \nabla \frac{1}{\theta}) \), with then \( \frac{\rho}{\theta} \) given constitutively and somehow postulated). We thus assume that \( \psi, \epsilon, h, \zeta, \pi \) and \( q \) depend a priori on \( Z \) and we deduce from (2.10) the following dissipation inequality:
\[
(\partial \frac{\psi}{\theta} - e) \frac{\partial \frac{\psi}{\theta}}{\partial t} - q \cdot \nabla \frac{1}{\theta} + \left( \frac{\pi - \mu}{\theta} + \frac{\partial \rho}{\partial t} \right) \frac{\partial \rho}{\partial t} + \frac{1}{\theta} (\partial \nabla \psi - \zeta) \cdot \nabla \frac{\partial \rho}{\partial t} + \frac{1}{\theta} \partial \nabla \psi \cdot \nabla \frac{\partial \rho}{\partial t} - \frac{1}{\theta} \partial \nabla \frac{\partial \rho}{\partial t} \frac{\partial \nabla \frac{\partial \rho}{\partial t}}{\partial t} + \mu \cdot \nabla h \leq 0 \tag{2.11}
\]
which has to be valid for every fields. Here, it is possible to choose a field \( Z \) such that \( Z, \frac{\partial \frac{\psi}{\theta}}{\partial t}, \frac{\partial \rho}{\partial t}, \nabla \frac{\partial \rho}{\partial t}, \frac{\partial \frac{\psi}{\theta}}{\partial t} \), and \( \frac{\partial \frac{\psi}{\theta}}{\partial t} \) take arbitrary prescribed values at some chosen point and time. Thus, since \( \frac{\partial \frac{\psi}{\theta}}{\partial t}, \frac{\partial \rho}{\partial t}, \nabla \frac{\partial \rho}{\partial t}, \frac{\partial \frac{\psi}{\theta}}{\partial t} \), and \( \frac{\partial \frac{\psi}{\theta}}{\partial t} \) appear linearly in (2.11), it follows that, necessarily,
\[
e = \frac{\partial \frac{\psi}{\theta}}{\partial t}, \tag{2.12}
\]

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so that \( s = -\partial_\theta \psi \), and

\[
\psi = \psi(\rho, \nabla \rho, \theta),
\]

as expected (in particular, the expressions for \( e \) and \( s \) actually follow from the Gibbs’ relation (1.7)). Moreover,

\[
\pi - \mu + \partial_\rho \psi = 0,
\]

\[
\zeta = \partial_\rho \psi.
\]

Indeed, otherwise, \( \frac{\partial^2}{\partial \theta^2}, \frac{\partial \rho}{\partial \theta}, \frac{\partial \nabla \rho}{\partial \theta}, \frac{\partial \nabla^2 \rho}{\partial \theta} \) and \( \frac{\partial \nabla^2 \rho}{\partial \theta} \) could be chosen to violate (2.11). There thus remains the dissipation inequality

\[
- q \cdot \nabla \frac{1}{\theta} + h \cdot \nabla \mu \leq 0,
\]

for every fields.

We now deduce from (1.11), (2.14) and (2.15) that

\[
\mu = \partial_\rho \psi - \text{div}(\partial_\rho \psi),
\]

i.e.

\[
\frac{\mu}{\theta} = \frac{1}{\theta} \partial_\rho \psi - \frac{1}{\theta} \text{div}(\partial_\rho \psi).
\]

Thus, instead of (1.6), we recover here the same expression of the chemical potential in terms of the free energy as in the isothermal theory (see [14]). An explanation for this fact could be given by noting that relation (1.6) essentially states that \( \mu/\theta \) coincides with the first variation of the rescaled total free energy, i.e.

\[
\frac{\mu}{\theta} = \delta_\rho \int_\Omega \frac{\psi}{\theta} dx.
\]

So, and also on account of (1.2)–(1.5), (1.2)–(1.6) seems to have a variational structure, at least with respect to \( \rho \). However, as we pointed out in the introduction, there is no reason why the free energy should obey a variational principle in the present nonisothermal setting.

Writing \( \frac{1}{\theta} \cdot \nabla \mu = h \cdot \nabla \frac{1}{\theta} - \mu h \cdot \nabla \frac{1}{\theta} \), we have the dissipation inequality

\[
- (q + \mu h) \cdot \nabla \frac{1}{\theta} + h \cdot \nabla \frac{\mu}{\theta} \leq 0,
\]

for every fields, which yields that (see [14], Appendix B)

\[
h = -A \nabla \frac{\mu}{\theta} - B \nabla \frac{1}{\theta},
\]

\[
q + \mu h = C \nabla \frac{\mu}{\theta} + D \nabla \frac{1}{\theta},
\]

where the matrices \( A, B, C \) and \( D \) depend on \( Z \) and are such that (2.20) is satisfied (which yields that \( A \) and \( D \) are, in some sense, positive semi-definite). Actually, these unknown constitutive moduli can also be viewed as some kind of constitutive relations. Thus, in some sense, one may say that, in Gurtin’s approach, the question of constitutive relations is pushed forward to a latter stage in the analysis. This
is nevertheless a weaker assumption (when compared with other approaches) and allows to obtain a wider class of models (see also Section 3).

Remark 2.1: We should note at this stage that, as already mentioned in the introduction, weaker forms of the entropy inequality (2.7) have been proposed. In particular, in [3], no a priori specification is made on the entropy flux (equal to \( q_\theta \) here). Then, based on an entropy principle (which postulates the existence of the entropy and of the entropy flux satisfying proper assumptions), the authors obtain restrictions on the constitutive equations. However, contrary to our approach, they make assumptions on the mass and heat fluxes and on the chemical potential which essentially mean that the theory developed in [3] is a thermodynamical theory near constant equilibria.

Thanks to (2.14) and (2.15), we can rewrite the energy equation (2.6) in the form

\[
\frac{\partial e}{\partial t} = - \text{div} q + \partial_\rho \psi \frac{\partial \rho}{\partial t} + \partial \tau_\rho \psi \cdot \nabla \frac{\partial \rho}{\partial t} - h \cdot \nabla \mu, \tag{2.23}
\]

which yields, in view of (2.22),

\[
\frac{\partial e}{\partial t} = - \text{div}(C\nabla \mu + D\nabla^1 \theta) + \partial_\rho \psi \frac{\partial \rho}{\partial t} + \partial \tau_\rho \psi \cdot \nabla \frac{\partial \rho}{\partial t} + \mu \text{ div } h, \tag{2.24}
\]

that is to say, with the mass balance (1.2),

\[
\frac{\partial e}{\partial t} = - \text{div}(C\nabla \mu + D\nabla^1 \theta) + \partial \tau_\rho \psi \cdot \nabla \frac{\partial \rho}{\partial t} + (\partial_\rho \psi - \mu) \frac{\partial \rho}{\partial t}. \tag{2.25}
\]

Using (2.17), we finally obtain the equation

\[
\frac{\partial e}{\partial t} = - \text{div}(C\nabla \mu + D\nabla^1 \theta - \partial \tau_\rho \psi). \tag{2.26}
\]

To sum up, we have the following nonisothermal Cahn-Hilliard system:

\[
\frac{\partial \rho}{\partial t} = \text{div}(A\nabla \mu + B\nabla^1 \theta), \tag{2.27}
\]

\[
\frac{\partial e}{\partial t} = - \text{div}(C\nabla \mu + D\nabla^1 \theta - \partial \tau_\rho \psi), \tag{2.28}
\]

\[
\mu = \partial_\rho \psi - \text{div}(\partial \tau_\rho \psi), \tag{2.29}
\]

\[
e = \partial_\theta \psi = \psi - \theta \partial_\theta \psi, \tag{2.30}
\]

where, here, (2.30) is a constitutive relation, whereas (2.29) corresponds to the microforce balance (1.11), written explicitly in terms of the constitutive relations (2.14)–(2.15). Therefore, (1.11) (or (2.29)) needs to be complemented with suitable boundary conditions.

A classical choice of free energy reads (see [1])

\[
\psi = -c_V \theta \ln \theta + c\rho^2 (\theta - \theta_c) + f(\rho) + \frac{\alpha(\rho, \theta)}{2} |\nabla \rho|^2, \tag{2.31}
\]

where \( c_V > 0, \ c > 0, \ \theta_c > 0 \) and \( f \) is usually a polynomial of degree 6. This gives rise to the relations
\[
\mu = 2c(\theta - \theta_c)\rho + \frac{1}{2}(\partial_\rho \alpha)|\nabla \rho|^2 + f'(\rho) - \text{div}(\alpha \nabla \rho),
\] (2.32)

\[
e = c_V\theta - c\theta_c\rho^2 + f(\rho) + \frac{1}{2}(\alpha - \theta \partial_\theta \alpha)|\nabla \rho|^2.
\] (2.33)

**Remark 2.2:** We note that, in relation (2.31), \(c_V\) is the specific heat, \(\theta_c\) has the meaning of a critical temperature and the quantity \(\ell(\rho) = -c\rho^2\) (with the minus sign) in the second term has the meaning of a latent heat function. More generally, it seems that, in concrete physical situations (see [22, 23] for more details), a latent heat of the form \(\ell(\rho) = -c\rho^2 + c_1\rho + c_2\), with \(c_1, c_2 = \text{Const.}\), is also relevant. Furthermore, many articles have been devoted to the case where the latent heat has a linear dependence on \(\rho\), i.e. \(\ell(\rho) = c_1\rho + c_2\), generally with \(c_1 > 0\). Finally, we have to note that \(f\) represents a potential associated with the phase separation process, which is possibly nonconvex in order to assign lower energy values to the pure states.

**Remark 2.3:** Other possible choices of free energy read (see [1])

\[
\psi = -c_V\theta^2 + c\rho^2(\theta - \theta_c) + f(\rho) + \frac{\alpha(\rho, \theta)}{2}|\nabla \rho|^2,
\] (2.34)

and

\[
\psi = -c_V\theta \ln(1 + \theta) + c\rho^2(\theta - \theta_c) + f(\rho) + \frac{\alpha(\rho, \theta)}{2}|\nabla \rho|^2.
\] (2.35)

In particular, “the entropic” contribution \(-c_V\theta^2\) in (2.34) appears in various classes of nonisothermal processes, such as phase transitions and thermoelastic systems (see [27]).

**Remark 2.4:** The mathematical analysis of models of the form (1.2)–(1.6) can be found, e.g., in [2] and [24]. The mathematical analysis of the models derived in this section seems however much more involved. To illustrate this, we consider for instance the case where \(A = D = I\) (the identity matrix), \(B = C = 0\) and \(\alpha = \text{Const.}\) and \(c = 0\) in (2.31). We then obtain the equations

\[
\frac{\partial \rho}{\partial t} = \Delta \frac{\mu}{\theta},
\] (2.36)

\[
\mu = f'(\rho) - \alpha \Delta \rho,
\] (2.37)

\[
c_V \frac{\partial \theta}{\partial t} + \Delta \frac{1}{\theta} = -f'(\rho) \frac{\partial \rho}{\partial t} + \alpha \frac{\partial \rho}{\partial t} \Delta \rho,
\] (2.38)

or, setting \(X = \frac{\rho}{\theta}\) and replacing the term \(\alpha \Delta \rho\) which appears in the last term in the right-hand side of (2.38) by its value given by (2.37),

\[
\frac{\partial \rho}{\partial t} = \Delta X,
\] (2.39)

\[
\theta X = f'(\rho) - \alpha \Delta \rho,
\] (2.40)

\[
c_V \frac{\partial \theta}{\partial t} + \Delta \frac{1}{\theta} = -\theta X \Delta X.
\] (2.41)
Here, the problem is that we do not know how to treat the term $\theta X \Delta X$. We note that we have the conservation of the energy here. Indeed, integrating (formally) (2.41) over the domain $\Omega$ occupied by the material, we obtain

$$c_v \frac{d}{dt} \int_\Omega \theta dx = - \int_\Omega \theta X \Delta X dx. \tag{2.42}$$

Multiplying then (2.40) by $\frac{\partial \rho}{\partial t}$ and integrating over $\Omega$, we have, thanks to (2.39) (we assume that the equations are supplemented with boundary conditions which allow to integrate by parts),

$$\frac{d}{dt} F(\rho) = \int_\Omega \theta X \Delta X dx, \tag{2.43}$$

where

$$F(\rho) = \int_\Omega (f(\rho) + \frac{\alpha}{2} |\nabla \rho|^2) dx. \tag{2.44}$$

We finally deduce from (2.42) and (2.43) the conservation of the energy

$$\frac{d}{dt} (F(\rho) + c_v \int_\Omega \theta dx) = 0. \tag{2.45}$$

### 3. Further generalization of the equations.

Following [14], we now also add $\frac{\partial \rho}{\partial t}$ (i.e. the kinetics) to the list of independent constitutive variables (we also recall that the working of the internal microforces are expressed through terms of this form).

Actually, we should note that the question of knowing which variables/functions to consider is not entirely solved by Gurtin’s approach and we still have to decide somehow which variable to add to the list of independent constitutive variables. We thus set $Z = (\rho, \nabla \rho, \frac{\partial \rho}{\partial t}, \mu \theta, \nabla \mu \theta, 1 \theta, \nabla 1 \theta)$. In that case, (2.10) yields the dissipation inequality

$$\left(\frac{\partial \psi}{\partial \theta} - e\right) \frac{\partial^2 \psi}{\partial \theta^2} - q \cdot \nabla 1 \theta + \frac{1}{\theta} (\pi - \mu + \partial_\psi \psi) \frac{\partial \psi}{\partial t} + \frac{1}{\theta} (\partial \nabla \psi - \zeta) \cdot \nabla \rho + \frac{1}{\theta} \frac{\partial^2 \rho}{\partial t^2} + \frac{1}{\theta} \frac{\partial \rho}{\partial t} \frac{\partial \nu}{\partial t} + \frac{1}{\theta} \frac{\partial \nabla \psi}{\partial t} + \frac{1}{\theta} \frac{\partial \nabla 1 \theta}{\partial t} + \frac{1}{\theta} \frac{\partial \nabla \mu}{\partial t} + h \cdot \nabla \mu \leq 0, \tag{3.1}$$

which has to be valid for every fields. We thus recover (2.12), (2.13) and (2.15) and there remains the dissipation inequality

$$- q \cdot \nabla 1 \theta + \frac{1}{\theta} (\pi - \mu + \partial_\psi \psi) \frac{\partial \rho}{\partial t} + h \cdot \nabla \mu \leq 0, \tag{3.2}$$

for every fields, which we rewrite as

$$-(q + \mu h) \cdot \nabla 1 \theta + \frac{1}{\theta} (\pi - \mu + \partial_\psi \psi) \frac{\partial \rho}{\partial t} + h \cdot \nabla \mu \leq 0, \tag{3.3}$$

for every fields. We then deduce from (3.3) that (see [14], Section 3.4 and Appendix B)

$$h = -\alpha \frac{\partial \rho}{\partial t} - A \nabla \mu \theta - B \nabla 1 \theta, \tag{3.4}$$
\[
\frac{1}{\theta}(\pi - \mu + \partial_\rho \psi) = -\beta \frac{\partial \rho}{\partial t} - b \cdot \nabla \frac{\mu}{\theta} - c \cdot \nabla \frac{1}{\theta}, \tag{3.5}
\]

\[
q + \mu h = d \frac{\partial \rho}{\partial t} + C \nabla \frac{\mu}{\theta} + D \nabla \frac{1}{\theta}, \tag{3.6}
\]

where the constitutive moduli \(A, B, C, D\) (4 matrices), \(a, b, c, d\) (4 vectors) and \(\beta\) (a scalar) depend on \(Z\) and are such that (3.3) is satisfied (this implies that \(\beta\) is positive and that \(A\) and \(D\) are, in some sense, positive semi-definite).

We now deduce from (3.5) that

\[
\mu \theta - b \cdot \nabla \frac{\mu}{\theta} = \pi \theta + \frac{1}{\theta} \partial_\rho \psi + \beta \frac{\partial \rho}{\partial t} + c \cdot \nabla \frac{1}{\theta}, \tag{3.7}
\]

which yields, in view of (1.11) and (2.15),

\[
\frac{\mu}{\theta} - b \cdot \nabla \frac{\mu}{\theta} = \beta \frac{\partial \rho}{\partial t} + c \cdot \nabla \frac{1}{\theta} + \frac{1}{\theta} \partial_\rho \psi - \frac{1}{\theta} \text{div}(\partial \nabla \rho \psi). \tag{3.8}
\]

Furthermore, proceeding as in Section 2, we can rewrite the energy equation (2.6) in the form

\[
\frac{\partial e}{\partial t} = -\text{div}\left(d \frac{\partial \rho}{\partial t} + C \nabla \frac{\mu}{\theta} + D \nabla \frac{1}{\theta} - \frac{\partial \rho}{\partial t} \partial \nabla \rho \psi\right) - \pi \frac{\partial \rho}{\partial t}, \tag{3.9}
\]

which yields, in view of (1.11) and (2.15),

\[
\frac{\partial e}{\partial t} = -\text{div}\left(d \frac{\partial \rho}{\partial t} + C \nabla \frac{\mu}{\theta} + D \nabla \frac{1}{\theta} - \frac{\partial \rho}{\partial t} \partial \nabla \rho \psi\right) - \frac{\partial \rho}{\partial t} \partial \nabla \rho \psi. \tag{3.10}
\]

To sum up, we have the following nonisothermal Cahn-Hilliard system:

\[
\frac{\partial \rho}{\partial t} = \text{div}\left(a \frac{\partial \rho}{\partial t} + A \nabla \frac{\mu}{\theta} + B \nabla \frac{1}{\theta}\right), \tag{3.11}
\]

\[
\frac{\mu}{\theta} - b \cdot \nabla \frac{\mu}{\theta} = \beta \frac{\partial \rho}{\partial t} + c \cdot \nabla \frac{1}{\theta} + \frac{1}{\theta} \partial_\rho \psi - \frac{1}{\theta} \text{div}(\partial \nabla \rho \psi), \tag{3.12}
\]

\[
\frac{\partial e}{\partial t} = -\text{div}\left(d \frac{\partial \rho}{\partial t} + C \nabla \frac{\mu}{\theta} + D \nabla \frac{1}{\theta} - \frac{\partial \rho}{\partial t} \partial \nabla \rho \psi\right) - \frac{\partial \rho}{\partial t} \partial \nabla \rho \psi. \tag{3.13}
\]

**Remark 3.1:** Taking \(b = 0\) and \(\beta = 0\) in (3.12) (we note however that, owing to the dissipation inequality (3.3), we should have \(\beta > 0\) if \(c \neq 0\); we thus take \(\beta = 0\) as a first approximation), we obtain

\[
\frac{\mu}{\theta} = \partial_\rho \psi - \frac{1}{\theta} \text{div}(\partial \nabla \rho \psi) + c \cdot \nabla \frac{1}{\theta}. \tag{3.14}
\]

We thus recover the constitutive relation (1.10) derived by Alt and Pawălow in [3], except for the second term in the right-hand side of (3.14) which is slightly different (we recall however that, in [3], the system is assumed to be close to a constant equilibrium; see also Section 2). Similarly, the constitutive equations for \(h\) and \(q\) are different from those derived in [3] (although they bear some resemblance). Thus, the equations obtained in this section may be viewed as extensions of the models of [3] to nonisotropic materials and to systems that are far from equilibrium. We could further generalize our models by adding \(\nabla \frac{\partial \rho}{\partial t}\) to the list of independent constitutive variables, thus allowing to develop a more general theory in which the microstress \(\zeta\) is dissipative. Another possible generalization consists in accounting
for the deformations of the material. To do so, we can proceed as in [14]; again, the models are essentially derived by adding proper quantities to the list of independent constitutive variables. Finally, the entropy flux $\Psi$, equal to $q/\theta$, is of the form

$$\Psi = -\mu h + \theta \frac{\partial \rho}{\partial t} + C\nabla \frac{\mu}{\theta} + \tilde{D} \nabla \frac{1}{\theta},$$

(3.15)

where $h$ is given by (3.4). Again, this expression bears some resemblance to the entropy flux obtained in [3] (we recall that, in [3], the entropy flux is not given a priori, but it is derived in a unique manner, up to normalization, based on an entropy principle). In particular, the term containing a multiplication of the chemical potential by the mass flux already appears in linear irreversible thermodynamics (see [12]; see also [3]).

4. The Ginzburg-Landau equation. We can study with a similar approach the Ginzburg-Landau equation. In that case, $W(R)$ is defined as in (2.2), while $M(R)$ vanishes (see [14]). Thus, we obtain, proceeding as in Section 2 and using the microforce balance (1.11),

$$\frac{\partial e}{\partial t} = -\text{div} q - \pi \frac{\partial \rho}{\partial t} + \zeta \cdot \nabla \frac{\partial \rho}{\partial t},$$

(4.1)

and we then have the following dissipation inequality:

$$\frac{\partial \psi}{\partial t} - e \frac{\partial \psi}{\partial t} \leq q \cdot \nabla \frac{1}{\theta} - \pi \frac{\partial \rho}{\theta} + \zeta \cdot \nabla \frac{\partial \rho}{\theta}.$$  

(4.2)

We take here $Z = (\rho, \nabla \rho, \frac{\partial \rho}{\theta}, \frac{1}{\theta}, \nabla \frac{1}{\theta})$ as independent constitutive variables (see [14]) and we obtain, assuming that $\psi, e, q, \pi$ and $\zeta$ depend on $Z$,

$$(\partial_\psi \psi - e) \frac{\partial \psi}{\partial t} - q \cdot \nabla \frac{1}{\theta} + \frac{1}{\theta} (\pi + \partial_\psi \psi) \frac{\partial \rho}{\partial t} + \frac{1}{\theta} (\partial_\psi \nabla \rho - \zeta) \cdot \frac{\partial \nabla \rho}{\partial t} + \frac{1}{\theta} \partial_\psi \psi \cdot \frac{\partial \nabla \rho}{\partial t} + \frac{1}{\theta} \partial_\psi \psi \cdot \frac{\partial \nabla \rho}{\partial t} \leq 0,$$

(4.3)

for every fields. We thus recover (2.12), (2.13) and (2.15) and there remains the dissipation inequality

$$\frac{1}{\theta} (\pi + \partial_\psi \psi) \frac{\partial \rho}{\partial t} - q \cdot \nabla \frac{1}{\theta} \leq 0,$$

(4.4)

for every fields, which yields that (see [14])

$$\frac{1}{\theta} (\pi + \partial_\psi \psi) = -\beta \frac{\partial \rho}{\partial t} - a \cdot \nabla \frac{1}{\theta},$$

(4.5)

where the constitutive moduli $\beta$ (a scalar), $a$, $b$ (2 vectors) and $B$ (a matrix) depend on $Z$ and are such that (4.4) is satisfied (which implies that $\beta$ is positive and that $B$ is, in some sense, positive semi-definite). We thus deduce from (1.11), (2.15) and (4.5) that

$$\beta \frac{\partial \rho}{\partial t} + a \cdot \nabla \frac{1}{\theta} + \frac{1}{\theta} \partial_\psi \psi - \frac{1}{\theta} \text{div}(\partial_\psi \psi) = 0,$$

(4.7)
and the energy equation (4.1) gives, using (1.11), (2.15) and (4.6),

\[ \frac{\partial e}{\partial t} = - \text{div}( b \frac{\partial \rho}{\partial t} + B \nabla \frac{1}{\theta} - \partial_{\psi} \rho \frac{\partial \rho}{\partial t} ). \]  

(4.8)

We now choose a free energy of the form (2.31), where we assume, for simplicity, that \( \beta \theta \) is a constant (which we still denote by \( \beta \)), that \( a = b = 0 \), that \( B = I \) and that \( \alpha \) is a constant. These values are consistent with the dissipation inequality (4.4); we note indeed that the absolute temperature is expected to be positive. We then have

\[ \partial_{\psi} \rho = 2c(\theta - \theta_c)\rho + f'(\rho), \]  

(4.9)

\[ \partial_{\psi} \rho = \alpha \nabla \rho, \]  

(4.10)

\[ e = c_v \theta - c_{\phi,c} \rho^2 + f(\rho) + \frac{\alpha}{2} |\nabla \rho|^2, \]  

(4.11)

and

\[ \frac{\partial e}{\partial t} = c_v \frac{\partial \theta}{\partial t} - 2c_{\phi,c} \rho \frac{\partial \rho}{\partial t} + f'(\rho) \frac{\partial \rho}{\partial t} + \alpha \nabla \rho \cdot \nabla \frac{\partial \rho}{\partial t}. \]  

(4.12)

It then follows from (4.7) that

\[ \beta \frac{\partial \rho}{\partial t} - \alpha \Delta \rho + 2c(\theta - \theta_c)\rho + f'(\rho) = 0, \]  

(4.13)

and it follows from (4.8) and (4.12) that

\[ c_v \frac{\partial \theta}{\partial t} + \Delta \frac{1}{\theta} = 2c_{\phi,c} \rho \frac{\partial \rho}{\partial t} - f'(\rho) \frac{\partial \rho}{\partial t} + \alpha \frac{\partial \rho}{\partial t} \Delta \rho. \]  

(4.14)

Replacing finally the term \( \alpha \Delta \rho \) which appears in the last term of the right-hand side of (4.14) by its value given by (4.13), we obtain the energy equation

\[ c_v \frac{\partial \theta}{\partial t} + \Delta \frac{1}{\theta} = \beta \left( \frac{\partial \rho}{\partial t} \right)^2 + 2c_{\phi,c} \rho \frac{\partial \rho}{\partial t}. \]  

(4.15)

To sum up, we have obtained the following nonisothermal Ginzburg-Landau system:

\[ \beta \frac{\partial \rho}{\partial t} - \alpha \Delta \rho + 2c(\theta - \theta_c)\rho + f'(\rho) = 0, \]  

(4.16)

\[ c_v \frac{\partial \theta}{\partial t} + \Delta \frac{1}{\theta} = \beta \left( \frac{\partial \rho}{\partial t} \right)^2 + 2c_{\phi,c} \rho \frac{\partial \rho}{\partial t}. \]  

(4.17)

A second consistent (with the dissipation inequality (4.4)) choice for \( B \) is \( B = \theta^2 I \) and we obtain in that case the following nonisothermal Ginzburg-Landau system:
\[
\beta \frac{\partial \rho}{\partial t} - \alpha \Delta \rho + 2c(\theta - \theta_c)\rho + f'(\rho) = 0, \quad (4.18)
\]

\[
c_V \frac{\partial \theta}{\partial t} - \Delta \theta = \beta \left( \frac{\partial \rho}{\partial t} \right)^2 + 2c\theta \rho \frac{\partial \rho}{\partial t}, \quad (4.19)
\]

We can note that these equations bear some resemblance to some of the models derived by Frémond in [13]. Actually, for a free energy of the form
\[
\psi = -c_V \theta \ln \theta + c_1 \rho (\theta - \theta_c) + f(\rho) + \alpha \frac{1}{2} |\nabla \rho|^2, \quad (4.20)
\]
(see Remark 2.2), with \( \alpha = \text{Const.} \), we recover exactly some of the models of Frémond. We could actually recover more general models of Frémond type by adding \( \nabla \frac{\partial \rho}{\partial t} \) to the list of independent constitutive variables.

**Remark 4.1:** We actually note that “intermediate” choices for \( B \) of the form
\[
B = B(\theta) \sim \left( \theta - \frac{1}{\theta} \right) I \quad (4.21)
\]
(or even generalizations of such \( Bs \) have also been considered in the literature (see, e.g., [9] [10]), for instance in the framework of the mathematical analysis of Penrose-Fife models [22 [23]. The meaning of the above expression of \( B \) seems to be that of describing a heat diffusion law which is singular as \( \theta \sim 0 \), while it has an approximately linear structure for large values of the temperature, as in the classical Fourier relation.

**Remark 4.2:** If we consider the free energies (2.34) and (2.35) (with \( \alpha = \text{Const.} \)), then the energy equations read
\[
c_V \frac{\partial \theta^2}{\partial t} - \Delta \varphi(\theta) = \beta \left( \frac{\partial \rho}{\partial t} \right)^2 + 2c\theta \rho \frac{\partial \rho}{\partial t}, \quad (4.22)
\]
and
\[
c_V \frac{\partial \theta^{1+\theta}}{\partial t} - \Delta \varphi(\theta) = \beta \left( \frac{\partial \rho}{\partial t} \right)^2 + 2c\theta \rho \frac{\partial \rho}{\partial t}, \quad (4.23)
\]
respectively, where \( \varphi(\theta) = \theta \) or \( -\frac{1}{\theta} \), or has a more general expression (see Remark 4.1).

**Remark 4.3:** The mathematical analysis of Frémond type models can be found, e.g., in [11], [16] and [17] (see also [25]). In particular, one can prove the existence of a global (in time) solution in one space dimension (in higher space dimensions, we generally only have the existence of local (in time) solutions, see [18]). Here, we can expect to have similar results for (4.16)–(4.17) and (4.18)–(4.19) (the same methods and techniques should apply here). Furthermore, we proved in [19] the global existence (and the uniqueness) of solutions for (4.16) and (4.22), with \( \varphi(\theta) = \theta \).
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