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Research Report

Thermodynamically consistent Cahn-Hilliard and Allen-Cahn models in elastic solids

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Abstract. The goal of this paper is to derive again the generalized Cahn-Hilliard and Allen-Cahn models in deformable continua introduced previously by E. Fried and M. E. Gurtin on the basis of a microforce balance. We use a different approach based on the second law in the form of the entropy principle according to I. Müller and I. S. Liu which leads to the evaluation of the entropy inequality with multipliers.

Both approaches provide the same systems of equations. In particular, our differential equation for the multiplier associated with the balance law for the order parameter turns out to be identical with the Fried-Gurtin microforce balance.

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1. Introduction

1.1. Motivation and goal

In a line of their papers E. Fried and M. E. Gurtin [8], [9], [10], [13] have developed a thermodynamical theory of phase transitions which is based on a microforce balance in addition to the basic balance laws and a mechanical version of the second law. Parallel to that theory M. Frémond [5], [6] has proposed a theory based on microscopic motions as a tool of modelling various phase transitions, specifically shape memory and damage problems. Despite of different ideas Fremond's approach bears some resemblance to the Fried-Gurtin theory.

Another approach to modelling phase transitions has been proposed in [1], [2] and applied in [23], [24], [25]. This approach consists in exploiting the second law in the form of the entropy principle according to I. Müller [21], [22] complemented by the Lagrange multipliers method suggested by I. S. Liu [18]. Such method leads to the evaluation of the entropy inequality with multipliers, known as the Müller-Liu entropy inequality. The Müller-Liu approach provides a systematic way of deriving restrictions on the interdependence of various physical quantities imposed by the second law. It represents important alternative to the so called Coleman-Noll approach [4] to the Clausius-Duhem inequality (see e.g. the more detailed accounts [20], [15]). It has been observed in [23] that assuming appropriate sets of constitutive variables and applying the multipliers-based approach it is possible to obtain generalized Allen-Cahn (Landau-Ginzburg) equations with kinetic and anisotropic effects which are identical with equations derived by Fried and Gurtin [8], [13] on the basis of the microforce balance.

The goal of this paper is to present the multipliers-based approach and compare the results obtained by means of it with the results due to Fried and Gurtin. For comparison we take two well-know models in materials science — the Cahn-Hilliard and Allen-Cahn equations and their generalizations for deformable continua. The coincidence of results, apart from indicating interesting connections, supports the usefulness of the multipliers-based approach for deriving other phase transition models. We remark that in recent years the Cahn-Hilliard and Allen-Cahn models in elastic solids have attracted a lot of mathematical interest (for up-to-date references see e.g. [3], [19], [17]).

The Cahn-Hilliard equation is a conservation law which describes phase separation process in binary alloys while the Allen-Cahn equation is a relaxation law describing ordering process in alloys. It is known from the materials science literature that elastic effects strongly influence the microstructure evolution in these processes. The chemical and elastic anisotropy, heterogeneity and the impact of external body forces are important factors as well. The Fried-Gurtin theory based on the microforce balance has allowed to encompass these effects into models. The generalized Cahn-Hilliard models have been derived in [13] while the generalized Allen-Cahn models in [8], [9], [13] and analysed further in [7]. The generalizations included anisotropic and heterogeneous effects, additional kinetic effects, multicomponent and constrained order parameters as well as the effects due to deformation of the material. Thermal effects have been suppressed except of [8] where a nonisothermal Allen-Cahn equation neglecting deformation has been considered. For the ease of direct comparison we suppress here thermal effects as well. We point out, however, that the

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multipliers-based approach can be in a straightforward manner extended to account for such effects. The nonisothermal Cahn-Hilliard and Allen-Cahn models in elastic solids will be the subject of a future work.

1.2. Review of the generalized Cahn-Hilliard and Allen-Cahn models

We review shortly the genralized Cahn-Hilliard and Allen-Cahn models derived by Fried and Gurtin. For consistency with our previous papers [17], [3] concerning mathematical aspects of the models we use a notation which differes from the original Fried-Gurtin notation. The correspondences are presented in detail in Sections 5, 6.

In case without elasticity the Cahn-Hilliard-Gurtin system for a three-dimensional body represents the mass and the microforce balances (see [13], Sec. 3.4):

$$
(1.1) \qquad
\begin{aligned}
&\dot{\chi} - \nabla \cdot (M \nabla w + h \dot{\chi}) = \tau, \\
&w - g \cdot \nabla w = -\nabla \cdot f_{,\nabla\chi}(\chi, \nabla\chi) + f_{,\chi}(\chi, \nabla\chi) + \beta \dot{\chi},
\end{aligned}
$$

where χ is the scalar, conserved order parameter representing the volume fraction of one of two components, w is the chemical potential, $f = \hat{f}(\chi, \nabla\chi)$ is the free energy density, superimposed dot denotes the material time derivative. Moreover, $M = (M_{ij})$ is the mobility tensor, $\beta \geq 0$ is the diffusional viscosity coefficient, $g = (g_i)$, $h = (h_i)$ are vectors accounting for anisotropic cross-coupling effects, and τ is an external supply of the order parameter. The quantities $M = \hat{M}(Z)$, $\beta = \hat{\beta}(Z)$, $g = \hat{g}(Z)$, $h = \hat{h}(Z)$ can in general depend on the set of variables $Z = \{\chi, D\chi, \chi_{,t}, w, Dw\}$ and are subject to the condition

$$
(1.2) \qquad
\begin{bmatrix} Dw \\ \chi_{,t} \end{bmatrix} \cdot \begin{bmatrix} M & h \\ g^T & \beta \end{bmatrix} \begin{bmatrix} Dw \\ \chi_{,t} \end{bmatrix} \geq 0 \text{ for all variables } Z.
$$

Here Dw and $\chi_{,t}$ are variables corresponding to the gradient ∇w and the time derivative $\dot{\chi}$, respectively. The relevant form of the free energy density is the Landau-Ginzburg one:

$$
(1.3) \qquad f(\chi, \nabla\chi) = \psi(\chi) + \frac{1}{2} \nabla\chi \cdot \Gamma(\chi) \nabla\chi,
$$

where $\psi(\chi)$ is a "coarse-grain" energy, a double-well potential whose wells define the phases, with the standard form

$$
(1.4) \qquad \psi(\chi) = \frac{1}{2} \chi^2 (1 - \chi)^2,
$$

and $\Gamma(\chi) = (\Gamma_{ij}(\chi))$ is a gradient energy tensor accounting for chemical heterogeneity. For free energy (1.3) equation $(1.1)_2$ becomes

$$
(1.5) \qquad w - g \cdot \nabla w = -\nabla \cdot (\Gamma(\chi) \nabla\chi) + \frac{1}{2} \nabla\chi \cdot \Gamma'(\chi) \nabla\chi + \psi'(\chi) + \beta\dot{\chi}.
$$

It is easy to see that for $g = h = 0$, $\tau = 0$, $M = mI$, $\Gamma = \gamma I$ where I is the unit tensor, and m, γ are positive constants, system $(1.1)_1$, (1.5) can be reduced to the form

$$
(1.6) \qquad \dot{\chi} - m\Delta(-\gamma\Delta\chi + \psi'(\chi) + \beta\dot{\chi}) = 0
$$

which for $\beta = 0$ represents the classical Cahn-Hilliard equation while for $\beta > 0$ the viscous Cahn-Hilliard equation.

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In case elastic effects are taken into account under assumption of infinitesimal deformations the relevant form of the free energy density is given by (see [13], Sec. 4.3):

$$(1.7) \qquad f(\varepsilon(\boldsymbol{u}), \chi, \nabla\chi) = W(\varepsilon(\boldsymbol{u}), \chi) + \psi(\chi) + \frac{1}{2}\nabla\chi \cdot \boldsymbol{\Gamma}(\chi)\nabla\chi$$

where

$$(1.8) \qquad W(\varepsilon(\boldsymbol{u}), \chi) = \frac{1}{2}(\varepsilon(\boldsymbol{u}) - \bar{\varepsilon}(\chi)) \cdot \mathbb{A}(\chi)(\varepsilon(\boldsymbol{u}) - \bar{\varepsilon}(\chi))$$

represents the elastic energy. Here $\boldsymbol{u} = (u_i)$ is the displacement vector, $\varepsilon(\boldsymbol{u}) = \frac{1}{2}(\nabla\boldsymbol{u} + \nabla\boldsymbol{u}^T)$ is the linearized strain tensor, $\mathbb{A}(\chi) = (A_{ijkl}(\chi))$ is the fourth order elasticity tensor and $\bar{\varepsilon}(\chi) = (\bar{\varepsilon}_{ij}(\chi))$ is the symmetric eigenstrain tensor. Correspondingly, the Cahn-Hilliard-Gurtin model in elastic solids based on free energy (1.7), (1.8) has the form of the mass and the microforce balances

$$(1.9) \qquad \begin{aligned} &\dot{\chi} - \nabla \cdot (\boldsymbol{M}\nabla w + \boldsymbol{h}\dot{\chi}) = \tau, \\ &w - \boldsymbol{g} \cdot \nabla w = -\nabla \cdot (\boldsymbol{\Gamma}(\chi)\nabla\chi) + \frac{1}{2}\nabla\chi \cdot \boldsymbol{\Gamma}'(\chi)\nabla\chi + \psi'(\chi) + W_{,\chi}(\varepsilon(\boldsymbol{u}), \chi) + \beta\dot{\chi} \end{aligned}$$

coupled with the linear momentum blance

$$(1.10) \qquad \ddot{\boldsymbol{u}} - \nabla \cdot W_{,\varepsilon}(\varepsilon(\boldsymbol{u}), \chi) = \boldsymbol{b},$$

where $\boldsymbol{b}$ is an external body force, and
(1.11)
$$\begin{aligned} &W_{,\chi}(\varepsilon(\boldsymbol{u}), \chi) = -\bar{\varepsilon}'(\chi) \cdot \mathbb{A}(\chi)(\varepsilon(\boldsymbol{u}) - \bar{\varepsilon}(\chi)) + \frac{1}{2}(\varepsilon(\boldsymbol{u}) - \bar{\varepsilon}(\chi)) \cdot \mathbb{A}'(\chi)(\varepsilon(\boldsymbol{u}) - \bar{\varepsilon}(\chi)), \\ &W_{,\varepsilon}(\varepsilon(\boldsymbol{u}), \chi) = \mathbb{A}(\chi)(\varepsilon(\boldsymbol{u}) - \bar{\varepsilon}(\chi)). \end{aligned}$$

Moreover, the quantities $\boldsymbol{M} = \hat{\boldsymbol{M}}(Z)$, $\beta = \hat{\beta}(Z)$, $\boldsymbol{g} = \hat{\boldsymbol{g}}(Z)$, $\boldsymbol{h} = \hat{\boldsymbol{h}}(Z)$ can depend on the set of variables $Z = \{\varepsilon(\boldsymbol{u}), \chi, D\chi, \chi_{,t}, w, Dw\}$ and are subject to the inequality (1.2) for all such variables Z. In view of the fact that the mechanical equilibrium is usually attained on a much faster time scale than diffusion in Gurtin's model (see [13], Sec. 4) a quasi-stationary approximation of (1.10), that is neglecting the inertial term $\ddot{\boldsymbol{u}}$, has been assumed.

The generalized Allen-Cahn equation derived by Fried and Gurtin (see [8], Sec. 2, [13], Sec. 2) represents the microforce balance

$$(1.12) \qquad \beta(\chi, \nabla\chi, \dot{\chi})\dot{\chi} + f_{,\chi}(\chi, \nabla\chi) - \nabla \cdot f_{,\nabla\chi}(\chi, \nabla\chi) = \tau.$$

Here χ is a scalar, nonconserved order parameter describing ordering process in alloys, $f = \hat{f}(\chi, \nabla\chi)$ is the free energy density, and $\beta = \hat{\beta}(\chi, \nabla\chi, \dot{\chi}) \geq 0$ is a kinetic coefficient (damping modulus). For the free energy (1.3) equation (1.12) becomes

$$(1.13) \qquad \beta(\chi, \nabla\chi, \dot{\chi})\dot{\chi} - \nabla \cdot (\boldsymbol{\Gamma}(\chi)\nabla\chi) + \frac{1}{2}\nabla\chi \cdot \boldsymbol{\Gamma}'(\chi)\nabla\chi + \psi'(\chi) = \tau.$$

It constitutes a broad generalization of the classical Allen-Cahn equation

$$(1.14) \qquad \beta\dot\chi - \gamma\Delta\chi + \psi'(\chi) = 0$$

which results from (1.13) setting $\beta = \text{const} > 0$, $\boldsymbol{\Gamma} = \gamma\boldsymbol{I}$, $\gamma = \text{const} > 0$ and $\tau = 0$.
The Allen-Cahn-Fried-Gurtin model with elasticity (under assumption of infinitesimal deformations) based on the free energy (1.7), (1.8) (see [9]) has the form of the microforce balance
$$(1.15)$$
$$\beta(\boldsymbol{\varepsilon}(\boldsymbol{u}),\chi,\nabla\chi,\dot\chi)\dot\chi - \nabla\cdot(\boldsymbol{\Gamma}(\chi)\nabla\chi) + \frac{1}{2}\nabla\chi\cdot\boldsymbol{\Gamma}'(\chi)\nabla\chi + \psi'(\chi) + W_{,\chi}(\boldsymbol{\varepsilon}(\boldsymbol{u}),\chi) = \tau$$

coupled with the linear momentum balance (1.10). Here the kinetic coefficient $\beta = \hat\beta(\boldsymbol{\varepsilon}(\boldsymbol{u}),$ $\chi,\nabla\chi,\dot\chi) \geq 0$ and $W_{,\chi}(\boldsymbol{\varepsilon}(\boldsymbol{u}),\chi)$, $W_{,\boldsymbol{\varepsilon}}(\boldsymbol{\varepsilon}(\boldsymbol{u}),\chi)$ are given by (1.11).

1.3. The multipliers-based approach

We derive the presented above models by employing the Müller-Liu multipliers-based approach. The application of this approach to phase transition problems requires a special procedure which has been suggested in [1], [2] and utilized in [23], [24], [25]. This procedure consists of three main steps.

In the first step we consider the system of balance laws with a set of constitutive variables relevant for the phase transition under consideration. Distinctive elements in this set are variables representing higher gradients of the order parameter and its time derivative. The presence of such variables is characteristic for theories involving free energies of Landau-Ginzburg type. In accordance with the principle of equipresence we assume that all quantities in balance laws are constitutive functions defined on this set of variables.

In the second step we postulate the free energy inequality with multipliers conjugated with the balance laws. Again, we assume that all quantities in this inequality, including multipliers, depend on the same constitutive set. Next, making no assumptions on the multipliers, we exploit the free energy inequality by using appropriately arranged algebraic operations. As a result we conclude a collection of algebraic restrictions on the constitutive equations.

In the third step we presuppose that the multiplier associated with the equation for the order parameter is an additional independent variable. Then, regarding algebraic restrictions obtained in the previous step, we deduce an extended system of equations including in addition to balance laws a differential equation for the multiplier. Moreover, we require this system to be consistent with the principle of frame indifference. The obtained system turns out to be identical with that resulting from the Fried-Gurtin theory based on the microforce balance. The most interesting conclusion from the comparison with their theory is that our differential equation for the multiplier is identical with their microforce balance. In view of that, at the concept level, our postulate of treating the multiplier as an additional independent variable corresponds to their postulate of an additional balance law for the microforce.

1.4. Plan of the paper

In Section 2 we introduce basic physical quantities, the balance laws, the constitutive equations, the entropy and the free energy inequality. The presented formulations allow for future extension of the theory by thermal effects.

In Section 3 we evaluate the free energy inequality restricting ourselves to the isothermal situation. The main results are stated in Theorems 3.1 and 3.2.

In Section 4 we introduce an extended model with the multiplier as an additional independent variable. The model combines various types of dynamics of the order parameter, in particular the conserved and the nonconserved one. The thermodynamical consistency of this model is examined in Theorem 4.1.

In Section 5 we consider the extended model in case of a conserved order parameter. It leads to the generalized Cahn-Hilliard system coupled with elasticity. We compare our results with the Gurtin theory.

In Section 6 we consider the extended model in case of a nonconserved order parameter. Then we conclude the generalized Allen-Cahn system coupled with elasticity. We compare results with the Fried-Gurtin theory.

1.5. Notation

We generally follow the notation in [14]. Vectors (tensor of the first order), tensors of the second order (referred simply to as tensors) and tensors of higher order are denoted by bold letters. Tensors of the second order are linear transformations of vectors into vectors. The unit tensor I is defined by $Iu = u$ for every vector u;
S^T, trS, S^{-1} and $\det S$, respectively, denote the transpose, trace, inverse, and determinant of a tensor S.
A dot designates the inner product, irrespective of the space in question: $u \cdot v$ is the inner product of vectors $u = (u_i)$ and $v = (v_i)$, $S \cdot R = tr(S^T R)$ is the inner product of tensors $S = (S_{ij})$ and $R = (R_{ij})$, $A^m \cdot B^m$ is the inner product of the m-th order tensors $A^m = (A^m_{i_1 \ldots i_m})$ and $B^m = (B^m_{i_1 \ldots i_m})$.
In Cartesian components,

$$(Su)_i = S_{ij}u_j, \quad (S^T)_{ij} = S_{ji}, \quad trS = S_{ii}, \quad u \cdot v = u_i v_i,$$
$$S \cdot R = S_{ij}R_{ij}, \quad A^m \cdot B^m = A^m_{i_1 \ldots i_m} B^m_{i_1 \ldots i_m}.$$

Here and throughout the summation convention over repeated indices is used.
The transpose of a tensor is defined by the requirement that

$$u \cdot Sv = (S^T u) \cdot v \text{ for all vectors } u \text{ and } v.$$

By $\mathbb{A} = (A_{ijkl})$ we denote the fourth order elasticity tensor which represents a symmetric linear transformation of symmetric tensors into symmetric tensors. We write $(\mathbb{A}\varepsilon)_{ij} = A_{ijkl}\varepsilon_{kl}$.
The term field signifies a function of a material point $x \in \mathbb{R}^3$ and time t. The superimposed dot $\dot{f}$ denotes the material time derivative of the field f (with respect to t holding x fixed),

∇ and $\nabla\cdot$ denote the material gradient and the divergence (with respect to $\boldsymbol{x}$ holding t fixed). For the divergence we use the convention of the contraction over the last index, e.g. $(\nabla \cdot S)_i = \partial S_{ij}/\partial x_j$.

We write $f_{,A} = \partial f/\partial A$ for the partial derivative of a function f with respect to the variable A (scalar or tensor). Specifically, for f scalar valued and $A^m = (A^m_{i_1...i_m})$ a tensor of order m, $f_{,A^m}$ is a tensor of order m with components $f_{,A^m_{i_1...i_m}}$.

Finally, for a function $f = f(\chi, \nabla\chi)$ we denote by $\delta f/\delta\chi$ its first variation with respect to χ:

$$\frac{\delta f}{\delta\chi} = f_{,\chi}(\chi, \nabla\chi) - \nabla \cdot f_{,\nabla\chi}(\chi, \nabla\chi).$$

2. Basic quantities. Balance laws and constitutive equations. Entropy and free energy inequalities

2.1. Basic quantities

Let $\Omega \subset \mathbb{R}^3$ be a bounded domain with a smooth boundary S, occupied by a solid body in a fixed reference configuration. Let $\boldsymbol{x} \in \Omega$ be the material point. The motion (deformation) of the body is denoted by $\boldsymbol{y}(\boldsymbol{x},t) = \boldsymbol{x} + \boldsymbol{u}(\boldsymbol{x},t)$, where $\boldsymbol{u}$ is the displacement. Further, let

$$F = \nabla\boldsymbol{y} = I + \nabla\boldsymbol{u},$$

subject to $\det F > 0$, be the deformation gradient, and $C = F^T F$, in components $C_{ij} = (\partial y_m/\partial x_i)(\partial y_m/\partial x_j)$, be the right Cauchy-Green strain tensor corresonding to F.

We study solid-solid transitions in a two-phase deformable body. We use an order parameter to characterize the notion of a phase and identify phase interfaces with thin transition zones within which the strain and the order parameter exhibit large gradients. To this end we consider the following fields in material representation:

ρ — mass density, assumed constant normalized to unity, $\rho \equiv 1$;
$S = (S_{ij})$ — first Piola-Kirchhoff stress tensor; $\boldsymbol{b} = (b_i)$ — external body force; χ — scalar order parameter; $\boldsymbol{j} = (j_i)$ — order parameter flux; r — order parameter production (scalar); τ — external source of the order parameter; e — internal energy; $\boldsymbol{q} = (q_i)$ — energy flux; g — external heat source; $\theta > 0$ — absolute temperature; η — entropy; $f = e - \theta\eta$ — Helmholtz free energy.

2.2. Balance laws and constitutive equations

Letting $\rho = 1$, the balance laws for the linear momentum, the angular momentum, the order parameter and the internal energy read as follows (see e.g. [26]):

(2.1)
$$\ddot{\boldsymbol{u}} - \nabla \cdot S = \boldsymbol{b},$$
$$SF^T = FS^T,$$
$$\dot{\chi} + \nabla \cdot \boldsymbol{j} - r = \tau,$$
$$\dot{e} + \nabla \cdot \boldsymbol{q} - S \cdot \dot{F} = g.$$

System (2.1) is closed by constitutive equations for the quantities S, j, r, e and q. To model phase transitions we consider the set of the following variables

$$(2.2) \qquad Y_\theta := \{F, \chi, D\chi, \dots, D^M \chi, \theta, \chi_{,t}\}, \quad M \in \mathbb{N}, \quad M \geq 2,$$

where $\chi_{,t}$ denotes a variable corresponding to the time derivative $\dot{\chi}$, and

$$D^m \chi = (\chi_{,i_1 \dots i_m})_{i_1, \dots, i_m = 1,2,3}, \quad 0 \leq m \leq M$$

is the m-th order tensor of variables corresponding to the m-th order gradient

$$\nabla^m \chi = \left(\frac{\partial^m \chi}{\partial \chi_{i_1} \dots \partial \chi_{i_m}} \right)_{i_1, \dots, i_m = 1,2,3}.$$

We use the convention $D^0 \chi = \chi$. In (2.2) the variable F represents mechanical properties, θ — thermal properties, χ and its higher gradients — chemical properties due to material heterogeneity, and $\chi_{,t}$ — viscous effects due to heterogeneity. For later purposes we split the set

$$(2.3) \qquad Y_\theta = \{Y_\theta^0, Y^1\}$$

into two subsets

$$(2.4) \qquad Y_\theta^0 := \{F, \chi, D\chi, \dots, D^M \chi, \theta\} \quad \text{and} \quad Y^1 := \{\chi_{,t}\}$$

which distinguish between the stationary variables and the nonstationary one vanishing at equilibrium. We assume the constitutive equations

$$(2.5) \qquad S = \hat{S}(Y_\theta), \quad j = \hat{j}(Y_\theta), \quad r = \hat{r}(Y_\theta), \quad e = \hat{e}(Y_\theta), \quad q = \hat{q}(Y_\theta)$$

with smooth functions $\hat{S}, \hat{j}, \hat{r}, \hat{e}, \hat{q}$. As common we do not assume the constitutive equations for the external sources b, τ and g. Because of the presence of tensors of order higher than one we supplement (2.5) by the following convention: Any constitutive function defined on the set Y_θ, say $\hat{j}(Y_\theta)$, is understood in the sense of the following extension

$$\hat{j}(F, \chi, D\chi, \dots, B^m + (B^m)^{skew}, \dots, \theta, \chi_{,t}) = \hat{j}(F, \chi, D\chi, \dots, B^m, \dots, \theta, \chi_{,t})$$

where B^m with $2 \leq m \leq M$ stands for the m-th order tensor corresponding to $D^m \chi$, and $(B^m)^{skew}$ denotes the skew part of B^m.

Such extension is used for all other constitutive functions. Consequently, for instance in case $D^2 \chi$, we can treat the variables $\chi_{,ij}$ and $\chi_{,ji}$ as independent despite of equality $\partial^2 \chi / \partial x_i \partial x_j = \partial^2 \chi / \partial x_j \partial x_i$. This fact is used in applying the chain rule in Theorem 3.1.

We point out that equation $(2.1)_3$ combines various types of dynamics of the order parameter:
— mixed conserved-nonconserved (mass balance with production term) $j \neq 0$ and $r \neq 0$;
— conserved (mass balance without production) $j \neq 0$ and $r \equiv 0$;
— nonconserved (evolution law for the order parameter) $j \equiv 0$ and $r \neq 0$.

Remark 2.1. In [23] it has been shown that in order to admit the free energy depending on $D^k\chi$, $k \in \mathbb{N}$, the set of constitutive variables has to include $D^{k-1}\chi_{,t}$. Since our goal here is to construct models with the free energy depending at most on $D\chi$ we have to admit $\chi_{,t}$ as the constitutive variable. $\square$

Remark 2.2. By virtue of the duality relation (see e.g. [2], [25]) thermal properties can be alternatively represented by the internal energy e or the entropy η. Then the set Y_θ is correspondingly replaced by the sets Y_e of Y_η which are defined by (2.2) with e or η in place of θ. $\square$

Remark 2.3. From the point of view of the axiom of frame indifference the appropriate measure of the strain is for instance the right Cauchy-Green strain tensor C (see e.g. [12]). However, as underlined in [13] the exploitation of the second principle is simpler using deformation gradient F as the constitutive variable. The restrictions imposed by the frame indifference are accounted for after deriving consequences from the second principle. $\square$

2.3. The Müller entropy principle

To derive restrictions on the constitutive functions (2.5) imposed by the second law we apply the entropy principle due to Müller [21], [22]. This principle states that there exists an entropy η and an entropy flux Ψ given by constitutive equations

$$(2.6) \qquad \eta = \hat{\eta}(Y_\theta), \quad \Psi = \hat{\Psi}(Y_\theta)$$

with smooth functions $\hat{\eta}$, $\hat{\Psi}$, such that for all solutions of the system of balance laws (2.1) with constitutive equations (2.5) (called thermodynamic processes) defined in a space-time domain $\Omega^{t_0} = \Omega \times (0, t_0)$ the following implication holds

$$(2.7) \qquad b = 0, \quad \tau = 0, \quad g = 0 \text{ in } \Omega^{t_0} \Rightarrow \sigma := \dot{\eta} + \nabla \cdot \Psi \geq 0 \text{ in } \Omega^{t_0}.$$

Remark 2.4. We recall two stronger versions of the Müller principle introduced in [2]. They can be useful whenever the existence of Liu multipliers is proved rigorously. In a slightly stronger version (2.7) is replaced by the following postulate: For all thermodynamic processes and all points $(x, t) \in \Omega^{t_0}$ it holds

$$(2.7') \qquad b(x, t) = 0, \quad \tau(x, t) = 0, \quad g(x, t) = 0 \Rightarrow \sigma(x, t) \geq 0.$$

An even stronger version asserts that there exists a scalar field σ_0 with a constitutive equation $\sigma_0 = \hat{\sigma}_0(Y_\theta, b, \tau, g)$, such that for all thermodynamic processes defined in Ω^{t_0} the following two conditions are satisfied

$$(2.7'') \qquad \sigma \geq \sigma_0 \text{ in } \Omega^{t_0} \text{ and } \hat{\sigma}_0(Y_\theta, 0, 0, 0) = 0$$

for all variables Y_θ. This version of the entropy principle describes the way it is used by Coleman and Noll [4] where, however, in contrast to the entropy principle formulated above it is assumed that Ψ and σ_0 are given by explicit formulas. $\square$

2.4. The Müller-Liu entropy inequality

The main step in the exploitation of the entropy principle is based on introducing the Lagrange multipliers with the purpose to replace the inequality in (2.7), which holds for all thermodynamic processes, by an inequality (called entropy inequality) which is satisfied for arbitrary fields. This idea is due to I. S. Liu [18].

For system (2.1) the entropy inequality reads as follows: There are multipliers

$$(2.8) \qquad \boldsymbol{\lambda_u} = \hat{\boldsymbol{\lambda}}_u(Y_\theta), \quad \lambda_\chi = \hat{\lambda}_\chi(Y_\theta), \quad \lambda_e = \hat{\lambda}_e(Y_\theta)$$

conjugated respectively with balances $(2.1)_1$, $(2.1)_3$ and $(2.1)_4$, such that the inequality

$$(2.9) \qquad \dot{\eta} + \nabla \cdot \boldsymbol{\Psi} - \boldsymbol{\lambda_u} \cdot (\ddot{\boldsymbol{u}} - \nabla \cdot \boldsymbol{S}) - \lambda_\chi(\dot{\chi} + \nabla \cdot \boldsymbol{j} - r) - \lambda_e(\dot{e} + \nabla \cdot \boldsymbol{q} - \boldsymbol{S} \cdot \dot{\boldsymbol{F}}) \geq 0$$

is satisfied for all fields $\boldsymbol{u}, \chi$ and θ.

Remark 2.5. Entropy inequality (2.9) implies the entropy principle with the strongest property (2.7″), that is for solutions of (2.1) it holds

$$(2.10) \qquad \sigma = \dot{\eta} + \nabla \cdot \boldsymbol{\Psi} \geq \hat{\boldsymbol{\lambda}}_u(Y_\theta) \cdot \boldsymbol{b} + \hat{\lambda}_\chi(Y_\theta)\tau + \hat{\lambda}_e(Y_\theta)g =: \hat{\sigma}_0(Y_\theta, \boldsymbol{b}, \tau, g).$$

Hence, entropy inequality (2.9) implies all three versions of the entropy principle. □

Remark 2.6. In a rigorous approach it has to be proved that entropy principle (2.7) implies entropy inequality (2.9). The proof requires a characterization of admissible sets of the system of partial differential equations under consideration and the verification of the Liu lemma [18]. For particular systems this question has been addressed in [18], [2] by means of the Cauchy-Kowalevsky theorem. Another approach to this question is to admit arbitrary sources in balance equations and postulate stronger version (2.7′) of the entropy principle (see [2], Sec. 4). □

As common in the literature (see e.g. [16], [27]) in the present paper we do not prove the entropy inequality (2.9) but take its validity for granted.

2.5. The free energy inequality

Assuming that the energy multiplier $\hat{\lambda}_e(Y_\theta) \neq 0$ for all Y_θ, inequality (2.9) can be rearranged to the following form

$$(2.11) \qquad \begin{aligned} &\left(e - \frac{\eta}{\lambda_e}\right)^{\cdot} + \nabla \cdot \left(\boldsymbol{q} - \frac{\boldsymbol{\Psi}}{\lambda_e}\right) - \boldsymbol{S} \cdot \dot{\boldsymbol{F}} + \frac{\boldsymbol{\lambda_u}}{\lambda_e} \cdot (\ddot{\boldsymbol{u}} - \nabla \cdot \boldsymbol{S}) \\ &+ \frac{\lambda_\chi}{\lambda_e}(\dot{\chi} + \nabla \cdot \boldsymbol{j} - r) + \eta \left(\frac{1}{\lambda_e}\right)^{\cdot} + \boldsymbol{\Psi} \cdot \nabla\left(\frac{1}{\lambda_e}\right) \leq 0 \end{aligned}$$

for all fields $\boldsymbol{u}, \chi, \theta$. Further, if we assume that the multiplier λ_e can be identified with the inverse of the absolute temperature, that is $\lambda_e = 1/\theta$, then by introducing the free energy

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in accordance with the Gibbs relation $f = e - \theta\eta$, inequality (2.11) takes the form of the so-called free energy (dissipation) inequality
(2.12)
$$\dot{f} + \nabla \cdot (q - \theta\Psi) - S \cdot \dot{F} + \theta\lambda_u \cdot (\ddot{u} - \nabla \cdot S) + \theta\lambda_\chi(\dot{\chi} + \nabla \cdot j - r) + \eta\dot{\theta} + \Psi \cdot \nabla\theta \le 0$$

for all fields u, χ, θ.

2.6. The free energy inequality in isothermal case

Assuming that system of balance laws (2.1) is satisfied at a given constant temperature $\theta = \bar{\theta} > 0$, we can reduce set of constitutive variables (2.3) to

$$(2.13) \qquad\qquad Y := Y_\theta|_{\theta=\bar{\theta}} = \{Y^0, Y^1\},$$

where
$$Y^0 := Y_\theta^0|_{\theta=\bar{\theta}} = \{F, \chi, D\chi, \dots, D^M\chi\}, \quad M \ge 2, \quad Y^1 := \{\chi_{,t}\}.$$

Since in such a case the relevant balance laws are $(2.1)_{1,2,3}$ (with $(2.1)_4$ satisfied identically) the constitutive equations (2.5) reduce to

$$(2.14) \qquad\qquad S = \hat{S}(Y), \quad j = \hat{j}(Y), \quad r = \hat{r}(Y).$$

Correspondingly, free energy inequality (2.12) reduces to

$$(2.15) \qquad \dot{f} + \nabla \cdot \Phi - S \cdot \dot{F} + \bar{\lambda}_u \cdot (\ddot{u} - \nabla \cdot S) + \lambda(\dot{\chi} + \nabla \cdot j - r) \le 0$$

for all fields u, χ, where $f = e - \bar{\theta}\eta$ is the free energy at $\theta = \bar{\theta}$, $\Phi = q - \bar{\theta}\Psi$ is the free energy flux at $\theta = \bar{\theta}$, and $\bar{\lambda}_u = \bar{\theta}\lambda_u$, $\lambda = \bar{\theta}\lambda_\chi$ are multipliers at $\theta = \bar{\theta}$. These quantities are given by constitutive equations

$$(2.16) \qquad f = \hat{f}(Y), \quad \Phi = \hat{\Phi}(Y), \quad \bar{\lambda}_u = \hat{\bar{\lambda}}_u(Y), \quad \lambda = \hat{\lambda}(Y).$$

3. Evaluation of the free energy inequality in isothermal case

3.1. Algebraic preliminaries

We prepare some simplifying notations. For $f = \hat{f}(Y)$ a smooth scalar function of its arguments and the set Y given by (2.13), we dentoe by $\partial_i^{Y^0} f$, $i = 1, 2, 3$, the algebraic version of the spatial derivative $\partial f/\partial x_i$ restricted to the set of variables Y^0 (applying differentiation by the chain rule):

$$\partial_i^{Y^0} f := f_{,F} \cdot F_{,i} + f_{,D^m\chi} \cdot D^m\chi_{,i},$$

and by $\nabla^{Y^0} f = (\partial_i^{Y^0} f)_{i=1,2,3}$ the corresponding algebraic version of the gradient ∇f restricted to the set Y^0. Similarly, for a smooth vector-valued function $\Phi = \hat{\Phi}(Y)$ with

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values in $\mathbb{R}^3$ we denote by $\nabla^{Y^0} \cdot \boldsymbol{\Phi}$ the algebraic version of the divergence $\nabla \cdot \boldsymbol{\Phi}$ restricted to the set Y^0:

$$\nabla^{Y^0} \cdot \boldsymbol{\Phi} := \Phi_{i,\boldsymbol{F}} \cdot F_{,i} + \Phi_{i,\boldsymbol{D}^m\chi} \cdot \boldsymbol{D}^m\chi_{,i}.$$

Throughout we use the summation convention with the indices $i,j = 1,2,3$ and $m = 0,1,\ldots,M$.

Moreover, we introduce the following subset of Y^0:

$$(3.1) \qquad \tilde{Y}^0 := \{\chi, \boldsymbol{D}\chi, \ldots, \boldsymbol{D}^{M-1}\chi\} = Y^0 \setminus \{\boldsymbol{F}, \boldsymbol{D}^M\chi\}.$$

For a function $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi)$ we denote by $\delta^{\tilde{Y}^0} f/\delta\chi$ the algebraic version of the first variation $\delta f/\delta\chi$ restricted to the subset $\tilde{Y}^0$:

$$(3.2) \qquad \frac{\delta^{\tilde{Y}^0} f}{\delta\chi} := f_{,\chi} - \nabla^{\tilde{Y}^0} \cdot f_{,\boldsymbol{D}\chi} = f_{,\chi} - f_{,\chi,i\chi}\chi_{,i} - f_{,\chi,i\chi,j}\chi_{,ji}.$$

3.2. The restrictions

Assuming constant temperature $\theta = \bar{\theta} > 0$ we consider system of balance laws $(2.1)_{1,2,3}$ with constitutive equations (2.14). To derive restrictions on these equations we postulate free energy inequality (2.15) complemented by equations (2.16). In addition we impose the following structural assumption

$$(A) \qquad \boldsymbol{\Phi}^0 = -\lambda^0 \boldsymbol{j}^0$$

where $\boldsymbol{\Phi}^0$, $\boldsymbol{j}^0$ and λ^0 denote stationary quantities defined by setting $\chi_{,t} = 0$ in the arguments Y, that is $\boldsymbol{\Phi}^0 := \hat{\boldsymbol{\Phi}}(Y^0, Y^1)|_{Y^1=\{0\}}$ and similarly for $\boldsymbol{j}^0, \lambda^0$.

We underline that assumption (A) represents the classical form of the relation between fluxes $\boldsymbol{\Phi}$ and $\boldsymbol{j}$ (see e.g. [22]). We prove the following

Theorem 3.1. *(Consistency with the free energy inequality)*
Let us consider balance laws $(2.1)_{1,2,3}$ with constitutive equations (2.14) ad $\theta = \bar{\theta} = \text{const}$.
Suppose that free energy inequality (2.15) with (2.16) is satisfied and assumption (A) holds true. Then the following relations are satisfied:
(i) multiplier of the linear momentum $\bar{\lambda}_{\boldsymbol{u}} = 0$;
(ii) free energy $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi)$;
(iii) stress tensor $S = \hat{S}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi) = \hat{f}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi)$;
(iv) free energy flux

$$\boldsymbol{\Phi} = -\lambda\boldsymbol{j} - \chi_{,t}[f_{,\boldsymbol{D}\chi} - \int_0^1 (\lambda_{,\chi,t}\boldsymbol{j})(Y^0, \tau\chi_{,t})d\tau];$$

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(v) compatibility conditions

(3.3)
$$\left[-f_{,\chi,i} + \int_0^1 (\lambda_{,\chi,t} j_i)(Y^0, \tau\chi_{,t}) d\tau\right]_{,F_{kl}} \chi_{,t} - j_i\lambda_{,F_{kl}} = 0,$$

$$\left[\int_0^1 (\lambda_{,\chi,t} j_i)(Y^0, \tau\chi_{,t}) d\tau\right]_{,\chi,i_1\ldots i_M} \chi_{,t} - j_i\lambda_{,\chi,i_1\ldots i_M} = 0$$

for all indices $i, k, l, i_1, \ldots, i_M$ with values equal $1, 2, 3$.
Moreover, there exists a scalar quantity $\tilde{a} = \hat{\tilde{a}}(Y)$ such that
(vi) multiplier $\lambda = \hat{\lambda}(Y)$ satisfies equation

(3.4)
$$-\lambda = \frac{\delta^{\tilde{Y}^0} f}{\delta\chi} + \nabla^{\tilde{Y}^0} \cdot \int_0^1 (\lambda_{,\chi,t} j)(Y^0, \tau\chi_{,t}) d\tau - \tilde{a}$$

with $\tilde{Y}^0$ and $\delta^{\tilde{Y}^0} f/\delta\chi$ defined by (3.1), (3.2);
(vii) the quantities $j = \hat{j}(Y)$, $r = \hat{r}(Y)$ and $\tilde{a} = \hat{\tilde{a}}(Y)$ satisfy the residual inequality

(3.5)
$$\nabla^{\tilde{Y}^0} \lambda \cdot j + \lambda r - \chi_{,t}\tilde{a} \geq 0 \quad \text{for all variables } Y.$$

Remark 3.1. In view of assertion (ii), $\delta^{\tilde{Y}^0} f/\delta\chi$ depends on the variables $\{F, \chi, D\chi, D^2\chi\}$. For that reason parameter M in the set Y has been assumed to satisfy condition $M \geq 2$. $\square$

Remark 3.2. Equation (3.4) resembles the expression for the chemical potential in the classical Cahn-Hilliard theory which is given as the first variation of the free energy with respect to the order parameter (compare (1.1)$_2$). In view of that we shall identify the negative of the multiplier, denoted by $w := -\lambda$, with the chemical potential. $\square$

Proof of Theorem 3.1. By inserting constitutive equations (2.14), (2.16) into free energy inequality (2.15) and applying the chain rule we arrive at the following algebraic inequality

(3.6)
$$f_{,\chi,t}\chi_{,tt} + f_{,F} \cdot F_{,t} + f_{,D^m\chi} \cdot D^m\chi_{,t} + \Phi_{,\chi,t} \cdot D\chi_{,t} + \nabla^{Y^0} \cdot \Phi - S \cdot F_{,t} + \bar{\lambda}_u \cdot u_{,tt}$$
$$- \bar{\lambda}_u \cdot (S_{,\chi,t} D\chi_{,t}) - \bar{\lambda}_u \cdot (\nabla^{Y^0} \cdot S) + \lambda\chi_{,t} + \lambda j_{,\chi,t} \cdot D\chi_{,t} + \lambda\nabla^{Y^0} \cdot j - \lambda r \leq 0$$

for all variables $\{W, Y\}$. Here

$$W := \{u_{,tt}, \chi_{,tt}, (D^m\chi_{,t})_{1 \leq m \leq M}, F_{,t}, DF, D^{M+1}\chi\}$$

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denotes the set of variables (called higher derivatives) in which the left-hand side of (3.6) is linear. The evaluation of (3.6) consists in deriving consequences from the linearity in the variables belonging to W. The linearity permits to conclude that the coefficients preceding these variables have to vanish identically. We proceed stepwise in the following order:

Step 1. By the linearity of the left-hand side of (3.6) in $u_{,tt}$ it follows that the corresponding coefficient has to vanish, that is $\bar{\lambda}_u = 0$. This shows (i).

Step 2. By the linearity in the variables $\chi_{,tt}$, $(D^m\chi_{,t})_{2\leq m\leq M}$, we read off that $f_{,\chi,t} = 0$, $f_{,D^m\chi} = 0$ for $2 \leq m \leq M$, so $f = \hat{f}(F, \chi, D\chi)$ which shows (ii).

Step 3. The linearity in $F_{,t}$ implies immediately (iii).

Step 4. From the linearity in $D\chi_{,t}$ we deduce that

$$(3.7) \qquad f_{,D\chi} + \Phi_{,\chi,t} + \lambda j_{,\chi,t} = 0.$$

We define now the vector $\tilde{\Phi}$ by

$$(3.8) \qquad \tilde{\Phi} := \Phi + \lambda j.$$

Clearly, by virtue of assumption (A),

$$(3.9) \qquad \tilde{\Phi}^0 = 0.$$

In view of (3.8) and (3.7),

$$(3.10) \qquad \tilde{\Phi}_{,\chi,t} = \Phi_{,\chi,t} + \lambda_{,\chi,t} j + \lambda j_{,\chi,t} = -f_{,D\chi} + \lambda_{,\chi,t} j.$$

Hence, recalling assertion (ii) and (3.9) we get

$$(3.11) \qquad \tilde{\Phi} = -f_{,D\chi}\chi_{,t} + \int_0^{\chi,t} (\lambda_{,\chi,t} j)(Y^0, \xi) d\xi = -\chi_{,t}\left[f_{,D\chi} - \int_0^1 (\lambda_{,\chi,t} j)(Y^0, \tau\chi_{,t}) d\tau\right].$$

From (3.8) and (3.11) we conclude (iv).

Step 5. It remains to consider the linearity in the variables DF and $D^{M+1}\chi$. In view of the previous results inequality (3.6) reduces to

$$(3.12) \qquad (f_{,\chi} + \lambda)\chi_{,t} + \nabla^{Y^0} \cdot \Phi + \lambda \nabla^{Y^0} \cdot j - \lambda r \leq 0$$

for all variables $\{Y, DF, D^{M+1}\chi\}$. We rearrange now the sum of the second and the third term on the left-hand side of (3.12) to the form

$$(3.13) \qquad \nabla^{Y^0} \cdot \Phi + \lambda \nabla^{Y^0} \cdot j = \nabla^{Y^0} \cdot \Phi + \nabla^{Y^0} \cdot (\lambda j) - \nabla^{Y^0}\lambda \cdot j = \nabla^{Y^0} \cdot \tilde{\Phi} - \nabla^{Y^0}\lambda \cdot j.$$

Next, in view of (3.11), using the definition of the restricted divergence $\nabla^{Y^0}\cdot$, we see that

$$(3.14) \qquad \nabla^{Y^0} \cdot \tilde{\Phi} = -\chi_{,t}\nabla^{Y^0} \cdot \left[f_{,D\chi} - \int_0^1 (\lambda_{,\chi,t} j)(Y^0, \tau\chi_{,t}) d\tau\right].$$

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Combining (3.13) and (3.14) inequality (3.12) becomes

$$(3.15) \quad \left(\lambda + f_{,\chi} + \nabla^{Y^0} \cdot \left[- f_{,D\chi} + \int\limits_0^1 (\lambda_{,\chi,t} j)(Y^0, \tau\chi_{,t}) d\tau \right]\right)\chi_{,t} - \nabla^{Y^0}\lambda \cdot j - \lambda r \le 0$$

for all variables $\{Y, DF, D^{M+1}\chi\}$. From (3.15), performing differentiation by the chain rule in terms involving $\nabla^{Y^0}\cdot$ and ∇^{Y^0} (restricting now to the subset $\tilde{Y}^0$) the linearity in the variables $F_{kl,i}$ and $\chi_{,i_1...i_M i}$ implies that the coefficients preceding these variables have to vanish for all indices $i, k, l, i_1, \ldots, i_M = 1, 2, 3$. This yields assertion (v).

Step 6. We proceed to derive conclusions from the inequality (3.15) which remains after taking into account (v). It reads

$$(3.16) \quad \left[\lambda + f_{,\chi} - \nabla^{\tilde{Y}^0} \cdot f_{,D\chi} + \nabla^{\tilde{Y}^0} \cdot \int\limits_0^1 (\lambda_{,\chi,t} j)(Y^0, \tau\chi_{,t}) d\tau \right]\chi_{,t} - \nabla^{\tilde{Y}^0}\lambda \cdot j - \lambda r \le 0$$

for all variables Y. Now let us define a scalar quantity $\tilde{a} = \hat{\tilde{a}}(Y)$ given by the squared parenthesis in (3.16):

$$(3.17) \qquad \tilde{a} := \lambda + f_{,\chi} - \nabla^{\tilde{Y}^0} \cdot f_{,D\chi} + \nabla^{\tilde{Y}^0} \cdot \int\limits_0^1 (\lambda_{,\chi,t} j)(Y^0, \tau\chi_{,t}) d\tau.$$

In view of (3.2) equality (3.17) yields assertion (vi). Finally, owing to (3.17), inequality (3.16) takes the form of the residual inequality (3.5). This shows assertion (vii) and thereby completes the proof. □

3.3. The restrictions in the nonconserved case

The statement of Theorem 3.1 simplifies greatly in case of the nonconserved dynamics of the order parameter. Then assumption (A) reads

$$(A)^{NC} \qquad\qquad\qquad\qquad \Phi = 0,$$

and we have

Theorem 3.2. *(Consistency with the free energy inequality in the nonconserved case)* Let us consider balance laws $(2.1)_{1,2,3}$ with constitutive equations (2.14) in the nonconserved case $j \equiv 0$, $r \ne 0$, at $\theta = \bar{\theta} = \text{const.}$ Suppose that the free energy inequality (2.15) with (2.16) is satisfied and assumption $(A)^{NC}$ holds true. Then the following relations are satisfied:
(i) $\bar{\lambda}_u = 0$;
(ii) $f = \hat{f}(F, \chi, D\chi)$;
(iii) $S = \hat{S}(F, \chi, D\chi) = f_{,F}(F, \chi, D\chi)$;

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(iv) $\Phi = -\chi_{,t}f_{,D\chi}$;

(v) $f_{,D\chi F} = 0$.

Moreover, there exists a scalar $\tilde{a} = \hat{\tilde{a}}(Y)$ such that

(iv) $-\lambda = \frac{\delta^{\varphi 0}}{\delta\chi}f - \tilde{a}$;

(vii) $\lambda r - \chi_{,t}\tilde{a} \geq 0$ for all variables Y.

4. Model with the multiplier as an additional independent variable

4.1. Model (M)

Regarding Theorem 3.1 we introduce an extended model in which the multipier λ is in addition to u and χ treated as an independent variable. We underline that such idea is admissible because theorem has been proved under no assumptions on λ. Recalling Remark 3.2 we identify the negative of the multiplier with the chemical potential

$$(4.1) \qquad\qquad w = -\lambda.$$

Assuming that w is a new independent variable we replace the set of variables Y by

$$(4.2) \qquad\qquad \mathcal{Z} := \{F, \chi, D\chi, D^2\chi, \chi_{,t}, w, Dw\}.$$

Here we do not consider space drivatives of order higher than 2.

The model with the multiplier, referred to as (M), is based on the following postulates:

(M1) The unknowns are the fields u, χ and w.

(M2) The free energy is given by

$$(4.3) \qquad\qquad f = \hat{f}(F, \chi, D\chi)$$

subject to the condition

$$(4.4) \qquad\qquad f_{,D\chi F} = 0.$$

(M3) The fields satisfy differential equations

$$(4.5) \qquad \begin{aligned} &\ddot{u} - \nabla \cdot S = b, \\ &\dot{\chi} + \nabla \cdot j - r = \tau, \\ &w - f_{,\chi} + \nabla \cdot f_{,\nabla\chi} + a = 0, \end{aligned}$$

where the stress tensor is given by

$$(4.6) \qquad\qquad S = \hat{S}(F, \chi, D\chi) = f_{,F}(F, \chi, D\chi),$$

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consistent with the condition

$$(4.7) \qquad\qquad SF^T = FS^T.$$

Moreover, the quantities $j = \hat{j}(\mathcal{Z})$, $r = \hat{r}(\mathcal{Z})$, $a = \hat{a}(\mathcal{Z})$ are subject to the dissipation inequality

$$(4.8) \qquad \mathcal{D} := -(Dw \cdot j + wr + \chi_{,t}a) \geq 0 \quad \text{for all variables } \mathcal{Z}.$$

(M4) In addition, in accordance with the principle of frame indifference, the constitutive equations

$$f = \hat{f}(F, \chi, D\chi), \quad S = \hat{S}(F, \chi, D\chi),$$
$$\xi = \hat{\xi}(F, \chi, D\chi) := f_{,D\chi}(F, \chi, D\chi),$$
$$j = \hat{j}(\mathcal{Z}), \quad r = \hat{r}(\mathcal{Z}), \quad a = \hat{a}(\mathcal{Z})$$

are assumed to be invariant under changes in observer, i.e. under transformations (see e.g. [13], Sec. 4.2)

$$f \to f, \quad S \to QS, \quad j \to j, \quad \xi \to \xi, \quad r \to r, \quad a \to a,$$
$$(F, \chi, D\chi, D^2\chi, \chi_{,t}, w, Dw) \to (QF, \chi, D\chi, D^2\chi, \chi_{,t}, w, Dw)$$

for all proper orthogonal tensors Q ($QQ^T = Q^TQ = I$ with det $Q > 0$). This leads to the following restrictions

$$(4.10) \qquad \begin{aligned} \hat{f}(F, \chi, D\chi) &= \hat{f}(C, \chi, D\chi), \\ \hat{S}(F, \chi, D\chi) &= F\bar{S}(C, \chi, D\chi), \\ \hat{\xi}(F, \chi, D\chi) &= \hat{\xi}(C, \chi, D\chi), \\ \hat{j}(\mathcal{Z}) &= \hat{j}(\bar{\mathcal{Z}}), \quad \hat{r}(\mathcal{Z}) = \hat{r}(\bar{\mathcal{Z}}), \quad \hat{a}(\mathcal{Z}) = \hat{a}(\bar{\mathcal{Z}}), \end{aligned}$$

where $\bar{\mathcal{Z}} := \{C, \chi, D\chi, D^2\chi, \chi_{,t}, w, Dw\}$ with $C = F^TF$ the right Cauchy-Green strain tensor. We note that by virtue of $(4.10)_2$ condition (4.7) is automatically satisfied (see e.g. [11]).

Remark 4.1. Equation $(4.5)_3$ is deduced from (3.4) after replacing the restricted first variation $\delta^{\hat{Y}^0} f / \delta\chi$ by the first variation $\delta f / \delta\chi$, and the terms

$$\nabla^{\hat{Y}^0} \cdot \int_0^1 (\lambda_{,\chi_{,t}} j)(Y^0, \tau\chi_{,t}) d\tau - \tilde{a}$$

by a scalar $a = \hat{a}(\mathcal{Z})$. In fact, in view of (4.3) and (4.4), the first variation

$$\frac{\delta f}{\delta\chi} = f_{,\chi} - \nabla \cdot f_{,D\chi} = \frac{\delta^{\hat{Y}^0} f}{\delta\chi}$$

is independent of the variables DF. Then, according to equation $(4.5)_3$, we have $a = \hat{a}(\mathcal{Z})$. This shows that the above mentioned replacements are well-founded. $\square$

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4.2. The solution of a dissipation inequality

Inequality (4.8) represents the standard thermodynamical inequality

$$(4.11) \qquad -X \cdot J(X, \omega) \geq 0 \quad \text{for all variables } \mathcal{Z} = \{X, \omega\},$$

where $X := (Dw, w, \chi_{,t})$ is a thermodynamical force, $J := (j, r, a)$ is a thermodynamical flux and $\omega := (F, \chi, D\chi, D^2\chi)$ is a vector of state variables. The solution of (4.11) can be characterized with the help of the following general result due to Gurtin [13], Appendix B: Let $J : \mathbb{R}^q \times \mathbb{R}^p \to \mathbb{R}^q$, $p, q \in \mathbb{N}$, be a smooth function satisfying inequality (4.11) for all $(X, \omega) \in \mathbb{R}^q \times \mathbb{R}^p$. Then

$$(4.12) \qquad J(X, \omega) = -B(X, \omega)X,$$

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

$$(4.13) \qquad X \cdot B(X, \omega)X \geq 0 \quad \text{for all } (X, \omega) \in \mathbb{R}^q \times \mathbb{R}^p.$$

We remark that because of the dependence of $B(X, \omega)$ on X, inequality (4.13) is weaker that positive semi-definiteness of $B(X, \omega)$. However, when $J(X, \omega)$ is linear in X for each ω, then

$$(4.14) \qquad J(X, \omega) = -B(\omega)X$$

with $B(\omega)$ positive semi-definite.

4.3. Thermodynamical consistency of model (M)

We shall show that model (M) is consistent with the second law of thermodynamics.

Theorem 4.1. *Model (M) satisfies the following free energy inequality with multipliers*

$$
(4.15) \quad
\begin{aligned}
& \left(f(F, \chi, \nabla\chi) + \frac{1}{2}|\dot{u}|^2 \right)^{\cdot} + \nabla \cdot (-S^T \dot{u} + wj - \dot{\chi} f_{,\nabla\chi}) \\
& + \Lambda_u \cdot (\ddot{u} - S) + \Lambda_\chi(\dot{\chi} + \nabla \cdot j - r) \\
& + \Lambda_w(w - f_{,\chi} + \nabla \cdot f_{,\nabla\chi} + a) + \Lambda_S \cdot (S - f_{,F}) \\
& = \nabla w \cdot j + wr + \dot{\chi} a = -\mathcal{D} \leq 0
\end{aligned}
$$

for all fields u, χ, w, where

$$(4.16) \qquad \Lambda_u = -\dot{u}, \quad \Lambda_\chi = -w, \quad \Lambda_w = \dot{\chi}, \quad \Lambda_S = \dot{F}$$

are multipliers conjugated respectively with equations $(4.5)_{1,2,3}$ and (4.6).

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Proof. Let u, χ, w be any fields and $\Lambda_u, \Lambda_\chi, \Lambda_w, \Lambda_S$ be defined by (4.16). Then, after simple rearrangements we arrive at the following identities:

$$\Lambda_u \cdot (\ddot{u} - \nabla \cdot S) + \Lambda_\chi(\dot{\chi} + \nabla \cdot j - r) + \Lambda_w(w - f_{,\chi} + \nabla \cdot f_{,\nabla\chi} + a) + \Lambda_S \cdot (S - f_{,F})$$

$$= -\dot{u} \cdot (\ddot{u} - \nabla \cdot S) - w(\dot{\chi} + \nabla \cdot j - r) + \dot{\chi}(w - f_{,\chi} + \nabla \cdot f_{,\nabla\chi} + a) + \dot{F} \cdot (S - f_{,F})$$

$$= \left[\left(\frac{1}{2}|\dot{u}|^2 \right)^{\cdot} + \nabla \cdot (S^T \dot{u}) - S \cdot \dot{F} \right] + [-w\dot{\chi} - \nabla \cdot (wj) + \nabla w \cdot j + wr]$$

$$+ [w\dot{\chi} - f_{,\chi}\dot{\chi} + \nabla \cdot (\dot{\chi} f_{,\nabla\chi}) - f_{,\nabla\chi} \cdot \nabla \dot{\chi} + \dot{\chi}a] + [S \cdot \dot{F} - f_{,F} \cdot \dot{F}]$$

$$= - \left(f(F, \chi, \nabla\chi) + \frac{1}{2}|\dot{u}|^2 \right)^{\cdot} + \nabla \cdot (S^T \dot{u} - wj + \dot{\chi} f_{,\nabla\chi}) + \nabla w \cdot j + wr + \dot{\chi}a.$$

This shows the equality in (4.15) while the inequality there results by virtue of (4.8). $\square$

Corollary 4.1. From (4.15) it follows that solutions of model (M) satisfy the following free energy (dissipation) inequality
(4.17)

$$\left(f(F, \chi, \nabla\chi) + \frac{1}{2}|\dot{u}|^2 \right)^{\cdot} + \nabla \cdot (-S^T \dot{u} + wj - \dot{\chi} f_{,\nabla\chi}) = -\mathcal{D} + \dot{u} \cdot b + wr \le \dot{u} \cdot b + wr.$$

Subtracting from (4.17) the balance equation for the kinetic energy

$$(4.18) \qquad \left(\frac{1}{2}|\dot{u}|^2 \right)^{\cdot} - \nabla \cdot (S^T \dot{u}) + S \cdot \dot{F} = \dot{u} \cdot b,$$

which follows by multiplying $(2.1)_1$ by $\dot{u}$, we obtain

$$(4.19) \qquad \dot{f} + \nabla \cdot \Phi - S \cdot \dot{F} = -\mathcal{D} + wr \le wr,$$

where

$$(4.20) \qquad \Phi := wj - \dot{\chi} f_{,\nabla\chi}$$

denotes the free energy flux. It is of interest to note that the structure of this flux remains in compatibility with assumption (A) postulated in Section 3. $\square$

Corollary 4.2. Integration of (4.17) over Ω yields

$$(4.21) \qquad \begin{aligned} & \left[\int_\Omega \left(f(F, \chi, \nabla\chi) + \frac{1}{2}|\dot{u}|^2 \right) dx \right]^{\cdot} + \int_S [-(Sn) \cdot \dot{u} + wn \cdot j - \dot{\chi}n \cdot f_{,\nabla\chi}] dS \\ & = \int_\Omega (\nabla w \cdot j + wr + \dot{\chi}a) dx + \int_\Omega (\dot{u} \cdot b + wr) dx \le \int_\Omega (\dot{u} \cdot b + wr) dx, \end{aligned}$$

where n denotes the unit outward normal to $S = \partial\Omega$. Hence, it follows that if the external sources vanish, that is $b = 0$, $r = 0$, and if the boundary conditions on S imply that

$$(4.22) \qquad (Sn) \cdot \dot{u} = 0, \quad wn \cdot j = 0, \quad \dot{\chi}n \cdot f_{,\nabla\chi} = 0,$$

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then solutions of model (M) satisfy

$$(4.23) \qquad \left[\int_\Omega \left(f(\boldsymbol{F}, \chi, \nabla\chi) + \frac{1}{2}|\dot{\boldsymbol{u}}|^2 \right) dx \right]^{\cdot} \leq 0.$$

This is the Lyapunov relation asserting that for model (M) the total energy is non-increasing on solutions paths. $\square$

4.4. Model $(M)_l$ in case of infinitesimal deformations

Here we deduce the corresponding model within linearized theory appropriate to situations in which the displacement gradient $\nabla\boldsymbol{u}$ is small. To this end it is appropriate to repeat considerations of Sections 2–4 assuming from the outset that the deformation is infinitesimal. Following arguments used in [13], Sec. 4.4, or [9], Sec. 6, we redefine $\boldsymbol{F}$ to be $\nabla\boldsymbol{u}$, and replace $(2.1)_2$ by the requirement that S be symmetric:

$$(4.24) \qquad S = S^T.$$

The steps leading to $(M1) - (M3)$ remain unchanged. Further, as in [13], Sec. 4.4, we conclude that invariance of the constitutive equations under infinitesimal rotations (i.e., repalcement of $\nabla\boldsymbol{u}$ by $\nabla\boldsymbol{u}+\boldsymbol{\Omega}$ with $\boldsymbol{\Omega}$ skew) implies that constitutive functions can depend on $\nabla\boldsymbol{u}$ only through the infinitesimal strain $\boldsymbol{\varepsilon}(\boldsymbol{u}) = (\nabla\boldsymbol{u} + \nabla\boldsymbol{u}^T)/2$. Consequently, the set of variables $\mathcal{Z}$ is repalced by

$$\mathcal{Z}_l := \{\boldsymbol{\varepsilon}(\boldsymbol{u}), \chi, D\chi, D^2\chi, \chi_{,t}, w, Dw\}.$$

Within linearized theory model $(M)_l$ is based on the following postulates:

$(M1)_l$ The unknowns are the fields $\boldsymbol{u}, \chi, w$.
$(M2)_l$ The free energy is given by

$$f = \hat{f}(\boldsymbol{\varepsilon}(\boldsymbol{u}), \chi, D\chi),$$

consistent with the condition $f_{,D\chi\boldsymbol{\varepsilon}} = \boldsymbol{0}$.
$(M3)_l$ The fields $\boldsymbol{u}, \chi, w$ satisfy equations (4.5), where S is given by

$$S = \hat{S}(\boldsymbol{\varepsilon}(\boldsymbol{u}), \chi, D\chi) = f_{,\boldsymbol{\varepsilon}}(\boldsymbol{\varepsilon}(\boldsymbol{u}), \chi, D\chi),$$

hence consistent with (4.24). Moreover, the quantities $\boldsymbol{j} = \hat{\boldsymbol{j}}(\mathcal{Z}_l)$, $r = \hat{r}(\mathcal{Z}_l)$, $a = \hat{a}(\mathcal{Z}_l)$ are subject to the dissipation inequality

$$\mathcal{D}_l := -(Dw \cdot \boldsymbol{j} + wr + \chi_{,t}a) \geq 0 \text{ for all variables } \mathcal{Z}_l.$$

5. The Cahn-Hilliard system coupled with elasticity

5.1. Model $(M)^C$ in the conserved case

We now specify model (M), denoted by $(M)^C$, in the conserved case $j \neq 0$, $r \equiv 0$. Then

(5.1) $$\mathcal{Z}^C := \mathcal{Z} = \{F, \chi, D\chi, D^2\chi, \chi_{,t}, w, Dw\},$$

and dissipation inequality (4.8) reduces to

(5.2) $$\mathcal{D}^C := -(Dw \cdot j + \chi_{,t}a) \geq 0 \quad \text{for all varialbes } \mathcal{Z}^C.$$

Recalling (4.12) the solution of (5.2) is given by

(5.3) $$\begin{bmatrix} j \\ a \end{bmatrix} = - \begin{bmatrix} M & h \\ g^T & \beta \end{bmatrix} \begin{bmatrix} Dw \\ \chi_{,t} \end{bmatrix},$$

where $M = \hat{M}(\mathcal{Z}^C)$ is a tensor in $\mathbb{R}^3$, $h = \hat{h}(\mathcal{Z}^C)$, $g = g(\mathcal{Z}^C)$ are vectors in $\mathbb{R}^3$, and $\beta = \hat{\beta}(\mathcal{Z}^C)$ is a scalar. These quantities are consistent with the inequality

(5.4) $$\begin{bmatrix} Dw \\ \chi_{,t} \end{bmatrix} \cdot \begin{bmatrix} M & h \\ g^T & \beta \end{bmatrix} \begin{bmatrix} Dw \\ \chi_{,t} \end{bmatrix} \geq 0 \quad \text{for all variables } \mathcal{Z}^C.$$

Equations (4.5), (4.6) together with (5.3) yield the following system of differential equations which represents model $(M)^C$ in the conserved case:

(5.5) $$\begin{aligned} &\ddot{u} - \nabla \cdot f_{,F}(F, \chi, \nabla\chi) = b, \\ &\dot{\chi} - \nabla \cdot (M\nabla w + h\dot{\chi}) = \tau, \\ &w - g \cdot \nabla w - f_{,\chi}(F, \chi, \nabla\chi) + \nabla \cdot f_{,\nabla\chi}(F, \chi, \nabla\chi) - \beta\dot{\chi} = 0, \end{aligned}$$

where $f = \hat{f}(F, \chi, D\chi)$ is subject to the condition $f_{,D\chi F} = 0$. Moreover, system (5.5) is supplemented by inequality (5.4) and invariance restrictions (4.10).

We recall that by virtue of Corollary 4.1, the solutions of (5.5) satisfy free energy inequality (4.19). For later comparison with Gurtin's theory we note that multiplying equation $(5.5)_2$ by w and subtracting the result from inequality (4.19), the latter becomes

(5.6) $$\dot{f} - S \cdot \dot{F} - (\nabla \cdot f_{,\nabla\chi} + w)\dot{\chi} - f_{,\nabla\chi} \cdot \nabla\dot{\chi} + j \cdot \nabla w \leq 0.$$

Finally, we specify model $(M)^C$ under assumption of infinitesimal deformations. It has the form

(5.7) $$\begin{aligned} &\ddot{u} - \nabla \cdot f_{,\epsilon}(\varepsilon(u), \chi, \nabla\chi) = b, \\ &\dot{\chi} - \nabla \cdot (M\nabla w + h\dot{\chi}) = \tau, \\ &w - g \cdot \nabla w - f_{,\chi}(\varepsilon(u), \chi, \nabla\chi) - \nabla \cdot f_{,\nabla\chi}(\varepsilon(u), \chi, \nabla\chi) - \beta\dot{\chi} = 0, \end{aligned}$$

with $f = \hat{f}(\varepsilon(u), \chi, D\chi)$ satisfying $f_{,D\chi\epsilon} = 0$, and the quantities $M = \hat{M}(\mathcal{Z}_l^C)$, $h = \hat{h}(\mathcal{Z}_l^C)$, $g = \hat{g}(\mathcal{Z}_l^C)$, $\beta = \hat{\beta}(\mathcal{Z}_l^C)$ consistent with the inequality (5.4) for all variables

$$\mathcal{Z}_l^C := \mathcal{Z}_l = \{\varepsilon(u), \chi, D\chi, D^2\chi, \chi_{,t}, w, Dw\}.$$

We point out that the Cahn-Hilliard-Gurtin model (1.9), (1.10) is a special case of system (5.7) corresponding to free energy (1.7), (1.8).

5.2. The Gurtin theory

To see in detail the connections between the presented multipliers-based approach and the microforce balance approach to the Cahn-Hilliard model with elasticity we recall here the main postulates of Gurtin's theory [13]. We use our notation with the following correspondences to the notation of [13]:

$\chi \leftrightarrow \rho$ order parameter, $w \leftrightarrow \mu$ chemical potential, $j \leftrightarrow h$ mass flux, $\tau \leftrightarrow m$ external mass supply, $h \leftrightarrow a$, $g \leftrightarrow b$ cross-coupling terms, $M \leftrightarrow A$ mobility tensor, $\mathbf{A} \leftrightarrow C$ elasticity tensor, $f \leftrightarrow \psi$ free energy.

The other notation is the same. Moreover, in [13] the following additional fields are considered as primitive quantities:

ξ — microstress (vector), π — internal microforce (scalar), γ — external microforce.

The postulates in [13] are:

(G1) The unknowns are the fields u, χ, w.

(G2) The underlying laws are the linear momentum balance in quasi-stationary approximation

$$(5.8) \qquad -\nabla \cdot S = b,$$

the angular momentum balance $(2.1)_2$, the mass balance $(2.1)_3$ $(r \equiv 0)$

$$(5.9) \qquad \dot{\chi} + \nabla \cdot j = \tau,$$

and the microforce balance

$$(5.10) \qquad \nabla \cdot \xi + \pi + \gamma = 0.$$

(G3) The second law is assumed in the form of the dissipation inequality (see [13], eq. (4.6))

$$(5.11) \qquad \dot{f} + \nabla \cdot (-S^T \dot{u} + wj - \dot{\chi}\xi) \leq \dot{u} \cdot b + w\tau + \dot{\chi}\gamma,$$

which in view of (5.8)–(5.10) is equivalent to (see [13], eq. (4.7))

$$(5.12) \qquad \dot{f} - S \cdot \dot{F} + (\pi - w)\dot{\chi} - \xi \cdot \nabla\dot{\chi} + j \cdot \nabla w \leq 0.$$

(G4) The set of constitutive variables (in case without kinetics) is

$$Z_0 := \{F, \chi, D\chi, w, Dw\}$$

and constitutive equations are (see [13], eq. (4.8))

$$(5.13) \qquad f = \hat{f}(Z_0), \quad S = \hat{S}(Z_0), \quad j = \hat{j}(Z_0), \quad \xi = \hat{\xi}(Z_0), \quad \pi = \hat{\pi}(Z_0).$$

(G5) The constitutive equations (5.13) are invariant under changes in observer, i.e., under transformations

$$(5.14) \qquad \begin{aligned} &f \to f, \quad S \to QS, \quad j \to j, \quad \xi \to \xi, \quad \pi \to \pi, \\ &(F, \chi, D\chi, w, Dw) \to (QF, \chi, D\chi, w, Dw) \end{aligned}$$

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for all orthogonal tensors Q. This leads to the restrictions

(5.15)
$$\hat{f}(Z_0) = \hat{f}(\bar{Z}_0), \quad \hat{S}(Z_0) = F\bar{S}(\bar{Z}_0), \quad \hat{j}(Z_0) = \hat{j}(\bar{Z}_0),$$
$$\hat{\xi}(Z_0) = \hat{\xi}(\bar{Z}_0), \quad \hat{\pi}(Z_0) = \hat{\pi}(\bar{Z}_0)$$

with $\bar{Z}_0 := (C, \chi, D\chi, w, Dw)$, $C = F^T F$. We add that restricted relations (5.15) are not used in the general development of the theory in [13] which is simpler in terms the deformation gradient F (see Remark 2.3).

We outline the main results proved in [13]:

— The compatibility of constitutive equations (5.13) with dissipation inequality (5.12) implies the following restrictions

(5.16)
$$f = \hat{f}(F, \chi, D\chi), \quad S = \hat{S}(F, \chi, D\chi) = f_{,F}(F, \chi, D\chi),$$
$$\xi = \hat{\xi}(F, \chi, D\chi) = f_{,D\chi}(F, \chi, D\chi),$$

(5.17)
$$\pi = \hat{\pi}(F, \chi, D\chi, w) = w - f_{,\chi}(F, \chi, D\chi),$$
$$j = -MDw$$

with tensor $M = \hat{M}(Z_0)$ consistent with the inequality

(5.18)
$$Dw \cdot MDw \geq 0 \quad \text{for all variables } Z_0.$$

— Balance laws (5.8)–(5.10) together with relations (5.16), (5.17) yield the system (see [13], eq. (4.15))

(5.19)
$$-\nabla \cdot f_{,F}(F, \chi, \nabla\chi) = b,$$
$$\dot{\chi} - \nabla \cdot (M\nabla w) = \tau,$$
$$w - f_{,\chi}(F, \chi, \nabla\chi) + \nabla \cdot f_{,\nabla\chi}(F, \chi, \nabla\chi) + \gamma = 0.$$

We note that this system is identical with (5.5) provided $\ddot{u} = 0$, $g = h = 0$, $\beta = \gamma = 0$ and the set Z^C replaced by Z_0.

— The considerations in [13], Sec. 3.4, 4.1 allow to deduce that inclusion of the kinetics in the constitutive variables, that is replacement of the set Z_0 in (G4) by

(5.20)
$$Z := \{F, \chi, D\chi, \chi_{,t}, w, Dw\},$$

leads to relations (5.16), and

(5.21)
$$\pi = w - f_{,\chi}(F, \chi, D\chi) + \pi_{dis},$$
$$j = -(MDw + h\chi_{,t}),$$
$$\pi_{dis} = -(g \cdot Dw + \beta\chi_{,t}),$$

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where π_{dis} represents dissipative part of the internal microforce, and the quantities $M = \hat{M}(Z)$, $h = \hat{h}(Z)$, $g = \hat{g}(Z)$, $\beta = \hat{\beta}(Z)$ are consistent with the inequality (5.4) for all variables Z. Then balance laws (5.8)–(5.10) together with relations (5.16), (5.21) yield the system which is identical with our system (5.5) if $\ddot{u} = 0$, $\gamma = 0$, and the set Z in place of $\mathcal{Z}^C$.

We summarize the comparison of the presented results by the following conclusions:

- The generalized Cahn-Hilliard models with elasticity obtained by two approaches have the same structure. The only differences are:
  - additional constraint on the free energy $f_{,D_X F} = 0$ in model $(M)^C$;
  - different sets of state variables: $\mathcal{Z}^C$ given by (5.1) in model $(M)^C$ and Z given by (5.20) in the Gurtin model.
- The term $f_{,\nabla\chi}(F, \chi, \nabla\chi)$ in differential equation (5.5)$_3$ for the chemical potential corresponds to the microstress while the term $w - f_{,\chi}(F, \chi, \nabla\chi)$ to the internal microforce.
- The quantity a in (5.3) corresponds to the dissipative part of the internal microforce.
- The free energy inequality (5.6) coincides with dissipation inequality (5.12) postulated in [13].
- Our postulate of treating the multiplier (chemical potential) as an independent variable corresponds to Gurtin's postulate of an additional balance law for the microforce and the assumption that system is far from equilibrium. The differential equations for the chemical potential and the microforce balance are identical.

6. The Allen-Cahn system coupled with elasticity

6.1. Model $(M)^{NC}$ in the nonconserved case

Here we specify model (M), denoted by $(M)^{NC}$, in the nonconserved case $j \equiv 0$, $r \neq 0$. Then the constitutive set $\mathcal{Z}$ reduces to

$$(6.1) \qquad \mathcal{Z}^{NC} := \{F, \chi, D\chi, D^2\chi, \chi_{,t}, w\},$$

and dissipation inequality (4.8) to

$$(6.2) \qquad \mathcal{D}^{NC} := -(wr + \chi_{,t}a) \geq 0 \quad \text{for all variables } \mathcal{Z}^{NC}.$$

By (4.12) the solution of (6.2) is given by

$$(6.3) \qquad \begin{bmatrix} r \\ a \end{bmatrix} = - \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix} \begin{bmatrix} w \\ \chi_{,t} \end{bmatrix},$$

where scalar coefficients $b_{kl} = \hat{b}_{kl}(\mathcal{Z}^{NC})$ are consistent with the inequality

$$(6.4) \qquad \begin{bmatrix} w \\ \chi_{,t} \end{bmatrix} \cdot \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix} \begin{bmatrix} w \\ \chi_{,t} \end{bmatrix} \geq 0 \quad \text{for all variables } \mathcal{Z}^{NC}.$$

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Consequently, equations (4.5), (4.6) together with (6.3) yield the following system which represents model $(M)^{NC}$ in the nonconserved case:

(6.5)
$$\ddot{u} - \nabla \cdot f_{,F}(F, \chi, \nabla\chi) = b,$$
$$\dot{\chi} + b_{11}w + b_{12}\dot{\chi} = \tau,$$
$$w - f_{,\chi}(F, \chi, \nabla\chi) + \nabla \cdot f_{,\nabla\chi}(F, \chi, \nabla\chi) - b_{21}w - b_{22}\dot{\chi} = 0,$$

where $f = \hat{f}(F, \chi, D\chi)$ is subject to the condition $f_{,D_\chi F} = 0$.
System (6.5) is supplemented by inequality (6.4) and the invariance restrictions (4.10). We recall that according to Corollary 4.1 the solutions of (6.5) satisfy free energy inequality (4.19) which now can be written in the form

(6.6)
$$\dot{f} - S \cdot \dot{F} - f_{,\nabla\chi} \cdot \nabla\dot{\chi} - (\nabla \cdot f_{,\nabla\chi})\dot{\chi} = -\mathcal{D}^{NC} + w\tau \le w\tau.$$

From $(6.5)_2$ and $(6.5)_3$ we can deduce a generalized Allen-Cahn equation. Specifically, it the coefficients b_{kl} are independent of w, i.e. $b_{kl} = \hat{b}_{kl}(F, \chi, D\chi, D^2\chi, \chi_{,t})$ and satisfy

(6.7)
$$b_{11} > 0, \quad b_{22} \ge 0, \quad b_{12} = b_{21} = 0,$$

then system $(6.5)_{2,3}$ upon eliminating w reduces to

(6.8)
$$\beta\dot{\chi} + f_{,\chi}(F, \chi, \nabla\chi) - \nabla \cdot f_{,\nabla\chi}(F, \chi, \nabla\chi) = \bar{\tau},$$

where $\bar{\tau} = \tau/b_{11}$ and $\beta = \hat{\beta}(F, \chi, D\chi, D^2\chi, \chi_{,t}) > 0$ is given by

(6.9)
$$\beta = \frac{1}{b_{11}} + b_{22}.$$

Moreover, dissipation (6.2) reduces to $\mathcal{D}^{NC} = \beta\chi_{,t}^2$.

In case of infinitesimal deformations system $(6.5)_1$, (6.8) is replaced by

(6.10)
$$\ddot{u} - \nabla \cdot f_{,\varepsilon}(\varepsilon(u), \chi, \nabla\chi) = b,$$
$$\beta\dot{\chi} + f_{,\chi}(\varepsilon(u), \chi, \nabla\chi) - \nabla \cdot f_{,\nabla\chi}(\varepsilon(u), \chi, \nabla\chi) = \bar{\tau},$$

where $\beta = \hat{\beta}(\varepsilon(u), \chi, D\chi, D^2\chi, \chi_{,t}) > 0$. We point out that the Allen-Cahn-Fried-Gurtin model (1.10), (1.15) is a special case of (6.10) corresponding to free energy (1.7), (1.8).

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6.2. The Fried-Gurtin theory

For comparison we outline here the main results of the Fried-Gurtin theory [9] focusing on its special case when the order parameter is unconstrained and scalar-valued (see [7]). We remark that the theory of [9] covers more general case where the order parameter is vector-valued and constrained. We use our notation with the correspondences to the notation of [9] indicated in Section 5.2 where now $\chi \leftrightarrow \varphi$ stands for a nonconserved order parameter.

The postulates in [9] are:

(FG1) The unknowns are the fields u and χ.

(FG2) The underlying laws are the linear and angular momentum balances $(2.1)_{1,2}$ and the microforce balance (5.10).

(FG3) The second law is assumed in the form of the dissipation inequality (see [9], eq. (2.13))

$$(6.11) \qquad \left(f + \frac{1}{2} |\dot{u}|^2 \right)^{\cdot} + \nabla \cdot (-S^T \dot{u} - \dot{\chi} \xi) \leq \dot{u} \cdot b + \dot{\chi} \gamma,$$

which on account of $(2.1)_1$ and (5.10) is equivalent to (see [9], eq. (2.14))

$$(6.12) \qquad \dot{f} - S \cdot \dot{F} - \xi \cdot \nabla \dot{\chi} + \pi \dot{\chi} \leq 0.$$

(FG4) The set of constitutive variables is given by

$$(6.13) \qquad Z = \{F, \chi, D\chi, \chi_{,t}\}$$

and constitutive equations are

$$(6.14) \qquad f = \hat{f}(Z), \quad S = \hat{S}(Z), \quad \xi = \hat{\xi}(Z), \quad \pi = \hat{\pi}(Z).$$

(FG5) Constitutive equations (6.14) are invariant under observer changes similarly as in (5.14).

We outline the main results obtained in [9]:

— The consistency of constitutive equations (6.14) with dissipation inequality (6.12) requires relations (5.16) and

$$(6.15) \qquad \begin{aligned} \pi &= -f_{,\chi}(F, \chi, D\chi) + \pi_{dis}, \\ \pi_{dis} &= \hat{\pi}_{dis}(F, \chi, D\chi, \chi_{,t}) = -\beta(F, \chi, D\chi, \chi_{,t})\chi_{,t} \end{aligned}$$

where $\beta = \hat{\beta}(F, \chi, D\chi, \chi_{,t}) \geq 0$ is a kinetic coefficient. Then (6.12) yields a dissipation balance (see [7], eq. (3.6))

$$(6.16) \qquad \dot{f} - S \cdot \dot{F} - \xi \cdot \nabla \dot{\chi} + \pi \dot{\chi} = -\beta(F, \chi, \nabla\chi, \dot{\chi})\dot{\chi} = \pi_{dis} \leq 0$$

which isolates a part of the internal microforce π_{dis} as the sole source of dissipation in the theory.

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— Balance laws $(2.1)_1$, (5.10) together with relations (5.16), (6.15) yield system (see [9], eq. (4.1))

$$(6.17) \quad \begin{aligned} &\ddot{u} - \nabla \cdot f_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \nabla\chi) = \boldsymbol{b}, \\ &\beta(\boldsymbol{F}, \chi, \nabla\dot{\chi}, \dot{\chi})\dot{\chi} + f_{,\chi}(\boldsymbol{F}, \chi, \nabla\chi) - \nabla \cdot f_{,\nabla\chi}(\boldsymbol{F}, \chi, \nabla\chi) - \gamma = 0 \end{aligned}$$

supplemented by the invariance restrictions.

We note that (6.17) coincides with $(6.5)_1$, (6.8) up to the difference in the constitutive dependence of β.

As in Section 5 we summarize the comparison by the following conclusions:

- The generalized Allen-Cahn models with elasticity obtained by two approaches have the same structure. The only differences are:
  — additional constraint $f_{,\boldsymbol{D}_{\chi}\boldsymbol{F}} = \boldsymbol{0}$ in model $(M)^{NC}$;
  — a broader constitutive dependence $\beta = \hat{\beta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \chi_{,t})$ in model $(M)^{NC}$.
- Allen-Cahn equation (6.8) corresponds to the microforce balance where $f_{,\nabla\chi}(\boldsymbol{F}, \chi, \nabla\chi)$ represents the microstress while $-(f_{,\chi} + \beta\dot{\chi})$ the internal microforce.
- Our free energy inequality (6.6) is consistent with the dissipation inequality (6.12) postulated in [9].

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