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A THERMODYNAMIC APPROACH TO PHASE-FIELD MODELLING OF THERMOELASTIC MATERIALS. PART I: THEORY

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ABSTRACT. The goal of this paper is to work out a thermodynamical setting for phase-field models with conserved and nonconserved order parameters in thermoelastic materials. Our approach consists in exploiting 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.

As the main result we obtain a general scheme of phase-field models which involves an arbitrary extra vector field. We explain the presence of such a field in the light of Edelen's decomposition theorem asserting a splitting of a solution of the dissipation inequality into a dissipative and a nondissipative part. For particular choices of this extra vector field we obtain known schemes with either modified entropy equation or modified energy equation. A detailed comparison with several known phase-field models, in particular Cahn–Hilliard and Allen–Cahn models in the presence of deformation and heat conduction, will be presented in Part II of the paper [Paw07].

Keywords: phase-field models, thermoelastic materials, order parameters, conserved and nonconserved dynamics.

Mathematic Subject Classification: 74A30, 35K25, 35Q72, 35L20.

CONTENTS

1. Introduction

1.1. Motivation and goal.

Phase-field approaches to modelling phase transitions in various conserved and nonconserved systems have gained a lot of popularity during the last years. Among the mostly known and broadly investigated we mention the Caginalp model of solid-liquid phase transitions [Cag86], Penrose–Fife models with conserved and nonconserved order parameter [PenFife90], [PenFife93], models due to Fried–Gurtin [FriGur93], [FriGur94], [FriGur96], [FriGur99], Gurtin [Gur96], Frémond [Frem02], [FremMi96], and Falk [Falk82], [Falk90] for phase transitions in solids, in particular phase separation, ordering in alloys, damage and shape memory problems.

The phase-field (or diffuse-interface) models postulate one or more quantities, named order parameters, as indicators of the state of the material, in addition to the usual ones such as temperature, elastic strain etc. In models of this type – on the contrary to sharp interface ones – the order parameters vary continuously in the medium, including the interfacial regions between the phases where they undergo large variations.

In accordance with a postulate of a smooth phase transition phase-field models are based on a free energy functional, called Landau–Grinzburg functional, which accounts not only for a volumetric energy but also for a surface energy of phase interfaces.

In most of the literature the derivations of phase-field models are based on variational arguments and adapt concepts from classical equilibrium thermodynamics in nonequilibrium situations.

Having in mind several objections to variational derivations, in particular not sufficient generality of postulated constitutive equations, E. Fried and M. E. Gurtin have developed in a line of their papers [FriGur93], [FriGur94], [FriGur96], [FriGur99], [Gur96] a thermodynamic theory of phase transitions 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 [Frem02], [FremMi96] has proposed a theory based on microscopic motions as a tool of modelling of various phase transitions, specifically shape memory and damage problems. Despite of different ideas Frémond's approach bears some resemblance to the Fried–Gurtin theory.

Another approach to modelling phase transitions has been proposed in [AltPaw95], [AltPaw96] and applied in [Paw00a], [Paw00b], [Paw00c]. This approach consists in exploiting the second law in the form of the entropy principle according to I. Müller [Mul85], complemented by the Lagrange multipliers method suggested by I. S. Liu [Liu72]. Such method leads to the evaluation of the entropy inequality with multipliers, known as the Müller–Liu inequality. Recently the multipliers-based approach was applied for deriving generalized Cahn–Hilliard and Allen–Cahn models coupled with elasticity (see [Paw06a]). A comparison with the Fried–Gurtin theory based on a microforce balance showed coincidence of results and several interesting connections.

We point out that the above mentioned thermodynamic approaches allow to obtain models with much more general structure than those introduced by variational arguments.

The goal of the present paper is to work out a general thermodynamic setting for phase-field models with conserved and nonconserved, scalar order parameters in thermoelastic materials by means of the multipliers-based approach. Our ultimate aim is to obtain a general class of thermodynamically consistent schemes for Cahn–Hilliard and Allen–Cahn models – two central equations in materials science – in the presence of deformation and heat conduction. This will be presented in Part II of the paper [Paw07] where we discuss the general thermodynamic scheme in several special situations and compare the results with the mentioned above well-known phase-field models. In particular, we shall consider there the Cahn–Hilliard and Allen–Cahn models coupled separately either with elasticity or with thermal efects. The latter case allows to enlighten a general question of particular interest in phase-field modelling whether to modify the energy or the entropy equation (for related discussion see e.g. [FGM06]). In this respect the answer given by the present paper is that both variants of the schemes with extra energy or extra entropy flux are thermodynamically consistent and arise in dependence on whether there appears or not a nondissipative (anomaly) thermodynamic flux in the system. More precisely, in the present paper we show that one can choose a nonstationary part (depending on the time derivative of the order parameter) of the energy flux in an arbitrary way not restricted by the entropy principle. This property, characteristic for models governed by gradient-type potentials, was observed firstly in [AltPaw96]. Here we explain this freedom in the light of Edelen's decomposition theorem [Ede73], [Ede74] which asserts a splitting of the solution of the dissipation inequality into a dissipative and a nondissipative part. Clearly, a final selection of this flux must follow from an additional analysis of the resulting model equations.

1.2. The multipliers-based approach.

Prior to presenting a general scheme of phase-field models we describe briefly the Müller–Liu multipliers-based approach. The application of this approach to phase transition models requires a special procedure which 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 entropy 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 entropy 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 multipliers associated with the equations for the order parameter and the energy are additional independent variables. Then, regarding algebraic restrictions obtained in the previous step, we deduce an extended system of equations including in addition to the balance laws the equations for the multipliers. Moreover, we require the resulting system to be consistent with the principle of frame indifference.

1.3. A general scheme of models.

We summarize the main result of the paper which yields a general scheme for phase-field models with conserved and nonconserved order parameters, governed by a first order gradient free energy in the presence of deformation and heat conduction.

We use the following notation: χ – order parameter, $\mathbf{u} = (u_i)$ – displacement, $\mathbf{F} = (F_{ij})$ – deformation gradient, μ – chemical potential, $\theta > 0$ – absolute temperature, f – free energy, e – internal energy, η – entropy, $\mathbf{q} = (q_i)$ – energy flux, $\boldsymbol{\Psi} = (\Psi_i)$ – enropy flux, $\mathbf{j} = (j_i)$ – order parameter flux, r – order parameter production, τ – external source of the order parameter, g – external heat source.

We assume that there are given a free energy $f = \widehat{f}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta)$ which is strictly concave with respect to θ, and a dissipation potential $\mathcal{D} = \widehat{\mathcal{D}}(\mathbf{X}; \omega)$

with

$$\mathbf{X} := \left(\frac{\mu}{\theta}, \mathrm{D}\frac{\mu}{\theta}, \mathrm{D}\frac{1}{\theta}, \chi_{,t}\right) \text{ – thermodynamic forces,}$$
$$\omega := (\mathbf{F}, \mathbf{DF}, \chi, \mathrm{D}\chi, \mathrm{D}^2\chi, \theta) \text{ – state variables,}$$

which is nonnegative, convex in $\mathbf{X}$ and such that $\mathcal{D}(\mathbf{0};\omega) = 0$. Here $\mathrm{D}\chi, \mathrm{D}^2\chi, \chi_{,t}$, etc. denote variables corresponding respectively to $\nabla\chi, \nabla^2\chi, \dot{\chi}$; superimposed dot denotes the material time derivative.

The unknowns are the fields $\mathbf{u}, \chi, \mu/\theta$ and $\theta > 0$ satisfying the following system of equations in $\Omega \subset \mathbb{R}^3$:

$$\begin{aligned} &\ddot{\mathbf{u}} - \nabla \cdot f_{,\mathbf{F}} = \mathbf{b}, \\ &\dot{\chi} + \nabla \cdot \mathbf{j} - r = \tau, \\ &\frac{\mu}{\theta} = \frac{\delta(f/\theta)}{\delta\chi} + \nabla\frac{1}{\theta} \cdot \mathbf{h}^{nd} + a^d, \\ &\dot{e} + \nabla \cdot \mathbf{q} - f_{,\mathbf{F}} \cdot \dot{\mathbf{F}} = g \end{aligned} \tag{1.1}$$

subject to appropriate initial and boundary conditions.

The subsequent equations in (1.1) represent respectively the linear momentum balance, the mass balance, a generalized equation for the chemical potential (equivalent to a microforce balance in Gurtins theory, see [Paw06a]) and the energy balance. Equation $(1.1)_2$ combines various types of dynamics of the order parameter:

- mixed type if $\mathbf{j} \neq \mathbf{0}$, $r \neq 0$;
- conserved if $\mathbf{j} \neq \mathbf{0}$, $r \equiv 0$;
- nonconserved if $\mathbf{j} \equiv \mathbf{0}, r \neq 0$.

The expression $\frac{\delta(f/\theta)}{\delta\chi}$ denotes the first variation of the rescaled free energy f/θ with respect to χ:

$$\frac{\delta(f/\theta)}{\delta\chi} = \left(\frac{f}{\theta}\right)_{,\chi} - \nabla \cdot \left(\frac{f_{,\mathrm{D}\chi}}{\theta}\right), \tag{1.2}$$

the internal energy $e = \widehat{e}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta)$ is given by the Gibbs relation

$$e = f - \theta f_{,\theta}, \tag{1.3}$$

and the energy flux $\mathbf{q}$ splits into a dissipative, $\mathbf{q}^d$, and a nondissipative, $-\dot{\chi}\mathbf{h}^{nd}$ (possibly zero), parts:

$$\mathbf{q} = \mathbf{q}^d - \dot{\chi}\mathbf{h}^{nd}. \tag{1.4}$$

The dissipative quantities

$$r \equiv r^d = \widehat{r}^d(\mathbf{X};\omega), \quad \mathbf{j} \equiv \mathbf{j}^d = \widehat{\mathbf{j}}^d(\mathbf{X};\omega),$$
$$\mathbf{q}^d = \widehat{\mathbf{q}}^d(\mathbf{X};\omega), \quad a^d = \widehat{a}^d(\mathbf{X};\omega), \tag{1.5}$$

denoting respectively the order parameter production, the order parameter flux, the heat flux, and a dissipative part of the rescaled chemical potential μ/θ, are given by

$$-r^d = \frac{\partial\mathcal{D}}{\partial(\mu/\theta)}, \quad -\mathbf{j}^d = \frac{\partial\mathcal{D}}{\partial\mathbf{D}(\mu/\theta)},$$
$$\mathbf{q}^d = \frac{\partial\mathcal{D}}{\partial\mathbf{D}(1/\theta)}, \quad a^d = \frac{\partial\mathcal{D}}{\partial\chi_{,t}}. \tag{1.6}$$

The dissipative quantities contribute to the dissipation inequality whereas nondissipative ones do not. The nondissipative flux $\mathbf{h}^{nd} = \widehat{\mathbf{h}}^{nd}(\mathbf{X};\omega)$ is an arbitrary vector field which is not restricted by the entropy principle. It should, however, like all other constitutive quantities in (1.1), be consistent with the frame indifference principle. This principle restricts the dependence on the deformation gradient $\mathbf{F}$. In particular, the free energy should satisfy

$$\widehat{f}(\mathbf{F},\chi,\mathbf{D}\chi,\theta) = \widehat{f}(\mathbf{C},\chi,\mathbf{D}\chi,\theta)$$

where $\mathbf{C} = \mathbf{F}^T\mathbf{F}$ is the right Cauchy–Green strain tensor; other quantities should transform appropriately (see Section 4).

It will be shown (see Corollary 4.2) that solutions of system (1.1) satisfy the following entropy equation and the inequality

$$\dot{\eta} + \nabla\cdot\mathbf{\Psi} = -\frac{\mu}{\theta}r^d - \nabla\frac{\mu}{\theta}\cdot\mathbf{j}^d + \nabla\frac{1}{\theta}\cdot\mathbf{q}^d + \dot{\chi}a^d + \frac{\mu}{\theta}\tau + \frac{g}{\theta}$$
$$\geq \frac{\mu}{\theta}\tau + \frac{g}{\theta}, \tag{1.7}$$

with the entropy flux $\mathbf{\Psi}$ given by

$$\mathbf{\Psi} = -\frac{\mu}{\theta}\mathbf{j}^d + \frac{1}{\theta}\mathbf{q}^d + \dot{\chi}\frac{f_{,\mathbf{D}\chi} - \mathbf{h}^{nd}}{\theta}. \tag{1.8}$$

The quantity

$$\Sigma(\mathbf{X};\omega) = -\frac{\mu}{\theta}r^d - \mathbf{D}\frac{\mu}{\theta}\cdot\mathbf{j}^d + \mathbf{D}\frac{1}{\theta}\cdot\mathbf{q}^d + \chi_{,t}\,a^d \geq 0$$

represents the dissipation of the system.

Another important property of system (1.1) is the Lyapunov relation (see Corollary 4.4) which asserts that if the external sources vanish, i.e. $\mathbf{b} = \mathbf{0}$,

$\tau = 0$, $g = 0$, and if the boundary conditions on S imply that

$$(f_{,\mathbf{F}}\,\mathbf{n}) \cdot \dot{\mathbf{u}} = 0, \quad \frac{\mu}{\theta}\mathbf{n} \cdot \mathbf{j} = 0, \quad \left(1 - \frac{\overline{\theta}}{\theta}\right) \mathbf{n} \cdot (\mathbf{q}^d - \dot{\chi}\mathbf{h}^{nd}) = 0, \tag{1.9}$$
$$\frac{\dot{\chi}}{\theta}\mathbf{n} \cdot f_{,\mathbf{D}\chi} = 0,$$

then solutions of (1.1) satisfy the inequality

$$\frac{d}{dt} \int_{\Omega} (e(\mathbf{F}, \chi, \mathbf{D}\chi, \theta) + \frac{1}{2}|\dot{\mathbf{u}}|^2 - \overline{\theta}\eta(\mathbf{F}, \chi, \mathbf{D}\chi, \theta))dx \le 0 \tag{1.10}$$

for some constant $\overline{\theta} > 0$. This provides the Lyapunov relation.

The distinguishing elements of system (1.1) are nonstandard energy and entropy fluxes, $\mathbf{q}$ and $\mathbf{\Psi}$, which contain extra nonstationary terms. As seen from (1.4), (1.5) and (1.8), the fluxes $\mathbf{\Psi}, \mathbf{q}$ and $\mathbf{j}$ are related by the condition

$$\mathbf{\Psi} + \frac{\mu}{\theta}\mathbf{j} - \frac{1}{\theta}\mathbf{q} = \dot{\chi}\frac{f_{,\mathbf{D}\chi}}{\theta}. \tag{1.11}$$

This condition shows that in phase-field models with a first-order gradient energy (i.e. $f_{,\mathbf{D}\chi} \neq \mathbf{0}$) at least one of the fluxes must include an extra nonstationary term with $\dot{\chi}$. We point on the two extreme choices of the nondissipative flux $\mathbf{h}^{nd}$:

(i) $\mathbf{h}^{nd} = \mathbf{0}$
leading to models with extra entropy flux

$$\mathbf{q} = \mathbf{q}^d, \quad \mathbf{\Psi} = -\frac{\mu}{\theta}\mathbf{j}^d + \frac{1}{\theta}\mathbf{q}^d + \dot{\chi}\frac{f_{,\mathbf{D}\chi}}{\theta};$$

(ii) $\mathbf{h}^{nd} = \mathbf{f}_{,\mathbf{D}\chi}$
leading to models with extra energy flux

$$\mathbf{q} = \mathbf{q}^d - \dot{\chi}f_{,\mathbf{D}\chi}, \quad \mathbf{\Psi} = -\frac{\mu}{\theta}\mathbf{j}^d + \frac{1}{\theta}\mathbf{q}^d.$$

With the above special choices of $\mathbf{h}^{nd}$, assuming standard forms of the free energy $f = \widehat{f}(\mathbf{F}, \chi, \mathbf{D}\chi, \theta)$ and the dissipation potential $\mathcal{D} = \widehat{\mathcal{D}}(\mathbf{X}; \omega)$, we can derive from system (1.1) several known phase-field models, in particular Penrose–Fife models (corresponding to $\mathbf{h}^{nd} = \mathbf{0}$), and Fried–Gurtin and Frémond models (corresponding to $\mathbf{h}^{nd} = f_{,\mathbf{D}\chi}$), see [Paw07].

1.4. **Plan of the paper.**

The paper is organized as follows:

In Section 2 we introduce basic physical quantities, the balance laws, the entropy principle, the entropy inequality with multipliers and the state spaces relevant for phase field models under consideration. We present thermodynamic Gibbs relations formulated alternatively either with respect to free energy or reduced free energy. Moreover, we present duality relations expressed either in terms of internal energy or entropy. These relations generalize the classical Legendre transformations to the case of gradient type potentials.

They are of a general importance in phase-field modelling as they allow to formulate equations equivalently with respect to temperature, entropy or energy as independent thermal variables.

In Section 3 we evaluate the entropy inequality with multipliers to select a class of thermodynamically consistent models. To this purpose we use there the state space with entropy as an independent variable and internal energy density as a thermodynamic potential. The obtained restrictions are stated in Theorems 3.1 and 3.2.

In Section 4 we introduce an extended model $(M)_\eta$ with the multipliers corresponding to mass and energy balances as additional independent variables. The model combines various types of dynamics of the order parameter and is expressed in terms of entropy as an independent variable. Next, making use of the duality relations, we give its equivalent formulation $(M)_\theta$ in terms of absolute temperature as an independent variable. The thermodynamic consistency of both formulations is stated in Theorems 4.1 and 4.2. Besides, we present the formulation of the model within the linearized elasticity theory.

In Sections 5 and 6 we present an alternative derivation of model $(M)_\theta$ by starting with the state space with internal energy as an independent variable. In Theorems 5.1 and 5.2 we state restrictions on the model in which entropy density plays the role of a thermodynamic potential.

In Section 6, following the procedure of Section 4, we introduce an extended model $(M)_e$ with the multipliers corresponding to mass and energy balances as additional independent variables. Finally, with the help of the duality relations we show that model $(M)_e$ can be transformed to the form $(M)_\vartheta$ expressed in terms of the inverse temperature $\vartheta = 1/\theta$. It turns out that models $(M)_\vartheta$ and $(M)_\theta$ are identical.

In Section 7 we are concerned with solutions of a general thermodynamic inequality which appears in all models. We recall two results on representations of such solutions, one due to Gurtin [Gur96] and the second one due to Edelen [Ede73]. The application of Edelen's decomposition theorem to the introduced models yields the splitting of the thermodynamic fluxes into a dissipative and a nondissipative part with extra nonstationary term.

In Section 8, taking into account the decomposition of the fluxes, we present a final scheme of phase-field models outlined above. We give also some standard examples of free energies and dissipation potentials. Besides, we present some equivalent forms of the model equations and discuss them for particular choices of the nondissipative energy flux. This way we prepare a stage for a comparison with phase-field models known in literature, to be presented in [Paw07].

In Appendix we present proofs of representation lemmas for solutions of a general thermodynamic inequality.

1.5. Notations.

We generally follow the notation in [Gur00]. Vectors (tensors 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 $\mathbf{I}$ is defined by $\mathbf{Iu} = \mathbf{u}$ for every vector $\mathbf{u}$;
$\mathbf{S}^T, tr\mathbf{S}, \mathbf{S}^{-1}$ and $\det \mathbf{S}$, respectively, denote the transpose, trace, inverse, and determinant of a tensor $\mathbf{S}$.

A dot designates the inner product, irrespective of the space in question: $\mathbf{u} \cdot \mathbf{v}$ is the inner product of vectors $\mathbf{u} = (u_i)$ and $\mathbf{v} = (v_i), \mathbf{S} \cdot \mathbf{R} = tr(\mathbf{S}^T\mathbf{R})$ is the inner product of tensors $\mathbf{S} = (S_{ij})$ and $\mathbf{R} = (R_{ij}), \mathbf{A}^m \cdot \mathbf{B}^m$ is the inner product of the m-th order tensors $\mathbf{A}^m = (A^m_{i_1 \dots i_m})$ and $\mathbf{B}^m = (B^m_{i_1 \dots i_m})$.

In Cartesian components,

$$
\begin{aligned}
&(\mathbf{Su})_i = S_{ij}u_j, \quad (\mathbf{S}^T)_{ij} = S_{ji}, \quad tr\mathbf{S} = S_{ii}, \quad \mathbf{u} \cdot \mathbf{v} = u_i v_i, \\
&\mathbf{S} \cdot \mathbf{R} = S_{ij}R_{ij}, \quad \mathbf{A}^m \cdot \mathbf{B}^m = A^m_{i_1 \dots i_m} B^m_{i_1 \dots i_m}.
\end{aligned}
$$

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

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

By $\mathbf{A} = (A_{ijkl})$ we denote the fourth order elasticity tensor which represents a symmetric linear transformation of symmetric tensors into symmetric tensors. We write $(\mathbf{A}\boldsymbol{\varepsilon})_{ij} = A_{ijkl}\varepsilon_{kl}$.
The term field signifies a function of a material point $\mathbf{x} \in \mathbb{R}^3$ and time t.
The superimposed dot, e.g. $\dot{f}$, denotes the material time derivative of the field f (with respect to t holding $\mathbf{x}$ fixed), ∇ and $\nabla\cdot$ denote the material gradient and the divergence (with respect to $\mathbf{x}$ holding t fixed).
For the divergence we use the convention of the contraction over the last index, e.g. $(\nabla \cdot \mathbf{S})_i = \partial S_{ij}/\partial x_j$.

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 $\mathbf{A}^m = (A^m_{i_1\ldots i_m})$ a tensor of order m, $f_{,\mathbf{A}^m}$ is a tensor of order m with components $f_{,A^m_{i_1\ldots i_m}}$.

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

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

In situations that may cause confusion we shall distinguish between functions and their values. Functions are denoted then by superimposed "$\wedge$" symbol, e.g. $f = \widehat{f}(\chi, \nabla\chi)$.

2. Thermodynamic foundations

2.1. **Basic quantities.**

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

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

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

We use a scalar order parameter to characterize the notion of a phase and identify phase interfaces with thin transition zones within which the order parameter exhibits large gradients.

We consider the following fields in material representation:

ρ – mass density, assumed constant normalized to unity, $\rho \equiv 1$,
$\mathbf{S} = (S_{ij})$ – first Piola–Kirchhoff stress tensor,
$\mathbf{b} = (b_i)$ – external body force,
χ – scalar order parameter,
$\mathbf{j} = (j_i)$ – order parameter flux,
r – order parameter production (scalar),
τ – external source of the order parameter,
e – internal energy,
$\mathbf{q} = (q_i)$ — energy flux,
g – external heat source,
$\theta > 0$ – absolute temperature, $\vartheta = 1/\theta$ – inverse temperature,

μ – chemical potential, $\overline{\mu} = \mu/\theta$ – rescaled chemical potential,
η – entropy, $f = e - \theta\eta$ – Helmholtz free energy,
$\phi = f/\theta$ – rescaled free energy.

Moreover, depending on the choice of thermal variable (see Section 2.5), we denote:
$e, \overline{e}, \widetilde{e}$ – internal energy respectively as a function of θ, ϑ and η,
$\eta, \overline{\eta}, \widetilde{\eta}$ – entropy respectively as a function of θ, ϑ and e.

2.2. Balance laws and the entropy principle.

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. [Silh97]):

$$\begin{aligned} &\ddot{\mathbf{u}} - \nabla \cdot \mathbf{S} = \mathbf{b}, \\ &\mathbf{S}\mathbf{F}^T = \mathbf{F}\mathbf{S}^T, \\ &\dot{\chi} + \nabla \cdot \mathbf{j} - r = \tau, \\ &\dot{e} + \nabla \cdot \mathbf{q} - \mathbf{S} \cdot \dot{\mathbf{F}} = g. \end{aligned} \tag{2.1}$$

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) $\mathbf{j} \neq \mathbf{0}$ and $r \neq 0$,
– conserved (mass balance without production) $\mathbf{j} \neq \mathbf{0}$ and $r \equiv 0$,
– nonconserved (evolution law for the order parameter) $\mathbf{j} \equiv \mathbf{0}$ and $r \neq 0$.

Balance laws (2.1) are closed by constitutive equations for the quantities $\mathbf{S}, \mathbf{j}, r, e$ and $\mathbf{q}$:

$$\mathbf{S} = \widehat{\mathbf{S}}(Y), \quad \mathbf{j} = \widehat{\mathbf{j}}(Y), \quad r = \widehat{r}(Y), \quad e = \widehat{e}(Y), \quad \mathbf{q} = \widehat{\mathbf{q}}(Y), \tag{2.2}$$

where Y denotes a set of independent constitutive variables (so-called state space) and $\widehat{\mathbf{S}}, \widehat{\mathbf{j}}, \widehat{r}, \widehat{e}, \widehat{\mathbf{q}}$ are smooth functions of their arguments. The set Y has to be chosen so that to reflect properly the material properties (see Section 2.3). As common we do not assume constitutive equations for the external sources $\mathbf{b}, \tau$ and g.

The entropy principle is used to derive restrictions on constitutive equations (2.2) and this way to select a class of thermodynamically consistent models.

We apply the entropy principle due to I. Müller [Mul85]. This principle states that there exists an entropy η and an entropy flux $\mathbf{\Psi}$ given by the constitutive equations

$$\eta = \widehat{\eta}(Y), \quad \mathbf{\Psi} = \widehat{\mathbf{\Psi}}(Y), \tag{2.3}$$

with smooth functions $\widehat{\eta}, \mathbf{\Psi}$ depending on the same set Y, such that for all solutions of the system of balance laws (2.1) with constitutive equations (2.2) (called thermodynamic processes) defined in a space-time domain $\Omega^{t_0} = \Omega \times (0, t_0)$ the following implication holds

$$\mathbf{b} = \mathbf{0},\ \tau = 0,\ g = 0 \text{ in } \Omega^{t_0} \Rightarrow \sigma := \dot{\eta} + \nabla \cdot \mathbf{\Psi} \geq 0 \text{ in } \Omega^{t_0}. \tag{2.4}$$

Remark 2.1. *We recall two stronger versions of the Müller entropy principle introduced in* [AltPaw96]. *They can be useful in the proofs of the existence of the multipliers in the exploitation of the entropy principle by means of the Lagrange multipliers method due to I. S. Liu* [Liu72].

In a slightly stronger version (2.4) is replaced by the following postulate: For all thermodynamic processes and all points $(\mathbf{x}, t) \in \Omega^{t_0}$ *it holds*

$$\mathbf{b}(\mathbf{x}, t) = \mathbf{0},\ \tau(\mathbf{x}, t) = 0,\ g(\mathbf{x}, t) = 0 \Rightarrow \sigma(\mathbf{x}, t) \geq 0. \tag{2.5}$$

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

$$\sigma \geq \sigma_0 \ \textit{in}\ \Omega^{t_0} \ \textit{and}\ \widehat{\sigma}_0(Y, \mathbf{0}, 0, 0) = 0. \tag{2.6}$$

for all variables Y. *This version of the entropy principle describes the way it is used by Coleman and Noll* [ColNol63] *where, however, in contrast to the entropy principle formulated above it is assumed that* $\mathbf{\Psi}$ *and* σ_0 *are given by explicit formulas.* ■

2.3. 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 (2.4), which holds for all thermodynamic processes, by an inequality (called entropy inequality) which is satisfied for arbitraty fields. This idea is due to I. S. Liu [Liu72].

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

$$\boldsymbol{\lambda}_{\mathbf{u}} = \widehat{\boldsymbol{\lambda}}_{\mathbf{u}}(Y), \quad \lambda_\chi = \widehat{\lambda}_\chi(Y), \quad \lambda_e = \widehat{\lambda}_e(Y) \tag{2.7}$$

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

$$\dot{\eta} + \nabla \cdot \mathbf{\Psi} - \boldsymbol{\lambda}_{\mathbf{u}} \cdot (\ddot{\mathbf{u}} - \nabla \cdot \mathbf{S}) - \lambda_\chi(\dot{\chi} + \nabla \cdot \mathbf{j} - r) - \lambda_e(\dot{e} + \nabla \cdot \mathbf{q} - \mathbf{S} \cdot \dot{\mathbf{F}}) \geq 0 \tag{2.8}$$

is satisfied for all fields corresponding to the state space Y.

Remark 2.2. *Entropy inequality* (2.8) *implies the entropy principle with the strongest property* (2.6), *that is for solutions of* (2.1) *it holds*

$$\sigma = \dot{\eta} + \nabla \cdot \Psi \geq \widehat{\lambda}_{\mathbf{u}}(Y) \cdot \mathbf{b} + \widehat{\lambda}_{\chi}(Y)\tau + \widehat{\lambda}_e(Y)g =: \widehat{\sigma}_0(Y, \mathbf{b}, \tau, g). \tag{2.9}$$

Hence, entropy inequality (2.8) implies all three versions of the entropy principle. ■

Remark 2.3. *In a rigorous approach it has to be proved that entropy principle* (2.4) *implies entropy inequality* (2.8). *The proof requires a characterization of admissible sets of the system of partial differential equations under consideration and the verification of the Liu lemma* [Liu72]. *For particular systems this question has been addressed in* [Liu72], [AltPaw96] *by means of the Cauchy–Kowalevsky theorem. Another approach to this question is to admit arbitrary sources in balance equations and postulate stronger version* (2.5) *of the entropy principle (see* [AltPaw96], *Sec. 4).* ■

As common in the literature (see e.g. [Wilm98]) in the present paper we do not prove the entropy inequality (2.8) but take its validity for granted.

2.4. State spaces for phase-field models.

For phase-field models governed by a first order gradient free energy $f = \widehat{f}(\mathbf{F}, \chi, \mathbf{D}\chi, \theta)$ the appropriate are the following state spaces which differ only by thermal variables:

$$\begin{aligned} Y_\theta &:= \{\mathbf{F}, \mathbf{DF}, \ldots, \mathbf{D}^M\mathbf{F}, \chi, \mathbf{D}\chi, \ldots, \mathbf{D}^K\chi, \theta, \mathbf{D}\theta, \ldots, D^L\theta, \chi_{,t}\}, \\ Y_e &:= \{\mathbf{F}, \mathbf{DF}, \ldots, \mathbf{D}^M\mathbf{F}, \chi, \mathbf{D}\chi, \ldots, \mathbf{D}^K\chi, e, \mathbf{D}e, \ldots, \mathbf{D}^Le, \chi_{,t}\}, \\ Y_\eta &:= \{\mathbf{F}, \mathbf{DF}, \ldots, \mathbf{D}^M\mathbf{F}, \chi, \mathbf{D}\chi, \ldots, \mathbf{D}^K\chi, \eta, \mathbf{D}\eta, \ldots, \mathbf{D}^L\eta, \chi_{,t}\} \end{aligned} \tag{2.10}$$

with integers M, K, L satisfying conditions $M, L \geq 1$ and $K \geq 2$. Here $\chi_{,t}$ denotes a variable corresponding to the time derivative $\dot{\chi}$,

$$\mathbf{D}^k\chi = (\chi_{,i_1\ldots i_k})_{i_1,\ldots,i_k=1,2,3}, \qquad 0 \leq k \leq K,$$

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

$$\nabla^k\chi = \left(\frac{\partial^k\chi}{\partial x_{i_1}\ldots\partial x_{i_k}}\right)_{i_1,\ldots,i_k=1,2,3},$$

similarly $\mathbf{D}^k\theta, \mathbf{D}^k e, \mathbf{D}^k\eta$. Further,

$$\mathbf{D}^m\mathbf{F} = (F_{ij,i_1\ldots i_m})_{i,j,i_1,\ldots,i_m=1,2,3}$$

is the $(2+m)$-th order tensor of variables corresponding to the m-th order gradient of tensor $\mathbf{F}$

$$\nabla^m \mathbf{F} = \left(\frac{\partial F_{ij}}{\partial x_{i_1} \ldots \partial x_{i_m}} \right)_{i,j,i_1,\ldots,i_m=1,2,3}.$$

We use the convention $\mathbf{D}^0\chi = \chi$.

Remark 2.4. *Tensor $\mathbf{F}$ and its gradients represent mechanical properties, χ and its gradients – chemical properties due to material heterogeneity, θ, e, η and their gradients – thermal properties, and $\chi_{,t}$ – viscous effects due to material heterogeneity.*

The distinguishing elements in (2.10) are variables corresponding to higher order space derivatives and the nonstationary variable $\chi_{,t}$. In [Paw00a] *it has been shown that in order to admit the free energy depending on $\mathbf{D}^p\chi, p \in \mathbb{N}$, the set of constitutive variables has to include $\mathbf{D}^{p-1}\chi_{,t}$. Since our goal in the present paper is to construct models with free energy depending at most on $\mathbf{D}\chi$ we must admit $\chi_{,t}$ as a constitutive variable.*

The kinetic variable $\chi_{,t}$ appears also in Fried–Gurtin's theory based on a microforce balance, see e.g. [FriGur93], [Gur96]. *In this theory $\chi_{,t}$ is related to the working of internal microforces.*

The higher gradients of $\mathbf{F}, \chi, \theta$ (or e, η) arise due to the first variation $\delta f/\delta\chi$ which appears in the model. In particular, in case $f = \widehat{f}(\mathbf{F}, \chi, \mathbf{D}\chi, \theta)$,

$$\begin{aligned}\frac{\delta f}{\delta \chi} &= f_{,\chi} - \nabla \cdot f_{,\mathbf{D}\chi} \\ &= f_{,\chi} - \sum_{i=1}^{3} (f_{,\chi_{,i}\mathbf{F}} \cdot \mathbf{F}_{,i} + f_{,\chi_{,i}\chi}\chi_{,i} + f_{,\chi_{,i}\theta}\theta_{,i}) - \sum_{i,j=1}^{3} f_{,\chi_{,i}\chi_{,j}}\chi_{,ji},\end{aligned}$$

which generates the variables $\mathbf{DF}, \mathbf{D}\chi, \mathbf{D}^2\chi, \mathbf{D}\theta$ in the state space Y_θ. For the clarity of further presentation we admit in (2.10) $M, L \geq 1$ and $K \geq 2$. ■

Remark 2.5. *The arbitrariness in the choice Y_θ, Y_e or Y_η results from the duality relations (Legendre transformations) presented in Section 2.5. We have found the choices of the state spaces Y_e and Y_η more straightforward for the exploitation of the entropy inequality in comparison with the space Y_θ. We mention that in some particular situations the state space Y_e has been used in* [Paw00b], *Y_η in* [Paw00c] *and Y_θ in* [AltPaw95]. ■

Remark 2.6. *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 $\mathbf{C}$. However, as underlined in* [Gur96] *the exploitation of the second principle is simpler using deformation gradient $\mathbf{F}$ as the constitutive variable.*

The restrictions imposed by the frame indifference are accounted for after deriving consequences from the second principle. ■

In Section 3 we shall work with the state space

$$Y \equiv Y_\eta. \tag{2.11}$$

In such a case the internal energy $\widetilde{e} = \widehat{\widetilde{e}}(\mathbf{F}, \chi, \mathbf{D}\chi, \eta)$ expressed as a function of entropy η will play the role of a thermodynamical potential. In view of the duality relations such potential is equivalent to the free energy $f = \widehat{f}(\mathbf{F}, \chi, \mathbf{D}\chi, \theta)$ (see Section 2.5). For later purposes let us split the state space

$$Y_\eta = \{Y^0, Y^1\} \tag{2.12}$$

into two subsets

$$Y^0 := \{\mathbf{F}, \mathbf{DF}, \dots, \mathbf{D}^M\mathbf{F}, \chi, \mathbf{D}\chi, \dots, \mathbf{D}^K\chi, \eta, \mathbf{D}\eta, \dots, \mathbf{D}^L\eta\} \tag{2.13}$$

and

$$Y^1 := \{\chi_{,t}\},$$

which dinstinguish between stationary variables and the nonstationary one vanishing at equilibrium. According to (2.2) the constitutive equations are

$$\mathbf{S} = \widehat{\mathbf{S}}(Y_\eta), \quad \mathbf{j} = \widehat{\mathbf{j}}(Y_\eta), \quad r = \widehat{r}(Y_\eta), \quad \widetilde{e} = \widehat{\widetilde{e}}(Y_\eta), \quad \mathbf{q} = \widehat{\mathbf{q}}(Y_\eta), \tag{2.14}$$

where $\widehat{\mathbf{S}}, \widehat{\mathbf{j}}, \widehat{r}, \widehat{\widetilde{e}}, \widehat{\mathbf{q}}$ are smooth functions of their arguments and $\widehat{\widetilde{e}}$ denotes the internal energy expressed as a function of the entropy η.

Because of the presence of tensors of order higher than one we supplement (2.14) by the following convention: Any constitutive function defined on the set Y_η, say $\widehat{\mathbf{j}}(Y_n)$, is understood in the sense of the following extension:

$$\begin{aligned}\widehat{\mathbf{j}}(F_{ij}, \dots, \mathbf{A}_{ij}^m + (\mathbf{A}_{ij}^m)^{skew}, \dots, \chi, \dots,\\ \mathbf{B}^k + (\mathbf{B}^k)^{skew}, \dots, \eta, \dots, \mathbf{C}^l + (\mathbf{C}^l)^{skew}, \dots)\\ = \widehat{\mathbf{j}}(F_{ij}, \dots, \mathbf{A}_{ij}^m, \dots, \chi, \dots, \mathbf{B}^k, \dots, \eta, \dots, \mathbf{C}^l, \dots),\end{aligned}$$

where $\mathbf{A}_{ij}^m$ with $2 \le m \le M$, $i, j = 1, 2, 3$, stands for the m-th order tensor corresponding to $\mathbf{D}^m F_{ij}$, $\mathbf{B}^k$ with $2 \le k \le K$ for the k-th order tensor corresponding to $\mathbf{D}^k\chi$, and $\mathbf{C}^l$ with $2 \le l \le L$ for the l-th order tensor corresponding to $\mathbf{D}^l\eta$, and where $(\mathbf{A}_{ij}^m)^{skew}$, $(\mathbf{B}^k)^{skew}$, $(\mathbf{C}^l)^{skew}$ denote respectively the skew parts of $\mathbf{A}_{ij}^m, \mathbf{B}^k$ and $\mathbf{C}^l$.

Such extension is used for all other constitutive functions. Consequently, for instance in case of $\mathbf{D}^2\chi$, we can treat the variables $\chi_{,ij}$ and $\chi_{,ji}$ as independent despite of the 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 Theorems 3.1 and 5.1.

2.5. Basic thermodynamic relations.

We present here some basic relations for continua characterized by a first order gradient free energy density

$$f = \widehat{f}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta). \tag{2.15}$$

In particular, we recall from [AltPaw96] the duality relations generalizing the classical Legendre transformations to the case of gradient energy (2.15).

Throughout this section, in order to avoid confusion, we distinguish between functions and their values by using superimposed "$\wedge$" symbol for functions. Let

$$\vartheta := \frac{1}{\theta} > 0 \tag{2.16}$$

denote the inverse temperature, and

$$\widehat{\phi}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta) := \vartheta \widehat{f}\left(\mathbf{F}, \chi, \mathrm{D}\chi, \frac{1}{\vartheta}\right), \tag{2.17}$$

or equivalently

$$\widehat{\phi}\left(\mathbf{F}, \chi, \mathrm{D}\chi, \frac{1}{\theta}\right) := \frac{1}{\theta}\widehat{f}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta),$$

be the rescaled free energy, known as the Massieu function (see e.g. [Silh97], Sec. 10.2.2).

The lemma below gives equivalent statements of the thermodynamic Gibbs relation formulated alternatively in terms of the free energy $f = \widehat{f}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta)$ or the rescaled free energy $\phi = \widehat{\phi}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta)$.

Lemma 2.1. *The Gibbs relation*

$$\begin{aligned} &\widehat{e}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta) - \widehat{f}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta) = \theta \widehat{\eta}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta), \\ &\widehat{\eta}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta) = -\widehat{f}_{,\theta}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta) \end{aligned} \tag{2.18}$$

is equivalent to

$$\begin{aligned} &\widehat{\phi}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta) + \widehat{\overline{\eta}}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta) = \vartheta \widehat{\overline{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta), \\ &\widehat{\overline{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta) = \widehat{\phi}_{,\vartheta}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta), \end{aligned} \tag{2.19}$$

where

$$\begin{aligned} &\widehat{\overline{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta) := \widehat{e}\left(\mathbf{F}, \chi, \mathrm{D}\chi, \frac{1}{\vartheta}\right), \\ &\widehat{\overline{\eta}}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta) := \widehat{\eta}\left(\mathbf{F}, \chi, \mathrm{D}\chi, \frac{1}{\vartheta}\right), \quad \vartheta = \frac{1}{\theta}. \end{aligned}$$

Proof. (2.18)$\Rightarrow$(2.19)
Relation $(2.19)_1$ results from $(2.18)_1$ directly on account of the definitions of $\vartheta, \phi, \overline{e}$ and $\overline{\eta}$. The equalities

$$\begin{aligned}
\widehat{\phi}_{,\vartheta}(\mathbf{F},\chi,\mathbf{D}\chi,\vartheta) &= \left(\vartheta\widehat{f}\left(\mathbf{F},\chi,\mathbf{D}\chi,\frac{1}{\vartheta}\right)\right)_{,\vartheta} \\
&= \widehat{f}\left(\mathbf{F},\chi,\mathbf{D}\chi,\frac{1}{\vartheta}\right) + \vartheta\widehat{f}_{,\theta}(\mathbf{F},\chi,\mathbf{D}\chi,\theta)\cdot\left(-\frac{1}{\vartheta^2}\right) \\
&= \widehat{f}(\mathbf{F},\chi,\mathbf{D}\chi,\theta) - \theta\widehat{f}_{,\theta}(\mathbf{F},\chi,\mathbf{D}\chi,\theta) \\
&\underset{(2.18)_2}{=} \widehat{f}(\mathbf{F},\chi,\mathbf{D}\chi,\theta) + \theta\widehat{\eta}(\mathbf{F},\chi,\mathbf{D}\chi,\theta) \\
&\underset{(2.18)_1}{=} \widehat{e}(\mathbf{F},\chi,\mathbf{D}\chi,\theta) = \widehat{\overline{e}}(\mathbf{F},\chi,\mathbf{D}\chi,\vartheta)
\end{aligned}$$

show that (2.18) implies $(2.19)_2$.

(2.18)$\Leftarrow$(2.19)
Relation $(2.18)_1$ results from $(2.19)_1$ directly by the definitions of $\vartheta, \phi, \overline{e}$ and $\overline{\eta}$. The equalities

$$\begin{aligned}
\widehat{f}_{,\theta}(\mathbf{F},\chi,\mathbf{D}\chi,\theta) &= \left(\theta\widehat{\phi}\left(\mathbf{F},\chi,\mathbf{D}\chi,\frac{1}{\theta}\right)\right)_{,\theta} \\
&= \widehat{\phi}\left(\mathbf{F},\chi,\mathbf{D}\chi,\frac{1}{\theta}\right) + \theta\widehat{\phi}_{,\vartheta}(\mathbf{F},\chi,\mathbf{D}\chi,\vartheta)\cdot\left(-\frac{1}{\theta^2}\right) \\
&= \widehat{\phi}(\mathbf{F},\chi,\mathbf{D}\chi,\vartheta) - \vartheta\widehat{\phi}_{,\vartheta}(\mathbf{F},\chi,\mathbf{D}\chi,\vartheta) \\
&\underset{(2.19)_2}{=} \widehat{\phi}(\mathbf{F},\chi,\mathbf{D}\chi,\vartheta) + \vartheta\widehat{\overline{e}}(\mathbf{F},\chi,\mathbf{D}\chi,\vartheta) \\
&\underset{(2.19)_1}{=} -\widehat{\overline{\eta}}(\mathbf{F},\chi,\mathbf{D}\chi,\vartheta) = -\widehat{\eta}(\mathbf{F},\chi,\mathbf{D}\chi,\theta)
\end{aligned}$$

show that (2.19) implies $(2.18)_2$. This completes the proof. ■

Let us introduce now, in accordance with the classical definition (see e.g. [Wood75], p. 31), the specific heat coefficient (heat capacity) by

$$c_0 = \widehat{c}_0(\mathbf{F},\chi,\mathbf{D}\chi,\theta) := \widehat{e}_{,\theta}(\mathbf{F},\chi,\mathbf{D}\chi,\theta). \tag{2.20}$$

Due to Gibbs relation (2.18), (2.19) the equivalent expressions for c_0 are as follows:

$$\begin{aligned}
\widehat{c}_0(\mathbf{F},\chi,\mathbf{D}\chi,\theta) &\underset{(2.18)_1}{=} (\widehat{f}(\mathbf{F},\chi,\mathbf{D}\chi,\theta) + \theta\widehat{\eta}(\mathbf{F},\chi,\mathbf{D}\chi,\theta))_{,\theta} \\
&\underset{(2.18)_2}{=} \theta\widehat{\eta}_{,\theta}(\mathbf{F},\chi,\mathbf{D}\chi,\theta) \\
&\underset{(2.18)_2}{=} -\theta\widehat{f}_{,\theta\theta}(\mathbf{F},\chi,\mathbf{D}\chi,\theta),
\end{aligned} \tag{2.21}$$

and

$$
\begin{aligned}
(2.22)\quad \widehat{\overline{c}}_0(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta) &:= \widehat{c}_0\left(\mathbf{F},\chi,\mathrm{D}\chi,\frac{1}{\vartheta}\right)\\
&= -\vartheta^2\widehat{\overline{e}}_{,\vartheta}(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta)\\
&\underset{(2.19)_2}{=} -\vartheta^2\widehat{\phi}_{,\vartheta\vartheta}(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta)\\
&= -\vartheta(\vartheta\widehat{\overline{e}}_{,\vartheta}(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta))\\
&\underset{(2.19)_1}{=} -\vartheta(\widehat{\phi}_{,\vartheta}(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta)\\
&\qquad +\widehat{\overline{\eta}}_{,\vartheta}(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta)-\widehat{\overline{e}}(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta))\\
&\underset{(2.19)_2}{=} -\vartheta\widehat{\overline{\eta}}_{,\vartheta}(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta).
\end{aligned}
$$

We shall assume now the standard thermodynamic condition

$$(2.23)\qquad \widehat{c}_0(\mathbf{F},\chi,\mathrm{D}\chi,\theta)>0$$

which is known as a thermal stability (see e.g. [Wood75], p. 34). In such a case the duality relations generalizing the classical Legendre tranformations to the case of gradient type potentials hold true. They allow to use alternatively the absolute temperature θ (or the inverse temperature ϑ), the entropy η or the internal energy $\overline{e}$ as independent thermal variables.

Firstly, let us note that as a direct consequence of relations in (2.21), (2.22) we have

Lemma 2.2. *Assume Gibbs relations* (2.18), (2.19). *Then the following statements are equivalent:*

(i) $\widehat{c}_0(\mathbf{F},\chi,\mathrm{D}\chi,\theta)>0$ *and* $\theta>0$,
(ii) $\widehat{e}(\mathbf{F},\chi,\mathrm{D}\chi,\theta)$ *is strictly increasing in* θ,
(iii) $\widehat{\eta}(\mathbf{F},\chi,\mathrm{D}\chi,\theta)$ *is strictly increasing in* θ,
(iv) $\widehat{f}(\mathbf{F},\chi,\mathrm{D}\chi,\theta)$ *is strictly concave in* θ,
(v) $\widehat{\overline{e}}(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta)$ *is strictly decreasing in* ϑ,
(vi) $\widehat{\overline{\eta}}(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta)$ *is strictly decreasing in* ϑ,
(vii) $\widehat{\phi}(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta)$ *is strictly concave in* ϑ.

In Lemma 2.3 below we present the dual formulations of Gibbs relations (2.18), (2.19) expressed respectively with respect to entropy η and internal energy $\overline{e}$ as independent thermal variables.

Under thermodynamic condition (2.23), it follows from Lemma 2.2 (iv), (vii) that $\theta\mapsto -\widehat{f}(\mathbf{F},\chi,\mathrm{D}\chi,\theta)$ is a strictly convex function and $\vartheta\mapsto\widehat{\phi}(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta)$ is a strictly concave function. Therefore the following conjugate functions are well-defined:

– the conjugate convex function

$$\widehat{\widehat{e}}(\mathbf{F},\chi,\mathrm{D}\chi,\eta) := \sup_{0<\overline{\theta}<+\infty} \{\overline{\theta}\eta + \widehat{f}(\mathbf{F},\chi,\mathrm{D}\chi,\theta)\} \le +\infty, \tag{2.24}$$

which is a lower semicontinuous strictly convex function of $\eta \in \mathbb{R}$, and

– the conjugate concave function

$$\widehat{\widehat{\eta}}(\mathbf{F},\chi,\mathrm{D}\chi,\overline{e}) := \inf_{0<\overline{\vartheta}<+\infty} \{\overline{\vartheta}\overline{e} - \widehat{\phi}(\mathbf{F},\chi,\mathrm{D}\chi,\overline{\vartheta})\} \ge -\infty, \tag{2.25}$$

which is an upper semicontinuous strictly concave function of $\overline{e} \in \mathbb{R}$.

Lemma 2.3. *Assume Gibbs relations* (2.18), (2.19) *and the condition* $\widehat{c}_0(\mathbf{F},\chi,\mathrm{D}\chi,\theta) > 0$. *Let the conjugate functions* $\widehat{\widehat{e}}(\mathbf{F},\chi,\mathrm{D}\chi,\eta)$ *and* $\widehat{\widehat{\eta}}(\mathbf{F},\chi,\mathrm{D}\chi,\overline{e})$ *be defined respectively by (2.24) and (2.25). Then the unique supremum in (2.24) is attained at*

$$\theta = \widehat{\theta}(\mathbf{F},\chi,\mathrm{D}\chi,\eta),$$

and is characterized by the following relations

$$\begin{aligned} &\widehat{\widehat{e}}(\mathbf{F},\chi,\mathrm{D}\chi,\eta) - \widehat{f}(\mathbf{F},\chi,\mathrm{D}\chi,\theta) = \theta\eta, \\ &\widehat{\widehat{e}}_{,\eta}(\mathbf{F},\chi,\mathrm{D}\chi,\eta) = \theta. \end{aligned} \tag{2.26}$$

The unique infimum in (2.25) is attained at

$$\vartheta = \widehat{\vartheta}(\mathbf{F},\chi,\mathrm{D}\chi,\overline{e}),$$

and is characterized by

$$\begin{aligned} &\widehat{\widehat{\eta}}(\mathbf{F},\chi,\mathrm{D}\chi,\overline{e}) + \widehat{\phi}(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta) = \vartheta\overline{e}, \\ &\widehat{\widehat{\eta}}_{,\overline{e}}(\mathbf{F},\chi,\mathrm{D}\chi,\overline{e}) = \vartheta. \end{aligned} \tag{2.27}$$

Proof. By Lemma 2.2 (iii) the map $\theta \mapsto \widehat{\eta}(\mathbf{F},\chi,\mathrm{D}\chi,\theta)$ is strictly increasing. Therefore, there exists the inverse map

$$\eta \mapsto \widehat{\theta}(\mathbf{F},\chi,\mathrm{D}\chi,\eta), \tag{2.28}$$

and the property $0 < \theta < +\infty$ is equivalent to $\eta_* < \eta < \eta^*$ with $\eta_* = \widehat{\eta}_*(\mathbf{F},\chi,\mathrm{D}\chi) \ge -\infty$ and $\eta_* = \widehat{\eta}_*(\mathbf{F},\chi,\mathrm{D}\chi) \le +\infty$. If $\eta_* < \eta < \eta^*$ then the supremum in (2.24) is uniquely attained at

$$\theta = \widehat{\theta}(\mathbf{F},\chi,\mathrm{D}\chi,\eta),$$

and then

$$\widehat{\widehat{e}}(\mathbf{F},\chi,\mathrm{D}\chi,\eta) = \theta\eta + \widehat{f}(\mathbf{F},\chi,\mathrm{D}\chi,\theta).$$

This shows $(2.26)_1$. To deduce $(2.26)_2$ note that the supremum in (2.24) implies the condition

$$\eta = -\widehat{f}_{,\theta}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta). \tag{2.29}$$

Hence, from $(2.26)_1$ and (2.28), (2.29) it follows that

$$\widetilde{e}_{,\eta}(\mathbf{F}, \chi, \mathrm{D}\chi, \eta) + \eta\widehat{\theta}_{,\eta}(\mathbf{F}, \chi, \mathrm{D}\chi, \eta) = \theta + \eta\widehat{\theta}_{,\eta}(\mathbf{F}, \chi, \mathrm{D}\chi, \eta)$$

which actually shows $(2.26)_2$.

We shall prove now (2.27). By Lemma 2.2(v), the map $\vartheta \mapsto \overline{e}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta)$ is strictly decreasing. Therefore there exists the inverse map

$$\overline{e} \mapsto \widehat{\vartheta}(\mathbf{F}, \chi, \mathrm{D}\chi, \overline{e}), \tag{2.30}$$

and the property $0 < \vartheta < +\infty$ is equivalent to $e_* < \overline{e} < e^*$ with $e_* = \widehat{e}_*(\mathbf{F}, \chi, \mathrm{D}\chi) \geq -\infty$ and $e^* = \widehat{e}^*(\mathbf{F}, \chi, \mathrm{D}\chi) \leq +\infty$. If $e_* < \overline{e} < e^*$ then the infimum in (2.25) is uniquely attained at

$$\vartheta = \widehat{\vartheta}(\mathbf{F}, \chi, \mathrm{D}\chi, \overline{e}),$$

and then

$$\widetilde{\eta}(\mathbf{F}, \chi, \mathrm{D}\chi, \overline{e}) = \vartheta\overline{e} - \widehat{\phi}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta).$$

This shows $(2.27)_1$. To conclude $(2.27)_2$ note that the infimum in (2.25) is characterized by

$$\overline{e} = \widehat{\phi}_{,\vartheta}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta). \tag{2.31}$$

Hence, $(2.27)_1$ and (2.30), (2.31) imply that

$$\widetilde{\eta}_{,\overline{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \overline{e}) + \overline{e}\widehat{\vartheta}_{,\overline{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \overline{e}) = \vartheta + \overline{e}\widehat{\vartheta}_{,\overline{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \overline{e})$$

which shows $(2.27)_2$. This completes the proof. ∎

Let us note that in view of Gibbs relation $(2.18)_1$ the equality $(2.26)_1$ implies that

$$\widehat{e}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta) = \widetilde{e}(\mathbf{F}, \chi, \mathrm{D}\chi, \widehat{\eta}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta)) \tag{2.32}$$

which shows that $\widetilde{e}$ is the internal energy expressed as a function of the entropy η.

Moreover, differentiating $(2.26)_1$, with respect to θ we see that

$$\widetilde{e}_{,\eta}\eta_{,\theta} - f_{,\theta} = \eta + \theta\eta_{,\theta}$$

with appropriate arguments. Hence, by virtue of $(2.26)_2$, it follows that

$$\widehat{\eta}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta) = -\widehat{f}_{,\theta}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta), \tag{2.33}$$

that is Gibbs relation $(2.18)_2$.

Similarly, in view $(2.19)_1$ it follows from (2.27) that

$$\widehat{\eta}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta) = \widehat{\widetilde{\eta}}(\mathbf{F}, \chi, \mathrm{D}\chi, \widehat{\overline{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta)) \tag{2.34}$$

which shows that $\widetilde{\eta}$ is the entropy expressed as a function of the internal energy $\overline{e}$. Moreover, differentiating $(2.27)_1$ with respect to ϑ leads to

$$\widetilde{\eta}_{,\overline{e}}\overline{e}_{,\vartheta} + \phi_{,\vartheta} = \overline{e} + \vartheta\overline{e}_{,\vartheta}$$

with appropriate arguments. Hence, on account of $(2.27)_2$, it follows that

$$\widehat{\overline{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta) = \widehat{\phi}_{,\vartheta}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta), \tag{2.35}$$

that is Gibbs relation $(2.19)_2$.

The above considerations show that under assumption of thermal stability $c_0 > 0$ the statements in Lemmas 2.1 and 2.3 are equivalent.

The presented duality relations allow to use instead of temperature θ (or inverse temperature ϑ) the entropy η or the internal energy $\overline{e}$ as thermal variables.

If η is considered as an independent variable then we have to insert into all constitutive equations the relation

$$\theta = \widehat{\theta}(\mathbf{F}, \chi, \mathrm{D}\chi, \eta),$$

together with the corresponding expression for the space derivatives

$$\theta_{,i} = \widehat{\theta}_{,\mathbf{F}} \cdot \mathbf{F}_{,i} + \widehat{\theta}_{,\chi}\chi_{,i} + \widehat{\theta}_{,\mathrm{D}\chi} \cdot \mathrm{D}\chi_{,i} + \widehat{\theta}_{,\eta}\eta_{,i}, \tag{2.36}$$

which is equivalent to

$$\eta_{,i} = \widehat{\eta}_{,\mathbf{F}} \cdot \mathbf{F}_{,i} + \widehat{\eta}_{,\chi}\chi_{,i} + \widehat{\eta}_{,\mathrm{D}\chi} \cdot \mathrm{D}\chi_{,i} + \widehat{\eta}_{,\theta}\theta_{,i}.$$

Similarly, choosing $\overline{e}$ as an independent variable we have to insert into constitutive equations

$$\vartheta = \widehat{\vartheta}(\mathbf{F}, \chi, \mathrm{D}\chi, \overline{e}),$$

and

$$\vartheta_{,i} = \widehat{\vartheta}_{,\mathbf{F}} \cdot \mathbf{F}_{,i} + \widehat{\vartheta}_{,\chi}\chi_{,i} + \widehat{\vartheta}_{,\mathrm{D}\chi} \cdot \mathrm{D}\chi_{,i} + \widehat{\vartheta}_{,\overline{e}}\overline{e}_{,i}, \tag{2.37}$$

which is equivalent to

$$\overline{e}_{,i} = \widehat{\overline{e}}_{,\mathbf{F}} \cdot \mathbf{F}_{,i} + \widehat{\overline{e}}_{,\chi}\chi_{,i} + \widehat{\overline{e}}_{,\mathrm{D}\chi} \cdot \mathrm{D}\chi_{,i} + \widehat{\overline{e}}_{,\vartheta}\vartheta_{,i}.$$

At this point it is of interest to note that if $\widehat{\eta}$ does not depend on $\mathrm{D}\chi$ (in Section 6 such a case is called energetic one) then the transformation between η and θ does not involve $\mathrm{D}\chi$, and the transformation between $\mathrm{D}\eta$ and $\mathrm{D}\theta$ does not involve $\mathrm{D}^2\chi$. Similarly, if $\widehat{\overline{e}}$ does not depend on $\mathrm{D}\chi$ (in Section 6 such a case is called entropic one) then the transformation between $\overline{e}$ and ϑ

does not involve $\mathrm{D}\chi$, and the transformation between $\mathrm{D}\overline{e}$ and $\mathrm{D}\vartheta$ does not involve $\mathrm{D}^2\chi$.

Below we express the specific heat coefficient in terms of the entropy and internal energy as independent variables.

Lemma 2.4. *Assume that duality relations* (2.26), (2.27) *hold.*

$$\begin{aligned}(2.38)\quad \widehat{c}_0(\mathbf{F},\chi,\mathrm{D}\chi,\theta)\Big|_{\theta=\widehat{\theta}(\mathbf{F},\chi,\mathrm{D}\chi,\eta)} &= -\theta\widehat{f}_{,\theta\theta}(\mathbf{F},\chi,\mathrm{D}\chi,\theta)\Big|_{\theta=\widehat{\theta}(\mathbf{F},\chi,\mathrm{D}\chi,\eta)}\\ &= \widehat{\theta}(\mathbf{F},\chi,\mathrm{D}\chi,\eta)\frac{1}{\widehat{\widehat{e}}_{,\eta\eta}(\mathbf{F},\chi,\mathrm{D}\chi,\eta)},\end{aligned}$$

and

$$\begin{aligned}(2.39)\quad \widehat{\widehat{c}}_0(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta)\Big|_{\vartheta=\widehat{\vartheta}(\mathbf{F},\chi,\mathrm{D}\chi,\overline{e})} &= -\vartheta^2\widehat{\phi}_{,\vartheta\vartheta}(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta)\Big|_{\vartheta=\widehat{\vartheta}(\mathbf{F},\chi,\mathrm{D}\chi,\overline{e})}\\ &= -\widehat{\vartheta}^2(\mathbf{F},\chi,\mathrm{D}\chi,\overline{e})\frac{1}{\widehat{\widehat{\eta}}_{,\overline{e}\,\overline{e}}(\mathbf{F},\chi,\mathrm{D}\chi,\overline{e})}.\end{aligned}$$

Proof. By $(2.21)_2$ and $(2.26)_2$ we have

$$\begin{aligned}\widehat{c}_0(\mathbf{F},\chi,\mathrm{D}\chi,\theta)\Big|_{\theta=\widehat{\theta}(\mathbf{F},\chi,\mathrm{D}\chi,\eta)} &\underset{(2.21)_2}{=} \theta\widehat{\eta}_{,\theta}(\mathbf{F},\chi,\mathrm{D}\chi,\theta)\Big|_{\theta=\widehat{\theta}(\mathbf{F},\chi,\mathrm{D}\chi,\eta)}\\ &= \widehat{\theta}(\mathbf{F},\chi,\mathrm{D}\chi,\eta)\frac{1}{\widehat{\theta}_{,\eta}(\mathbf{F},\chi,\mathrm{D}\chi,\eta)}\\ &\underset{(2.26)_2}{=} \widehat{\theta}(\mathbf{F},\chi,\mathrm{D}\chi,\eta)\frac{1}{\widehat{\widehat{e}}_{,\eta\eta}(\mathbf{F},\chi,\mathrm{D}\chi,\eta)}\end{aligned}$$

which shows (2.38).

Similarly, by $(2.22)_2$ and $(2.27)_2$,

$$\begin{aligned}\widehat{\widehat{c}}_0(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta)\Big|_{\vartheta=\widehat{\vartheta}(\mathbf{F},\chi,\mathrm{D}\chi,\overline{e})} &\underset{(2.22)_2}{=} -\vartheta^2\widehat{\widehat{e}}_{,\vartheta}(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta)\Big|_{\vartheta=\widehat{\vartheta}(\mathbf{F},\chi,\mathrm{D}\chi,\overline{e})}\\ &= -\widehat{\vartheta}^2(\mathbf{F},\chi,\mathrm{D}\chi,\overline{e})\frac{1}{\widehat{\vartheta}_{,\overline{e}}(\mathbf{F},\chi,\mathrm{D}\chi,\overline{e})}\\ &\underset{(2.27)_2}{=} -\widehat{\vartheta}^2(\mathbf{F},\chi,\mathrm{D}\chi,\overline{e})\frac{1}{\widehat{\widehat{\eta}}_{,\overline{e}\,\overline{e}}(\mathbf{F},\chi,\mathrm{D}\chi,\overline{e})}.\end{aligned}$$

This shows (2.39) and completes the proof. ■

For further use we recall also the formulas which relate the first variations with respect to the order parameter χ of the thermodynamical potentials $\widehat{f}(\mathbf{F},\chi,\mathrm{D}\chi,\theta)$, $\widehat{\phi}(\mathbf{F},\chi,\mathrm{D}\chi,\vartheta)$, $\widehat{\widehat{e}}(\mathbf{F},\chi,\mathrm{D}\chi,\eta)$ and $\widehat{\widehat{\eta}}(\mathbf{F},\chi,\mathrm{D}\chi,\overline{e})$.

Lemma 2.5. *The following relations are satisfied*

$$(2.40)\quad \begin{aligned} \frac{\delta \widehat{f}}{\delta \widehat{\chi}}(\mathbf{F},\mathbf{DF},\chi,\mathbf{D}\chi,\mathbf{D}^2\chi,\theta,\mathbf{D}\theta) &= \frac{\delta \widehat{\widehat{e}}}{\delta \chi}(\mathbf{F},\mathbf{DF},\chi,\mathbf{D}\chi,\mathbf{D}^2\chi,\eta,\mathbf{D}\eta),\\ \frac{\delta \widehat{\phi}}{\delta \chi}(\mathbf{F},\mathbf{DF},\chi,\mathbf{D}\chi,\mathbf{D}^2\chi,\vartheta,\mathbf{D}\vartheta) &= -\frac{\delta \widehat{\widehat{\eta}}}{\delta \chi}(\mathbf{F},\mathbf{DF},\chi,\mathbf{D}\chi,\mathbf{D}^2\chi,\overline{e},\mathbf{D}\overline{e}),\end{aligned}$$

where $\theta, \mathbf{D}\theta$ *and* $\eta, \mathbf{D}\eta$ *are related by the formulas*

$$\begin{aligned} &\theta = \widehat{\theta}(\mathbf{F},\chi,\mathbf{D}\chi,\eta),\\ &\theta_{,i} = \widehat{\theta}_{,\mathbf{F}}\cdot\mathbf{F}_{,i} + \widehat{\theta}_{,\chi}\chi_{,i} + \widehat{\theta}_{,\mathbf{D}\chi}\cdot\mathbf{D}\chi_{,i} + \widehat{\theta}_{,\eta}\eta_{,i},\end{aligned}$$

and $\vartheta, \mathbf{D}\vartheta$ *and* $\overline{e}, \mathbf{D}\overline{e}$ *by*

$$\begin{aligned} &\vartheta = \widehat{\vartheta}(\mathbf{F},\chi,\mathbf{D}\chi,\overline{e}),\\ &\vartheta_{,i} = \widehat{\vartheta}_{,\mathbf{F}}\cdot\mathbf{F}_{,i} + \widehat{\vartheta}_{,\chi}\chi_{,i} + \widehat{\vartheta}_{,\mathbf{D}\chi}\cdot\mathbf{D}\chi_{,i} + \widehat{\vartheta}_{,\overline{e}}\overline{e}_{,i}.\end{aligned}$$

Proof (see [AltPaw96], Sec. 11). We use duality relations (2.26), (2.27). From $(2.26)_1$ it follows that

$$\widehat{f}(\mathbf{F},\chi,\mathbf{D}\chi,\theta) = -\theta\widehat{\eta}(\mathbf{F},\chi,\mathbf{D}\chi,\theta) + \widehat{\widehat{e}}(\mathbf{F},\chi,\mathbf{D}\chi,\widehat{\eta}(\mathbf{F},\chi,\mathbf{D}\chi,\theta)).$$

Hence, using $(2.26)_2$, we infer the equalities

$$(2.41)\quad \begin{aligned} \widehat{f}_{,\mathbf{F}} &= -\theta\widehat{\eta}_{,\mathbf{F}} + \widehat{\widehat{e}}_{,\mathbf{F}} + \widehat{\widehat{e}}_{,\eta}\widehat{\eta}_{,\mathbf{F}} = \widehat{\widehat{e}}_{,\mathbf{F}},\\ \widehat{f}_{,\chi} &= -\theta\widehat{\eta}_{,\chi} + \widehat{\widehat{e}}_{,\chi} + \widehat{\widehat{e}}_{,\eta}\widehat{\eta}_{,\chi} = \widehat{\widehat{e}}_{,\chi},\\ \widehat{f}_{,\mathbf{D}\chi} &= -\theta\widehat{\eta}_{,\mathbf{D}\chi} + \widehat{\widehat{e}}_{,\mathbf{D}\chi} + \widehat{\widehat{e}}_{,\eta}\widehat{\eta}_{,\mathbf{D}\chi} = \widehat{\widehat{e}}_{,\mathbf{D}\chi}\end{aligned}$$

with appropriate arguments. From $(2.41)_{2,3}$ we deduce that

$$\frac{\delta\widehat{f}}{\delta\chi} = \widehat{f}_{,\chi} - \nabla\cdot\widehat{f}_{,\mathbf{D}\chi} = \widehat{\widehat{e}}_{,\chi} - \nabla\cdot\widehat{\widehat{e}}_{,\mathbf{D}\chi} = \frac{\delta\widehat{\widehat{e}}}{\delta\chi},$$

which shows $(2.40)_1$.

Similarly, from $(2.27)_1$ it follows that

$$\widehat{\phi}(\mathbf{F},\chi,\mathbf{D}\chi,\vartheta) = \vartheta\widehat{\overline{e}}(\mathbf{F},\chi,\mathbf{D}\chi,\vartheta) - \widehat{\overline{\eta}}(\mathbf{F},\chi,\mathbf{D}\chi,\widehat{\overline{e}}(\mathbf{F},\chi,\mathbf{D}\chi,\vartheta)).$$

Hence using $(2.27)_2$ it follows that

$$(2.42)\quad \begin{aligned} \widehat{\phi}_{,\mathbf{F}} &= \vartheta\widehat{\overline{e}}_{,\mathbf{F}} - \widehat{\widehat{\eta}}_{,\mathbf{F}} - \widehat{\widehat{\eta}}_{,\overline{e}}\widehat{\overline{e}}_{,\mathbf{F}} = -\widehat{\widehat{\eta}}_{,\mathbf{F}},\\ \widehat{\phi}_{,\chi} &= \vartheta\widehat{\overline{e}}_{,\chi} - \widehat{\widehat{\eta}}_{,\chi} - \widehat{\widehat{\eta}}_{,\overline{e}}\widehat{\overline{e}}_{,\chi} = -\widehat{\widehat{\eta}}_{,\chi},\\ \widehat{\phi}_{,\mathbf{D}\chi} &= \vartheta\widehat{\overline{e}}_{,\mathbf{D}\chi} - \widehat{\widehat{\eta}}_{,\mathbf{D}\chi} - \widehat{\widehat{\eta}}_{,\overline{e}}\widehat{\overline{e}}_{,\mathbf{D}\chi} = -\widehat{\widehat{\eta}}_{,\mathbf{D}\chi},\end{aligned}$$

with appropriate arguments.

From $(2.42)_{2,3}$,

$$\frac{\delta\widehat{\phi}}{\delta\chi}=\widehat{\phi}_{,\chi}-\nabla\cdot\widehat{\phi}_{,\mathbf{D}\chi}=-\widehat{\widetilde{\eta}}_{,\chi}-\nabla\cdot\widehat{\widetilde{\eta}}_{,\mathbf{D}\chi}=-\frac{\delta\widehat{\widetilde{\eta}}}{\delta\chi}$$

which shows $(2.40)_2$. Thereby the proof is completed. ■

3. Evaluation of the entropy inequality – entropy as an independent variable

3.1. The entropy inequality.

Let us consider balance laws (2.1) with constitutive equations (2.14) and the state space Y_η defined by $(2.10)_3$:

$$\begin{aligned}&\ddot{\mathbf{u}}-\nabla\cdot\mathbf{S}=\mathbf{b},\\&\mathbf{S}\mathbf{F}^T=\mathbf{F}\mathbf{S}^T,\\&\dot{\chi}+\nabla\cdot\mathbf{j}-r=\tau,\\&\dot{\widetilde{e}}+\nabla\cdot\mathbf{q}-\mathbf{S}\cdot\dot{\mathbf{F}}=g,\end{aligned}$$

where

$$\begin{aligned}&\mathbf{S}=\widehat{\mathbf{S}}(Y_\eta),\quad \mathbf{j}=\widehat{\mathbf{j}}(Y_\eta),\quad r=\widehat{r}(Y_\eta),\quad \widetilde{e}=\widehat{\widetilde{e}}(Y_\eta),\quad \mathbf{q}=\widehat{\mathbf{q}}(Y_\eta),\\&Y_\eta=\{Y^0,Y^1\},\\&Y^0=\{\mathbf{F},\mathbf{D}\mathbf{F},\dots,\mathbf{D}^M\mathbf{F},\chi,\mathbf{D}\chi,\dots,\mathbf{D}^K\chi,\eta,\mathbf{D}\eta,\dots,\mathbf{D}^L\eta\},\\&Y^1=\{\chi_{,t}\}.\end{aligned}$$

To select a class of thermodynamically consistent models we impose the entropy inequality with multipliers (2.8) which in case of state variables Y_η reads as follows:

$$\dot{\eta}+\nabla\cdot\mathbf{\Psi}-\boldsymbol{\lambda}_{\mathbf{u}}\cdot(\ddot{\mathbf{u}}-\nabla\cdot\mathbf{S})-\lambda_\chi(\dot{\chi}+\nabla\cdot\mathbf{j}-r)-\lambda_e(\dot{\widetilde{e}}+\nabla\cdot\mathbf{q}-\mathbf{S}\cdot\dot{\mathbf{F}})\geq 0 \tag{3.1}$$

for all fields $\mathbf{u},\chi$ and η, where

$$\mathbf{\Psi}=\widehat{\mathbf{\Psi}}(Y_\eta),\quad \boldsymbol{\lambda}_{\mathbf{u}}=\widehat{\boldsymbol{\lambda}}_{\mathbf{u}}(Y_\eta),\quad \lambda_\chi=\widehat{\lambda}_\chi(Y_\eta),\quad \lambda_e=\widehat{\lambda}_e(Y_\eta) \tag{3.2}$$

are respectively the entropy flux and the multipliers conjugated with the balance laws for the linear momentum, order parameter and energy.

3.2. Algebraic preliminaries.

We prepare some simplifying notations. For $f=\widehat{f}(Y_\eta)$ a smooth scalar function of its arguments, we denote 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):

$$\partial_i^{Y^0} f := \sum_{m=0}^{M} f_{,\mathbf{D}^m\mathbf{F}} \cdot \mathbf{D}^m\mathbf{F}_{,i} + \sum_{k=0}^{K} f_{,\mathbf{D}^k\chi} \cdot \mathbf{D}^k\chi_{,i} + \sum_{l=0}^{L} f_{,\mathbf{D}^l\eta} \cdot \mathbf{D}^l\eta_{,i},$$

and by $\nabla^{Y^0} f = (\partial_i^{Y_0} f)_{i=1,2,3}$ the corresponding gradient ∇f restricted to the set Y^0.

Similarly, for a smooth vector-valued function $\mathbf{\Phi} = \widehat{\mathbf{\Phi}}(Y_\eta)$ with values in $\mathbb{R}^3$ we denote by $\nabla^{Y^0} \cdot \mathbf{\Phi}$ the algebraic version of the divergence $\nabla \cdot \mathbf{\Phi}$ restricted to the set Y^0, viz.

$$\nabla^{Y^0} \cdot \mathbf{\Phi} := \sum_{i=1}^{3} \left[\sum_{m=0}^{M} \Phi_{i,\mathbf{D}^m\mathbf{F}} \cdot \mathbf{D}^m\mathbf{F}_{,i} + \sum_{k=0}^{K} \Phi_{i,\mathbf{D}^k\chi} \cdot \mathbf{D}^k\chi_{,i} + \sum_{l=0}^{L} \Phi_{i,\mathbf{D}^l\eta} \cdot \mathbf{D}^l\eta_{,i} \right].$$

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

$$\begin{aligned} \widetilde{Y}^0 &:= Y^0 \setminus \{\mathbf{D}^M\mathbf{F}, \mathbf{D}^K\chi, \mathbf{D}^L\eta\} \\ &= \{\mathbf{F}, \mathbf{DF}, \dots, \mathbf{D}^{M-1}\mathbf{F}, \chi, \mathbf{D}\chi, \dots, \mathbf{D}^{K-1}\chi, \eta, \mathbf{D}\eta, \dots, \mathbf{D}^{L-1}\eta\}. \end{aligned} \tag{3.3}$$

For a function $f = \widehat{f}(Y_\eta)$ we denote by $\delta^{\widetilde{Y}^0} f/\delta\chi$ the algebraic version of the first variation $\delta f/\delta\chi$ restricted to the subset $\widetilde{Y}^0$:

$$\begin{aligned} \frac{\delta^{\widetilde{Y}^0} f}{\delta\chi} &= f_{,\chi} - \nabla^{\widetilde{Y}^0} \cdot f_{,\mathbf{D}\chi} \\ &= f_{,\chi} - \sum_{i=1}^{3} \left[\sum_{m=0}^{M-1} f_{,\chi_{,i}\mathbf{D}^m\mathbf{F}} \cdot \mathbf{D}^m\mathbf{F}_{,i} + \sum_{k=0}^{K-1} f_{,\chi_{,i}\mathbf{D}^k\chi} \cdot \mathbf{D}^k\chi_{,i} + \sum_{l=0}^{L-1} f_{,\chi_{,i}\mathbf{D}^l\eta} \cdot \mathbf{D}^l\eta_{,i} \right]. \end{aligned}$$

Let us note that $\nabla^{\widetilde{Y}^0} \cdot f_{,\mathbf{D}\chi}$ does not exceed the set Y_η.

If the constitutive dependence of f is restricted to $f = \widehat{f}(\mathbf{F}, \chi, \mathbf{D}\chi, \eta)$ then the above definition coincides with the algebraic version of the first variation $\delta f/\delta\chi$:

$$\frac{\delta^{\widetilde{Y}^0} f}{\delta\chi} = f_{,\chi} - \sum_{i=1}^{3} \left[f_{,\chi_{,i}\mathbf{F}} \cdot \mathbf{F}_{,i} + \sum_{j=1}^{3} f_{,\chi_{,i}\chi_{,j}} \chi_{,ji} + f_{,\chi_{,i}\eta}\eta_{,i} \right] = \frac{\delta f}{\delta\chi}. \tag{3.4}$$

Moreover, in such a case it holds

$$\nabla^{\widetilde{Y}^0} f = \nabla f.$$

3.3. The restrictions.

We impose the following two structural assumptions:
– the nondegeneracy condition for the internal energy

$$\widetilde{e}_{,\eta}(Y_\eta) > 0 \quad \text{for all } Y_\eta; \tag{3.5}$$

– the relation between stationary entropy, energy and mass fluxes

$$\mathbf{\Psi}^0 = \lambda_\chi^0 \mathbf{j}^0 + \lambda_e^0 \mathbf{q}^0 \tag{3.6}$$

where $\mathbf{\Psi}^0$, $\mathbf{j}^0$, $\mathbf{q}^0$, λ_χ^0 and λ_e^0 are stationary quantities defined by setting $\chi_{,t} = 0$ in Y_η, that is $\mathbf{\Psi}^0 := \widehat{\mathbf{\Psi}}(Y^0, Y^1)|_{Y^1=\{0\}}$, and similarly for other quantities.

We underline that assumption (3.5) expresses the strict positivity of the absolute temperature θ (see $(2.26)_2$). The relation (3.6) is standard in the classical thermodynamic theory without gradients (see e.g. [Mul85]).

We prove the following

Theorem 3.1. *(Consistency with the entropy inequality).*
Let us consider balance laws (2.1) *with constitutive equations* (2.14). *Suppose that entropy inequality* (3.1), (3.2) *is satisfied and assumptions* (3.5), (3.6) *hold true. Then the following relations are satisfied:*

(i) multiplier of the linear momentum $\boldsymbol{\lambda}_{\mathbf{u}} = \mathbf{0}$;
(ii) internal energy $\widetilde{e} = \widetilde{\widehat{e}}(\mathbf{F}, \chi, \mathbf{D}\chi, \eta)$;
(iii) energy multiplier

$$\lambda_e = \widehat{\lambda}_e(\mathbf{F}, \chi, \mathbf{D}\chi, \eta) = \frac{1}{\widetilde{e}_{,\eta}(\mathbf{F}, \chi, \mathbf{D}\chi, \eta)} > 0; \tag{3.7}$$

(iv) stress tensor

$$\mathbf{S} = \widehat{\mathbf{S}}(\mathbf{F}, \chi, \mathbf{D}\chi, \eta) = \widetilde{e}_{,\mathbf{F}}(\mathbf{F}, \chi, \mathbf{D}\chi, \eta); \tag{3.8}$$

(v) entropy flux

$$\mathbf{\Psi} = \lambda_\chi \mathbf{j} + \lambda_e \mathbf{q} + \chi_{,t}\left[\lambda_e \widetilde{e}_{,\mathbf{D}\chi} - \int_0^1 (\lambda_{\chi,\chi_{,t}} \mathbf{j})(Y^0, \tau\chi_{,t}) d\tau\right]; \tag{3.9}$$

(vi) compatibility conditions

$$\begin{aligned} &\chi_{,t}\left[-\int_0^1 (\lambda_{\chi,\chi_{,t}} j_i)(Y^0, \tau\chi_{,t}) d\tau\right]_{,\mathbf{D}^M\mathbf{F}} + \lambda_{\chi,\mathbf{D}^M\mathbf{F}} j_i = \mathbf{0}, \\ &\chi_{,t}\left[-\int_0^1 (\lambda_{\chi,\chi_{,t}} j_i)(Y^0, \tau\chi_{,t}) d\tau\right]_{,\mathbf{D}^K\chi} + \lambda_{\chi,\mathbf{D}^K\chi} j_i = \mathbf{0}, \\ &\chi_{,t}\left[-\int_0^1 (\lambda_{\chi,\chi_{,t}} j_i)(Y^0, \tau\chi_{,t}) d\tau\right]_{,\mathbf{D}^L\eta} + \lambda_{\chi,\mathbf{D}^L\eta} j_i = 0 \end{aligned} \tag{3.10}$$

for $i = 1, 2, 3$.
Moreover, there exists a scalar quantity $a = \widehat{a}(Y_\eta)$ *such that*
(vii) multiplier $\lambda_\chi = \widehat{\lambda}_\chi(Y_\eta)$ *satisfies the equation*

$$-\lambda_\chi = \lambda_e \frac{\delta\widetilde{e}}{\delta\chi} - \nabla\lambda_e \cdot \widetilde{e}_{,\mathrm{D}\chi} + \nabla^{\widetilde{Y}^0} \cdot \int_0^1 (\lambda_{\chi,\chi,_t}\mathbf{j})(Y^0, \tau\chi_{,t})d\tau + a; \tag{3.11}$$

(viii) the quantities $r = \widehat{r}(Y_\eta)$, $\mathbf{j} = \widehat{\mathbf{j}}(Y_\eta)$, $\mathbf{q} = \widehat{\mathbf{q}}(Y_\eta)$ *and* $a = \widehat{a}(Y_\eta)$ *satisfy the residual inequality*

$$\lambda_\chi r + \nabla^{\widetilde{Y}^0}\lambda_\chi \cdot \mathbf{j} + \nabla\lambda_e \cdot \mathbf{q} + \chi_{,t}a \geq 0 \tag{3.12}$$

for all variables Y_η.

Remark 3.1. *By assertion (ii),* $\delta\widetilde{e}/\delta\chi$ *depends on the variables* $\{\mathbf{F}, \mathbf{DF}, \chi, \mathrm{D}\chi, \mathrm{D}^2\chi, \eta, \mathrm{D}\eta\}$. *For that reason it was assumed in constitutive sets* (2.10) *that* $M, L \geq 1$ *and* $K \geq 2$. ∎

Remark 3.2. *In view of thermodynamical relation* $(2.26)_2$ *assertion (ii) implies that the energy multiplier* λ_e *corresponds to the inverse of the absolute temperature*

$$\lambda_e \leftrightarrow \frac{1}{\theta}.$$

Moreover, in view of thermodynamical relation $(2.40)_1$, *equation* (3.11) *for* $-\lambda_\chi$ *resembles the expression for the chemical potential in the classical Cahn–Hilliard theory which for* $\theta = \text{const}$ *is given by* $\mu = \delta f/\delta\chi$. *Thus, the form* (3.11) *suggests that the negative of the multiplier* $-\lambda_\chi$ *corresponds to a generalized (rescaled) chemical potential*

$$-\lambda_\chi \leftrightarrow \overline{\mu} := \frac{\mu}{\theta}.$$

The above correspondences will be precised in Section 4. ∎

Proof of Theorem 3.1. By inserting constitutive equations (2.14), (3.2) into entropy inequality (3.1) and applying the chain rule we arrive at the following algebraic inequality

$$\begin{aligned}
&\eta_{,t} + \mathbf{\Psi}_{,\chi,_t} \cdot \mathrm{D}\chi_{,t} + \nabla^{Y^0} \cdot \mathbf{\Psi} - \boldsymbol{\lambda}_\mathbf{u} \cdot \mathbf{u}_{,tt} + \boldsymbol{\lambda}_\mathbf{u} \cdot (\mathbf{S}_{,\chi,_t}\mathrm{D}\chi_{,t}) \\
&+\boldsymbol{\lambda}_\mathbf{u} \cdot (\nabla^{Y^0} \cdot \mathbf{S}) - \lambda_\chi\chi_{,t} - \lambda_\chi\mathbf{j}_{,\chi,_t} \cdot \mathrm{D}\chi_{,t} - \lambda_\chi\nabla^{Y^0} \cdot \mathbf{j} + \lambda_\chi r \\
&-\lambda_e \sum_{m=0}^{M} \widetilde{e}_{,\mathrm{D}^m\mathbf{F}} \cdot \mathrm{D}^m\mathbf{F}_{,t} - \lambda_e \sum_{k=0}^{K} \widetilde{e}_{,\mathrm{D}^k\chi} \cdot \mathrm{D}^k\chi_{,t} - \lambda_e \sum_{l=0}^{L} \widetilde{e}_{,\mathrm{D}^l\eta} \cdot \mathrm{D}^l\eta_{,t} \\
&-\lambda_e\widetilde{e}_{,\chi,_t}\chi_{,tt} - \lambda_e\mathbf{q}_{,\chi,_t} \cdot \mathrm{D}\chi_{,t} - \lambda_e\nabla^{Y^0} \cdot \mathbf{q} + \lambda_e\mathbf{S} \cdot \mathbf{F}_{,t} \geq 0
\end{aligned} \tag{3.13}$$

for all variables $\{W, Y_\eta\}$. Here

$$W := \{\mathbf{u}_{,tt}, \chi_{,tt}, (\mathbf{D}^m\mathbf{F}_{,t})_{0\le m\le M}, (\mathbf{D}^k\chi_{,t})_{1\le k\le K}, (\mathbf{D}^l\eta_{,t})_{0\le l\le L}, \mathbf{D}^{M+1}\mathbf{F}, \mathbf{D}^{K+1}\chi, \mathbf{D}^{L+1}\eta\}$$

denotes the set of variables (called higher derivatives) in which the left-hand side of (3.13) is linear. The evaluation of (3.13) 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 (3.13) in $\mathbf{u}_{,tt}$ it follows that the corresponding coefficient has to vanish, that is $\boldsymbol{\lambda}_\mathbf{u} = \mathbf{0}$. This shows (i).

Step 2. By the linearity in the variables $(\mathbf{D}^m\mathbf{F}_{,t})_{1\le m\le M}$, $(\mathbf{D}^k\chi_{,t})_{2\le k\le K}$, $(\mathbf{D}^l\eta_{,t})_{1\le l\le L}$, $\chi_{,tt}$ we read off that $\widetilde{e}_{,\mathbf{D}^m\mathbf{F}} = \mathbf{0}$ for $1 \le m \le M$, $\widetilde{e}_{,\mathbf{D}^k\chi} = \mathbf{0}$ for $2 \le k \le K$, $\widetilde{e}_{,\mathbf{D}^l\eta} = \mathbf{0}$ for $1 \le l \le L$ and $\widetilde{e}_{,\chi_{,t}} = 0$. Hence, the constitutive dependence of $\widetilde{e}$ is restricted to $\widetilde{e} = \widetilde{\widetilde{e}}(\mathbf{F}, \chi, \mathbf{D}\chi, \eta)$ which shows (ii).

Step 3. The linearity in $\eta_{,t}$ implies that

$$1 - \lambda_e \widetilde{e}_{,\eta} = 0,$$

so, in view of assumption (3.5) and (ii) we infer (iii).

Step 4. By the linearity in $\mathbf{F}_{,t}$,

$$\lambda_e \mathbf{S} - \lambda_e \widetilde{e}_{,\mathbf{F}} = \mathbf{0}.$$

Hence, since $\lambda_e > 0$, assertion (iv) follows.

Step 5. From the linearity in $\mathbf{D}\chi_{,t}$ we deduce that

$$\boldsymbol{\Psi}_{,\chi_{,t}} - \lambda_\chi \mathbf{j}_{,\chi_{,t}} - \lambda_e \widetilde{e}_{,\mathbf{D}\chi} - \lambda_e \mathbf{q}_{,\chi_{,t}} = \mathbf{0}. \tag{3.14}$$

Let us define the vector

$$\widetilde{\boldsymbol{\Psi}} := \boldsymbol{\Psi} - \lambda_\chi \mathbf{j} - \lambda_e \mathbf{q}. \tag{3.15}$$

By virtue of assumption (3.6),

$$\widetilde{\boldsymbol{\Psi}}^0 = \mathbf{0}. \tag{3.16}$$

From (3.15), using (3.14) and (iii), we get

$$\begin{aligned} \widetilde{\boldsymbol{\Psi}}_{,\chi_{,t}} &= \boldsymbol{\Psi}_{,\chi_{,t}} - \lambda_{\chi,\chi_{,t}} \mathbf{j} - \lambda_\chi \mathbf{j}_{,\chi_{,t}} - \lambda_e \mathbf{q}_{,\chi_{,t}} \\ &= \lambda_e \widetilde{e}_{,\mathbf{D}\chi} - \lambda_{\chi,\chi_{,t}} \mathbf{j}. \end{aligned} \tag{3.17}$$

Hence, in view of (3.16) and (ii), (iii), it follows that

$$\widetilde{\Psi} = \lambda_e \widetilde{e}_{,\mathbf{D}\chi} \chi_{,t} - \int_0^{\chi_{,t}} (\lambda_{\chi,\chi_{,t}} \mathbf{j})(Y^0, \xi) d\xi = \chi_{,t} \left[\lambda_e \widetilde{e}_{,\mathbf{D}\chi} - \int_0^1 (\lambda_{\chi,\chi_{,t}} \mathbf{j})(Y^0, \tau\chi_{,t}) d\tau \right]. \tag{3.18}$$

From (3.15) and (3.18) we conclude (v).

Step 6. It remains to examine the linearity in the variables $\mathbf{D}^{M+1}\mathbf{F}, \mathbf{D}^{K+1}\chi$, $\mathbf{D}^{L+1}\eta$. In view of the results obtained in the previous steps, inequality (3.13) is reduced to

$$-(\lambda_\chi + \lambda_e \widetilde{e}_{,\chi})\chi_{,t} + \lambda_\chi r + \nabla^{Y^0} \cdot \Psi - \lambda_\chi \nabla^{Y^0} \cdot \mathbf{j} - \lambda_e \nabla^{Y^0} \cdot \mathbf{q} \geq 0 \tag{3.19}$$

for all variables $\{\mathbf{D}^{M+1}\mathbf{F}, \mathbf{D}^{K+1}\chi, \mathbf{D}^{L+1}\eta, Y_\eta\}$. We rearrange now the sum of the last three terms on the left-hand side of (3.19) to the form

$$\begin{aligned} &\nabla^{Y^0} \cdot \Psi - \lambda_\chi \nabla^{Y^0} \cdot \mathbf{j} - \lambda_e \nabla^{Y^0} \cdot \mathbf{q} \\ &= \nabla^{Y^0} \cdot (\Psi - \lambda_\chi \mathbf{j} - \lambda_e \mathbf{q}) + \nabla^{Y^0} \lambda_\chi \cdot \mathbf{j} + \nabla^{Y^0} \lambda_e \cdot \mathbf{q} \\ &= \nabla^{Y^0} \cdot \widetilde{\Psi} + \nabla^{Y^0} \lambda_\chi \cdot \mathbf{j} + \nabla^{Y^0} \lambda_e \cdot \mathbf{q}. \end{aligned} \tag{3.20}$$

Further, in view of (3.18), using the definition of the restricted divergence $\nabla^{Y^0}\cdot$, we obtain

$$\nabla^{Y^0} \cdot \widetilde{\Psi} = \chi_{,t} \left[\nabla^{Y^0} \cdot (\lambda_e \widetilde{e}_{,\mathbf{D}\chi}) - \nabla^{Y^0} \cdot \int_0^1 (\lambda_{\chi,\chi_{,t}} \mathbf{j})(Y^0, \tau\chi_{,t}) d\tau \right]. \tag{3.21}$$

Consequently, by combining (3.20) and (3.21), inequality (3.19) is transformed to

$$\begin{aligned} &\chi_{,t} \left[-\lambda_\chi - \lambda_e \widetilde{e}_{,\chi} + \nabla^{Y^0} \cdot (\lambda_e \widetilde{e}_{,\mathbf{D}\chi}) - \nabla^{Y^0} \cdot \int_0^1 (\lambda_{\chi,\chi_{,t}} \mathbf{j})(Y^0, \tau\chi_{,t}) d\tau \right] \\ &+ \lambda_\chi r + \nabla^{Y^0} \lambda_\chi \cdot \mathbf{j} + \nabla^{Y^0} \lambda_e \cdot \mathbf{q} \geq 0 \end{aligned} \tag{3.22}$$

for all variables $\{\mathbf{D}^{M+1}\mathbf{F}, \mathbf{D}^{K+1}\chi, \mathbf{D}^{L+1}\eta, Y_\eta\}$.

From (3.22), performing differentiation by the chain rule in terms involving $\nabla^{Y^0}\cdot$ and ∇^{Y^0} (restricting now to the subset $\widetilde{Y}^0$), the linearity in the variables $\mathbf{D}^{M+1}\mathbf{F}, \mathbf{D}^{K+1}\chi$ and $\mathbf{D}^{L+1}\eta$ implies that the coefficients preceding these variables have to vanish. Hence, recalling (ii) and (iii), we conclude (vi).

Step 7. We shall derive conclusions from inequality (3.22) which remains after taking into account (vi). It reads

$$\chi_{,t}\left[-\lambda_\chi - \lambda_e\widetilde{e}_{,\chi} + \nabla^{\widetilde{Y}^0}\cdot(\lambda_e\widetilde{e}_{,\mathbf{D}\chi}) - \nabla^{\widetilde{Y}^0}\cdot\int_0^1(\lambda_{\chi,\chi,_t}\mathbf{j})(Y^0,\tau\chi_{,t})d\tau\right] + \lambda_\chi r + \nabla^{\widetilde{Y}^0}\lambda_\chi\cdot\mathbf{j} + \nabla^{\widetilde{Y}^0}\lambda_e\cdot\mathbf{q} \geq 0 \tag{3.23}$$

for all variables Y_η. Now, let us define a scalar quantity $a = \widehat{a}(Y_\eta)$ given by the squared parenthesis in (3.23), viz.

$$\begin{aligned} a &:= -\lambda_\chi - \lambda_e\widetilde{e}_{,\chi} + \nabla^{\widetilde{Y}^0}\cdot(\lambda_e\widetilde{e}_{,\mathbf{D}\chi}) - \nabla^{\widetilde{Y}^0}\cdot\int_0^1(\lambda_{\chi,\chi,_t}\mathbf{j})(Y^0,\tau\chi_{,t})d\tau \\ &= -\lambda_\chi - \lambda_e(\widetilde{e}_{,\chi} - \nabla^{\widetilde{Y}^0}\cdot\widetilde{e}_{,\mathbf{D}\chi}) + \nabla^{\widetilde{Y}^0}\lambda_e\cdot\widetilde{e}_{,\mathbf{D}\chi} \\ &\quad -\nabla^{\widetilde{Y}^0}\cdot\int_0^1(\lambda_{\chi,\chi,_t}\mathbf{j})(Y^0,\tau\chi_{,t})d\tau. \end{aligned} \tag{3.24}$$

Let us note that on account of (ii) and (iii) it holds

$$\nabla^{\widetilde{Y}^0}\cdot(\lambda_e\widetilde{e}_{,\mathbf{D}\chi}) = \nabla\cdot(\lambda_e\widetilde{e}_{,\mathbf{D}\chi}), \qquad \nabla^{\widetilde{Y}^0}\lambda_e = \nabla\lambda_e, \tag{3.25}$$

so that, recalling (3.4),

$$\frac{\delta^{\widetilde{Y}^0}\widetilde{e}}{\delta\chi} = \widetilde{e}_{,\chi} - \nabla^{\widetilde{Y}^0}\cdot\widetilde{e}_{,\mathbf{D}\chi} = \frac{\delta\widetilde{e}}{\delta\chi}.$$

Using these equalities we conclude from (3.24) assertion (vii). Finally, owing to (3.24), inequality (3.23) takes the form of the residual inequality (3.12). This shows assertion (viii) and thereby completes the proof. ■

3.4. 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 (3.6) reads

$$\mathbf{\Psi}^0 = \lambda_e^0\mathbf{q}^0, \tag{3.26}$$

and we have

Theorem 3.2. *(Consistency with the entropy inequality in the nonconserved case).*
Let us consider balance laws (2.1) with constitutive equations (2.14) in the nonconserved case $\mathbf{j} \equiv \mathbf{0}, r \neq 0$. Suppose that the entropy inequality (3.1), (3.2) is satisfied and assumptions (3.5), (3.26) hold true. Then the following relations are satisfied:

(i) $\boldsymbol{\lambda}_{\mathbf{u}} = \mathbf{0}$;
(ii) $\widetilde{e} = \widehat{\widetilde{e}}(\mathbf{F},\chi,\mathbf{D}\chi,\eta)$;

(iii) $\lambda_e = \widehat{\lambda}_e(\mathbf{F}, \chi, \mathbf{D}\chi, \eta) = \dfrac{1}{\widetilde{e}_{,\eta}(\mathbf{F}, \chi, \mathbf{D}\chi, \eta)} > 0;$

(iv) $\mathbf{S} = \widehat{\mathbf{S}}(\mathbf{F}, \chi, \mathbf{D}\chi, \eta) = \widetilde{e}_{,\mathbf{F}}(\mathbf{F}, \chi, \mathbf{D}\chi, \eta);$

(v) $\mathbf{\Psi} = \lambda_e \mathbf{q} + \chi_{,t}\lambda_e \widetilde{e}_{,\mathbf{D}\chi}.$

Moreover, there exists a scalar field $a = \widehat{a}(Y_\eta)$ *such that*

(vi) $-\lambda_\chi = \lambda_e \dfrac{\delta \widetilde{e}}{\delta \chi} - \nabla \lambda_e \cdot \widetilde{e}_{,\mathbf{D}\chi} + a;$

(vii) $\lambda_\chi r + \nabla \lambda_e \cdot \mathbf{q} + \chi_{,t} a \geq 0$ *for all variables* Y_η.

4. Extended models $(M)_\eta$ and $(M)_\theta$ based on entropy and absolute temperature as independent variables

4.1. Multipliers as additional independent variables.

Regarding Theorem 3.1 (and Theorem 3.2 as a special case) we introduce an extended model in which the multipliers λ_χ and λ_e are in addition to $\mathbf{u}, \chi$ and η treated as independent variables. Such idea is admissible because theorem has been proved under no assumptions on λ_χ and λ_e.

Our claim on the structure of the extended model is based on the following modifications of the statements of Theorem 3.1:

— We replace the state space Y_η in $(2.10)_3$ by

$$\mathcal{Z}_\eta := \{\mathbf{F}, \mathbf{DF}, \chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \eta, \mathbf{D}\eta, \lambda_\chi, \mathbf{D}\lambda_\chi, \lambda_e, \mathbf{D}\lambda_e, \chi_{,t}\}. \tag{4.1}$$

This set includes all variables which will appear in the extended model. The higher derivatives $\mathbf{D}^m\mathbf{F}, \mathbf{D}^k\chi, \mathbf{D}^l\eta$ for $m, l \geq 2, k \geq 3$ are irrelevant (see Remark 3.1).

— Regarding λ_χ as an independent variable we set all expressions involving its derivatives with respect to $\chi_{,t}, \mathbf{D}^M\mathbf{F}, \mathbf{D}^K\chi, \mathbf{D}^L\eta$ identically equal zero and consequently replace $\nabla^{\widetilde{Y}^0}\lambda_\chi$ by $\nabla\lambda_\chi$.

Formally, with such modifications the statements (i)–(iv) of Theorem 3.1 remain unchanged, (vi) is automatically satisfied and (v), (vii), (viii) are respectively replaced by:

$(\widetilde{\text{v}})$ $\mathbf{\Psi} = \lambda_\chi \mathbf{j} + \lambda_e \mathbf{q} + \chi_{,t}\lambda_e \widetilde{e}_{,\mathbf{D}\chi};$

$(\widetilde{\text{vii}})$ $-\lambda_\chi = \lambda_e \dfrac{\delta \widetilde{e}}{\delta \chi} - \nabla \lambda_e \cdot \widetilde{e}_{,\mathbf{D}\chi} + a;$

$(\widetilde{\text{viii}})$ the quantities $r = \widehat{r}(\mathcal{Z}_\eta)$, $\mathbf{j} = \widehat{\mathbf{j}}(\mathcal{Z}_\eta)$, $\mathbf{q} = \widehat{\mathbf{q}}(\mathcal{Z}_\eta)$ and $a = \widehat{a}(\mathcal{Z}_\eta)$ satisfy the inequality

$$\lambda_\chi r + \mathbf{D}\lambda_\chi \cdot \mathbf{j} + \mathbf{D}\lambda_e \cdot \mathbf{q} + \chi_{,t} a \geq 0 \tag{4.2}$$

for all variables $\mathcal{Z}_\eta$ in (4.1).

In Section 4.3 it will be proved that the above mentioned modifications lead to a model which is consistent with the entropy principle.

4.2. Model $(M)_\eta$ – formulation with internal energy $\widetilde{e} = \widehat{\widetilde{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \eta)$ as a thermodynamic potential.

The extended model, referred further to as $(M)_\eta$, is based on the following postulates:

$(M1)_\eta$ The unknowns are the fields $\mathbf{u}, \chi, \eta$ and $\lambda_\chi, \lambda_e > 0$.

$(M2)_\eta$ A thermodynamic potential is the internal energy

$$\widetilde{e} = \widehat{\widetilde{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \eta), \tag{4.3}$$

subject to the condition

$$\widetilde{e}_{,\eta} > 0 \text{ for all arguments } (\mathbf{F}, \chi, \mathrm{D}\chi, \eta). \tag{4.4}$$

$(M3)_\eta$ The fields $\mathbf{u}, \chi, \eta, \lambda_\chi$ and λ_e satisfy the differential equations

$$\begin{aligned} &\ddot{\mathbf{u}} - \nabla \cdot \mathbf{S} = \mathbf{b}, \\ &\dot{\chi} + \nabla \cdot \mathbf{j} - r = \tau, \\ &-\lambda_\chi = \lambda_e \frac{\delta \widetilde{e}}{\delta \chi} - \nabla \lambda_e \cdot \widetilde{e}_{,\mathrm{D}\chi} + a, \\ &[\widetilde{e}(\mathbf{F}, \chi, \mathrm{D}\chi, \eta)]^{\cdot} + \nabla \cdot \mathbf{q} - \mathbf{S} \cdot \dot{\mathbf{F}} = g, \\ &\lambda_e \widetilde{e}_{,\eta} - 1 = 0, \end{aligned} \tag{4.5}$$

where $\mathbf{S}$ is given by

$$\mathbf{S} = \widetilde{e}_{,\mathbf{F}}, \tag{4.6}$$

consistent with the condition

$$\mathbf{S}\mathbf{F}^T = \mathbf{F}\mathbf{S}^T. \tag{4.7}$$

Moreover, the quantities $r = \widehat{r}(\mathcal{Z}_\eta)$, $\mathbf{j} = \widehat{\mathbf{j}}(\mathcal{Z}_\eta)$, $\mathbf{q} = \widehat{\mathbf{q}}(\mathcal{Z}_\eta)$ and $a = \widehat{a}(\mathcal{Z}_\eta)$, with $\mathcal{Z}_\eta$ given by (4.1), are subject to the dissipation inequality (4.2).

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

$$\begin{aligned} &\widetilde{e} = \widehat{\widetilde{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \eta), \quad \mathbf{S} = \widehat{\mathbf{S}}(\mathbf{F}, \chi, \mathrm{D}\chi, \eta), \\ &\boldsymbol{\xi} = \widehat{\boldsymbol{\xi}}(\mathbf{F}, \chi, \mathrm{D}\chi, \eta) := \widetilde{e}_{,\mathrm{D}\chi}(\mathbf{F}, \chi, \mathrm{D}\chi, \eta), \\ &\mathbf{j} = \widehat{\mathbf{j}}(\mathcal{Z}_\eta), \quad \mathbf{q} = \widehat{\mathbf{q}}(\mathcal{Z}_\eta), \quad r = \widehat{r}(\mathcal{Z}_\eta), \quad a = \widehat{a}(\mathcal{Z}_\eta) \end{aligned}$$

are assumed to be invariant under changes in observer, i.e. under transformations (see e.g. [Gur96], Sec. 4.2)

$$\begin{aligned}
&\widetilde{e} \to \widetilde{e},\ \mathbf{S} \to \mathbf{PS},\ \boldsymbol{\xi} \to \boldsymbol{\xi},\ \mathbf{j} \to \mathbf{j},\ \mathbf{q} \to \mathbf{q},\ r \to r,\ a \to a,\\
&\{\mathbf{F}, \mathbf{DF}, \chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \eta, \mathbf{D}\eta, \lambda_\chi, \mathbf{D}\lambda_\chi, \lambda_e, \mathbf{D}\lambda_e, \chi_{,t}\}\\
&\to \{\mathbf{PF}, \mathbf{PDF}, \chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \eta, \mathbf{D}\eta, \lambda_\chi, \mathbf{D}\lambda_\chi, \lambda_e, \mathbf{D}\lambda_e, \chi_{,t}\}
\end{aligned}$$

for all proper orthogonal tensors $\mathbf{P}(\mathbf{PP}^T = \mathbf{P}^T\mathbf{P} = \mathbf{I}$ with $\det \mathbf{P} > 0)$. This leads to the following restrictions

$$\begin{aligned}
(4.8)\quad &\widehat{\widetilde{e}}(\mathbf{F}, \chi, \mathbf{D}\chi, \eta) = \widehat{\widetilde{e}}(\mathbf{C}, \chi, \mathbf{D}\chi, \eta),\\
&\widehat{\mathbf{S}}(\mathbf{F}, \chi, \mathbf{D}\chi, \eta) = \mathbf{F}\widehat{\widehat{\mathbf{S}}}(\mathbf{C}, \chi, \mathbf{D}\chi, \eta),\\
&\widehat{\boldsymbol{\xi}}(\mathbf{F}, \chi, \mathbf{D}\chi, \eta) = \widehat{\boldsymbol{\xi}}(\mathbf{C}, \chi, \mathbf{D}\chi, \eta),\\
&\widehat{\mathbf{j}}(\mathcal{Z}_\eta) = \widehat{\mathbf{j}}(\overline{\mathcal{Z}}_\eta),\quad \widehat{\mathbf{q}}(\mathcal{Z}_\eta) = \widehat{\mathbf{q}}(\overline{\mathcal{Z}}_\eta),\quad \widehat{r}(\mathcal{Z}_\eta) = \widehat{r}(\overline{\mathcal{Z}}_\eta),\quad \widehat{a}(\mathcal{Z}_\eta) = \widehat{a}(\overline{\mathcal{Z}}_\eta)
\end{aligned}$$

where

$$\overline{\mathcal{Z}}_\eta := \{\mathbf{C}, \mathbf{DC}, \chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \eta, \mathbf{D}\eta, \lambda_\chi, \mathbf{D}\lambda_\chi, \lambda_e, \mathbf{D}\lambda_e, \chi_{,t}\},$$

with $\mathbf{C} = \mathbf{F}^T\mathbf{F}$ the right Cauchy–Green strain tensor. We note that by virtue of $(4.8)_2$, condition (4.7) is automatically satisfied (see e.g. [Gur96]).

4.3. **Thermodynamic consistency of model** $(M)_\eta$.

We shall prove that model $(M)_\eta$ is consistent with the second law of thermodynamics.

Theorem 4.1. *System* (4.5) *with relations* (4.3), (4.6) *and* (4.2) *satisfies the following entropy inequality with multipliers*

$$\begin{aligned}
(4.9)\qquad &\dot{\eta} + \nabla\cdot\boldsymbol{\Psi} - \boldsymbol{\Lambda}_{\mathbf{u}}\cdot(\ddot{\mathbf{u}} - \nabla\cdot\mathbf{S}) - \Lambda_\chi(\dot{\chi} + \nabla\cdot\mathbf{j} - r)\\
&-\Lambda_{\lambda_\chi}(\lambda_\chi + \lambda_e\widetilde{e}_{,\chi} - \lambda_e\nabla\cdot\widetilde{e}_{,\mathbf{D}\chi} - \nabla\lambda_e\cdot\widetilde{e}_{,\mathbf{D}\chi} + a)\\
&-\Lambda_e(\dot{\widetilde{e}} + \nabla\cdot\mathbf{q} - \mathbf{S}\cdot\dot{\mathbf{F}}) - \Lambda_{\lambda_e}(\lambda_e\widetilde{e}_{,\eta} - 1) - \boldsymbol{\Lambda}_{\mathbf{S}}\cdot(\mathbf{S} - \widetilde{e}_{,\mathbf{F}})\\
&= \lambda_\chi r + \nabla\lambda_\chi\cdot\mathbf{j} + \nabla\lambda_e\cdot\mathbf{q} + \dot{\chi}a \geq 0
\end{aligned}$$

for all fields $\mathbf{u}, \chi, \eta, \lambda_\chi, \lambda_e$. *The corresponding multipliers are given by*

$$\begin{aligned}
(4.10)\qquad &\boldsymbol{\Lambda}_{\mathbf{u}} = \mathbf{0},\quad \Lambda_\chi = \lambda_\chi,\quad \Lambda_{\lambda_\chi} = -\dot{\chi},\\
&\Lambda_e = \lambda_e,\quad \Lambda_{\lambda_e} = -\dot{\eta},\quad \boldsymbol{\Lambda}_{\mathbf{S}} = \lambda_e\dot{\mathbf{F}},
\end{aligned}$$

and the entropy flux is

$$(4.11)\qquad \boldsymbol{\Psi} = \lambda_\chi\mathbf{j} + \lambda_e\mathbf{q} + \dot{\chi}\lambda_e\widetilde{e}_{,\mathbf{D}\chi}.$$

Proof. Let $\mathbf{u}, \chi, \eta, \lambda_\chi, \lambda_e$ be any fields and $\mathbf{\Lambda_u}, \Lambda_\chi, \Lambda_{\lambda_\chi}, \Lambda_e, \Lambda_{\lambda_e}, \mathbf{\Lambda_S}$ be defined by (4.10). Then, after simple rearrangements, we arrive at the following identities:

$$\begin{aligned}
&\mathbf{\Lambda_u} \cdot (\ddot{\mathbf{u}} - \nabla \cdot \mathbf{S}) + \Lambda_\chi(\dot\chi + \nabla \cdot \mathbf{j} - r) \\
&+\Lambda_{\lambda_\chi}(\lambda_\chi + \lambda_e \widetilde{e}_{,\chi} - \nabla \cdot (\lambda_e \widetilde{e}_{,\mathbf{D}\chi}) + a) + \Lambda_e(\dot{\widetilde{e}} + \nabla \cdot \mathbf{q} - \mathbf{S} \cdot \dot{\mathbf{F}}) \\
&+\Lambda_{\lambda_e}(\lambda_e \widetilde{e}_{,\eta} - 1) + \mathbf{\Lambda_S} \cdot (\mathbf{S} - \widetilde{e}_{,\mathbf{F}}) \\
=\ & \lambda_\chi(\dot\chi + \nabla \cdot \mathbf{j} - r) - \dot\chi(\lambda_\chi + \lambda_e \widetilde{e}_{,\chi} - \nabla \cdot (\lambda_e \widetilde{e}_{,\mathbf{D}\chi}) + a) \\
&+\lambda_e(\widetilde{e}_{,\mathbf{F}} \cdot \dot{\mathbf{F}} + \widetilde{e}_{,\chi}\dot\chi + \widetilde{e}_{,\mathbf{D}\chi} \cdot \nabla\dot\chi + \widetilde{e}_{,\eta}\dot\eta + \nabla \cdot \mathbf{q} - \mathbf{S} \cdot \dot{\mathbf{F}}) \\
&-\dot\eta(\lambda_e \widetilde{e}_{,\eta} - 1) + \lambda_e \dot{\mathbf{F}} \cdot (\mathbf{S} - \widetilde{e}_{,\mathbf{F}}) \\
=\ & \dot\eta + \nabla \cdot (\lambda_\chi \mathbf{j} + \lambda_e \mathbf{q} + \dot\chi \lambda_e \widetilde{e}_{,\mathbf{D}\chi}) - \lambda_\chi r - \nabla\lambda_\chi \cdot \mathbf{j} - \nabla\lambda_e \cdot \mathbf{q} - \dot\chi a.
\end{aligned}$$

This shows the equality in (4.9). In turn, the inequality in (4.9) results by virtue of dissipation inequality (4.2). Thereby the proof is completed. ■

Corollary 4.1. *From* (4.9) *it follows that the solutions of system* (4.5) *with* (4.3), (4.6), (4.2) *(thermodynamic processes) satisfy the following entropy equation and inequality*

$$\text{(4.12)} \qquad \begin{aligned} \dot\eta + \nabla \cdot \mathbf{\Psi} &= \lambda_\chi r + \nabla\lambda_\chi \cdot \mathbf{j} + \nabla\lambda_e \cdot \mathbf{q} + \dot\chi a + \lambda_\chi \tau + \lambda_e g \\ &\geq \lambda_\chi \tau + \lambda_e g, \end{aligned}$$

where the entropy flux $\mathbf{\Psi}$ *is given by* (4.11). *It is of interest to note that the structure of* $\mathbf{\Psi}$ *remains in compatibility with assumption* (3.6) *postulated in Theorem 3.1.*

4.4. **Model** $(M)_\theta$ **– formulation with free energy** $f = \widehat{f}(\mathbf{F}, \chi, \mathbf{D}\chi, \theta)$ **as a thermodynamic potential.**

Here we present an equivalent formulation of model $(M)_\eta$, expressed in terms of the absolute temperature θ as an independent thermal variable and the Helmholtz free energy $f = \widehat{f}(\mathbf{F}, \chi, \mathbf{D}\chi, \theta)$ as a thermodynamic potential. To this purpose we assume thermal stability condition $c_0 = \widehat{c}_0(\mathbf{F}, \chi, \mathbf{D}\chi, \theta) > 0$ under which duality relations (2.26) hold true.

If $c_0 > 0$ then Lemma 2.4 implies that

$$\text{(4.13)} \qquad \begin{aligned} &\text{the map } \eta \mapsto \widetilde{e}(\mathbf{F}, \chi, \mathbf{D}\chi, \eta) \text{ is strictly convex,} \\ &\text{so the map } \eta \mapsto \widetilde{e}_{,\eta}(\mathbf{F}, \chi, \mathbf{D}\chi, \eta) \text{ is strictly increasing.} \end{aligned}$$

From now on we shall assume that $\widetilde{e}$ satisfies (4.13) in addition to (4.4), i.e.

$$\text{(4.14)} \qquad \begin{aligned} &\widetilde{e} = \widetilde{e}(\mathbf{F}, \chi, \mathbf{D}\chi, \eta) \text{ is strictly convex as a function of } \eta, \\ &\text{and such that } \widetilde{e}_{,\eta} > 0 \text{ for all arguments } (\mathbf{F}, \chi, \mathbf{D}\chi, \eta). \end{aligned}$$

Under such assumption the duality relations (2.26) are satisfied. Consequently, by $(4.5)_5$ and $(2.26)_2$, it follows that

$$\lambda_e = \frac{1}{\widetilde{e}_{,\eta}} = \frac{1}{\theta} \tag{4.15}$$

which means that the energy multiplier can be identified with the inverse temperature. Clearly, the assumption $\widetilde{e}_{,\eta} > 0$ is equivalent to $\theta > 0$. Moreover, the requirement (4.13) means that

(4.16) the map $\eta \mapsto \widehat{\theta}(\mathbf{F}, \chi, \mathrm{D}\chi, \eta)$ is strictly increasing, so there exists a well-defined inverse map $\theta \mapsto \widehat{\eta}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta)$.

Further, in view of equalities (2.38), the strict convexity of $\widetilde{e} = \widehat{\widetilde{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \eta)$ with respect to η is equivalent to the strict concavity of $f = \widehat{f}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta)$ with respect to θ. Hence, the assumption (4.14) expressed in terms of f reads:

(4.17) $f = \widehat{f}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta)$ is strictly concave with respect to $\theta > 0$.

In addition, recalling (2.41), we have the equalities

$$\widetilde{e}_{,\mathbf{F}} = f_{,\mathbf{F}}, \quad \widetilde{e}_{,\chi} = f_{,\chi}, \quad \widetilde{e}_{,\mathrm{D}\chi} = f_{,\mathrm{D}\chi}, \quad \frac{\delta \widetilde{e}}{\delta \chi} = \frac{\delta f}{\delta \chi} \tag{4.18}$$

with appropriate arguments. Hence, by $(4.18)_1$, equation (4.6) takes the form

$$\mathbf{S} = f_{,\mathbf{F}}.$$

Further, in view of (2.32) and (2.33), we have

$$\begin{aligned} \widehat{e}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta) &= \widehat{\widetilde{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \widehat{\eta}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta)) \\ &= \widehat{f}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta) + \theta \widehat{\eta}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta) \end{aligned}$$

with

$$\widehat{\eta}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta) = -\widehat{f}_{,\theta}(\mathbf{F}, \chi, \mathrm{D}\chi, \theta).$$

Let us turn to the multiplier λ_χ. Recalling Remark 3.2, we shall identify $-\lambda_\chi$ with a rescaled chemical potential

$$-\lambda_\chi = \overline{\mu} := \frac{\mu}{\theta}. \tag{4.19}$$

Then, on account of (4.15) and (4.18), equation $(4.5)_3$ yields

$$\overline{\mu} = \frac{1}{\theta}\frac{\delta f}{\delta \chi} - \nabla\frac{1}{\theta}\cdot f_{,\mathbf{D}\chi} + a = \frac{\delta(f/\theta)}{\delta\chi} + a. \tag{4.20}$$

In view of relations (4.15), (4.16), (4.19) and $(2.36)_2$ the state space $\mathcal{Z}_\eta$ in (4.1) is replaced by

$$\mathcal{Z}_\theta := \left\{\mathbf{F}, \mathbf{DF}, \chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \theta, \mathbf{D}\frac{1}{\theta}, \overline{\mu}, \mathbf{D}\overline{\mu}, \chi_{,t}\right\}, \quad \overline{\mu} = \frac{\mu}{\theta}. \tag{4.21}$$

The above considerations lead to the following formulation of model $(M)_\eta$, referred further as $(M)_\theta$, expressed in terms of θ as an independent thermal variable:

$(M1)_\theta$ The unknowns are the fields $\mathbf{u}, \chi, \overline{\mu} = \mu/\theta$ and $\theta > 0$.

$(M2)_\theta$ A thermodynamic potential is the free energy $f = \widehat{f}(\mathbf{F}, \chi, \mathbf{D}\chi, \theta)$ satisfying (4.17).

$(M3)_\theta$ The fields $\mathbf{u}, \chi, \overline{\mu} = \mu/\theta$ and θ satisfy the system of equations

$$\begin{aligned}
&\ddot{\mathbf{u}} - \nabla\cdot\mathbf{S} = \mathbf{b},\\
&\dot{\chi} + \nabla\cdot\mathbf{j} - r = \tau,\\
&\overline{\mu} = \frac{\delta(f/\theta)}{\delta\chi} + a,\\
&\dot{e} + \nabla\cdot\mathbf{q} - \mathbf{S}\cdot\dot{\mathbf{F}} = g,
\end{aligned} \tag{4.22}$$

where

$$\begin{aligned}
&e = \widehat{e}(\mathbf{F}, \chi, \mathbf{D}\chi, \theta) = \widehat{f}(\mathbf{F}, \chi, \mathbf{D}\chi, \theta) + \theta\widehat{\eta}(\mathbf{F}, \chi, \mathbf{D}\chi, \theta),\\
&\eta = \widehat{\eta}(\mathbf{F}, \chi, \mathbf{D}\chi, \theta) = -f_{,\theta}(\mathbf{F}, \chi, \mathbf{D}\chi, \theta),\\
&\frac{\delta(f/\theta)}{\delta\chi} = \frac{f_{,\chi}}{\theta} - \nabla\cdot\left(\frac{f_{,\mathbf{D}\chi}}{\theta}\right),
\end{aligned} \tag{4.23}$$

and $\mathbf{S}$ is given by

$$\mathbf{S} = f_{,\mathbf{F}}, \tag{4.24}$$

consistent with the condition

$$\mathbf{S}\mathbf{F}^T = \mathbf{F}\mathbf{S}^T. \tag{4.25}$$

Moreover, the quantities $r = \widehat{r}(\mathcal{Z}_\theta)$, $\mathbf{j} = \widehat{\mathbf{j}}(\mathcal{Z}_\theta)$, $\mathbf{q} = \widehat{\mathbf{q}}(\mathcal{Z}_\theta)$ and $a = \widehat{a}(\mathcal{Z}_\theta)$ are subject to the dissipation inequality

$$-\overline{\mu}r - \mathbf{D}\overline{\mu}\cdot\mathbf{j} + \mathbf{D}\frac{1}{\theta}\cdot\mathbf{q} + \chi_{,t}a \geq 0 \tag{4.26}$$

for all variables $\mathcal{Z}_\theta$ in (4.21).

$(M4)_\theta$ The constitutive equations have to be invariant under changes in observer (see (4.8)).

Remark 4.1. *It is seen that in both presented above formulations $(M)_\eta$ and $(M)_\theta$ the fundamental problem is that of obtaining all solutions of dissipation inequalities* (4.2) *and* (4.26) *and thereby all possible constitutive relations for the quantities $r, \mathbf{j}, \mathbf{q}$ and a. We address this question in Section 5.* ∎

Model $(M)_\theta$, similarly as $(M)_\eta$, is consistent with the second law of thermodynamics.

Theorem 4.2. *System* (4.22)–(4.26) *satisfies the following entropy inequality with multipliers*

$$
\begin{aligned}
(4.27)\qquad & \dot\eta + \nabla\cdot\boldsymbol{\Psi} - \boldsymbol{\Lambda}_{\mathbf{u}}\cdot(\ddot{\mathbf{u}} - \nabla\cdot\mathbf{S}) - \Lambda_\chi(\dot\chi + \nabla\cdot\mathbf{j} - r)\\
& -\Lambda_{\overline{\mu}}\left(-\overline{\mu} + \frac{f_{,\chi}}{\theta} - \nabla\cdot\frac{f_{,\mathbf{D}\chi}}{\theta} + a\right) - \Lambda_e(\dot e + \nabla\cdot\mathbf{q} - \mathbf{S}\cdot\dot{\mathbf{F}})\\
& -\boldsymbol{\Lambda}_{\mathbf{S}}\cdot(\mathbf{S} - f_{,\mathbf{F}}) = -\overline{\mu}r - \nabla\overline{\mu}\cdot\mathbf{j} + \nabla\frac{1}{\theta}\cdot\mathbf{q} + \dot\chi a \ge 0
\end{aligned}
$$

for all fields $\mathbf{u}, \chi, \overline{\mu} = \mu/\theta$ and θ. The multipliers are given by

$$
(4.28)\qquad \boldsymbol{\Lambda}_{\mathbf{u}} = \mathbf{0},\quad \Lambda_\chi = -\overline{\mu},\quad \Lambda_{\overline{\mu}} = -\dot\chi,\quad \Lambda_e = \frac{1}{\theta},\quad \boldsymbol{\Lambda}_{\mathbf{S}} = \frac{\dot{\mathbf{F}}}{\theta},
$$

and the entropy flux is

$$
(4.29)\qquad \boldsymbol{\Psi} = -\overline{\mu}\mathbf{j} + \frac{1}{\theta}\mathbf{q} + \dot\chi\frac{f_{,\mathbf{D}\chi}}{\theta}.
$$

Proof. Let $\mathbf{u}, \chi, \overline{\mu}$ and θ be any fields and $\boldsymbol{\Lambda}_{\mathbf{u}}$, Λ_χ, $\Lambda_{\overline{\mu}}$, Λ_e and $\boldsymbol{\Lambda}_{\mathbf{S}}$ be defined by (4.28). Then

$$
\begin{aligned}
& \boldsymbol{\Lambda}_{\mathbf{u}}\cdot(\ddot{\mathbf{u}} - \nabla\cdot\mathbf{S}) + \Lambda_\chi(\dot\chi + \nabla\cdot\mathbf{j} - r) + \Lambda_{\overline{\mu}}\left(-\overline{\mu} + \frac{f_{,\chi}}{\theta} - \nabla\cdot\frac{f_{,\mathbf{D}\chi}}{\theta} + a\right)\\
& +\Lambda_e(\dot e + \nabla\cdot\mathbf{q} - \mathbf{S}\cdot\dot{\mathbf{F}}) + \boldsymbol{\Lambda}_{\mathbf{S}}\cdot(\mathbf{S} - f_{,\mathbf{F}})\\
& = -\overline{\mu}(\dot\chi + \nabla\cdot\mathbf{j} - r) - \dot\chi\left(-\overline{\mu} + \frac{f_{,\chi}}{\theta} - \nabla\cdot\frac{f_{,\mathbf{D}\chi}}{\theta} + a\right)\\
& +\frac{1}{\theta}(\dot e + \nabla\cdot\mathbf{q} - \mathbf{S}\cdot\dot{\mathbf{F}}) + \frac{\dot{\mathbf{F}}}{\theta}\cdot(\mathbf{S} - f_{,\mathbf{F}}) \equiv I.
\end{aligned}
$$

Taking into account that

$$
\begin{aligned}
\dot e &= (f + \theta\eta)^{\cdot} = f_{,\mathbf{F}}\cdot\dot{\mathbf{F}} + f_{,\chi}\dot\chi + f_{,\mathbf{D}\chi}\cdot\nabla\dot\chi + f_{,\theta}\dot\theta + \theta\dot\eta + \eta\dot\theta\\
&= \theta\dot\eta + f_{,\mathbf{F}}\cdot\dot{\mathbf{F}} + f_{,\chi}\dot\chi + f_{,\mathbf{D}\chi}\cdot\nabla\dot\chi,
\end{aligned}
$$

a simple rearrangements lead to

$$
\begin{aligned}
I &= -\overline{\mu}\nabla\cdot\mathbf{j} + \overline{\mu}r + \dot{\chi}\nabla\cdot\frac{f_{,\mathbf{D}\chi}}{\theta} - \dot{\chi}a + \dot{\eta} + \frac{f_{,\mathbf{D}\chi}}{\theta}\cdot\nabla\dot{\chi} + \frac{1}{\theta}\nabla\cdot\mathbf{q} \\
&= \dot{\eta} + \nabla\cdot\left[-\overline{\mu}\mathbf{j} + \frac{1}{\theta}\mathbf{q} + \dot{\chi}\frac{f_{,\mathbf{D}\chi}}{\theta}\right] \\
&\quad + \overline{\mu}r + \nabla\overline{\mu}\cdot\mathbf{j} - \nabla\frac{1}{\theta}\cdot\mathbf{q} - \dot{\chi}a.
\end{aligned}
$$

This shows the equality in (4.27). The inequality in (4.27) is a consequence of (4.26). ∎

Now we collect some important implications of the above theorem.

Corollary 4.2. *The solutions of system* (4.22)–(4.26) *satisfy the entropy equation and inequality*

$$
\begin{aligned}
\dot{\eta} + \nabla\cdot\boldsymbol{\Psi} &= -\frac{\mu}{\theta}r - \nabla\frac{\mu}{\theta}\cdot\mathbf{j} + \nabla\frac{1}{\theta}\cdot\mathbf{q} + \dot{\chi}a - \frac{\mu}{\theta}\tau + \frac{g}{\theta} \\
&\geq -\frac{\mu}{\theta}\tau + \frac{g}{\theta},
\end{aligned}
\tag{4.30}
$$

where $\boldsymbol{\Psi}$ *is given by* (4.29).

Corollary 4.3. *The solutions of system* (4.22)–(4.26) *satisfy the following availability identity*

$$
\begin{aligned}
&\left(e + \frac{1}{2}|\dot{\mathbf{u}}|^2 - \overline{\theta}\eta\right)^{\cdot} + \nabla\cdot[-\mathbf{S}^T\dot{\mathbf{u}} + \mathbf{q} - \overline{\theta}\boldsymbol{\Psi}] \\
&= -\overline{\theta}\left(-\frac{\mu}{\theta}r - \nabla\frac{\mu}{\theta}\cdot\mathbf{j} + \nabla\frac{1}{\theta}\cdot\mathbf{q} + \dot{\chi}a\right) + \dot{\mathbf{u}}\cdot\mathbf{b} + g - \overline{\theta}\left(-\frac{\mu}{\theta}\tau + \frac{g}{\theta}\right),
\end{aligned}
\tag{4.31}
$$

where $\overline{\theta} = \text{const} > 0$.

Proof. Multiplying $(4.22)_1$ by $\dot{\mathbf{u}}$ we obtain the balance equation for the kinetic energy

$$
\left(\frac{1}{2}|\dot{\mathbf{u}}|^2\right)^{\cdot} - \nabla\cdot(\mathbf{S}^T\dot{\mathbf{u}}) + \mathbf{S}\cdot\dot{\mathbf{F}} = \dot{\mathbf{u}}\cdot\mathbf{b}.
\tag{4.32}
$$

Summing up (4.32), energy equation $(4.22)_4$ and entropy equation $(4.30)_1$ multiplied by $-\overline{\theta}$ we obtain (4.31). ∎

Corollary 4.4. *The solutions of* (4.22)–(4.26) *satisfy the Lyapunov relation. In fact, integration of* (4.31) *over* Ω *gives*

$$\begin{aligned}
(4.33)\qquad & \frac{d}{dt}\int_\Omega \left(e+\frac{1}{2}|\dot{\mathbf{u}}|^2-\overline{\theta}\eta\right)dx \\
&+\int_S \left[-(\mathbf{Sn})\cdot\dot{\mathbf{u}}+\mathbf{n}\cdot\mathbf{q}-\overline{\theta}\mathbf{n}\cdot\left(-\frac{\mu}{\theta}\mathbf{j}+\frac{1}{\theta}\mathbf{q}+\dot{\chi}\frac{f_{,\mathbf{D}\chi}}{\theta}\right)\right]dS \\
&=-\int_\Omega \overline{\theta}\left(-\frac{\mu}{\theta}r-\nabla\frac{\mu}{\theta}\cdot\mathbf{j}+\nabla\frac{1}{\theta}\cdot\mathbf{q}+\dot{\chi}a\right)dx \\
&+\int_\Omega \left[\dot{\mathbf{u}}\cdot\mathbf{b}+g-\overline{\theta}\left(-\frac{\mu}{\theta}\tau+\frac{g}{\theta}\right)\right]dx \\
&\le \int_\Omega \left[\dot{\mathbf{u}}\cdot\mathbf{b}+g-\overline{\theta}\left(-\frac{\mu}{\theta}\tau+\frac{g}{\theta}\right)\right]dx,
\end{aligned}$$

where $\mathbf{n}$ *denotes the unit outward normal to* $S=\partial\Omega$. *Hence, it follows that if the external sources vanish, i.e.*

$$\mathbf{b}=\mathbf{0},\qquad g=0,\qquad \tau=0,$$

and if the boundary conditions on S *imply that*

$$(4.34)\qquad (\mathbf{Sn})\cdot\dot{\mathbf{u}}=0,\quad \frac{\mu}{\theta}\mathbf{n}\cdot\mathbf{j}=0,\quad \left(1-\frac{\overline{\theta}}{\theta}\right)\mathbf{n}\cdot\mathbf{q}=0,\quad \frac{\dot{\chi}}{\theta}\mathbf{n}\cdot f_{,\mathbf{D}\chi}=0,$$

then solutions of system (4.22)–(4.26) satisfy

$$(4.35)\qquad \frac{d}{dt}\int_\Omega (e(\mathbf{F},\chi,\mathbf{D}\chi,\theta)+\frac{1}{2}|\dot{\mathbf{u}}|^2-\overline{\theta}\eta(\mathbf{F},\chi,\mathbf{D}\chi,\theta))dx\le 0.$$

This is the Lyapunov relation asserting that the function $e+\frac{1}{2}|\dot{\mathbf{u}}|^2-\overline{\theta}\eta$, *called equilibrium free energy, is nonincreasing on solutions paths.* ∎

4.5. Model $(M)_\theta$ in case of infinitesimal deformations.

Here we deduce the corresponding model within the linearized theory appropriate to situations in which the displacement gradient $\nabla\mathbf{u}$ 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 [Gur96], Sec. 4.4 or [FriGur94], Sec. 6, we redefine $\mathbf{F}$ to be $\nabla\mathbf{u}$, and replace $(2.1)_2$ by the requirement that $\mathbf{S}$ be symmetric

$$(4.36)\qquad \mathbf{S}=\mathbf{S}^T.$$

The steps leading to $(M1)_\eta-(M3)_\eta$ and $(M1)_\theta-(M3)_\theta$ remain unchanged. Further, as in [Gur96], Sec. 4.4, we conclude that the invariance of the constitutive equations under infinitesimal rotations (i.e., replacement of $\nabla\mathbf{u}$ by

$\nabla \mathbf{u} + \boldsymbol{\Omega}$ with $\boldsymbol{\Omega}$ skew) implies that constitutive functions can depend on $\nabla \mathbf{u}$ through the infinitesimal strain

$$\varepsilon(\mathbf{u}) = \frac{1}{2}(\nabla \mathbf{u} + \nabla \mathbf{u}^T).$$

Consequently, the set of variables $\mathcal{Z}_\theta$ in (4.21) is replaced by

$$\mathcal{Z}_\theta^l = \{\varepsilon(\mathbf{u}), \mathbf{D}\varepsilon(\mathbf{u}), \chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \theta, \mathbf{D}\frac{1}{\theta}, \overline{\mu}, \mathbf{D}\overline{\mu}, \chi_{,t}\}, \qquad \overline{\mu} = \frac{\mu}{\theta}.$$

Summarizing, within the linearized theory model $(M)_\theta$ is based on the following postulates:

$(M1)_\theta^l$ The unknowns are the fields $\mathbf{u}, \chi, \overline{\mu} = \mu/\theta$ and $\theta > 0$.

$(M2)_\theta^l$ The free energy is given by

$$f = \widehat{f}(\varepsilon(\mathbf{u}), \chi, \mathbf{D}\chi, \theta),$$

satisfying the requirement (4.17) of strict concavity with respect to $\theta > 0$.

$(M3)_\theta^l$ The fields $\mathbf{u}, \chi, \overline{\mu}$ and θ satisfy equations (4.22), where $\mathbf{S}$ is given by

$$\mathbf{S} = \widehat{\mathbf{S}}(\varepsilon(\mathbf{u}), \chi, \mathbf{D}\chi, \theta) = f_{,\varepsilon}(\varepsilon(\mathbf{u}), \chi, \mathbf{D}\chi, \theta),$$

hence consistent with (4.36).
Moreover, the quantities $r = \widehat{r}(\mathcal{Z}_\theta^l), \mathbf{j} = \widehat{\mathbf{j}}(\mathcal{Z}_\theta^l), \mathbf{q} = \widehat{\mathbf{q}}(\mathcal{Z}_\theta^l)$ and $a = \widehat{a}(\mathcal{Z}_\theta^l)$ are subject to the dissipation inequality

$$-\overline{\mu} r - \mathbf{D}\overline{\mu} \cdot \mathbf{j} + \mathbf{D}\frac{1}{\theta} \cdot \mathbf{q} + \chi_{,t} a \geq 0$$

for all variables $\mathcal{Z}_\theta^l$.

5. Alternative approach – internal energy as an independent variable

To show the role of the duality relations we present in this and the next section an alternative derivation of model $(M)_\theta$. More precisely, in evaluating the entropy inequality we shall use — in contrast to Section 3 — the internal energy as an independent variable and the entropy density as a corresponding thermodynamic potential.

5.1. The entropy inequality.

Let us consider balance laws (2.1) with the constitutive equations

$$\mathbf{S} = \widehat{\mathbf{S}}(Y_e), \quad \mathbf{j} = \widehat{\mathbf{j}}(Y_e), \quad r = \widehat{r}(Y_e), \quad \mathbf{q} = \widehat{\mathbf{q}}(Y_e), \tag{5.1}$$

where Y_e is the state space with the internal energy as a thermal variable (see $(2.10)_2$):

$$Y_e := \{\mathbf{F}, \mathbf{DF}, \ldots, \mathbf{D}^M\mathbf{F}, \chi, \mathbf{D}\chi, \ldots \mathbf{D}^K\chi, e, \mathbf{D}e, \ldots \mathbf{D}^L e, \chi_{,t}\}$$

where $M, L \geq 1$ and $K \geq 2$.

Similarly as in (2.12) we introduce the spliting

$$Y_e = \{Y^0, Y^1\} \tag{5.2}$$

where

$$Y^0 := \{\mathbf{F}, \mathbf{DF}, \ldots, \mathbf{D}^M\mathbf{F}, \chi, \mathbf{D}\chi, \ldots \mathbf{D}^K\chi, e, \mathbf{D}e, \ldots \mathbf{D}^L e\}$$

and

$$Y^1 := \{\chi_{,t}\}.$$

To select a class of thermodynamically consistent models we impose the entropy inequality with multipliers (2.8) which in case of state variables Y_e takes the form

$$\dot{\widetilde{\eta}} + \nabla\cdot\mathbf{\Psi} - \boldsymbol{\lambda}_{\mathbf{u}}\cdot(\ddot{\mathbf{u}} - \nabla\cdot\mathbf{S}) - \lambda_\chi(\dot{\chi} + \nabla\cdot\mathbf{j} - r) - \lambda_e(\dot{e} + \nabla\cdot\mathbf{q} - \mathbf{S}\cdot\dot{\mathbf{F}}) \geq 0 \tag{5.3}$$

for all fields $\mathbf{u}, \chi$ and e, where

(5.4)

$$\widetilde{\eta} = \widehat{\widetilde{\eta}}(Y_e), \quad \mathbf{\Psi} = \widehat{\mathbf{\Psi}}(Y_e), \quad \boldsymbol{\lambda}_{\mathbf{u}} = \widehat{\boldsymbol{\lambda}}_{\mathbf{u}}(Y_e), \quad \lambda_\chi = \widehat{\lambda}_\chi(Y_e), \quad \lambda_e = \widehat{\lambda}_e(Y_e)$$

are respectively the entropy expressed as a function of the energy, the entropy flux and the multipliers conjugated with the balance laws for the linear momentum, order parameter and energy.

5.2. The restrictions.

We impose the following two structural assumptions:
- the nondegeneracy condition for the entropy

$$\widetilde{\eta}_{,e}(Y_e) > 0 \quad \text{for all } Y_e; \tag{5.5}$$

- the relation between stationary entropy, energy and mass fluxes

$$\mathbf{\Psi}^0 = \lambda_\chi^0\mathbf{j}^0 + \lambda_e^0\mathbf{q}^0 \tag{5.6}$$

where $\mathbf{\Psi}^0, \mathbf{j}^0, \mathbf{q}^0, \lambda_\chi^0$ and λ_e^0 are stationary quantities defined by setting $\chi_{,t} = 0$ in the set Y_e, i.e. $\mathbf{\Psi}^0 := \widehat{\mathbf{\Psi}}(Y^0, Y^1)|_{Y^1=\{0\}}$ and similarly for other quantities.

We prove the following

Theorem 5.1 (Consistency with the entropy inequality). *Let us consider balance (2.1) with constitutive equations (5.1). Suppose that entropy inequality (5.3) is satisfied and assumptions (5.5), (5.6) hold true. Then the following relations are satisfied:*

(i) multiplier of the linear momentum $\boldsymbol{\lambda}_{\mathbf{u}} = \mathbf{0}$;

(ii) entropy $\widetilde{\eta} = \widehat{\widetilde{\eta}}(\mathbf{F}, \chi, \mathbf{D}\chi, e)$;

(iii) multiplier of the energy equation

$$\lambda_e = \widehat{\lambda}_e(\mathbf{F}, \chi, \mathbf{D}\chi, e) = \widetilde{\eta}_{,e}(\mathbf{F}, \chi, \mathbf{D}\chi, e) > 0; \tag{5.7}$$

(iv) stress tensor

$$\mathbf{S} = \widehat{\mathbf{S}}(\mathbf{F}, \chi, \mathbf{D}\chi, e) = -\frac{1}{\lambda_e(\mathbf{F}, \chi, \mathbf{D}\chi, e)}\widetilde{\eta}_{,\mathbf{F}}(\mathbf{F}, \chi, \mathbf{D}\chi, e); \tag{5.8}$$

(v) entropy flux

$$\boldsymbol{\Psi} = \lambda_\chi \mathbf{j} + \lambda_e \mathbf{q} - \chi_{,t}\left[\widetilde{\eta}_{,\mathbf{D}\chi} + \int_0^1 (\lambda_{\chi,\chi_{,t}}\mathbf{j})(Y^0, \tau\chi_{,t})d\tau\right]; \tag{5.9}$$

(vi) compatibility conditions

$$\begin{aligned}
&\chi_{,t}\left[-\int_0^1 (\lambda_{\chi,\chi_{,t}} j_i)(Y^0, \tau\chi_{,t})d\tau\right]_{,\mathbf{D}^M\mathbf{F}} + \lambda_{\chi,\mathbf{D}^M\mathbf{F}} j_i = \mathbf{0},\\
&\chi_{,t}\left[-\int_0^1 (\lambda_{\chi,\chi_{,t}} j_i)(Y^0, \tau\chi_{,t})d\tau\right]_{,\mathbf{D}^K\chi} + \lambda_{\chi,\mathbf{D}^K\chi} j_i = \mathbf{0},\\
&\chi_{,t}\left[-\int_0^1 (\lambda_{\chi,\chi_{,t}} j_i)(Y^0, \tau\chi_{,t})d\tau\right]_{,\mathbf{D}^L e} + \lambda_{\chi,\mathbf{D}^L e} j_i = \mathbf{0}
\end{aligned} \tag{5.10}$$

for $i = 1, 2, 3$.

Moreover, there exists a scalar quantity $a = \widehat{a}(Y_e)$ *such that*

(vii) multiplier $\lambda_\chi = \widehat{\lambda}_\chi(Y_e)$ *satisfies the equation*

$$-\lambda_\chi = -\frac{\delta\widetilde{\eta}}{\delta\chi} + \nabla^{\widetilde{Y}^0}\cdot\int_0^1 (\lambda_{\chi,\chi_{,t}}\mathbf{j})(Y^0, \tau\chi_{,t})d\tau + a, \tag{5.11}$$

where

$$\begin{aligned}
\widetilde{Y}^0 &:= Y^0 \setminus \{\mathbf{D}^M\mathbf{F}, \mathbf{D}^K\chi, \mathbf{D}^L e\}\\
&= \{\mathbf{F}, \mathbf{DF}, \dots, \mathbf{D}^{M-1}\mathbf{F}, \chi, \mathbf{D}\chi, \dots, \mathbf{D}^{K-1}\chi, e, \mathbf{D}e, \dots \mathbf{D}^{L-1}e\},\\
\frac{\delta\widetilde{\eta}}{\delta\chi} &= \frac{\delta^{\widetilde{Y}^0}\widetilde{\eta}}{\delta\chi} = \widetilde{\eta}_{,\chi} - \nabla\cdot\widetilde{\eta}_{,\mathbf{D}\chi};
\end{aligned}$$

(viii) the quantities $r = \widehat{r}(Y_e)$, $\mathbf{j} = \widehat{\mathbf{j}}(Y_e)$, $\mathbf{q} = \widehat{\mathbf{q}}(Y_e)$ *and* $a = \widehat{a}(Y_e)$ *satisfy the residual inequality*

$$\lambda_\chi r + \nabla^{\widetilde{Y}^0}\lambda_\chi \cdot \mathbf{j} + \nabla\lambda_e \cdot \mathbf{q} + \chi_{,t}a \geq 0 \tag{5.12}$$

for all variables Y_e.

Proof of Theorem 5.1. By inserting constitutive equations (5.1), (5.4) into entropy inequality (5.3) and applying the chain rule we arrive at the algebraic ineqality:

$$\begin{aligned}(5.13)\quad & \sum_{m=0}^{M}\widetilde{\eta}_{,\mathbf{D}^m\mathbf{F}} \cdot \mathbf{D}^m\mathbf{F}_{,t} + \sum_{k=0}^{K}\widetilde{\eta}_{,\mathbf{D}^k\chi} \cdot \mathbf{D}^k\chi_{,t} + \sum_{l=0}^{L}\widetilde{\eta}_{,\mathbf{D}^l e} \cdot \mathbf{D}^l e_{,t}\\ & + \widetilde{\eta}_{,\chi_t}\chi_{,tt} + \mathbf{\Psi}_{,\chi_t} \cdot \mathbf{D}\chi_{,t} + \nabla^{Y^0} \cdot \mathbf{\Psi} - \boldsymbol{\lambda}_\mathbf{u} \cdot \mathbf{u}_{,tt}\\ & + \lambda_\mathbf{u} \cdot (\mathbf{S}_{,\chi_{,t}}\mathbf{D}\chi_{,t}) + \lambda_\mathbf{u} \cdot (\nabla^{Y^0} \cdot \mathbf{S}) - \lambda_\chi\chi_{,t} - \lambda_\chi\mathbf{j}_{,\chi_{,t}} \cdot \mathbf{D}\chi_{,t}\\ & - \lambda_\chi\nabla^{Y^0} \cdot \mathbf{j} + \lambda_r r - \lambda_e e_{,t} - \lambda_e\mathbf{q}_{,\chi_{,t}} \cdot \mathbf{D}\chi_{,t} - \lambda_e\nabla^{Y^0} \cdot \mathbf{q} + \lambda_e\mathbf{S} \cdot \mathbf{F}_{,t} \geq 0\end{aligned}$$

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

$$\begin{aligned}W := \{&\mathbf{u}_{,tt}, \chi_{,tt}, (\mathbf{D}^m\mathbf{F}_{,t})_{0\leq m\leq M}, (\mathbf{D}^k\chi_{,t})_{1\leq k\leq K}, (\mathbf{D}^l e_{,t})_{0\leq l\leq L},\\ &\mathbf{D}^{M+1}\mathbf{F}, \mathbf{D}^{K+1}\chi, \mathbf{D}^{L+1}e\}\end{aligned}$$

denotes the set of variables in which the left-hand side of (5.13) is linear. Further procedure consists in deriving consequences from the linearity in the variables belonging to the set W.

Step 1. By the linearity of the left-hand side of (5.13) in $\mathbf{u}_{,tt}$ it follows that the corresponding coefficient preceding this variable has to vanish, i.e. $\boldsymbol{\lambda}_\mathbf{u} = \mathbf{0}$. This shows (i).

Step 2. By the linearity in the variables $(\mathbf{D}^m\mathbf{F}_{,t})_{1\leq m\leq M}$, $(\mathbf{D}^k\chi_{,t})_{2\leq k\leq K}$, $(\mathbf{D}^l e_{,t})_{1\leq l\leq L}$, $\chi_{,tt}$ we read off that $\widetilde{\eta}_{,\mathbf{D}^m\mathbf{F}} = \mathbf{0}$ for $1 \leq m \leq M$, $\widetilde{\eta}_{,\mathbf{D}^k\chi} = \mathbf{0}$ for $2 \leq k \leq K$, $\widetilde{\eta}_{,\mathbf{D}^l e} = \mathbf{0}$ for $1 \leq l \leq L$ and $\widetilde{\eta}_{,\chi_{,t}} = 0$. Hence, the constitutive dependence of $\widetilde{\eta}$ is restricted to $\widetilde{\eta} = \widehat{\widetilde{\eta}}(\mathbf{F}, \chi, \mathbf{D}\chi, e)$ which shows (ii).

Step 3. The linearity in $e_{,t}$ implies that

$$\widetilde{\eta}_{,e} - \lambda_e = 0.$$

Hence, in view of (ii) and assumption (5.5) we conclude (iii).

Step 4. By the linearity in $\mathbf{F}_{,t}$,

$$\widetilde{\eta}_{,\mathbf{F}} + \lambda_e\mathbf{S} = \mathbf{0},$$

so, due to assumption (5.5), (ii) and (iii) we infer (iv).

Step 5. From the linearity in $\mathbf{D}\chi_{,t}$ we deduce that

$$\widetilde{\eta}_{,\mathbf{D}\chi} + \boldsymbol{\Psi}_{,\chi,t} - \lambda_\chi \mathbf{j}_{,\chi,t} - \lambda_e \mathbf{q}_{,\chi,t} = \mathbf{0}. \tag{5.14}$$

Next, let us define the vector

$$\widetilde{\boldsymbol{\Psi}} := \boldsymbol{\Psi} - \lambda_\chi \mathbf{j} - \lambda_e \mathbf{q}. \tag{5.15}$$

By virtue of assumption (5.6),

$$\widetilde{\boldsymbol{\Psi}}^0 = \mathbf{0}. \tag{5.16}$$

From (5.15), using (5.14) and (iii), we get

$$\begin{aligned} \widetilde{\boldsymbol{\Psi}}_{,\chi,t} &= \boldsymbol{\Psi}_{,\chi,t} - \lambda_{\chi,\chi,t}\mathbf{j} - \lambda_\chi \mathbf{j}_{,\chi,t} - \lambda_e \mathbf{q}_{,\chi,t} \\ &= -\widetilde{\eta}_{,\mathbf{D}\chi} - \lambda_{\chi,\chi,t}\mathbf{j}. \end{aligned} \tag{5.17}$$

Hence, in view of (5.16), (ii) and (iii), it follows that

$$\begin{aligned} \widetilde{\boldsymbol{\Psi}} &= -\widetilde{\eta}_{,\mathbf{D}\chi}\chi_{,t} - \int_0^{\chi,t} (\lambda_{\chi,\chi,t}\mathbf{j})(Y^0,\xi)d\xi \\ &= -\chi_{,t}\left[\widetilde{\eta}_{,\mathbf{D}\chi} + \int_0^1 (\lambda_{\chi,\chi,t}\mathbf{j})(Y^0,\tau\chi_{,t})d\tau\right]. \end{aligned} \tag{5.18}$$

From (5.15) and (5.18) we conclude (v).

Step 6. It remains to examine the linearity in the variables $\mathbf{D}^{M+1}\mathbf{F}, \mathbf{D}^{K+1}\chi$ and $\mathbf{D}^{L+1}e$. On account of the results obtained in the previous steps, inequality (5.13) is reduced to

$$(\widetilde{\eta}_{,\chi} - \lambda_\chi)\chi_{,t} + \lambda_\chi r + \nabla^{Y^0}\cdot\boldsymbol{\Psi} - \lambda_\chi \nabla^{Y^0}\cdot\mathbf{j} - \lambda_e \nabla^{Y^0}\cdot\mathbf{q} \geq 0 \tag{5.19}$$

for all variables $\{\mathbf{D}^{M+1}\mathbf{F}, \mathbf{D}^{K+1}\chi, \mathbf{D}^{L+1}e, Y_e\}$. We rearrange now the sum of the last three terms on the right-hand side of (5.19) to the form

$$\begin{aligned} &\nabla^{Y^0}\cdot\boldsymbol{\Psi} - \lambda_\chi\nabla^{Y^0}\cdot\mathbf{j} - \lambda_e\nabla^{Y^0}\cdot\mathbf{q} \\ &= \nabla^{Y^0}\cdot(\boldsymbol{\Psi} - \lambda_\chi\mathbf{j} - \lambda_e\mathbf{q}) + \nabla^{Y^0}\lambda_\chi\cdot\mathbf{j} + \nabla^{Y^0}\lambda_e\cdot\mathbf{q} \\ &= \nabla^{Y^0}\cdot\widetilde{\boldsymbol{\Psi}} + \nabla^{Y^0}\lambda_\chi\cdot\mathbf{j} + \nabla^{Y^0}\lambda_e\cdot\mathbf{q}. \end{aligned} \tag{5.20}$$

Further, in view of (5.18), recalling the definition of $\nabla^{Y^0}\cdot$ (see Section 3.2), it follows that

$$\nabla^{Y^0}\cdot\widetilde{\boldsymbol{\Psi}} = -\chi_{,t}\left[\nabla^{Y^0}\cdot\widetilde{\eta}_{,\mathbf{D}\chi} + \nabla^{Y^0}\cdot\int_0^1 (\lambda_{\chi,\chi,t}\mathbf{j})(Y^0,\tau\chi_{,t})d\tau\right]. \tag{5.21}$$

Consequently, by combining (5.20) and (5.21), inequality (5.19) is transformed to

$$\begin{aligned}(5.22)\qquad &\chi_{,t}\left[-\lambda_\chi + \widetilde{\eta}_{,\chi} - \nabla^{Y^0}\cdot\widetilde{\eta}_{,\mathbf{D}\chi} - \nabla^{Y^0}\cdot\int_0^1(\lambda_{\chi,\chi,_t}\mathbf{j})(Y^0,\tau\chi_{,t})d\tau\right]\\ &+\lambda_\chi r + \nabla^{Y^0}\lambda_\chi\cdot\mathbf{j} + \nabla^{Y^0}\lambda_e\cdot\mathbf{q}\geq 0\end{aligned}$$

for all variables $\{\mathbf{D}^{M+1}\mathbf{F}, \mathbf{D}^{K+1}\chi, \mathbf{D}^{L+1}e, Y_e\}$.

From (5.22), performing differentiation by the chain rule in terms involving $\nabla^{Y^0}\cdot$ and ∇^{Y^0} (restricting now to the subset $\widetilde{Y}^0$), the linearity in the variables $\mathbf{D}^{M+1}\mathbf{F}, \mathbf{D}^{K+1}\chi$ and $\mathbf{D}^{L+1}e$ implies that the coefficients preceding these variables have to vanish. Hence, recalling (ii) and (iii), we conclude (vi).

Step 7. On account of (vi) inequality (5.22) becomes

$$\begin{aligned}(5.23)\qquad &\chi_{,t}\left[-\lambda_\chi + \widetilde{\eta}_{,\chi} - \nabla^{\widetilde{Y}^0}\cdot\widetilde{\eta}_{,\mathbf{D}\chi} - \nabla^{\widetilde{Y}^0}\cdot\int_0^1(\lambda_{\chi,\chi,_t}\mathbf{j})(Y^0,\tau\chi_{,t})d\tau\right]\\ &\qquad\qquad+\lambda_\chi r + \nabla^{\widetilde{Y}^0}\lambda_\chi\cdot\mathbf{j} + \nabla^{\widetilde{Y}^0}\lambda_e\cdot\mathbf{q}\geq 0\end{aligned}$$

for all variables Y_e. Now, let us define a scalar quantity $a = \widehat{a}(Y_e)$ given by the squared parenthesis in (5.23), viz.

$$(5.24)\qquad a := -\lambda_\chi + \widetilde{\eta}_{,\chi} - \nabla^{\widetilde{Y}^0}\cdot\widetilde{\eta}_{,\mathbf{D}\chi} - \nabla^{\widetilde{Y}^0}\cdot\int_0^1(\lambda_{\chi,\chi,_t}\mathbf{j})(Y^0,\tau\chi_{,t})d\tau.$$

Let us note that on account of (ii) and (iii),

$$(5.25)\qquad \nabla^{\widetilde{Y}^0}\cdot\widetilde{\eta}_{,\mathbf{D}\chi} = \nabla\cdot\widetilde{\eta}_{,\mathbf{D}\chi},\qquad \nabla^{\widetilde{Y}^0}\lambda_e = \nabla\lambda_e,$$

so that, recalling (3.4),

$$\frac{\delta^{\widetilde{Y}^0}\widetilde{\eta}}{\delta\chi} = \widetilde{\eta}_{,\chi} - \nabla^{\widetilde{Y}^0}\cdot\widetilde{\eta}_{,\mathbf{D}\chi} = \frac{\delta\widetilde{\eta}}{\delta\chi}.$$

Consequently,

$$a = -\lambda_\chi + \frac{\delta\widetilde{\eta}}{\delta\chi} - \nabla^{\widetilde{Y}^0}\cdot\int_0^1(\lambda_{\chi,\chi,_t}\mathbf{j})(Y^0,\tau\chi_{,t})d\tau.$$

This shows assertion (vii). Finally, in view of (5.24), and $(5.25)_2$, inequality (5.23) takes the form of the residual inequality (5.12). This shows assertion (viii) and thereby completes the proof. ∎

5.3. The restrictions in the nonconserved case.

As in Section 3, it is of interest to distinguish thermodynamic restrictions in the nonconserved case ($\mathbf{j} \equiv \mathbf{0}$). Then assumption (5.6) reduces to

$$\boldsymbol{\Psi}^0 = \lambda_e^0 \mathbf{q}^0, \tag{5.26}$$

and Theorem 3.1 specializes to

Theorem 5.2. *(Consistency with the entropy inequality in the nonconserved case).*
Let us consider balance laws (2.1) *with constitutive equations* (5.1) *in the nonconserved case* $\mathbf{j} \equiv \mathbf{0}, r \neq 0$. *Suppose that the entropy inequality* (5.3), *is satisfied and assumptions* (5.5), (5.26) *hold true. Then the following relations are satisfied:*

(i) $\boldsymbol{\lambda}_{\mathbf{u}} = \mathbf{0}$;
(ii) $\widetilde{\eta} = \widehat{\widetilde{\eta}}(\mathbf{F}, \chi, \mathrm{D}\chi, e)$;
(iii) $\lambda_e = \widehat{\lambda}_e(\mathbf{F}, \chi, \mathrm{D}\chi, e) = \widetilde{\eta}_{,e}(\mathbf{F}, \chi, \mathrm{D}\chi, e) > 0$;
(iv) $\mathbf{S} = \widehat{\mathbf{S}}(\mathbf{F}, \chi, \mathrm{D}\chi, e) = -\dfrac{1}{\lambda_e(\mathbf{F}, \chi, \mathrm{D}\chi, e)} \widetilde{\eta}_{,\mathbf{F}}(\mathbf{F}, \chi, \mathrm{D}\chi, e)$;
(v) $\boldsymbol{\Psi} = \lambda_e \mathbf{q} - \chi_{,t} \widetilde{\eta}_{,\mathrm{D}\chi}$.
Moreover, there exists a scalar field $a = \widehat{a}(Y_\eta)$ *such that*
(vi) $-\lambda_\chi = -\dfrac{\delta \widetilde{\eta}}{\delta \chi} + a$;
(vii) $\lambda_\chi r + \nabla \lambda_e \cdot \mathbf{q} + \chi_{,t} a \geq 0$ *for all variables* Y_e.

6. Extended models $(M)_e$ and $(M)_\vartheta$ based on internal energy and inverse temperature as independent variables

6.1. Multipliers as additional independent variables.

On the basis of Theorem 5.1, following the idea described in Section 4, we introduce an extended model in which the multipliers λ_χ and λ_e are in addition to $\mathbf{u}, \chi$ and e treated as independent variables. The extended model is based on the following modifications of the statements of Theorem 5.1:
— We replace the state space Y_e in (5.1) by

$$\mathcal{Z}_e := \{\mathbf{F}, \mathrm{D}\mathbf{F}, \chi, \mathrm{D}\chi, \mathrm{D}^2\chi, e, \mathrm{D}e, \lambda_\chi, \mathrm{D}\lambda_\chi, \lambda_e, \mathrm{D}\lambda_e, \chi_{,t}\}. \tag{6.1}$$

This set includes all variables which will appear in the extended model. The higher derivatives $\mathrm{D}^m\mathbf{F}, \mathrm{D}^k\chi, \mathrm{D}^l e$ for $m, l \geq 2, k \geq 3$ are irrelevant.
— Regarding λ_χ as an independent variable we set all expressions involving its

derivatives with respect to $\chi_{,t}, \mathbf{D}^M\mathbf{F}, \mathbf{D}^K\chi, \mathbf{D}^L e$ equal zero and replace $\nabla^{\widetilde{Y}^0}\lambda_\chi$ by $\nabla\lambda_\chi$.

Formally, with such modifications statements (i)–(iv) of Theorem 5.1 remain unchanged, (vi) is automatically satisfied and (v), (vii), (viii) are respectively replaced by:

$(\widetilde{\mathrm{v}})$ $\boldsymbol{\Psi} = \lambda_\chi \mathbf{j} - \lambda_e \mathbf{q} - \chi_{,t}\widetilde{\eta}_{,\mathbf{D}\chi}$;

$(\widetilde{\mathrm{vii}})$ $-\lambda_\chi = -\dfrac{\delta\widetilde{\eta}}{\delta\chi} + a$;

$(\widetilde{\mathrm{viii}})$ the quantities $r = \widehat{r}(\mathcal{Z}_e)$, $\mathbf{j} = \widehat{\mathbf{j}}(\mathcal{Z}_e)$, $\mathbf{q} = \widehat{\mathbf{q}}(\mathcal{Z}_e)$ and $a = \widehat{a}(\mathcal{Z}_e)$ satisfy the inequality

(6.2) $$\lambda_\chi r + \mathbf{D}\lambda_\chi \cdot \mathbf{j} + \mathbf{D}\lambda_e \cdot \mathbf{q} + \chi_{,t} a \geq 0$$

for all variables $\mathcal{Z}_e$ in (6.1).

6.2. Model $(M)_e$ – formulation with entropy $\widetilde{\eta} = \widehat{\widetilde{\eta}}(\mathbf{F}, \chi, \mathbf{D}\chi, e)$ as a thermodynamic potential.

The extended model, referred further to as $(M)_e$, is based on the following postulates:

$(M1)_e$ The unknowns are the fields $\mathbf{u}, \chi, e$ and $\lambda_\chi, \lambda_e > 0$.

$(M2)_e$ A thermodynamic potential is the entropy

(6.3) $$\widetilde{\eta} = \widehat{\widetilde{\eta}}(\mathbf{F}, \chi, \mathbf{D}\chi, e),$$

subject to the condition

(6.4) $$\widetilde{\eta}_{,e} > 0 \text{ for all arguments } (\mathbf{F}, \chi, \mathbf{D}\chi, e).$$

$(M3)_e$ The fields $\mathbf{u}, \chi, e, \lambda_\chi$ and λ_e satisfy the differential equations

(6.5) $$\begin{aligned} &\ddot{\mathbf{u}} - \nabla \cdot \mathbf{S} = \mathbf{b}, \\ &\dot{\chi} + \nabla \cdot \mathbf{j} - r = \tau, \\ &-\lambda_\chi = -\frac{\delta\widetilde{\eta}}{\delta\chi} + a, \\ &\dot{e} + \nabla \cdot \mathbf{q} - \mathbf{S} \cdot \dot{\mathbf{F}} = g, \\ &\lambda_e - \widetilde{\eta}_{,e} = 0, \end{aligned}$$

where $\mathbf{S}$ is given by

(6.6) $$\mathbf{S} = -\frac{1}{\lambda_e}\widetilde{\eta}_{,\mathbf{F}},$$

consistent with the condition

(6.7) $$\mathbf{S}\mathbf{F}^T = \mathbf{F}\mathbf{S}^T.$$

Moreover, the quantities $r = \widehat{r}(\mathcal{Z}_e)$, $\mathbf{j} = \widehat{\mathbf{j}}(\mathcal{Z}_e)$, $\mathbf{q} = \widehat{\mathbf{q}}(\mathcal{Z}_e)$ and $a = \widehat{a}(\mathcal{Z}_e)$ are subject to the dissipation inequality (6.2).

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

$$\begin{aligned}
&\widetilde{\eta} = \widehat{\widetilde{\eta}}(\mathbf{F}, \chi, \mathbf{D}\chi, e), \qquad \mathbf{S} = \widehat{\mathbf{S}}(\mathbf{F}, \chi, \mathbf{D}\chi, e),\\
&\boldsymbol{\xi} = \widehat{\boldsymbol{\xi}}(\mathbf{F}, \chi, \mathbf{D}\chi, e) := \widetilde{\eta}_{,\mathbf{D}\chi}(\mathbf{F}, \chi, \mathbf{D}\chi, e),\\
&\mathbf{j} = \widehat{\mathbf{j}}(\mathcal{Z}_e), \quad \mathbf{q} = \widehat{\mathbf{q}}(\mathcal{Z}_e), \quad r = \widehat{r}(\mathcal{Z}_e), \quad a = \widehat{a}(\mathcal{Z}_e)
\end{aligned}$$

are assumed to be invariant under changes in observer, similarly as in (4.8).

6.3. Thermodynamic consistency of model $(M)_e$.

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

Theorem 6.1. *System* (6.5) *with relations* (6.3), (6.6) *and* (6.2) *satisfies the following entropy inequality with multipliers*

$$\begin{aligned}
(6.8)\qquad &[\widetilde{\eta}(\mathbf{F}, \chi, \mathbf{D}\chi, e)]^{\cdot} + \nabla \cdot \boldsymbol{\Psi} - \boldsymbol{\Lambda}_{\mathbf{u}} \cdot (\ddot{\mathbf{u}} - \nabla \cdot \mathbf{S}) - \Lambda_\chi(\dot{\chi} + \nabla \cdot \mathbf{j} - r)\\
&-\Lambda_{\lambda_\chi}(\lambda_\chi - \widetilde{\eta}_{,\chi} + \nabla \cdot \widetilde{\eta}_{,\mathbf{D}\chi} + a)\\
&-\Lambda_e(\dot{e} + \nabla \cdot \mathbf{q} - \mathbf{S} \cdot \dot{\mathbf{F}}) - \Lambda_{\lambda_e}(\lambda_e - \widetilde{\eta}_{,e}) - \boldsymbol{\Lambda}_{\mathbf{S}} \cdot \left(\mathbf{S} + \frac{1}{\lambda_e}\widetilde{\eta}_{,\mathbf{F}}\right)\\
&= \lambda_\chi r + \nabla\lambda_\chi \cdot \mathbf{j} + \nabla\lambda_e \cdot \mathbf{q} + \dot{\chi} a \geq 0
\end{aligned}$$

for all fields $\mathbf{u}, \chi, e, \lambda_\chi, \lambda_e$. *The corresponding multipliers are given by*

$$\begin{aligned}
(6.9)\qquad &\boldsymbol{\Lambda}_{\mathbf{u}} = \mathbf{0}, \quad \Lambda_\chi = \lambda_\chi, \quad \Lambda_{\lambda_\chi} = -\dot{\chi},\\
&\Lambda_e = \lambda_e, \quad \Lambda_{\lambda_e} = -\dot{e}, \quad \boldsymbol{\Lambda}_{\mathbf{S}} = \lambda_e \dot{\mathbf{F}},
\end{aligned}$$

and the entropy flux is

$$(6.10)\qquad \boldsymbol{\Psi} = \lambda_\chi \mathbf{j} + \lambda_e \mathbf{q} - \dot{\chi}\widetilde{\eta}_{,\mathbf{D}\chi}.$$

Proof. Let $\mathbf{u}, \chi, e, \lambda_\chi, \lambda_e$ be any fields and $\boldsymbol{\Lambda}_{\mathbf{u}}, \Lambda_\chi, \Lambda_{\lambda_\chi}, \Lambda_e, \Lambda_{\lambda_e}, \boldsymbol{\Lambda}_{\mathbf{S}}$ be defined by (6.9). Then simple rearrangements lead to the following identities:

$$\begin{aligned}
&\boldsymbol{\Lambda}_{\mathbf{u}} \cdot (\ddot{\mathbf{u}} - \nabla \cdot \mathbf{S}) + \Lambda_\chi(\dot{\chi} + \nabla \cdot \mathbf{j} - r)\\
&+\Lambda_{\lambda_\chi}(\lambda_\chi - \widetilde{\eta}_{,\chi} + \nabla \cdot \widetilde{\eta}_{,\mathbf{D}\chi} + a) + \Lambda_e(\dot{\widetilde{e}} + \nabla \cdot \mathbf{q} - \mathbf{S} \cdot \dot{\mathbf{F}})\\
&+\Lambda_{\lambda_e}(\lambda_e - \widetilde{\eta}_{,e}) + \boldsymbol{\Lambda}_{\mathbf{S}} \cdot \left(\mathbf{S} + \frac{1}{\lambda_e}\dot{\mathbf{F}}\right)
\end{aligned}$$

$$\begin{aligned}
&= \lambda_\chi(\dot\chi + \nabla\cdot\mathbf{j} - r) - \dot\chi(\lambda_\chi - \widetilde\eta_{,\chi} + \nabla\cdot\widetilde\eta_{,\mathbf{D}\chi}) + a) \\
&\quad +\lambda_e(\dot e + \nabla\cdot\mathbf{q} - \mathbf{S}\cdot\dot{\mathbf{F}}) - \dot e(\lambda_e - \widetilde\eta_{,e}) \\
&\quad +\lambda_e\dot{\mathbf{F}}\cdot\left(\mathbf{S} + \frac{1}{\lambda_e}\widetilde\eta_{,\mathbf{F}}\right) \\
&= \widetilde\eta_{,\mathbf{F}}\cdot\dot{\mathbf{F}} + \widetilde\eta_{,\chi}\dot\chi + \widetilde\eta_{,\mathbf{D}\chi}\cdot\nabla\dot\chi + \widetilde\eta_{,e}\dot e \\
&\quad +\nabla\cdot(\lambda_\chi\mathbf{j} + \lambda_e\mathbf{q} - \dot\chi\widetilde\eta_{,\mathbf{D}\chi}) - \lambda_\chi r - \nabla\lambda_\chi\cdot\mathbf{j} - \nabla\lambda_e\cdot\mathbf{q} - \dot\chi a \\
&= [\widetilde\eta(\mathbf{F},\chi,\mathbf{D}\chi,e)]^{\cdot} + \nabla\cdot\mathbf{\Psi} - \lambda_\chi r - \nabla\lambda_\chi\cdot\mathbf{j} - \nabla\lambda_e\cdot\mathbf{q} - \dot\chi a.
\end{aligned}$$

This shows the equality in (6.8). The inequality in (6.8) is a consequence of dissipation inequality (6.2). The proof is completed. ■

Corollary 6.1. *From* (6.8) *it follows that solutions of system* (6.5) *with* (6.3), (6.6), (6.2) *satisfy the following entropy equation and inequality*

$$(6.11)\quad [\widetilde\eta(\mathbf{F},\chi,\mathbf{D}\chi,e)]^{\cdot} + \nabla\cdot\mathbf{\Psi} = \lambda_\chi r + \nabla\lambda_\chi\cdot\mathbf{j} + \nabla\lambda_e\cdot\mathbf{q} + \dot\chi a + \lambda_\chi\tau + \lambda_e g \geq \lambda_\chi\tau + \lambda_e g,$$

where the entropy flux $\mathbf{\Psi}$ *is given by* (6.10).

6.4. Model $(M)_\vartheta$ – formulation with rescaled free energy $\phi = \widehat\phi(\mathbf{F},\chi,\mathbf{D}\chi,\vartheta)$ as a thermodynamic potential.

Under assumption of thermal stability

$$(6.12)\qquad \overline{c}_0 = \widehat{\overline{c}}_0(\mathbf{F},\chi,\mathbf{D}\chi,\vartheta) = \widehat{c}_0\left(\mathbf{F},\chi,\mathbf{D}\chi,\frac{1}{\vartheta}\right) > 0$$

model $(M)_e$ can be equivalently expressed in terms of the inverse temperature ϑ as an independent thermal variable and the reduced free energy $\phi = \widehat\phi(\mathbf{F},\chi,\mathbf{D}\chi,\vartheta)$ as a thermodynamic potential.

If $\overline{c}_0 > 0$ then duality relations (2.27) hold true. For notational consistency with (2.27), in view of the transformation between the inverse temperature ϑ and the internal energy $\overline{e}$, let us set now $e = \overline{e}$ in the statement of $(M)_e$.

According to Lemma 2.4, if $\overline{c}_0 > 0$ then

(6.13) the map $\overline{e} \mapsto \widetilde\eta(\mathbf{F},\chi,\mathbf{D}\chi,\overline{e})$ is strictly concave, so the map $\overline{e} \mapsto \widetilde\eta_{,\overline{e}}(\mathbf{F},\chi,\mathbf{D}\chi,\overline{e})$ is strictly decreasing.

From now on we shall assume that $\widetilde\eta$ satisfies (6.13) in addition to (6.4), i.e.

(6.14) $\widetilde\eta = \widehat{\widetilde\eta}(\mathbf{F},\chi,\mathbf{D}\chi,\overline{e})$ is strictly concave as a function of $\overline{e}$, and such that $\widetilde\eta_{,\overline{e}} > 0$ for all arguments $(\mathbf{F},\chi,\mathbf{D}\chi,\overline{e})$.

Under such assumption the duality relations (2.27) are satisfied. Consequently, by $(6.5)_5$ and $(2.27)_2$, it follows that

$$\lambda_e = \widetilde{\eta}_{,\overline{e}} = \vartheta \tag{6.15}$$

which means that the energy multiplier can be identified with the inverse temperature. Clearly, the assumption $\widetilde{\eta}_{,\overline{e}} > 0$ is equivalent to $\vartheta > 0$.
Moreover, the requirement (6.13) means that

(6.16) the map $\overline{e} \mapsto \widehat{\vartheta}(\mathbf{F}, \chi, \mathrm{D}\chi, \overline{e})$ is strictly decreasing,
so there exists a well-defined inverse map $\vartheta \mapsto \widehat{\overline{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta)$.

Further, in view of the equalities (2.39), the strict concavity of $\widetilde{\eta} = \widehat{\widetilde{\eta}}(\mathbf{F}, \chi, \mathrm{D}\chi, \overline{e})$ with respect to $\overline{e}$ is equivalent to the strict concavity of $\phi = \widehat{\phi}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta)$ with respect to ϑ. Hence, the assumption (6.14) expressed in terms of ϕ reads:

(6.17) $\phi = \widehat{\phi}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta)$ is strictly concave with respect to $\vartheta > 0$.

In addition, recalling (2.42),

$$-\widetilde{\eta}_{,\mathbf{F}} = \phi_{,\mathbf{F}}, \quad -\widetilde{\eta}_{,\chi} = \phi_{,\chi}, \quad -\widetilde{\eta}_{,\mathrm{D}\chi} = \phi_{,\mathrm{D}\chi}, \quad -\frac{\delta\widetilde{\eta}}{\delta\chi} = \frac{\delta\phi}{\delta\chi} \tag{6.18}$$

with appropriate arguments.

Similarly as in Section 4, we shall identify $-\lambda_\chi$ with a rescaled chemical potential

$$-\lambda_\chi = \overline{\mu} := \vartheta\mu. \tag{6.19}$$

Then, on account of $(6.18)_4$, equation $(6.5)_3$ becomes

$$\overline{\mu} = \frac{\delta\phi}{\delta\chi} + a. \tag{6.20}$$

Further, by (6.15) and $(6.18)_1$, equation (6.6) is transformed to the form

$$\mathbf{S} = \frac{1}{\vartheta}\phi_{,\mathbf{F}}. \tag{6.21}$$

Moreover, by virtue of (2.34) and (2.35)

$$\begin{aligned} \widehat{\eta}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta) &= \widehat{\widetilde{\eta}}(\mathbf{F}, \chi, \mathrm{D}\chi, \widehat{\overline{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta)) \\ &= -\widehat{\phi}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta) + \vartheta\widehat{\overline{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta) \end{aligned} \tag{6.22}$$

with

$$\widehat{\overline{e}}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta) = \widehat{\phi}_{,\vartheta}(\mathbf{F}, \chi, \mathrm{D}\chi, \vartheta).$$

In view of relations (6.15), (6.16), (6.19) and $(2.37)_2$ the state space $\mathcal{Z}_e$ in (6.1) (with $e = \overline{e}$) is replaced by

$$\mathcal{Z}_\vartheta := \left\{\mathbf{F}, \mathrm{D}\mathbf{F}, \chi, \mathrm{D}\chi, \mathrm{D}^2\chi, \vartheta, \mathrm{D}\vartheta, \overline{\mu}, \mathrm{D}\overline{\mu}, \chi_{,t}\right\}, \quad \overline{\mu} = \vartheta\mu. \tag{6.23}$$

Summarizing the above conclusions, we arrive at the following formulation of model $(M)_e$, referred further as $(M)_\vartheta$, expressed in terms of ϑ as an independent thermal variable:

$(M1)_\vartheta$ The unknowns are the fields $\mathbf{u}, \chi, \overline{\mu} = \vartheta\mu$ and $\vartheta > 0$.

$(M2)_\vartheta$ A thermodynamic potential is the reduced free energy $\phi = \widehat{\phi}(\mathbf{F}, \chi, \mathbf{D}\chi, \vartheta)$ satisfying (6.17).

$(M3)_\vartheta$ The fields $\mathbf{u}, \chi, \overline{\mu} = \vartheta\mu$ and ϑ satisfy the system of equations

$$
\begin{aligned}
&\ddot{\mathbf{u}} - \nabla\cdot\mathbf{S} = \mathbf{b},\\
&\dot{\chi} + \nabla\cdot\mathbf{j} - r = \tau,\\
&\overline{\mu} = \frac{\delta\phi}{\delta\chi} + a,\\
&\dot{\overline{e}} + \nabla\cdot\mathbf{q} - \mathbf{S}\cdot\dot{\mathbf{F}} = g,
\end{aligned}
\tag{6.24}
$$

where

$$
\begin{aligned}
&\overline{e} = \widehat{\overline{e}}(\mathbf{F}, \chi, \mathbf{D}\chi, \vartheta) = \widehat{\phi}_{,\vartheta}(\mathbf{F}, \chi, \mathbf{D}\chi, \vartheta),\\
&\widehat{\phi}(\mathbf{F}, \chi, \mathbf{D}\chi, \vartheta) + \widehat{\overline{\eta}}(\mathbf{F}, \chi, \mathbf{D}\chi, \vartheta) = \vartheta\widehat{\overline{e}}(\mathbf{F}, \chi, \mathbf{D}\chi, \vartheta),\\
&\frac{\delta\phi}{\delta\chi} = \phi_{,\chi} - \nabla\cdot\phi_{,\mathbf{D}\chi},
\end{aligned}
\tag{6.25}
$$

and $\mathbf{S}$ is given by

$$
\mathbf{S} = \frac{1}{\vartheta}\phi_{,\mathbf{F}},
\tag{6.26}
$$

consistent with the condition

$$
\mathbf{S}\mathbf{F}^T = \mathbf{F}\mathbf{S}^T.
$$

Moreover, the quantities $r = \widehat{r}(\mathcal{Z}_\vartheta)$, $\mathbf{j} = \widehat{\mathbf{j}}(\mathcal{Z}_\vartheta)$, $\mathbf{q} = \widehat{\mathbf{q}}(\mathcal{Z}_\vartheta)$ and $a = \widehat{a}(\mathcal{Z}_\vartheta)$ are subject to the dissipation inequality

$$
-\overline{\mu}r - \mathbf{D}\overline{\mu}\cdot\mathbf{j} + \mathbf{D}\vartheta\cdot\mathbf{q} + \chi_{,t}a \geq 0
\tag{6.27}
$$

for all variables $\mathcal{Z}_\vartheta$ in (6.23).

$(M4)_\vartheta$ The constitutive equations have to be invariant under changes in observer, like in (4.8).

Since

$$
\vartheta = \frac{1}{\theta}, \quad \widehat{\phi}\left(\mathbf{F}, \chi, \mathbf{D}\chi, \frac{1}{\theta}\right) = \frac{1}{\theta}\widehat{f}(\mathbf{F}, \chi, \mathbf{D}\chi, \theta),
$$

the strict concavity of f with respect to θ is equaivalent to the strict concavity of ϕ with respect to ϑ (see Lemma 2.2), and Gibbs relations in (4.23) are equivalent to that in (6.25) (see Lemma 2.1), it is immediate to see that models $(M)_\theta$ and $(M)_\vartheta$ are identical.

Thus, we can conclude that the approaches with entropy or, alternatively, with energy as independent thermal variables lead to the same final model with temperature as thermal variable.

7. General solution of the dissipation inequality. Application to model $(M)_\theta$

7.1. **Thermodynamic setting.**

In this section we are concerned with solving dissipation inequalities that appear in all presented models $(M)_\eta$, $(M)_\theta$, $(M)_e$ and $(M)_\vartheta$ (see (4.2), (4.26), (6.2), (6.27)). To be specific, let us consider inequality (4.26) in model $(M)_\theta$:

$$-\overline{\mu}\widehat{r}(\mathcal{Z}_\theta) - \mathbf{D}\overline{\mu}\cdot\widehat{\mathbf{j}}(\mathcal{Z}_\theta) + \mathbf{D}\frac{1}{\theta}\cdot\widehat{\mathbf{q}}(\mathcal{Z}_\theta) + \chi_{,t}\widehat{a}(\mathcal{Z}_\theta) \geq 0$$

for all variables

$$Z_\theta = \left\{\mathbf{F}, \mathbf{DF}, \chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \theta, \mathbf{D}\frac{1}{\theta}, \overline{\mu}, \mathbf{D}\overline{\mu}, , \chi_{,t}\right\}, \qquad \overline{\mu} = \frac{\mu}{\theta}.$$

Let us identify the variables $(\overline{\mu}, \mathbf{D}\overline{\mu}, \mathbf{D}\frac{1}{\theta}, \chi_{,t})$ with the radius vector, $\mathbf{X}$, of E^N:

$$\mathbf{X} := \left(\overline{\mu}, \mathbf{D}\overline{\mu}, \mathbf{D}\frac{1}{\theta}, \chi_{,t}\right), \tag{7.1}$$

called thermodynamic forces. Correspondingly, let us identify $(-r, -\mathbf{j}, \mathbf{q}, a)$ with the radius vector, $\mathbf{J}$, of E^N:

$$\mathbf{J} := (-r, -\mathbf{j}, \mathbf{q}, a), \tag{7.2}$$

called thermodynamic fluxes. Finally, let us identify the remaining variables from the set $\mathcal{Z}_\theta$ (not belonging to $\mathbf{X}$) with the radius vector, $\boldsymbol{\omega}$, of E^p:

$$\boldsymbol{\omega} = (\mathbf{F}, \mathbf{DF}, \chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \theta), \tag{7.3}$$

called state variables.

With such notation (4.26) is transformed to the following well-known form of the thermodynamic inequality

$$\begin{aligned} \Sigma(\mathbf{X};\boldsymbol{\omega}) &:= -\overline{\mu}r - \mathbf{D}\overline{\mu}\cdot\mathbf{j} + \mathbf{D}\frac{1}{\theta}\cdot\mathbf{q} + \chi_{,t}a \\ &= \mathbf{X}\cdot\mathbf{J}(\mathbf{X};\boldsymbol{\omega}) \geq 0 \end{aligned} \tag{7.4}$$

for all variables $\{\mathbf{X};\boldsymbol{\omega}\} = \mathcal{Z}_\theta$.

We recall two results on the representation of solutions of thermodynamic inequality (7.4).

The first, due to Gurtin [Gur96], gives a representation in terms of a linear transformation which satisfies in a certain sense the semi-definiteness condition. The second one is the decomposition theorem due to Edelen [Ede73] which represents a special case of the Helmholtz theorem in vector analysis. This theorem asserts a splitting of the solution of the dissipation inequality into a dissipative and a nondissipative part. The application of this theorem to problem $(M)_\theta$ allows to draw interesting conclusions regarding the structure of the quantities in (7.2). It turns out that the nonstationary parts of these quantities may in general contribute to nondissipative thermodynamic fluxes. In other words, if not excluded, such anomaly fluxes are not restricted by the second law. In class of models we are concerned with, involving free energy of gradient type, the key role plays the nondissipative energy flux. The free choice of this flux together with a relation between energy and entropy fluxes (see (8.5) below) allows to enlighten a question of recent interest (see [FGM06]) whether in phase-field models one has to modify energy or entropy equation.

Our answer will be that both variants are correct and arise due to particular choices of the nonstationary energy flux (see Section 8.3).

7.2. Representation of solutions to the dissipation inequality.

Lemma 7.1. *(see* [Gur96]*, Appendix B).*
Let $\mathbf{X}$ *be a generic element of an* N*-dimensional vector space* E^N *with inner product* $\mathbf{X}\cdot\mathbf{Y}$*, let* ω *be a generic element of a* p*-dimensional vector space* E^p*, and let* $\mathbf{J}(\mathbf{X};\omega) := E^N \times E^p \to E^N$ *be a smooth function satisfying inequality*

$$\mathbf{X}\cdot\mathbf{J}(\mathbf{X};\omega) \geq 0 \quad \textit{for all } (\mathbf{X};\omega) \in E^N \times E^p. \tag{7.5}$$

Then $\mathbf{J}$ *is given by*

$$\mathbf{J}(\mathbf{X};\omega) = \mathbf{B}(\mathbf{X};\omega)\mathbf{X}, \tag{7.6}$$

with $\mathbf{B}(\mathbf{X};\omega)$*, for each* $(\mathbf{X};\omega)$*, a linear transformation from* E^N *into* E^N*, consistent with the inequality*

$$\mathbf{X}\cdot\mathbf{B}(\mathbf{X};\omega)\mathbf{X} \geq 0 \quad \textit{for all } (\mathbf{X};\omega) \in E^N \times E^p. \tag{7.7}$$

The mapping $\mathbf{B}(\mathbf{X};\omega)$ *is given by*

$$\mathbf{B}(\mathbf{X};\omega) = \int_0^1 \nabla_{(\tau\mathbf{X})}\mathbf{J}(\tau\mathbf{X};\omega)d\tau, \tag{7.8}$$

where $\nabla_{\mathbf{X}}$ *denotes the gradient with respect to* $\mathbf{X}$.

For reader's convenience the proof of this lemma is given in Appendix.

We remark that because of the dependence of $\mathbf{B}(\mathbf{X};\omega)$ on $\mathbf{X}$, inequality (7.7) is weaker than positive semidefiniteness of $\mathbf{B}(\mathbf{X};\omega)$. However, when $\mathbf{J}(\mathbf{X};\omega)$ is linear in $\mathbf{X}$ for each ω, then

$$\mathbf{J}(\mathbf{X};\omega) = \mathbf{B}(\omega)\mathbf{X} \tag{7.9}$$

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

The second lemma yields a decomposition result

Lemma 7.2. *(see* [Ede73], *Corollary p. 220).*
Let $\mathbf{X}$ *stand for elements of an* N*-dimensional vector space* E^N *with inner product* $\mathbf{X}\cdot\mathbf{Y}$, *let* ω *stand for an element of a* p*-dimensional vector space* E^p, *and let* $\mathbf{J}(\mathbf{X};\omega) : E^N \times E^p \to E^N$ *be a mapping which is continuous in* ω *and of class* C^1 *in* $\mathbf{X}$. *There exists a scalar-valued function* $\mathcal{D}(\mathbf{X};\omega)$ *that is unique to within an added function of* ω, *and a unique vector-valued function* $\mathbf{U}(\mathbf{X};\omega)$ *such that*

$$\begin{aligned} &\mathbf{J}(\mathbf{X};\omega) = \nabla_{\mathbf{X}}\mathcal{D}(\mathbf{X};\omega) + \mathbf{U}(\mathbf{X};\omega), \\ &\mathbf{X}\cdot\mathbf{U}(\mathbf{X};\omega) = 0, \qquad \mathbf{U}(0;\omega) = \mathbf{0}. \end{aligned} \tag{7.10}$$

The mappings $\mathcal{D}(\mathbf{X};\omega)$ *and* $\mathbf{U}(\mathbf{X};\omega)$ *are given by*

$$\begin{aligned} \mathcal{D}(\mathbf{X};\omega) &= \int_0^1 \mathbf{X}\cdot\mathbf{J}(\tau\mathbf{X};\omega)d\tau, \\ U_i(\mathbf{X};\omega) &= \int_0^1 \tau X_j \left\{ \frac{\partial J_i(\tau\mathbf{X};\omega)}{\partial(\tau X_j)} - \frac{\partial J_j(\tau\mathbf{X};\omega)}{\partial(\tau X_i)} \right\} d\tau. \end{aligned} \tag{7.11}$$

Moreover, if $\mathbf{J}(\mathbf{X};\omega)$ *is of class* C^2 *in* $\mathbf{X}$, *then* $\mathcal{D}(\mathbf{X};\omega)$ *is of class* C^2 *in* $\mathbf{X}$, *and the symmetry relations*

$$\nabla_{\mathbf{X}} \wedge (\mathbf{J}(\mathbf{X};\omega) - \mathbf{U}(\mathbf{X};\omega)) = \mathbf{0}, \tag{7.12}$$

where „$\wedge$" denotes the exterior product operation, are satisfied identically on $E^N \times E^p$.

This lemma represents a special case of a more general decomposition theorem proved in [Ede73]. For a clarity, in Appendix we present a direct, simplified proof of this special case.

We point out important implications and interpretations of the latter lemma. Firstly, in view of $(7.10)_2$, dissipation inequality (7.4) reduces to

$$\Sigma(\mathbf{X};\omega) = \mathbf{X}\cdot\mathbf{J}(\mathbf{X};\omega) = \mathbf{X}\cdot\nabla_{\mathbf{X}}\mathcal{D}(\mathbf{X};\omega) \geq 0. \tag{7.13}$$

It is thus only the part $\nabla_{\mathbf{X}}\mathcal{D}(\mathbf{X};\omega)$ of the thermodynamic fluxes $\mathbf{J}(\mathbf{X};\omega)$ that contributes to the rate of entropy production. The function $\mathcal{D}(\mathbf{X};\omega)$ can thus be interpreted as a dissipation potential. In other words, Edelen's theorem asserts that there exists a dissipation potential $\mathcal{D}(\mathbf{X};\omega)$ for every system of constitutive relations that satisfies the dissipation inequality. In fact, it follows directly from (7.13) that $\Sigma(\mathbf{X};\omega)$ and $\mathcal{D}(\mathbf{X};\omega)$ stay in the relation

$$\mathcal{D}(\mathbf{X};\omega)=\int_0^1 \Sigma(\tau\mathbf{X};\omega)\frac{d\tau}{\tau}. \tag{7.14}$$

By (7.13) and (7.14) it follows that $\mathcal{D}(\mathbf{X};\omega)$ is nonnegative, convex and achives its absolute minimum of zero for $\mathbf{X}=\mathbf{0}$.

The vector $\mathbf{U}(\mathbf{X};\omega)$ can be interpreted as the nondissipative part of the thermodynamic fluxes $\mathbf{J}(\mathbf{X};\omega)$ because $\mathbf{X}\cdot\mathbf{U}(\mathbf{X};\omega)=0$ and hence $\mathbf{U}$ makes no contribution to the dissipation Σ for any values of $\mathbf{X}$ and ω.

The symmetry relations (7.12) assert that reciprocity relations are always satisfied by any solution of the dissipation inequality, although it is $\mathbf{J}-\mathbf{U}$ rather than just $\mathbf{J}$ that satisfies them. In this sense (7.12) generalize the Onsager reciprocity relations of linear theory of irreversible processes to the nonlinear case. More precisely, it follows from (7.12) that

$$\nabla_X\wedge\mathbf{J}=\mathbf{0},\ \text{i.e. } \partial J_i/\partial X_j=\partial J_j/\partial X_i, \qquad i,j=1,\dots,N,$$

when and only when the nondissipative part $\mathbf{U}$ of the thermodynamic fluxes vanishes identically on $E^N\times E^p$.

7.3. Decomposition of the fluxes.

According to Theorem 4.2, the entropy flux $\mathbf{\Psi}$ contains the nonstationary term $\dot\chi f_{,\mathbf{D}\chi}/\theta$ (see (4.29)). This suggests that one should look more carefully on other possible nonstationary terms comming from the constitutive quantities $\mathbf{q}$, $\mathbf{j}$ and r. As mentioned before, of particular interest is the energy flux $\mathbf{q}$.

Let us assume, without loss of generality, the following splitting of $\mathbf{q}=\widehat{\mathbf{q}}(\mathcal{Z}_\theta)$:

$$\mathbf{q}=\mathbf{q}^0-\chi_{,t}\mathbf{h}, \tag{7.15}$$

where $\mathbf{q}^0$ stands for a stationary (heat) flux which does not depend on $\chi_{,t}$, i.e.

$$\mathbf{q}^0=\widehat{\mathbf{q}}^0(\mathcal{Z}_\theta^0)$$

with

$$\mathcal{Z}_\theta^0:=\mathcal{Z}_\theta|_{\chi,t=0}=\left\{\mathbf{F},\mathbf{DF},\chi,\mathbf{D}\chi,\mathbf{D}^2\chi,\theta,\mathbf{D}\frac{1}{\theta},\overline{\mu},\mathbf{D}\overline{\mu},0\right\},$$

and $\mathbf{h}$ (possibly equal zero) stands for a nonstationary flux, i.e.

$$\mathbf{h}=\widehat{\mathbf{h}}(\mathcal{Z}_\theta),\qquad \mathcal{Z}_\theta=\left\{\mathbf{F},\mathbf{DF},\chi,\mathbf{D}\chi,\mathbf{D}^2\chi,\theta,\mathbf{D}\frac{1}{\theta},\overline{\mu},\mathbf{D}\overline{\mu},\chi_{,t}\right\}.$$

Further, in accordance with Edelen's decomposition theorem, let us assume that there may exist a nondissipative (anomaly) flux in the system and that it is due to the nonstationary flux $\mathbf{h}$. More precisely, let us assume that $\mathbf{q}$ in (7.15) splits into a dissipative, $\mathbf{q}^d$, and a nondissipative (extra), $\mathbf{q}^{nd}$, parts:

$$\mathbf{q} = \mathbf{q}^d + \mathbf{q}^{nd}, \tag{7.16}$$

where

$$\mathbf{q}^d := \mathbf{q}^0 - \chi_{,t}\mathbf{h}^d, \qquad \mathbf{q}^{nd} := -\chi_{,t}\mathbf{h}^{nd}, \tag{7.17}$$

and

$$\mathbf{h} = \mathbf{h}^d + \mathbf{h}^{nd} \tag{7.18}$$

with $\mathbf{h}^d = \widehat{\mathbf{h}}^d(\mathcal{Z}_\theta)$ and $\mathbf{h}^{nd} = \widehat{\mathbf{h}}^{nd}(\mathcal{Z}_\theta)$ denoting respectively a dissipative and a nondissipative part of the flux $\mathbf{h}$ (each of them can be zero).

Similarly, one could select nondissipative parts of the quantities r and $\mathbf{j}$ in (4.26). For simplicity we omit this, however, assuming that

$$r \equiv r^d, \qquad \mathbf{j} \equiv \mathbf{j}^d \qquad (r^{nd} = 0,\ \mathbf{j}^{nd} = \mathbf{0}). \tag{7.19}$$

With splittings (7.16)–(7.19) dissipation inequality (4.26) can be transformed into the following decomposed form:

$$\begin{aligned} \Sigma(\mathbf{X};\boldsymbol{\omega}) &= -\overline{\mu}r^d - \mathbf{D}\overline{\mu}\cdot\mathbf{j}^d + \mathbf{D}\frac{1}{\theta}\cdot\mathbf{q}^d + \chi_{,t}a^d \\ &\quad -\mathbf{D}\frac{1}{\theta}\cdot(\chi_{,t}\mathbf{h}^{nd}) + \chi_{,t}\mathbf{D}\frac{1}{\theta}\cdot\mathbf{h}^{nd} \\ &\equiv \mathbf{X}\cdot(\mathbf{J}^d(\mathbf{X};\boldsymbol{\omega}) + \mathbf{U}(\mathbf{X};\boldsymbol{\omega})) \\ &= \mathbf{X}\cdot\mathbf{J}^d(\mathbf{X};\boldsymbol{\omega}) \geq 0, \end{aligned} \tag{7.20}$$

where

$$\begin{aligned} a^d &:= a - \mathbf{D}\frac{1}{\theta}\cdot\mathbf{h}^{nd}, \\ \mathbf{J}^d &:= (-r^d, -\mathbf{j}^d, \mathbf{q}^d, a^d), \\ \mathbf{X} &:= \left(\overline{\mu}, \mathbf{D}\overline{\mu}, \mathbf{D}\frac{1}{\theta}, \chi_{,t}\right), \end{aligned} \tag{7.21}$$

and

$$\mathbf{U} := \left(0, \mathbf{0}, -\chi_{,t}\mathbf{h}^{nd}, \mathbf{D}\frac{1}{\theta}\cdot\mathbf{h}^{nd}\right)$$

satisfies

$$\mathbf{X}\cdot\mathbf{U}(\mathbf{X};\boldsymbol{\omega}) = 0 \quad \text{and} \quad \mathbf{U}(\mathbf{0};\boldsymbol{\omega}) = \mathbf{0}.$$

Thus, a^d may be interpreted as a dissipative part of the quantity a in the equation for the chemical potential (see $(4.22)_3$), $\mathbf{J}^d$ as a dissipative part of the thermodynamic fluxes $\mathbf{J}$ and $\mathbf{U}$ as their nondissipative part.

Moreover, by virtue Lemma 7.2, the dissipative flux $\mathbf{J}^d$ in (7.21) is characterized by

$$\mathbf{J}^d(\mathbf{X};\omega) = \nabla_{\mathbf{X}}\mathcal{D}(\mathbf{X};\omega), \tag{7.22}$$

where $\mathcal{D}(\mathbf{X};\omega)$ is a dissipation potential which is nonnegative, convex in $\mathbf{X}$ and such that it achives its absolute minimum of zero at $\mathbf{X} = \mathbf{0}$.

Let us add that an equivalent characterization of flux $\mathbf{J}^d$, according to Lemma 5.1, is:

$$\mathbf{J}^d(\mathbf{X};\omega) = \mathbf{B}(\mathbf{X};\omega)\mathbf{X},$$

with $\mathbf{B}(\mathbf{X},\omega)$, being a linear transformation from E^N into E^N, consistent with the inequality

$$\mathbf{X}\cdot\mathbf{B}(\mathbf{X};\omega)\mathbf{X} \geq 0 \quad \text{for all } (\mathbf{X};\omega) \in E^N \times E^p.$$

8. A scheme of phase-field models with conserved and nonconserved order parameters

8.1. **Formulation.**

On account of representation (7.20)–(7.22) of dissipation inequality (4.26), the formulation $(M)_\theta$ presented in Section 4 leads to the following scheme of phase-field models with a first order gradient energy.

Let the state space be

$$\mathcal{Z}_\theta = \left\{\mathbf{F}, \mathbf{DF}, \chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \theta, \mathbf{D}\frac{1}{\theta}, \frac{\mu}{\theta}, \mathbf{D}\frac{\mu}{\theta}, \chi_{,t}\right\}. \tag{8.1}$$

There are given a free energy $f = \widehat{f}(\mathbf{F},\chi,\mathbf{D}\chi,\theta)$ which is strictly concave with respect to θ, and a dissipation potential $\mathcal{D} = \widehat{\mathcal{D}}(\mathbf{X};\omega)$ with

$$\begin{aligned}\mathbf{X} &:= \left(\frac{\mu}{\theta}, \mathbf{D}\frac{\mu}{\theta}, \mathbf{D}\frac{1}{\theta}, \chi_{,t}\right),\\ \omega &:= (\mathbf{F}, \mathbf{DF}, \chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \theta), \qquad \{\mathbf{X};\omega\} = \mathcal{Z}_\theta,\end{aligned}$$

which is nonnegative, convex in $\mathbf{X}$ and such that $\mathcal{D}(\mathbf{0};\omega) = 0$. The unknowns are the fields $\mathbf{u}, \chi, \overline{\mu} = \mu/\theta$ and $\theta > 0$ satisfying the following system of equations:

(8.2)
$$\begin{aligned}
&\ddot{\mathbf{u}} - \nabla \cdot f_{,\mathbf{F}} = \mathbf{b},\\
&\dot{\chi} + \nabla \cdot \mathbf{j} - r = \tau,\\
&\frac{\mu}{\theta} = \frac{\delta(f/\theta)}{\delta\chi} + \nabla\frac{1}{\theta} \cdot \mathbf{h}^{nd} + a^d,\\
&\dot{e} + \nabla \cdot \mathbf{q} - f_{,\mathbf{F}} \cdot \dot{\mathbf{F}} = g,
\end{aligned}$$

where

(8.3)
$$\begin{aligned}
&e = f - \theta f_{,\theta}, \qquad \mathbf{q} = \mathbf{q}^d - \dot{\chi}\mathbf{h}^{nd},\\
&-r \equiv -r^d = \mathcal{D}_{,(\mu/\theta)}, \qquad -\mathbf{j} \equiv -\mathbf{j}^d = \mathcal{D}_{,\mathbf{D}(\mu/\theta)},\\
&\mathbf{q}^d = \mathcal{D}_{,\mathbf{D}(1/\theta)}, \qquad a^d = \mathcal{D}_{,\chi_{,t}},
\end{aligned}$$

and a nondissipative flux $\mathbf{h}^{nd} = \widehat{\mathbf{h}}^{nd}(\mathbf{X};\omega)$ is an arbitrary vector field not restricted by the entropy principle.

Remark 8.1. *The solutions of system (8.2), (8.3) satisfy entropy inequality (4.30) which on account of (7.20) takes the form*

(8.4)
$$\begin{aligned}
\dot{\eta} + \nabla \cdot \mathbf{\Psi} &= -\frac{\mu}{\theta}r^d - \nabla\frac{\mu}{\theta} \cdot \mathbf{j}^d + \nabla\frac{1}{\theta} \cdot \mathbf{q}^d + \dot{\chi}a^d - \frac{\mu}{\theta}\tau + \frac{g}{\theta}\\
&\geq -\frac{\mu}{\theta}\tau + \frac{g}{\theta},
\end{aligned}$$

where

(8.5)
$$\begin{aligned}
\mathbf{\Psi} &= -\frac{\mu}{\theta}\mathbf{j}^d + \frac{1}{\theta}(\mathbf{q}^d - \dot{\chi}\mathbf{h}^{nd}) + \dot{\chi}\frac{f_{,\mathbf{D}\chi}}{\theta}\\
&\equiv \mathbf{\Psi}^d + \dot{\chi}\mathbf{\Psi}^{nd}
\end{aligned}$$

with

$$\mathbf{\Psi}^d := -\frac{\mu}{\theta}\mathbf{j}^d + \frac{1}{\theta}\mathbf{q}^d, \qquad \mathbf{\Psi}^{nd} := \frac{f_{,\mathbf{D}\chi} - \mathbf{h}^{nd}}{\theta}.$$

It is of interest to note that the extra energy term, $\mathbf{h}^{nd}$, and the extra entropy term, $\mathbf{\Psi}^{nd}$, defined above, are linked by the Gibbs-like relation

(8.6)
$$\mathbf{h}^{nd} + \theta\mathbf{\Psi}^{nd} = f_{,\mathbf{D}\chi}. \ \blacksquare$$

8.2. Examples of thermodynamic potentials.

To set a stage for a comparison with phase-field models known in literature, to be presented separately in [Paw07], we collect here some typical models of free energies and dissipation potentials. Moreover, we discuss system (8.2)–(8.3) in two extreme cases.

A general model of free energy describing phase transitions in solids has a separable Landau–Ginzburg form

$$f(\mathbf{F},\chi,\mathbf{D}\chi,\theta) = f_*(\theta) + W(\mathbf{F},\chi,\theta) + \psi(\chi,\theta) + f_G(\chi,\mathbf{D}\chi,\theta) \tag{8.7}$$

with the subsequent terms representing respectively thermal energy, elastic energy, chemical energy and gradient energy which corresponds to diffused phase interfaces.

A typical example of $f_*(\theta)$, associated with constant thermal specific heat $c_v > 0$, is

$$f_*(\theta) = -c_v\theta\log\left(\frac{\theta}{\theta_1}\right) + c_v\theta + \bar{c} \tag{8.8}$$

with a positive constant θ_1, and some constant $\bar{c}$ immaterial from the point of view of differential equations.

An example of elastic energy $W(\mathbf{F},\chi,\theta)$ for phase separation in a binary $a-b$ alloy in case of infinitesimal deformations is (see e.g. [DreyMul00], [BonCDGSS02]):

$$W(\varepsilon(\mathbf{u}),\chi,\theta) = \frac{1}{2}(\varepsilon(\mathbf{u}) - \bar{\varepsilon}(\chi,\theta))\cdot\mathbf{A}(\chi)(\varepsilon(\mathbf{u}) - \bar{\varepsilon}(\chi,\theta)), \tag{8.9}$$

where $\varepsilon(\mathbf{u}) = (\nabla\mathbf{u} + \nabla\mathbf{u}^T)/2$ is the infinitesimal strain tensor, $\mathbf{A}(\chi)$ is the fourth order elasticity tensor (in general depending on χ because of different elastic properties of the phases), and $\bar{\varepsilon}(\chi,\theta)$ is the eigenstrain tensor accounting for different thermal expansions of the phases. Tensors $\mathbf{A}(\chi)$ and $\bar{\varepsilon}(\chi,\theta)$ are defined by

$$\begin{aligned} \mathbf{A}(\chi) &= (1 - z(\chi,\theta))\mathbf{A}_a + z(\chi,\theta)\mathbf{A}_b, \\ \bar{\varepsilon}(\chi,\theta) &= (\theta - \theta_R)[(1 - z(\chi,\theta))\boldsymbol{\alpha}_a + z(\chi,\theta)\boldsymbol{\alpha}_b], \end{aligned} \tag{8.10}$$

where $\mathbf{A}_a, \mathbf{A}_b$ are constant elasticity tensors of phases a, b, $\boldsymbol{\alpha}_a$ and $\boldsymbol{\alpha}_b$ are the matrices of thermal expansion coefficients of these phases, θ_R is a reference temperature, and $z(\chi,\theta)$ is so called shape function given by

$$z(\chi,\theta) = \frac{\chi_a(\theta) - \chi}{\chi_a(\theta) - \chi_b(\theta)}.$$

It interpolates between temperature-dependent equilibrium concentrations $\chi_a(\theta))$ and $\chi_b(\theta))$ of the $a-b$ phase diagram.

The chemical (or coarse-grain) energy $\psi(\chi,\theta)$ characterizes the energetic favorability of the individual phases and typically has the form of a double-well potential. A well-known example at $\theta = \text{const}$ is given by

$$\psi_0(\chi) = \frac{1}{4}(\chi^2 - 1)^2, \tag{8.11}$$

where the values ± 1 correspond to the pure phases (after rescaling χ).
For nonisothermal phase transitions a relevant form of $\psi(\chi,\theta)$, proposed by Penrose and Fife [PenFife93], is

$$\psi(\chi,\theta) = \frac{\theta}{4\theta_0}\psi_0(\chi) + \left(1 - \frac{\theta}{\theta_0}\right)(-a\chi^2 + b\chi + c), \tag{8.12}$$

where $\theta_0 > 0$ is a transition temperature and a, b, c are some constants whose choice depends on the system under consideration.

A typical example of an isotropic gradient energy is

$$f_G(\chi, \mathbf{D}\chi, \theta) = \frac{1}{2}\gamma(\chi,\theta)|\mathbf{D}\chi|^2 \tag{8.13}$$

with a positive function $\gamma(\chi,\theta)$ being a small interfacial parameter. In applications to concrete systems one can distinguish two special cases of temperature-dependence of the parameter γ.

In the first one, which we call energetic, the gradient term is fully contained in the internal energy and the entropy is purely volumetric. On the contrary, in the second case, which we call entropic, the internal energy is volumetric whereas the gradient term is fully contained in the entropy. More precisely, these cases can be characterized with the help of Gibbs relation (2.18) as follows:

— gradient energy of energetic type $\gamma = \overline{\gamma}(\chi) > 0$

$$e_{,\mathbf{D}\chi} = (f - \theta f_{,\theta})_{,\mathbf{D}\chi} = f_{,\mathbf{D}\chi} = \gamma\mathbf{D}\chi \Leftrightarrow \eta_{,\mathbf{D}\chi} = -f_{,\theta\mathbf{D}\chi} = -\gamma_{,\theta}\mathbf{D}\chi = \mathbf{0}, \tag{8.14}$$

— gradient energy of entropic type $\gamma = \theta\overline{\gamma}(\chi) > 0$

$$\begin{aligned} e_{,\mathbf{D}\chi} &= (f - \theta f_{,\theta})_{,\mathbf{D}\chi} = (\gamma - \theta\gamma_{,\theta})\mathbf{D}\chi = \mathbf{0} \Leftrightarrow \\ \theta\eta_{,\mathbf{D}\chi} &= -\theta f_{,\theta\mathbf{D}\chi} = -\theta\gamma_{,\theta}\mathbf{D}\chi = -\gamma\mathbf{D}\chi = -f_{,\mathbf{D}\chi}. \end{aligned} \tag{8.15}$$

We present now some standard examples of the dissipation potential $\mathcal{D}(\mathbf{X};\omega)$ in (8.2), (8.3). For simplicity, let us assume the splitting

$$\mathcal{D}(\mathbf{X};\omega) = \mathcal{D}_1\left(\frac{\mu}{\theta};\omega\right) + \mathcal{D}_2\left(\mathbf{D}\frac{\mu}{\theta};\omega\right) + \mathcal{D}_3\left(\mathbf{D}\frac{1}{\theta};\omega\right) + \mathcal{D}_4(\chi_{,t};\omega), \tag{8.16}$$

and restrict ourselves to the situation near thermodynamical equilibrium with potentials $\mathcal{D}_k, k = 1,2,3,4,$ of second degree of homogeneity in the variables $\frac{\mu}{\theta}, \mathbf{D}\frac{\mu}{\theta}, \mathbf{D}\frac{1}{\theta}$ and $\chi_{,t}$, respectively. The potential $\mathcal{D}_1$ corresponds to a nonconserved order parameter dynamics whereas $\mathcal{D}_2$ to a conserved one. The simplest examples are

$$\mathcal{D}_1 = \frac{1}{2}\alpha\left(\frac{\mu}{\theta}\right)^2, \quad \mathcal{D}_2 = \frac{1}{2}M\left|\mathbf{D}\frac{\mu}{\theta}\right|^2, \tag{8.17}$$

where α and M are positive coefficients, M representing a diffusional mobility. According to (8.3) such potentials yield the following laws:

— for the production term

$$r^d = -\mathcal{D}_{,(\mu/\theta)} = -\alpha\frac{\mu}{\theta}, \quad \alpha > 0, \tag{8.18}$$

— for the mass flux

$$\mathbf{j}^d = -\mathcal{D}_{,\mathbf{D}(\mu/\theta)} = -M\mathbf{D}\frac{\mu}{\theta}, \quad M > 0. \tag{8.19}$$

The potential $\mathcal{D}_3$ corresponds to the heat conduction. A typical example which governs the isotropic Fourier law is

$$\mathcal{D}_3 = \frac{1}{2}k|\mathbf{D}\log\theta|^2 = \frac{1}{2}k\theta^2\left|\mathbf{D}\frac{1}{\theta}\right|^2, \tag{8.20}$$

where $k > 0$ is the heat conductivity coefficient. Then, according to (8.3),

$$\mathbf{q}^d = \mathcal{D}_{,\mathbf{D}(1/\theta)} = k\theta^2\mathbf{D}\frac{1}{\theta} = -k\mathbf{D}\theta, \quad k > 0. \tag{8.21}$$

Finally, the potential $\mathcal{D}_4$ corresponds to viscous diffusive effects with an example

$$\mathcal{D}_4 = \frac{1}{2}\beta\chi_{,t}^2 \tag{8.22}$$

where $\beta > 0$ is a viscosity coefficient. By (8.3) such potential yields the following law

$$a^d = \mathcal{D}_{,\chi_{,t}} = \beta\chi_{,t}, \quad \beta > 0. \tag{8.23}$$

8.3. **Special forms of model equations.**

For a further discussion we collect some equivalent forms of equations $(8.2)_3$ and $(8.2)_4$ for the chemical potential and the internal energy. First, let us note that $(8.2)_3$ can be rewritten as

$$\frac{\mu}{\theta} = \frac{1}{\theta}\frac{\delta f}{\delta\chi} - \nabla\frac{1}{\theta}\cdot(f_{,\mathbf{D}\chi} - \mathbf{h}^{nd}) + a^d, \tag{8.24}$$

or, using (8.6), as

$$\mu = \frac{\delta f}{\delta\chi} + \nabla\theta\cdot\mathbf{\Psi}^{nd} + \theta a^d.$$

Next, introducing the specific heat coefficient (see (2.21))

$$c_0 = -\theta f_{,\theta\theta},$$

and taking into account that

$$\dot{e} = (f - \theta f_{,\theta})_{,\mathbf{F}}\cdot\dot{\mathbf{F}} + (f - \theta f_{,\theta})_{,\chi}\dot{\chi} + (f - \theta f_{,\theta})_{,\mathbf{D}\chi}\cdot\nabla\dot{\chi} - \theta f_{,\theta\theta}\dot{\theta},$$

the internal energy equation $(8.2)_4$ can be rewritten in the following temperature form

$$c_0\dot{\theta}+\nabla\cdot(\mathbf{q}^d-\dot{\chi}\mathbf{h}^{nd})+(f-\theta f_{,\theta})_{,\chi}\dot{\chi}+(f-\theta f_{,\theta})_{,\mathbf{D}\chi}\cdot\nabla\dot{\chi}-\theta f_{,\theta\mathbf{F}}\cdot\dot{\mathbf{F}}=g. \tag{8.25}$$

Equations (8.24) and (8.25) suggest two extreme choices of the flux $\mathbf{h}^{nd}$:

$$\mathbf{h}^{nd}=\mathbf{0},\ \text{so}\ \mathbf{\Psi}^{nd}=\frac{f_{,\mathbf{D}\chi}}{\theta}\ \text{(extra entropy flux)}, \tag{8.26}$$

and

$$\mathbf{h}^{nd}=f_{,\mathbf{D}\chi},\ \text{so}\ \mathbf{\Psi}^{nd}=\mathbf{0}\ \text{(extra energy flux)}. \tag{8.27}$$

The corresponding schemes take then the following forms:

(i) Scheme with extra entropy flux: $\mathbf{h}^{nd}=\mathbf{0}$, $\mathbf{\Psi}^{nd}=f_{,\mathbf{D}\chi}/\theta$

$$\begin{aligned}
&\ddot{\mathbf{u}}-\nabla\cdot f_{,\mathbf{F}}=\mathbf{b},\\
&\dot{\chi}+\nabla\cdot\mathbf{j}^d-r^d=\tau,\\
&\frac{\mu}{\theta}=\frac{\delta(f/\theta)}{\delta\chi}+a^d,\\
&c_0\dot{\theta}+\nabla\cdot\mathbf{q}^d+(f-\theta f_{,\theta})_{,\chi}\dot{\chi}+(f-\theta f_{,\theta})_{,\mathbf{D}\chi}\cdot\nabla\dot{\chi}\\
&\qquad-\theta f_{,\theta\mathbf{F}}\cdot\dot{\mathbf{F}}=g,
\end{aligned} \tag{8.28}$$

with $r^d,\mathbf{j}^d,\mathbf{q}^d,a^d$ given in (8.3). Such scheme satisfies the entropy inequality of the form

$$\begin{aligned}
\dot{\eta}+\nabla\cdot\left[-\frac{\mu}{\theta}\mathbf{j}^d+\frac{1}{\theta}\mathbf{q}^d+\dot{\chi}\frac{f_{,\mathbf{D}\chi}}{\theta}\right]
&=-\frac{\mu}{\theta}r^d-\nabla\frac{\mu}{\theta}\cdot\mathbf{j}^d+\nabla\frac{1}{\theta}\cdot\mathbf{q}^d+\dot{\chi}a^d-\frac{\mu}{\theta}\tau+\frac{g}{\theta}\\
&\geq-\frac{\mu}{\theta}\tau+\frac{g}{\theta}.
\end{aligned} \tag{8.29}$$

(ii) Scheme with extra energy flux: $\mathbf{h}^{nd}=f_{,\mathbf{D}\chi}$, $\mathbf{\Psi}^{nd}=\mathbf{0}$

$$\begin{aligned}
&\ddot{\mathbf{u}}-\nabla\cdot f_{,\mathbf{F}}=\mathbf{b},\\
&\dot{\chi}+\nabla\cdot\mathbf{j}^d-r^d=\tau,\\
&\frac{\mu}{\theta}=\frac{1}{\theta}\frac{\delta f}{\delta\chi}+a^d,\\
&c_0\dot{\theta}+\nabla\cdot(\mathbf{q}^d-\dot{\chi}f_{,\mathbf{D}\chi})+(f-\theta f_{,\theta})_{,\chi}\dot{\chi}+(f-\theta f_{,\theta})_{,\mathbf{D}\chi}\cdot\nabla\dot{\chi}\\
&\qquad-\theta f_{,\theta\mathbf{F}}\cdot\dot{\mathbf{F}}=g,
\end{aligned} \tag{8.30}$$

with r^d,j^d,q^d,a^d given in (8.3). Such scheme satisfies the entropy inequality of the form

$$
\begin{aligned}
(8.31)\qquad \dot\eta + \nabla\cdot\left[-\frac{\mu}{\theta}\cdot\mathbf{j}^d + \frac{1}{\theta}\mathbf{q}^d\right]
&= -\frac{\mu}{\theta}r^d - \nabla\frac{\mu}{\theta}\cdot\mathbf{j}^d + \nabla\frac{1}{\theta}\cdot\mathbf{q}^d + \dot\chi a^d - \frac{\mu}{\theta}\tau + \frac{g}{\theta}\\
&\geq -\frac{\mu}{\theta}\tau + \frac{g}{\theta}.
\end{aligned}
$$

We remark that, regarding the structure of the energy equation, scheme (i) with extra entropy flux falls into the frame of Penrose–Fife models with conserved and nonconserved order parameters [PenFife90], [PenFife93], Caginalp model [Cag86], and several other models with modified entropy equation, e.g. models in [AltPaw90], [AltPaw92], [FGM06].

Scheme (ii) with extra energy flux is in turn consistent with models for nonconserved order parameters proposed by Fried–Gurtin [FriGur93], Frémond [Frem02] and Miranville–Schimperna [MirSchim05a]. Besides, if higher gradients of deformation are admitted then scheme (ii) with modified energy equation turns out to be consistent with the theory by Falk [Falk82], [Falk90] for shape memory alloys and by Dunn–Serrin [DunnSer85] for higher grade materials (see [Paw00c], [PawZaj03]).

In view of applications it is of interest to consider schemes (i) and (ii) in case of entropic and energetic gradient energies. If the gradient energy (8.13) is of entropic type

$$\gamma(\chi,\theta) = \theta\overline{\gamma}(\chi) > 0,$$

then scheme (i) with extra entropy flux reduces to the form:

$$
(8.32)\qquad
\begin{aligned}
&\ddot{\mathbf{u}} - \nabla\cdot f_{,\mathbf{F}} = \mathbf{b},\\
&\dot\chi + \nabla\cdot\mathbf{j}^d - r^d = \tau,\\
&\frac{\mu}{\theta} = \frac{f_{,\chi}}{\theta} - \nabla\cdot(\overline{\gamma}\nabla\chi) + a^d,\\
&c_0\dot\theta + \nabla\cdot\mathbf{q}^d + (f-\theta f_{,\theta})_{,\chi}\dot\chi - \theta f_{,\theta\mathbf{F}}\cdot\dot{\mathbf{F}} = g.
\end{aligned}
$$

In turn, if the gradient energy (8.13) is of energetic type

$$\gamma(\chi,\theta) = \overline{\gamma}(\chi) > 0,$$

then scheme (ii) with extra energy flux becomes

$$
(8.33)\qquad
\begin{aligned}
&\ddot{\mathbf{u}} - \nabla\cdot f_{,\mathbf{F}} = \mathbf{b},\\
&\dot\chi + \nabla\cdot\mathbf{j}^d - r^d = \tau,\\
&\mu = f_{,\chi} - \nabla\cdot(\overline{\gamma}\nabla\chi) + \theta a^d,\\
&c_0\dot\theta + \nabla\cdot\mathbf{q}^d + \dot\chi[f_{,\chi} - \nabla\cdot(\overline{\gamma}\nabla\chi)] - \theta f_{,\theta\chi}\dot\chi - \theta f_{,\theta\mathbf{F}}\cdot\dot{\mathbf{F}} = g.
\end{aligned}
$$

A detailed comparison of the above presented schemes with several models known in literature will be presented in Part II [Paw07].

Appendix

Proof of Lemma 7.1. According to (7.5), for $\lambda > 0$

$$\lambda\mathbf{X}\cdot\mathbf{J}(\lambda\mathbf{X};\omega) \geq 0 \quad \text{for all } (\mathbf{X};\omega)\in E^N\times E^p,$$

and hence

$$\mathbf{X}\cdot\mathbf{J}(\lambda\mathbf{X};\omega) \geq 0 \quad \text{for all } (\mathbf{X};\omega).$$

Thus, letting $\lambda\to 0$, $\mathbf{X}\cdot\mathbf{J}(\mathbf{0};\omega)\geq 0$ for all $(\mathbf{X};\omega)$, which implies that

$$\mathbf{J}(\mathbf{0};\omega) = \mathbf{0}. \tag{A.1}$$

In view of (A.1), denoting

$$\widetilde{\mathbf{J}} = \mathbf{J}(\tau\mathbf{X};\omega),$$

it follows that

$$\begin{aligned}\mathbf{J}(\mathbf{X};\omega) &= \mathbf{J}(\mathbf{X};\omega) - \mathbf{J}(\mathbf{0};\omega) = \int_0^1 \frac{d}{d\tau}\widetilde{\mathbf{J}}\,d\tau \\ &= \int_0^1 \frac{\partial\widetilde{\mathbf{J}}}{\partial(\tau X_j)}X_j\,d\tau \\ &= \left\{\int_0^1 \nabla_{(\tau\mathbf{X})}\mathbf{J}(\tau\mathbf{X};\omega)\,d\tau\right\}\mathbf{X}.\end{aligned}$$

Hence denoting

$$\mathbf{B}(\mathbf{X};\omega) = \int_0^1 \nabla_{(\tau\mathbf{X})}\mathbf{J}(\tau\mathbf{X};\omega)\,d\tau,$$

which for each $(\mathbf{X};\omega)$ defines a linear transformation from E^N into E^N, we have

$$\mathbf{J}(\mathbf{X};\omega) = \mathbf{B}(\mathbf{X};\omega)\mathbf{X} \quad \text{for all } (\mathbf{X};\omega). \tag{A.2}$$

A general solution $\mathbf{J}$ of inequality (7.5) is therefore given by (A.2) with $\mathbf{B}(\mathbf{X};\omega)$, for each $(\mathbf{X};\omega)$ a linear transformation from E^N into E^N consistent with the inequality

$$\mathbf{X}\cdot\mathbf{B}(\mathbf{X};\omega)\mathbf{X} \geq 0 \quad \text{for all } (\mathbf{X};\omega). \tag{A.3}$$

This proves the lemma. ■

Proof of Lemma 7.2. Let $\mathcal{D}(\mathbf{X};\omega)$ be constructed in accord with $(7.11)_1$. Since $\mathbf{J}(\mathbf{X};\omega)$ is of class C^1 in $\mathbf{X}$, $\mathcal{D}(\mathbf{X};\omega)$ is of class C^1 in $\mathbf{X}$ as well. Further, let

$$\widetilde{\mathbf{J}} = \mathbf{J}(\tau\mathbf{X};\omega).$$

Then

$$\text{(A.4)} \qquad \begin{aligned} \frac{\partial \mathcal{D}}{\partial X_i} &= \int_0^1 \left\{ \widetilde{J}_i + \tau X_j \frac{\partial \widetilde{J}_j}{\partial(\tau X_i)} \right\} d\tau \\ &= \int_0^1 \left\{ \widetilde{J}_i + \tau X_j \frac{\partial \widetilde{J}_i}{\partial(\tau X_j)} \right\} d\tau \\ &\quad + \int_0^1 \tau X_j \left\{ \frac{\partial \widetilde{J}_j}{\partial(\tau X_i)} - \frac{\partial \widetilde{J}_i}{\partial(\tau X_j)} \right\} d\tau \\ &= I_1 + I_2. \end{aligned}$$

Since

$$\frac{d}{d\tau}\widetilde{J}_i = \frac{\partial \widetilde{J}_i}{\partial(\tau X_j)} X_j,$$

an integration by parts in I_1 gives

$$\text{(A.5)} \qquad I_1 = \int_0^1 \left\{ \widetilde{J}_i + \tau \frac{d}{d\tau}\widetilde{J}_i \right\} d\tau = \tau \widetilde{J}_i \Big|_0^1 = J_i(\mathbf{X};\omega).$$

Thus, from (A.4) and (A.5) it follows that

$$\begin{aligned} J_i(\mathbf{X};\omega) &= \frac{\partial \mathcal{D}}{\partial X_i} - I_2 \\ &= \frac{\partial \mathcal{D}}{\partial X_i} + \int_0^1 \tau X_j \left\{ \frac{\partial \widetilde{J}_i}{\partial(\tau X_j)} - \frac{\partial \widetilde{J}_j}{\partial(\tau X_i)} \right\} d\tau. \end{aligned}$$

When substitution $(7.11)_2$ is used, we obtain

$$J_i(\mathbf{X};\omega) = \frac{\partial \mathcal{D}}{\partial X_i} + U_i(\mathbf{X};\omega)$$

which shows decomposition $(7.10)_1$.

It now follows directly from $(7.11)_2$ that $(7.10)_2$ is satisfied:

$$\mathbf{X}\cdot\mathbf{U}(\mathbf{X};\omega) = \int_0^1 \tau X_i X_j \left\{ \frac{\partial J_i(\tau\mathbf{X};\omega)}{\partial(\tau X_j)} - \frac{\partial J_j(\tau\mathbf{X};\omega)}{\partial(\tau X_i)} \right\} d\tau = 0,$$

and

$$\mathbf{U}(\mathbf{0};\omega) = \mathbf{0}.$$

It remains to show the uniqueness of the decomposition. Clearly,

$$\mathbf{J} = \nabla_{\mathbf{X}}\mathcal{D}_1 + \mathbf{U}_1 = \nabla_{\mathbf{X}}\mathcal{D}_2 + \mathbf{U}_2$$

with

$$\mathbf{X}\cdot\mathbf{U}_1 = \mathbf{X}\cdot\mathbf{U}_2 = 0,$$

imply that

$$\mathbf{U}_1 - \mathbf{U}_2 = \nabla_{\mathbf{X}}(\mathcal{D}_2 - \mathcal{D}_1) \tag{A.6}$$

and

$$\mathbf{X} \cdot (\mathbf{U}_1 - \mathbf{U}_2) = \mathbf{X} \cdot \nabla_{\mathbf{X}}(\mathcal{D}_2 - \mathcal{D}_1) = 0. \tag{A.7}$$

Since $\mathcal{D}_1$ and $\mathcal{D}_2$ are C^1 functions of $\mathbf{X}$, the difference $\mathcal{D} = \mathcal{D}_2 - \mathcal{D}_1$ is a C^1 function of $\mathbf{X}$. However, the only C^1 solution of (A.7) is given by

$$\mathcal{D}_2 = \mathcal{D}_1 + \mathcal{D}(\mathbf{0}; \omega). \tag{A.8}$$

Hence, $\mathcal{D}$ is unique to within an additive function of ω. When (A.8) is substituted into (A.6), we obtain

$$\mathbf{U}_1 = \mathbf{U}_2. \tag{A.9}$$

This establishes the uniqueness of the decomposition $(7.10)_1$.

Finally, if $\mathbf{J}(\mathbf{X}; \omega)$ is of class C^2 in $\mathbf{X}$, then $\mathcal{D}(\mathbf{X}; \omega)$ is of class C^2 in $\mathbf{X}$ as well. Then exterior differentiation of $(7.10)_1$ with respect to $\mathbf{X}$ gives (7.12). This completes the proof. ■

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