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A thermodynamic framework for phase-field models: Theory and applications

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Contents

Abstract

The goal of this work is to develop a thermodynamic setting for phase-field (diffused-interface) models with conserved and nonconserved scalar order parameters in thermoelastic materials. Our approach consists in exploiting the second law of thermodynamics in the form of the entropy principle according to I. Müller complemented by the Lagrange multipliers method suggested by I.Shih Liu. Such method leads to the evaluation of the entropy inequality with multipliers, known as the Müller-Liu inequality. By a rigorous exploitation of this inequality, combined with the application of the dual approach (with entropy or internal energy as independent thermal variable), we obtain in Part I a general scheme of phase-field models which involves an arbitrary "extra" vector field. For particular choices of this extra vector field we obtain known phase-field schemes with either modified entropy equation or/and modified energy equation. A detailed comparison with several well-known phase-field models, in particular models by Penrose and Fife, Caginalp, Fried and Gurtin, Falk, Frémond et al., Umantsev et al., is presented in Part II of this work.

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1. Introduction

1.1. Motivation and goal. In classical thermodynamics phase boundaries are considered as singular surfaces. The corresponding models, usually referred to as free boundary problems include in particualr one-and two-phase Stefan problems of parabolic or parabolic-elliptic type, and the Muscat problem. They have been studied intensively in the beginning of the eighties last century (see, e.g., [131], [120], [89], [122], [100]).
The concept of interfacial energy (or interface tension) does not follow from internal properties of the system (such as the energy density function) but is added ad hoc to the interface according to experimentally observed values. As pointed out by Falk [62] this approach is most unsatisfactory when both phases contain the same material, as in the case of a liquid-vapor interface or the interface between partially miscible fluids. To improve this situation in 1893 van der Waals [144], and somewhat later in 1901 Korteweg [91], included terms depending on the density gradient into the constitutive equation for the energy. As a consequence not only the interface energy arises in a natural way but also the interface becomes diffuse.
This type of gradient energy theory has been investigated for mixtures by Cahn and Hillard [34], [35], Cahn [36], and for gas-liquid interfaces by Felderhof [63], Widom [147]. In elasticity the theory with the gradient of the deformation influencing the energy dates back to Toupin [138]. The van der Waals-Korteweg theory has been reconsidered in various aspects in Aifantis [1], [2], Aifantis and Serrin [3], [4], Alexiades and Aifantis [11], Slemrod [135], [136], [137], Dunn and Serrin [49].

In the last three decades the gradient-type approach has become a popular tool for the investigations not only in the liquid-vapour transitions but also in the theory of continuous solid-liquid and solid-solid phase transitions. The corresponding model equations are usually referred to as phase-field (or diffused-interface) models.

The phase-field dynamical models of solid-liquid type with conserved and/or nonconserved order parameter are the concern of the present work.

Among the mostly known and broadly investigated we mention the Caginalp model of solid-liquid phase transitions [21], [22], [23], Penrose-Fife models with conserved and nonconserved order parameter [129], [130], models due to Fried and Gurtin [72], [73], [74], [75], Gurtin [83], Frémond [70], [71], and Falk [57], [61], [62] for phase transitions in solids, in particular phase separation, ordering in alloys, damage and shape memory problems. We mention also phase-field models with nonconserved order parameter due to Umantsev and Roĭtburd [141], Umantsev [139], [140], [142], and Umantsev and Olson [143].

For overvew see, e.g., Carach, Chen and Fife [38], Chen [39], Umantsev [140], Emmerich [51], Singer-Loginowa and Singer [134], Heida, Malek, and Rajagopal [86], and the monograph by Brokate and Sprekels [20].

As noted by Penrose-Fife [129] the phase-field equations were apparently first suggested by Langer [94] on the basis of a similar model, called "Model C" by Halperin, Hohenberg, and Ma [85]. Such equations were first studied analytically and numerically by Fix [67], [68], Caginalp [21], Langer [94]. Independently, phase-field equations were proposed by Collins-Levine [42] to model crystal growth.

The theory of phase-field models has been advanced by Caginalp and co-workers in a series of papers [22], [23], [24], [25], [26], [28], [29], [30], [31], [32], [33] [27]. As a matter of fact it was just the lack of a proper thermodynamic setting of the original Caginalp's model that gave rise in the neintieth of the last century to a number of so-called thermodynamically consistent models of phase transitions, in particular models by Penrose and Fife [129], [130], [66], [64], Alt and the author [5], [6], [7], [9], [10], Wang et al. [145].

The phase-field (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.

According to a postulate of a smooth phase transition the phase-field models are based on a free energy functional, called Landau-Ginzburg functional, often called Ginzburg-Landau functional, named after V. L. Ginzburg and L. Landau mathematical theory of superconductivity. This functional 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. In particular, the Penrose-Fife models with conserved and nonconserved order parameters have been derived by means of variational arguments.

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 [72], [73], [74], [75], [83] 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 of thermodynamics. Parallel to that theory M. Frémond [70], [71] 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 beeen proposed by H.W. Alt and the author in [9], [10] and applied further in [123], [124], [125], [126], [127], [128]. This approach consists in exploiting the second law in the form of the entropy principle according to I. Müller [114], [115], [116], complemented by the Lagrange multipliers method suggested by I-Shih Liu [96]. Such method leads to the evaluation of the entropy inequality with multipliers, known as the Müller-Liu inequality. In [126] the multipliers-based approach was applied for deriving generalized Cahn-Hilliard and Allen-Cahn models coupled with elasticity with suppressed thermal effects. A comparison with the Fried-Gurtin theory based on a microforce balance showed coincidence of results and several interesting connections.

Various generalized isothermal Cahn-Hilliard and Allen-Cahn models based on a microforce balance have attracted a lot of mathematical interest, see, e.g., [101], [102], [103].

It should be pointed out that the above mentioned thermodynamic approaches allow to obtain models with much more general structure than those introduced by variational arguments.

The nonisothermal phase-field models based on the Fried-Gurtin concept of a microforce balance have been further developed and studied mathematically by Miranville and Schimperna [104], [105].

The phase-field and irreversible phase transitions models based on Frémond's theory of microscopic motions (admitting nonsmooth thermodynamic functions) have been studied by Bonfanti, Frémond, and Luterotti [17], [18], Bonetti et al. [16], Colli et al. [41], Laurençont, Schimperna, and Stefanelli [95], Luterotti, Schimparna, and Stefanelli [99], Schimperna and Stefanelli [132].

Recently several phase-field approaches to nonisothermal phase transitions with broad range of applications have been advanced by Fabrizio, Giorgi, and Morro [53], [54], [55], Fabrizio [52], Gentili and Giorgi [80], Giorgi [81], Morro [109], [110], [111], [112], [113]. The applications included in particular model for ice-water transition which allows for superheating and undercooling, model for the transition in superconducting materials, materials with thermal memory, second-sound transition in solids, as well as Cahn-Hilliard fluids.

We mention also diffuse interface model for rapid phase transfomation in nonequilibrium system, proposed by Galenko and Jou [77].

The goal of the present work is to set up 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 the Cahn-Hilliard and the Allen-Cahn models – two central equations in materials science – in the presence of deformation and heat conduction. This is presented in Part II of this work where we discuss a 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 generalized Cahn-Hilliard and the Allen-Cahn models coupled separately either with elasticity or with thermal effects. 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 by "extra" terms (for related discussion see, e.g., [53] and [113]).

Let us note that to the class of models which involve an "extra" entropy flux belong, e.g., models by Penrose and Fife [129], [130], Caginalp [23]. Alt and the author [5], [7], Falk [62], Fabrizio, Giorgi, and Morro [53], Morro [112].

On the other hand, to the class of models which involve an "extra" energy flux belong, e.g., models by Aifantis [1], [2], Dunn and Serrin [49], Umantsev [139], Umantsev and Roĭtburd [141], Fried and Gurtin [72], Frémond [70], Bonfanti, Frémond, and Luterotti [17], [18], Miranville and Schimperna [104], and Benzoni-Gavage et al. [12].

In relation to models modified by extra energy or/and entropy fluxes, the answer given by the present work is that both variants of the schemes with extra energy or/and extra entropy fluxes are thermodynamically consistent. More precisely, we prove 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 potentiales, was observed firstly in [10] by a rigorous analytical exploitation of the second law of thermodynamics in the form of the Müller-Liu entropy inequality. Following the ideas in [9], [10], we worked out in a number of papers [123], [124], [125], [127], [128] a special procedure of exploiting the Müller-Liu entropy inequality, combined with a dual approach. The dual approach consists in choosing internal energy or entropy as independent thermal variable for the exploitation of the entropy inequality, and afterwards applying the duality relations (Legendre transformations) to formulate the resulting equations in terms of the absolute temperature. Using such approach we derive here schemes involving an arbitrary vector field. Clearly, a final selection of this field must follow from an additional analysis of the resulting model equations.

What is of interest, extra energy and entropy fluxes are also allowed to appear in phase-field models of Cahn-Hilliard fluids, proposed by A. Morro [113].

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 based on a dual approach. The procedure consits 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. According to the principle of equipresence we assume that all quantities in balance laws are constitutive functions defined on this set of variables.

The dual approach with internal energy or entropy as independent thermal variable is valid under assumption of strict positivity of the specific heat (so-called thermal stability condition). We have found such approach more straightforward in comparison with the one using the absolute temperature as primary independent variable. Let us mention that phase-field systems with internal energy as thermal variable have been introduced, e.g., by Halperin, Hohenberg and Ma [85], Penrose and Fife [129], Galenko and Jou [77]. Multicomponent systems with entropy as independent thermal variable have been derived, e.g., by Falk [62]. To illustrate the role of the duality relations in evaluating the entropy inequality, in this work we present both approaches with entropy and energy as independent thermal 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 invariance, often referred to as frame indifference (see, e.g., [133, Sec. 9.3.2]).,

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

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. The motion of the body is denoted by $\boldsymbol{y}(\boldsymbol{X},t) = \boldsymbol{X} + \boldsymbol{u}(\boldsymbol{X},t)$, where $\boldsymbol{u} = (u_i)$ is the displacement vector; $\boldsymbol{F} = \nabla \boldsymbol{y} = \boldsymbol{I} + \nabla \boldsymbol{u}$, subject to the condition $\det \boldsymbol{F} > 0$, is the deformation gradient.

We deal with the following quantities in the material representation:

$\varrho_0 = \varrho_0(\boldsymbol{X}) > 0$ – mass density given once and for all along with the body and the fixed reference configuration,
$\boldsymbol{S} = (S_{ij})$ – referential stress tensor,
$\boldsymbol{b} = (b_i)$ – specific body force,
χ – scalar order parameter (phase variable),
$\boldsymbol{j} = (j_i)$ – order parameter flux,
r – specific rate of produciton of the phase variable,
τ – specific rate of supply of the phase variable from the exterior,
μ – chemical potential,
$\theta > 0$ – absolute temperature,
$\bar{\mu} = \mu/\theta$ – rescaled chemical potential,
$\boldsymbol{q} = (q_i)$ – referential heat flux vector,
g – specific rate of supply of heat,
e – specific internal energy,
η – specific entropy,
$f = e - \theta\eta$ – free energy (Helmholtz) function,
$\phi = f/\theta$ – rescaled free energy,
σ – specific entropy production,
$\boldsymbol{\Psi} = (\Psi_i)$ – referential entropy flux,
$c_{\boldsymbol{F}}$ – specific heat at constant deformation.

If elastic effects are suppressed or in case of fluids c_F is denoted by c_ν and is called specific heat at constant volume (see [133]).

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

$$\mathcal{X} := \left(\frac{\mu}{\theta}, \boldsymbol{D}\frac{\mu}{\theta}, \boldsymbol{D}\frac{1}{\theta}, \chi_{,t}\right) \qquad \text{— thermodynamic forces,}$$
$$\omega := (\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta) \quad \text{— state variables,}$$

which is nonnegative, convex in $\mathcal{X}$ and such that $\mathcal{D}(\boldsymbol{0};\omega) = 0$. Above $\boldsymbol{D}\chi$, $\boldsymbol{D}^2\chi$, $\chi_{,t}$, etc. denote variables corresponding to $\nabla\chi$, $\nabla^2\chi$, $\dot{\chi}$, respectively. Here and in what follows all derivatives are material; ∇ and $\nabla\cdot$ are the gradient and the divergence with respect to material point $\boldsymbol{X}$, superimposed dot denotes the material time derivative.
A general scheme of phase-field models, denoted $(PF)_\theta$, is as follows.

The unknowns are the fields $\boldsymbol{u}, \chi, \bar{\mu} := \frac{\mu}{\theta}$ and $\theta > 0$ satisfying the following system of differential equations in $\Omega \subset \mathbb{R}^3$ and time $t \in [0, T]$, $T > 0$:

$$\begin{aligned}
&\varrho_0\ddot{\boldsymbol{u}} - \nabla\cdot\boldsymbol{S} = \varrho_0\boldsymbol{b},\\
&\varrho_0\dot{\chi} + \nabla\cdot\boldsymbol{j}^d - \varrho_0 r^d = \varrho_0\tau,\\
&\varrho_0\frac{\mu}{\theta} = \frac{\delta(\varrho_0 f/\theta)}{\delta\chi} + \boldsymbol{h}^e\cdot\nabla\frac{1}{\theta} + a^d,\\
&\varrho_0\dot{e} + \nabla\cdot(\boldsymbol{q}^d - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S}\cdot\dot{\boldsymbol{F}} = g,
\end{aligned} \tag{1.1}$$

subject to appropriate initial and boundary conditions. Here

$$\begin{aligned}
&e = \hat{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) - \theta\hat{f}_{,\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta),\\
&\boldsymbol{S} = \varrho_0\hat{f}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta), \text{ satisfying } \boldsymbol{S}\boldsymbol{F}^T = \boldsymbol{F}\boldsymbol{S}^T,
\end{aligned} \tag{1.2}$$

and $r^d = \hat{r}^d(\mathcal{X};\omega)$, $\boldsymbol{j}^d = \hat{\boldsymbol{j}}^d(\mathcal{X};\omega)$, $\boldsymbol{q}^d = \hat{\boldsymbol{q}}^d(\mathcal{X};\omega)$, $a^d = \hat{a}^d(\mathcal{X};\omega)$ are subject to the residual dissipation inequality

$$\varrho_0\sigma := -\frac{\mu}{\theta}\varrho_0 r^d - \boldsymbol{D}\frac{\mu}{\theta}\cdot\boldsymbol{j}^d + \boldsymbol{D}\frac{1}{\theta}\cdot\boldsymbol{q}^d + \chi_{,t}\cdot a^d \geq 0 \tag{1.3}$$

for all variables $\{\mathcal{X};\omega\} =: \mathcal{Z}_\theta$.
The quantity σ is the specific entropy production. The superscript d indicates that the quantity is dissipative, thus contributes to the entropy production. By the Edelen decomposition theorem (see Section 4.2), the quantities r^d, $\boldsymbol{j}^d$, $\boldsymbol{q}^d$, a^d are given by

$$\begin{aligned}
&-\varrho_0 r^d = \frac{\partial\mathcal{D}}{\partial(\mu/\theta)}, \quad -\boldsymbol{j}^d = \frac{\partial\mathcal{D}}{\partial\boldsymbol{D}(\mu/\theta)}, \quad \boldsymbol{q}^d = \frac{\partial\mathcal{D}}{\partial\boldsymbol{D}(1/\theta)},\\
&a^d = \frac{\partial\mathcal{D}}{\partial\chi_{,t}}.
\end{aligned} \tag{1.4}$$

The subsequent equations in (1.1) represent correspondingly the linear momentum balance, the balance equation for the order parameter, a generalized equation for the chemical potential (equivalent to a microforce balance in the Fried-Gurtin theory, see Chapters 9, 10), and the internal energy balance. Equation $(1.1)_2$ combines various types of dynamics of the order parameter:

– mixed type if $\boldsymbol{j}^d \neq \mathbf{0}$, $r^d \neq 0$;

– conserved if $\boldsymbol{j}^d \neq \mathbf{0}$, $r^d \equiv 0$;

– nonconserved if $\boldsymbol{j}^d \equiv \mathbf{0}$, $r^d \neq 0$.

The expression $\delta(\varrho_0 f/\theta)/\delta\chi$ denotes the first variation of the rescaled free energy f/θ with respect to χ:

$$\frac{\delta(\varrho_0 f/\theta)}{\delta\chi} = \left(\frac{\varrho_0 f}{\theta}\right)_{,\chi} - \nabla \cdot \left(\frac{\varrho_0 f_{,\boldsymbol{D}\chi}}{\theta}\right). \tag{1.5}$$

The first equation in (1.2) represents the thermodynamic Gibbs relation assumed to be valid in case of gradient type potentials. The second equation in (1.2) is the standard constitutive equation for the stress tensor.

The characteristic nonstandard element in system (1.1) is the nondissipative extra vector field $\boldsymbol{h}^e = \hat{\boldsymbol{h}}^e(\mathcal{X};\omega)$ which contributes to the nonstationary energy flux (superscript e indicates energy). The vector field $\boldsymbol{h}^e$ is not restricted by the entropy principle. It should, however, like all other constitutive quantities in (1.1), be consistent with the frame invariance principle. This principle restricts the dependence on the deformation gradient $\boldsymbol{F}$. In particular, the free energy should satisfy

$$\hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) = \hat{f}(\boldsymbol{C}, \chi, \boldsymbol{D}\chi, \theta),$$

where $\boldsymbol{C} = \boldsymbol{F}^T\boldsymbol{F}$ is the right Cauchy-Green strain tensor; other quantities should transform appropriately (see Section 6.1).

Apart from this restriction the vector field $\boldsymbol{h}^e$ is an arbitrary quantity that may be selected, e.g., on a basis of an additional analysis of the resulting equations. We shall present some physically realistic examples of vector $\boldsymbol{h}^e$ which lead to phase-field models well-known in the literature (see Chapters 9, 10 for a detailed discussion).

Prior to do this, let us summarize the main properties of model $(PF)_\theta$, i.e., system (1.1)–(1.3).

It will be proved (see Corollary 6.8 and Remark 7.1) that sufficiently regular solutions of system (1.1)–(1.3) satisfy the following entropy equation and inequality

$$\varrho_0\dot{\eta} + \nabla \cdot \boldsymbol{\Psi} = \varrho_0\sigma - \frac{\mu}{\theta}\varrho_0\tau + \frac{\varrho_0 g}{\theta} \geq -\frac{\mu}{\theta}\varrho_0\tau + \frac{\varrho_0 g}{\theta} \tag{1.6}$$

with the entropy production $\varrho_0\sigma$ given by (1.3), and the entropy flux admitting the splitting

$$\boldsymbol{\Psi} = -\frac{\mu}{\theta}\boldsymbol{j}^d + \frac{1}{\theta}\boldsymbol{q}^d + \dot{\chi}\frac{\varrho_0 f_{,\boldsymbol{D}\chi} - \boldsymbol{h}^e}{\theta} \equiv \boldsymbol{\Psi}^d + \dot{\chi}\boldsymbol{h}^\eta. \tag{1.7}$$

Above

$$\boldsymbol{\Psi}^d := -\frac{\mu}{\theta}\boldsymbol{j}^d + \frac{1}{\theta}\boldsymbol{q}^d \tag{1.8}$$

is the standard entropy flux associated with the dissipative fluxes, and

$$\dot{\chi}\boldsymbol{h}^\eta \quad \text{with} \quad \boldsymbol{h}^\eta := \frac{1}{\theta}(\varrho_0 f_{,\boldsymbol{D}\chi} - \boldsymbol{h}^d) \tag{1.9}$$

is an extra nonequilibrium entropy flux.

It is of importance to note that according to the splitting (1.7), the extra nonequilibrium energy flux, $-\dot{\chi}\boldsymbol{h}^e$, and the extra nonequilibrium entropy flux, $\dot{\chi}\boldsymbol{h}^\eta$, are linked by the equality

$$\dot{\chi}(\boldsymbol{h}^e + \theta\boldsymbol{h}^\eta) = \dot{\chi}\varrho_0 f_{,\boldsymbol{D}\chi}, \quad \text{i.e.,} \quad \boldsymbol{h}^e + \theta\boldsymbol{h}^\eta = \varrho_0 f_{,\boldsymbol{D}\chi}. \tag{1.10}$$

Another important property of model $(PF)_\theta$ (1.1)–(1.3) is the Lyapunov relation (see Corollary 6.11 and Remark 7.1) which asserts that if the external sources vanish, i.e., $\boldsymbol{b} = \boldsymbol{0}$, $\tau = 0$, $g = 0$, and if the boundary conditions on the domain boundary S imply that

$$\begin{aligned} &(\boldsymbol{S}\boldsymbol{n}) \cdot \dot{\boldsymbol{u}} = 0, \quad \frac{\mu}{\theta}\boldsymbol{n} \cdot \boldsymbol{j} = 0, \quad \left(1 - \frac{\bar{\theta}}{\theta}\right)\boldsymbol{n} \cdot (\boldsymbol{q}^d - \dot{\chi}\boldsymbol{h}^e) = 0, \\ &\frac{\dot{\chi}}{\theta}\boldsymbol{n} \cdot f_{,\boldsymbol{D}\chi} = 0, \end{aligned} \tag{1.11}$$

where $\boldsymbol{n}$ denotes the unit outward normal to $S = \partial\Omega$, and $\bar{\theta} > 0$ is some constant, then solutions of system (1.1)–(1.3) satisfy the inequality

$$\frac{d}{dt}\int_\Omega \varrho_0\Big(e(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) + \frac{1}{2}|\dot{\boldsymbol{u}}|^2 - \bar{\theta}\eta(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)\Big)dx \leq 0. \tag{1.12}$$

This provides the Lyapunov relation.

One can see that the distinguishing elements in system (1.1)–(1.3) are nonstandard energy and entropy fluxes, $\boldsymbol{q}$ and $\boldsymbol{\Psi}$ which contain extra nonstationary terms. The relation (1.10) indicates that in phase-field models with the first-order gradient free energy (i.e., $f_{,\boldsymbol{D}\chi} \neq \boldsymbol{0}$) at least one of the fluxes must include an extra nonstationary term with $\dot{\chi}$.

We point now on model $(PF)_\theta$ with some physically realistic extra energy and entropy terms $\boldsymbol{h}^e$ and $\boldsymbol{h}^\eta$:

(PF)(i) extra energy and extra entropy terms

$$\boldsymbol{h}^e = \varrho_0 e_{,\boldsymbol{D}\chi} \quad \text{and} \quad \boldsymbol{h}^\eta = -\varrho_0 \eta_{,\boldsymbol{D}\chi};$$

(PF)(ii) zero extra energy term and extra entropy term

$$\boldsymbol{h}^e = \boldsymbol{0} \quad \text{and} \quad \boldsymbol{h}^\eta = \frac{1}{\theta}\varrho_0 f_{,\boldsymbol{D}\chi};$$

(PF)(iii) extra energy term and zero extra entropy term

$$\boldsymbol{h}^e = \varrho_0 f_{,\boldsymbol{D}\chi} \quad \text{and} \quad \boldsymbol{h}^\eta = \boldsymbol{0}.$$

The corresponding systems $(PF)_\theta$ are formulated in Section 7.4. Here we point out that with the above special choices of the extra term $\boldsymbol{h}^e$, assuming standard forms of the free energy $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ and the dissipation potential $\mathcal{D} = \hat{\mathcal{D}}(\mathcal{X}; \omega)$, we can derive from system (1.1)–(1.3) several known phase-field models with conserved and nonconserved order parameter, including the cases with suppressed either elastic or thermal effects.

1.4. Plan. Part I (Theory) consists of Chapters 2–7. In Chapter 2 we introduce basic physical quantities, the balance equations, the state spaces relevant for phase-field models under consideration and the constitutive relations. In Section 2.4 we present briefly the standard formulation of the second law of thermodynamics in the form of the Clausius-Duhem inequality and the Coleman-Noll approach of exploiting this inequality. In Section 2.5 we introduce the entropy principle due to I. Müller. This principle complemented by the multipliers metod proposed by I-Shih Liu is considered as an important alternative to the Coleman-Noll approach. In Section 2.6 we formulate the Müller-Liu inequality with multipliers for the system of our concern.

In Chapter 3 we present basic thermodynamic Gibbs relations formulated alternatively either with respect to the free energy or the rescaled free energy. Moreover, we present the Legendre duality relations for systems described by the gradient-type free energy $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$, e.g., the Landau-Ginzburg free energy. Such relations – well known for classical systems with volumetric free energies – in case of of gradient-type free energies are not so common. Since in the present work they play a crucial role we present them in a detailed way.

The exploitation of the entropy inequality always leads to the inequality type condition on the constitutive functions, called the *residual dissipation inequality.* In Chapter 4 we record two results known in the literature on the representation of solutions to the dissipation inequality. The first one is the decomposition theorem due to D.G.B. Edelen and the second one is the theorem due to M.E. Gurtin. In subsequent chapters we shall repeatedly make use of these representation results.

In Chapter 5 we are dealing with the evaluation of the entropy inequality introduced in Section 2.6 to select a class of thermodynamically consistent phase-field models. The applied procedure is combined with the dual approach. To illustrate the role of the duality relations in this procedure we present two alternative approaches of evaluating the entropy inequality which use either the entropy or the internal energy as independent thermal variable. In Section 5.1 we use the state space with the entropy as the independent variable and the internal energy density as a corresponding thermodynamic potential. The obtained restrictions on the constitutive relations are stated in Theorem 5.1 in case of mixed conserved-nonconserved dynamics of the order parameter, and in Theorem 5.4 for the nonconserved dynamics.

In Section 5.2 we present an alternative evaluation of the entropy inequality using the state space with the internal energy as independent thermal variable and the entropy density as a corresponding thermodynamic potential. The considerations parallel those in Section 5.1. The obtained restrictions on the constitutive relations are stated in Theorems 5.5 and in Theorem 5.6 in the nonconserved case.

On the basis of the obtained results, in Chapter 6 we introduce two classes of extended phase-field models $(PF)_\eta$ and $(PF)_e$, in which the multipliers corresponding to the balance equations for the order parameter and the internal energy are treated as independent variables. Then, on account of the duality relations, we give equivalent formulations, $(PF)_\theta$ and $(PF)_\vartheta$, of models $(PF)_\eta$ and $(PF)_e$, with absolute temperature θ and inverse temperature $\vartheta = 1/\theta$ in place of entropy η and internal energy e, respectively. It turns out that models $(PF)_\vartheta$ and $(PF)_\theta$ are identical. The characteristic feature of all presented models is the presence of an "extra" nondissipative vector field $\boldsymbol{h}^e$ which contributes to the nonstationary (depending on the time derivative of the phase variable)

energy and entropy fluxes as well as to the equation for the multiplier associated with the balance equation for the phase variable (identified with the rescaled chemical potential). This extra vector field is nondissipative, that is not restricted by the second law of thermodynamics.
It has to be selected in consitency with the frame invariance, but besides this it is an arbitrary quantity.

In literature it is common to formulate models with the absolute temperature as the independent thermal variable and the free energy as the corresponding thermodynamic potential. For this reason in Chapter 7 we focus our attention on the extended phase-field model $(PF)_\theta$. We present physically realistic examples of this model which depend on the specific choice of the extra vector field $\boldsymbol{h}^e$. These examples will be used in Part II to dissuss relations of model $(PF)_\theta$ to well-known phase-field models with conserved and nonconserved order parameters. Moreover, for further references we present separately model $(PF)_\theta$ with suppressed elastic effects or with suppressed thermal effects.

Part II (Applications) consists of Chapters 8–10. Here our aim is to unify various well-kown approaches to phase-field modelling by revising their arguments in the light of the theory presented in Part I.

In Chapter 8, to set a stage for a comparision with known models, we collect some typical examples of the free energies and dissipation potentials.

In Chapter 9 we discuss relation of our model $(PF)_\theta$ to well-known phase-field models with conserved order parameter, in particular the Penrose-Fife model, the model with the rescaled free energy, the Caginalp model, the Falk's model, the Cahn-Hilliard-de Gennes model for polymer phase separation, and the Gurtin model based on a microforce balance for the Cahn-Hilliard system coupled with elasticity.

In Chapter 10 we perform similar comparison of model $(PF)_\theta$ with well-known phase-field models with nonconserved order parameter. These include the Penrose-Fife model, the Caginalp model, the Fried-Gurtin model based on a microforce balance and its extension due to Miranville-Schimperna, and the Frémond model based on microscopic motions.

REMARK 1.1. In citing works we have tried to be objective as possible. Any omission of due references is a personal shortcoming and certainly not intentional. We apologize if we have not rendered justice to various significant contributions.

1.5. Notation. We generally follow the notation of the monograph by M.E. Gurtin [84]. 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.
The unit tensor $\boldsymbol{I}$ is defined by $\boldsymbol{I}\boldsymbol{u} = \boldsymbol{u}$ for every vector $\boldsymbol{u}$; $\boldsymbol{S}^T$, $tr\boldsymbol{S}$, $\boldsymbol{S}^{-1}$ and det $\boldsymbol{S}$, respectively, denote the transpose, trace, inverse, and determinant of a tensor $\boldsymbol{S}$.

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

In Cartesian components

$$(\boldsymbol{S}\boldsymbol{u})_i = S_{ij}u_j, \quad (\boldsymbol{S}^T)_{ij} = S_{ji}, \quad tr\boldsymbol{S} = S_{ii}, \quad \boldsymbol{u}\cdot\boldsymbol{v} = u_iv_i,$$
$$\boldsymbol{S}\cdot\boldsymbol{R} = S_{ij}R_{ij}, \quad \boldsymbol{A}^m\cdot\boldsymbol{B}^m = A^m_{i_1\cdots i_m}B^m_{i_1\cdots i_m}.$$

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

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

By $\boldsymbol{A} = (A_{ijkl})$ we denote the fourth order elasticity tensor which represents a symmetric linear transformation of symmetric tensors into symmetric tensors. We write $(\boldsymbol{A}\boldsymbol{\varepsilon})_{ij} = (A_{ijkl}\varepsilon_{kl})_{ij}$.

The term field signifies a function of a material point $\boldsymbol{X} \in \mathbb{R}^3$ and time t.
The superimposed dot, e.g., $\dot{f}$, denotes the material time derivative of the field f (with respect to t holding $\boldsymbol{X}$ fixed), ∇ and $\nabla\cdot$ denote the material gradient and the divergence (with respect to $\boldsymbol{X}$ holding t fixed).

For the divergence we use the convention of the contraction over the last index, e.g., $(\nabla\cdot\boldsymbol{S})_i = \partial S_{ij}/\partial x_j$.

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

For a function $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ we denote by $\delta f/\delta\chi$ its first variation with respect to χ, defined by the identity

$$\frac{d}{d\alpha}\int_\Omega f(\boldsymbol{F}, \chi + \alpha\zeta, \nabla\chi + \alpha\nabla\zeta, \theta)d\boldsymbol{X}|_{\alpha=0} =: \int_\Omega \frac{\delta f}{\delta\chi}\zeta d\boldsymbol{X} \quad \text{for all } \zeta \in C_0^\infty(\Omega).$$

This gives the following representation

$$\frac{\delta f}{\delta\chi} = f_{,\chi}(\boldsymbol{F}, \chi, \nabla\chi, \theta) - \nabla\cdot f_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \nabla\chi, \theta). \tag{1.13}$$

In situations that may cause confusion we shall distinguish between functions and their values. Functions are then denoted by "hats", e.g., $f = \hat{f}(F, \chi, \boldsymbol{D}\chi, \theta)$.

Finally, let us add a comment on the numbering used in this work. Equations are numbered sectionwise within each chapter. For example (2.3.1) stands for the first equation in the Section 3 of Chapter 2. If this equation is referred to within Chapter 2 itself, it is simply cited as (3.1). Theorems, Lemmas, Corollaries, and Remarks are also numbered sectionwise within each chapter; typical examples are Theorem 5.1, Remark 2.1, Corollary 6.11, and so on.

Part I

Theory

2. Balance equations, state spaces, constitutive relations, and the entropy inequality

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. The material particles are identified with the positions $\boldsymbol{X} \in \Omega$ they occupy in this fixed reference configuration. The motion (deformation) of the body is denoted by

$$\boldsymbol{y}(\boldsymbol{X}, t) = \boldsymbol{X} + \boldsymbol{u}(\boldsymbol{X}, t), \tag{1.1}$$

where $\boldsymbol{u} = (u_i)$ is the dispacement vector. The motion velocity is $\boldsymbol{v} = \dot{\boldsymbol{y}}$. Further,

$$\boldsymbol{F} = \nabla \boldsymbol{y} = \boldsymbol{I} + \nabla \boldsymbol{u}, \tag{1.2}$$

subject to the condition $\det \boldsymbol{F} > 0$, is the deformation gradient, and

$$\boldsymbol{C} = \boldsymbol{F}^T \boldsymbol{F}, \quad \text{in components} \quad C_{ij} = \frac{\partial y_m}{\partial X_i} \frac{\partial y_m}{\partial X_j},$$

is the right Cauchy-Green strain tensor corresponding to $\boldsymbol{F}$. Above and hereafter the summation convention is used. Moreover, let

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

denote the infinitesimal (small) strain tensor. The linear map

$$\varepsilon(\boldsymbol{u}) \mapsto \boldsymbol{A}\varepsilon(\boldsymbol{u}) := \lambda trace \varepsilon(\boldsymbol{u}) \boldsymbol{I} + 2\mu\varepsilon(\boldsymbol{u}),$$

where λ, μ are the Lame constants satisfying $\mu > 0$, $3\lambda + 2\mu > 0$, $\boldsymbol{I} = (\delta_{ij})$ is the unit matrix, represents the Hooke's law for a homogeneous isotropic material. Here $\boldsymbol{A} = (A_{ijkl})$ with

$$A_{ijkl} = \lambda \delta_{ij} \delta_{kl} + \mu(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$$

is the fourth order elasticity tensor satisfying the symmetry conditions

$$A_{ijkl} = A_{jikl}, \quad A_{ijkl} = A_{ijlk}, \quad A_{ijkl} = A_{klij}.$$

In considerations of this work we follow the terminology of the monograph by M. Šilhavý [133]. More precisely, we deal with the following quantities in the material representation:

ϱ_0 – referential mass density,
$\boldsymbol{S} = (S_{ij})$ – referential (first Piola-Kirchhoff) stress tensor,
$\boldsymbol{b} = (b_i)$ – specific body force (specific means the amount of the quantity per unit mass),
χ – specific volume density of one of the two phases, referred to as *an order parameter* or *phase variable*.

In some theories order parameters are defined clearly in terms of concentrations or the arrangements of the atoms on lattices; however other nonconserved order parameter fields are often defined only in phenomenological terms. For various examples of conserved and nonconserved order parameters we refer e.g., to the monograph by M. Brocate and J. Sprekels [20];

$\boldsymbol{j} = (j_i)$ – referential flux vector of the phase variable, refferred also to as the referential mass flux if χ represents the concentration,
r – specific rate of production of the phase variable,
τ – specific rate of supply of the phase variable from the exterior,
$\theta > 0$ – absolute temperature,
$\vartheta = 1/\theta$ – inverse temperature,
$\boldsymbol{q} = (q_i)$ – referential (Piola-Kirchhoff) heat flux vector,
g – specific rate of supply of heat,
e – specific internal energy,
η – specific entropy,
$f = e - \theta\eta$ – free energy (Helmholtz function),
$\phi = f/\theta$ – rescaled free energy,
σ – specific entropy production (dissipation scalar),
$\boldsymbol{\Psi}$ – referential entropy flux,
μ – chemical potential,
$\bar{\mu} = \mu/\theta$ – rescaled chemical potential,
c_F – specific heat at constant deformation.

In the case of fluids or if the elastic effects are suppressed, i.e., $\boldsymbol{x} = \boldsymbol{y}(\boldsymbol{X}, t) = \boldsymbol{X}$, $\boldsymbol{v} = \boldsymbol{0}$, $\boldsymbol{F} = \boldsymbol{I}$, $\varrho = \varrho_0 / \det \boldsymbol{F} = \varrho_0$, then the specific heat at constant deformation is usually called the specific heat at constant volume and is denoted by c_ν, where $\nu = \det \boldsymbol{F}/\varrho_0 = 1/\varrho$ is the specific volume (see [133], Chap. 11).

Moreover, depending on the choice of independent thermal variable (see Chapter 3), we denote:

$e = \hat{e}(\theta)$, $\bar{e} = \hat{\bar{e}}(\vartheta)$, $\tilde{e} = \hat{\tilde{e}}(\eta)$ – specific internal energy as a function of θ, ϑ and η, respectively;
$\eta = \hat{\eta}(\theta)$, $\bar{\eta} = \hat{\bar{\eta}}(\vartheta)$, $\tilde{\eta} = \hat{\tilde{\eta}}(e)$ – specific entropy as a function of θ, ϑ and e, respectively.

2.2. Balance equations. Let us consider the local material forms of the balance equations for mass, linear momentum, angular momentum and total energy (cf., e.g., [133])

$$
\begin{aligned}
&\dot{\varrho}_0 = 0,\\
&\varrho_0 \ddot{\boldsymbol{y}} - \nabla \cdot \boldsymbol{S} = \varrho_0 \boldsymbol{b},\\
&\boldsymbol{S}\boldsymbol{F}^T = \boldsymbol{F}\boldsymbol{S}^T,\\
&\varrho_0 \left(e + \frac{1}{2}|\dot{\boldsymbol{y}}|^2 \right)^{\cdot} + \nabla \cdot (-\boldsymbol{S}^T \dot{\boldsymbol{y}} + \boldsymbol{q}) = \varrho_0 (\boldsymbol{b} \cdot \dot{\boldsymbol{y}} + g).
\end{aligned}
\tag{2.1}
$$

The equation of balance of energy $(2.1)_4$ admits the reduced form

$$\varrho_0 \dot{e} + \nabla \cdot \boldsymbol{q} - \boldsymbol{S} \cdot \dot{\boldsymbol{F}} = \varrho_0 g. \tag{2.2}$$

The reduced form (2.2) follows by multiplying scalarly the linear momentum equation $(2.1)_2$ by $\boldsymbol{v} = \dot{\boldsymbol{y}}$ and using the identity

$$\begin{aligned} \boldsymbol{v} \cdot (\nabla \cdot \boldsymbol{S}) &= v_i \partial_{X_j} S_{ij} = \partial_{X_j} (S^T_{ji} v_i) - S_{ij} \partial_{X_j} v_i \\ &= \nabla \cdot (\boldsymbol{S}^T \boldsymbol{v}) - \boldsymbol{S} \cdot \dot{\boldsymbol{F}}, \end{aligned}$$

to get the equation

$$\frac{1}{2} \varrho_0 (|\boldsymbol{v}|^2)^{\cdot} - \nabla \cdot (\boldsymbol{S}^T \boldsymbol{v}) + \boldsymbol{S} \cdot \dot{\boldsymbol{F}} = \varrho_0 \boldsymbol{v} \cdot \boldsymbol{b}. \tag{2.3}$$

Now, subtacting (2.3) from $(2.1)_4$ yields (2.2). We remind that $\nabla \cdot$ denotes the material divergence operator.

The system (2.1) is considered along with the local material form of the balance equation for the phase variable

$$\varrho_0 \dot{\chi} + \nabla \cdot \boldsymbol{j} - \varrho_0 r = \varrho_0 \tau, \tag{2.4}$$

where the quantities $\boldsymbol{j}$ and r represent the referential flux and the specific rate of production of the phase variable. We assume that both $\boldsymbol{j}$ and r are constitutive quantities, and one of them can be identically equal zero. The scalar τ represents the specific rate of supply of the phase variable from the exterior (not a constitutive quantity).

Equation (2.4) may describe various types of dynamics of the phase variable (see, e.g., [20]):

- mixed conserved-nonconserved when $\boldsymbol{j} \neq \boldsymbol{0}$ and $r \neq 0$,
- conserved when $\boldsymbol{j} \neq \boldsymbol{0}$ and $r \equiv 0$,
- nonconserved when $\boldsymbol{j} \equiv \boldsymbol{0}$ and $r \neq 0$.

In a common terminology due to Hohenberg and Halperin [87] equation (2.4) with a conserved order parameter is referred to as Model B of phase transitions while in the case of a nonconserved order parameter as Model A.

We shall assume that the referential mass density

$$\varrho_0 = \varrho_0(\boldsymbol{X}) > 0 \tag{2.5}$$

is a positive function given once and for all along with the body and the fixed reference configuration. Then system (2.1), (2.4), expressed in terms of the displacement $\boldsymbol{u}$, takes on the following reduced form:

$$\begin{aligned} &\varrho_0 \ddot{\boldsymbol{u}} - \nabla \cdot \boldsymbol{S} = \varrho_0 \boldsymbol{b}, \\ &\boldsymbol{S}\boldsymbol{F}^T = \boldsymbol{F}\boldsymbol{S}^T, \\ &\varrho_0 \dot{\chi} + \nabla \cdot \boldsymbol{j} - \varrho_0 r = \varrho_0 \tau, \\ &\varrho_0 \dot{e} + \nabla \cdot \boldsymbol{q} - \boldsymbol{S} \cdot \dot{\boldsymbol{F}} = \varrho_0 g. \end{aligned} \tag{2.6}$$

The system (2.6) is closed by constitutive relations for the quantities $\boldsymbol{S}$, $\boldsymbol{j}$, r, e and $\boldsymbol{q}$:

$$\boldsymbol{S} = \hat{\boldsymbol{S}}(Y), \quad \boldsymbol{j} = \hat{\boldsymbol{j}}(Y), \quad r = \hat{r}(Y), \quad e = \hat{e}(Y), \quad \boldsymbol{q} = \hat{\boldsymbol{q}}(Y), \tag{2.7}$$

where Y denotes a set of independent constitutive variables (state space), and $\hat{\boldsymbol{S}}$, $\hat{\boldsymbol{j}}$, $\hat{r}$, $\hat{e}$, $\hat{\boldsymbol{q}}$ are smooth functions of their arguments.

The set Y has to be chosen so that to reflect the material properties. As common, we do not assume constitutive relations for the external sources $\boldsymbol{b}$, τ and g.

2.3. State spaces. To derive phase-field models governed by a first order gradient free energy

$$f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta),$$

one may use the following state spaces which differ by the choice of thermal variables as θ, η, or e:

$$\begin{aligned} Y_\theta &:= \{\boldsymbol{F}, \boldsymbol{DF}, \ldots, \boldsymbol{D}^M\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \ldots, \boldsymbol{D}^K\chi, \theta, \boldsymbol{D}\theta, \ldots, \boldsymbol{D}^L\theta, \chi_{,t}\}, \\ Y_\eta &:= \{\boldsymbol{F}, \boldsymbol{DF}, \ldots, \boldsymbol{D}^M\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \ldots, \boldsymbol{D}^K\chi, \eta, \boldsymbol{D}\eta, \ldots, \boldsymbol{D}^L\eta, \chi_{,t}\}, \\ Y_e &:= \{\boldsymbol{F}, \boldsymbol{DF}, \ldots, \boldsymbol{D}^M\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \ldots, \boldsymbol{D}^K\chi, e, \boldsymbol{D}e, \ldots, \boldsymbol{D}^L e, \chi_{,t}\} \end{aligned} \tag{3.1}$$

with integers M, K, L satisfying the conditions $M, L \geq 1$ and $K \geq 2$.

To avoid confusions above and hereafter we distinguish variables from functions by a different notation. Thus, $\chi_{,t}$ is a variable corresponding to time derivative $\dot{\chi}$ evaluated at $(\boldsymbol{X}, t)$, and

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

is the k-th order tensor of variables corresponding to the k-th order gradient of χ with respect to $\boldsymbol{X}$

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

evaluated at $(\boldsymbol{X}, t)$; similarly $\boldsymbol{D}^l\theta$, $\boldsymbol{D}^l e$ and $\boldsymbol{D}^l\eta$, $0 \leq l \leq L$.

Finally,

$$\boldsymbol{D}^m\boldsymbol{F} = (F_{ij,i_1\ldots,i_m})_{i,j,i_1,\ldots,i_m=1,2,3}, \quad 0 \leq m \leq M,$$

is the $(2+m)$-th order tensor of variables corresponding to the m-th order gradient ot tensor $\boldsymbol{F} = (F_{ij})$

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

evaluated at $(\boldsymbol{X}, t)$.
We use the convention

$$\boldsymbol{D}^0\chi = \chi.$$

Remark 2.1. Tensor $\boldsymbol{F}$ and its gradients represent mechanical properties, χ and its gradients – structural properties due to material heterogeneity, θ, η, e and their gradients – thermal properties, and $\chi_{,t}$ – viscous effects due to material heterogeneity.

The distinguishing elements in state spaces (3.1) are variables corresponding to higher order space derivatives and the nonstationary varible $\chi_{,t}$. It can be shown (see [123]) that in order to admit the free energy depending on $\boldsymbol{D}^p\chi, p \in \boldsymbol{N}$, the set of constitutive variables has to include $\boldsymbol{D}^{p-1}\chi_{,t}$. Since our goal is to construct models with free energy depending at most on $\boldsymbol{D}\chi$ we must admit $\chi_{,t}$ as a constitutive variable.

The kinetic constitutive variable $\chi_{,t}$ appears also in Fried-Gurtin's theory based on a microforce balance, see, e.g. [72], [83]. In this theory $\chi_{,t}$ is related to the working of internal microforces.

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

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

generates the variables $\boldsymbol{DF}$, $\boldsymbol{D}\chi$, $\boldsymbol{D}^2\chi$, $\boldsymbol{D}\theta$ in the state space Y_θ. However, for some generality and the clarity of further presentation we do not restrict ourselves to $M = 1$, $L = 1$, $K = 2$, but admit $M, L \geq 1$ and $K \geq 2$.

REMARK 2.2. The arbitrary choice of the state space Y_θ, Y_η, or Y_e results from the duality relations which will be presented in Chapter 3. We have found the choices of the spaces Y_η and Y_e more straightforward for the exploitation of the entropy inequality than the space Y_θ. Let us mention that in some particular situations the state space Y_e has been used in [124], Y_η in [125] and Y_θ in [9].

REMARK 2.3. From the point of view of the axiom of frame invariance the appropriate measure of the strain is for instance the right Cauchy-Green strain tensor $\boldsymbol{C}$ as a constitutive variable. However, as underlinded, e.g., in Gurtin [83], the exploitation of the second law of thermodynamics is simpler using the deformation gradient $\boldsymbol{F}$ as the constitutive variable. The restrictions imposed by the frame invariance are then accounted for after deriving consequences from the second law.

2.4. The Clausius-Duhem inequality and the Coleman-Noll procedure. The *Clausius-Duhem inequality* is commonly used formulation of the second law of thermodynamics of continua. According to rational thermodynamics interpretation the second law is the requirement that the entropy production in any thermodynamic process must be nonnegative. The requirement that a particular material satisfies the second law imposes restrictions on the admissible constitutive relations. Within the field of rational thermodynamics approaches of various degree of complexity have been developed to fulfill the second law. Among them one finds the classical irreversible thermodynamics (cf. [45]), the Coleman-Noll approach to the Clausius-Duhem inequality (cf., e.g., [40], [82], [133]), and the Müller-Liu approach which will be discussed in the next sections. For review articles covering all these approaches we refer to Hutter [88], Muschik et al. [117], [118], Papenfuss and Forest [121].

The commonly known local form of the Clausius-Duhem inequality in the material description has the form (see Silhavý [133, Chap. 3.7])

$$\varrho_0\dot{\eta} + \nabla \cdot \frac{\boldsymbol{q}}{\theta} \geq \varrho_0\frac{g}{\theta}, \tag{4.1}$$

where it is postulated that there exist the absolute temperature $\theta > 0$ and the specific entropy given by a constitutive equation $\eta = \hat{\eta}(Y)$ with some state space Y, and that the referential entropy flux, $\boldsymbol{q}/\theta$, is determined as a quotient of the referential heat flux vector $\boldsymbol{q}$ and the absolute temperature θ.

The systematic procedure of exploiting the Clausius-Duhem inequality has been devised by B. D. Coleman and W. Noll [40] and is widely known as the Coleman-Noll procedure.

In case of a viscoelastic body with heat conduction, governed by the system of balance laws (2.1), the Coleman-Noll approach to inequality (4.1) relies on assuming the state space

$$Y := \{\boldsymbol{F}, \theta, \boldsymbol{D}\theta, \boldsymbol{F}_{,t}\}, \tag{4.2}$$

where $\boldsymbol{F}$, θ, $\boldsymbol{D}\theta$, $\boldsymbol{F}_{,t}$ represent variables corresponding to $\boldsymbol{F}$, θ, $\nabla\theta$, $\dot{\boldsymbol{F}}$, evaluated at a point $(\boldsymbol{X}, t)$, The important assumption in the Coleman-Noll approach is that the body force $\boldsymbol{b}$ and the external supply of heat g can be chosen arbitrarily so that to admit any deformation-temperature path $(\boldsymbol{y}, \theta)$ as a solution of system (2.1) with constitutive equations

$$\boldsymbol{S} = \hat{\boldsymbol{S}}(Y), \quad \boldsymbol{q} = \hat{\boldsymbol{q}}(Y), \quad e = \hat{e}(Y), \quad \eta = \hat{\eta}(Y), \tag{4.3}$$

where the state space is given by (4.2).
The pair $(\boldsymbol{y}, \theta)$ is then called an *admissible thermodynamic process.* The form of constitutive equations (4.3), (4.2) is determined by the requirement that system (2.1) must satisfy the Clausius-Duhem inequality (4.1).

Since the state space (4.2) uses the absolute temperature as the independent thermal variable, it is common to restate the Clausius-Duhem inequality (4.1) to the form of the dissipation inequality

$$\varrho_0 \dot{f} - \boldsymbol{S} \cdot \dot{\boldsymbol{F}} + \varrho_0 \eta \dot{\theta} + \frac{1}{\theta} \boldsymbol{q} \cdot \nabla\theta \leq 0 \tag{4.4}$$

as it contains the time derivative of θ, where $f = e - \theta\eta$ is the free energy. We refer to Šilhavý [133, Proposition 9.2.2], for the proof of consequences of the Clausius-Duhem inequality on constitutive relations (4.3), (4.2).

2.5. The Müller entropy principle and the multipliers method of its exploitation. The entropy principle due to I. Müller [115], [116] complemented by the multipliers method proposed by I-Shih Liu [96], [97], [98] is considered as an important alternative to the Coleman-Noll approach to the Clausius-Duhem inequality. The Müller-Liu approach has the same purpose as the Coleman-Noll procedure, namely to find restrictions on the constitutive relations. It is, however, much less restrictive, thus designated for more general classes of materials. In particular, it does not postulate a priori the structure of the entropy flux as $\boldsymbol{q}/\theta$ (see (4.1)), and is formulated for supply-free processes. In the present work we shall apply the Müller-Liu approach combined with the duality method to system (2.6), (2.7) with the purpose to find restrictions on the constitutive relations (2.7) and this way to select a class of thermodynamically consistent models.

We formulate the local version of the entropy principle due to I. Müller, specified to system (2.6) in material form, with the constitutive relations (2.7).

The Müller entropy principle states that there exist a specific entropy η and a referential entropy flux $\boldsymbol{\Psi}$, given by the constitutive relations

$$\eta = \hat{\eta}(Y), \quad \boldsymbol{\Psi} = \hat{\boldsymbol{\Psi}}(Y), \tag{5.1}$$

with smooth functions $\hat{\eta}$, $\hat{\boldsymbol{\Psi}}$, depending on the same set Y as $\hat{\boldsymbol{S}}$, $\hat{\boldsymbol{j}}$, $\hat{r}$, $\hat{e}$, $\hat{\boldsymbol{q}}$, such that for all solutions of the system of balance laws (2.6) with constitutive equations (2.7) (called thermodynamic processes) defined in a space-time domain $\Omega^{t_0} = \Omega \times (0, t_0)$, $t_0 > 0$, the following implication holds:

$$\boldsymbol{b} = \boldsymbol{0}, \quad \tau = 0, \quad g = 0 \quad \text{in} \quad \Omega^{t_0} \Rightarrow \varrho_0 \sigma := \varrho_0 \dot{\eta} + \nabla \cdot \boldsymbol{\Psi} \geq 0 \quad \text{in} \quad \Omega^{t_0}, \tag{5.2}$$

where the scalar σ denotes the *specific entropy production*. In other words, for supply-free thermodynamic processes the local entropy production has to be nonnegative. We point out that in the above formulation the entropy flux is a constitutive quantity and all external sources are omitted.

For further discussion in Section 2.6 of a rigorous exploitation of the Müller entropy principle by means of the Lagrange multipliers method due to I-Shih Liu [96], we recall two stronger versions of the implication (5.2) which have been firstly formulated in [10]. In a slightly stronger version (5.2) may be replaced by the following postulate:

For all thermodynamic processes and all points $(\boldsymbol{X}, t) \in \Omega^{t_0}$, it holds

$$\boldsymbol{b}(\boldsymbol{X}, t) = \boldsymbol{0}, \ \tau(\boldsymbol{X}, t) = 0, \ g(\boldsymbol{X}, t) = 0 \Rightarrow \varrho_0(\boldsymbol{X}) \sigma(\boldsymbol{X}, t) \geq 0, \tag{5.3}$$

where $\varrho_0(\boldsymbol{X}) > 0$ (see (2.5)).

One may formulate even stronger version of (5.2) as follows.

There exists a scalar field σ_0 with a constitutive equation $\sigma_0 = \hat{\sigma}_0(Y, \boldsymbol{b}, \tau, g)$, such that for all thermodynamic processes defined in Ω^{t_0} the following two conditions are satisfied

$$\sigma \geq \sigma_0 \quad \text{in} \quad \Omega^{t_0} \quad \text{and} \quad \hat{\sigma}_0(Y, \boldsymbol{0}, 0, 0) = 0 \quad \text{for all variables } Y. \tag{5.4}$$

The latter version of the entropy principle describes the way it is used in the Coleman-Noll procedure where, however, on the contrary to (5.4), it is assumed that the entropy flux $\boldsymbol{\Psi}$ and the quantity σ_0 are given by the explicit formulas.

We notice, that obviously, the strongest version (5.4) implies the two weaker ones, that is

$$(5.4) \Rightarrow (5.3) \Rightarrow (5.2).$$

2.6. The Müller-Liu entropy inequality. The main step in the exploitation of the entropy principle is based on introducing multipliers corresponding to the balance equations with the purpose of replacing the inequality in (5.2), which is required to hold only for thermodynamic processes, by an inequality that is satisfied for arbitrary fields. This idea is due to I-Shih Liu [96].

For system (2.6) the entropy inequality with multipliers, which we shortly call *the entropy inequality*, reads as follows: There are multipliers

$$\boldsymbol{\lambda}_{\boldsymbol{u}} = \hat{\boldsymbol{\lambda}}_{\boldsymbol{u}}(Y) \in \mathbb{R}^3, \quad \lambda_\chi = \hat{\lambda}_\chi(Y) \in \mathbb{R}, \quad \lambda_e = \hat{\lambda}_e(Y) \in \mathbb{R}, \tag{6.1}$$

conjugated respectively with balance equations $(2.6)_{1,3,4}$ for the linear momentum, the phase variable and the internal energy, such that the inequality

$$\varrho_0 \dot{\eta} + \nabla \cdot \boldsymbol{\Psi} - \boldsymbol{\lambda}_{\boldsymbol{u}}(\varrho_0 \ddot{\boldsymbol{u}} - \nabla \cdot \boldsymbol{S}) - \lambda_\chi(\varrho_0 \dot{e} + \nabla \cdot \boldsymbol{q} - \boldsymbol{S} \cdot \dot{\boldsymbol{F}}) \geq 0 \tag{6.2}$$

is satisfied for all fields of independent variables $\boldsymbol{u}$, χ, θ.

The quantities $\boldsymbol{\lambda}_u$, λ_χ, λ_e are usually called *the Lagrange multipliers* because the replacement of the inequality in (5.2) by (6.2) is a reminiscent of the manner the Lagrange multipliers are used in the analysis of extremal problems with constraints.

After inserting the constitutive equations and performing differentiation the inequality (6.2) becomes an algebraic condition on the constitutive functions. We shall refer to such condition as *the algebraic entropy inequality.* Therefore, after establishing the entropy inequality (6.2) the exploitation of the entropy principle reduces to algebraic considerations.

It is of interest to notice that the entropy inequality (6.2) implies the entropy principle with the strongest property (5.4). More precisely, it follows from (6.2) that for all thermodynamic processes (i.e., solutions of system (2.6) with constitutive relations (2.7)) it holds

$$\begin{aligned} \varrho_0 \sigma = \varrho_0 \dot{\eta} + \nabla \cdot \boldsymbol{\Psi} &\geq \varrho_0 [\hat{\boldsymbol{\lambda}}_u(Y) \cdot \boldsymbol{b} + \hat{\lambda}_\chi(Y)\tau + \hat{\lambda}_e(Y) g] \\ &=: \varrho_0 \hat{\sigma}_0(Y, \boldsymbol{b}, \tau, g) \end{aligned} \tag{6.3}$$

with $\hat{\sigma}_0(Y, \mathbf{0}, 0, 0) = 0$.
This means that whenever the entropy inequality (6.2) holds then all three presented versions of the entropy principle are satisfied.

REMARK 2.4. In a rigorous Müller-Liu approach (cf. [96], [97]) one has to prove that the entropy principle in the weakest version (5.2) implies the entropy inequality (6.2). The proof requires a characterization of local solutions to the system of partial differential equations under consideration and the verification of the *Liu lemma* [96]. For some systems this hard problem has been addressed in [96] by employing the Cauchy-Kowalewskaya theorem.

The local solvability via the Cauchy-Kowalewskaya theorem has been also used in [10] in the study of phase-field models with a conserved order parameter. For more detailed discussion concerned with the treatment of supply-free processes we refer to [133, Chap. 9.5].

Since the rigorous derivation of the entropy inequality is in general a complicated mathematical task, in literature (see, e.g., [148], [149], [150], [90]) it is common, however, not always expressed explicitly, to take the validity of the entropy inequality for granted.

3. Basic thermodynamic relations

In this chapter we present basic thermodynamic relations, in particular the Legendre duality relations, for systems described by the gradient-type free energy $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$. Such relations-well known for classical systems with volumetric free energies – in case of gradient-type systems are not so common, see, e.g., [129], [10]. Since in the present work they play a crucial role in the rigorous derivation of the phase field models we present them in a detailed way.

We remark that analogous duality relations are also true for thermoelastic phase-field models governed by the free energy $f = \hat{f}(\boldsymbol{F}, \boldsymbol{DF}, \theta)$ involving first gradient of the deformation gradient $\boldsymbol{F}$ which plays the role of the order parameter.
For the corresponding theory related to modelling of shape memory alloys we refer to [125].

To avoid possible confusions throughout this chapter we shall carefully distinguish between functions and their values by using superimposed "$\wedge$" symbol in case of functions.

3.1. The inverse temperature and the rescaled free energy. Let

$$f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) \tag{1.1}$$

be a given gradient-type free energy.
Apart from the absolute temperature $\theta > 0$ we introduce the inverse temperature

$$\vartheta := \frac{1}{\theta} > 0. \tag{1.2}$$

Moreover, in addition to the free energy (1.1) we introduce the corresponding rescaled free energy, defined by

$$\hat{\phi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) := \vartheta \hat{f}\left(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \frac{1}{\vartheta}\right), \tag{1.2}$$

or equaivalently,

$$\hat{\phi}\left(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \frac{1}{\theta}\right) := \frac{1}{\theta}\hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta). \tag{1.3}$$

The rescaled free energy is commonly known as the *Massieu function* (see, e.g., Šilhavý [133], Chap. 10.2.2).

3.2. Thermodynamic relations with temperature and inverse temperature as independent variables. We present equivalent formulations of the basic thermodynamic Gibbs relations betwen gradient-type free energy, rescaled free energy, entropy and internal energy. In classical thermostatics such relations are expressed in the form (see, e.g., Wilmański [149], Appendix A)

$$f = e - \theta\eta, \quad \eta = -f_{,\theta}. \tag{2.1}$$

As common in the literature on phase-field models (see, e.g., [7], [20], [85], [129], [130], [133]) we postulate the validity of the classical relations (2.1) in case of gradient-type free energy (1.1).

LEMMA 3.1 (Equivalance of thermodynamic relations with temperature and inverse temperature). *Assume the thermodynamic relations with $\theta > 0$ as independent thermal variable:*

$$\begin{aligned} &\hat{e}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) - \hat{f}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) = \theta\eta,\\ &\eta = -\hat{f}_{,\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta). \end{aligned} \tag{2.2}$$

The relations (2.2) are equivalent to the following ones expressed in terms of $\vartheta = 1/\theta$ as independent variable:

$$\begin{aligned} &\hat{\phi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) + \hat{\bar{\eta}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) = \vartheta\bar{e},\\ &\bar{e} = \hat{\phi}_{,\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta), \end{aligned} \tag{2.3}$$

where $\vartheta = 1/\theta$ is the inverse temperature, and $\bar{e}$, $\bar{\eta}$ denote internal energy and entropy as functions of the inverse temperature:

$$\begin{aligned} &\bar{e} = \hat{\bar{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) := \hat{e}\left(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\frac{1}{\vartheta}\right),\\ &\bar{\eta} = \hat{\bar{\eta}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) := \hat{\eta}\left(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\frac{1}{\vartheta}\right) \quad \text{with} \quad \frac{1}{\vartheta} = \theta. \end{aligned} \tag{2.4}$$

Proof. "(2.2) $\Rightarrow$ (2.3)": Multiplying (2.2) by $\vartheta = 1/\theta$ gives

$$\vartheta\hat{f}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) + \hat{\eta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) = \vartheta\hat{e}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta),$$

which by definitions of ϕ, $\bar{e}$ and $\bar{\eta}$ proves $(2.3)_1$. Simultaneously, the equalities

$$\begin{aligned} \hat{\phi}_{,\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) &= \left(\vartheta\hat{f}\left(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\frac{1}{\vartheta}\right)\right)_{,\vartheta}\\ &= \hat{f}\left(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\frac{1}{\vartheta}\right) + \vartheta\hat{f}_{,\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)\cdot\left(-\frac{1}{\vartheta^2}\right)\\ &= \hat{f}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) - \theta\hat{f}_{,\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)\\ &= \hat{f}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) + \theta\hat{\eta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) && \text{(by } (2.2)_2)\\ &= \hat{e}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) && \text{(by } (2.2)_1)\\ &\hat{\bar{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) && \text{(by } (2.4)_1) \end{aligned}$$

prove that (2.2) implies $(2.3)_2$.

"(2.2) $\Leftarrow$ (2.3)": The relation $(2.2)_1$ results immediately from $(2.3)_1$ by definitions of ϑ, ϕ, $\bar{e}$, and $\bar{\eta}$. In turn the equalities

$$\begin{aligned}
\hat{f}_{,\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) &= \Big(\theta\hat{\phi}\Big(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\frac{1}{\theta}\Big)\Big)_{,\theta} \\
&= \hat{\phi}\Big(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\frac{1}{\theta}\Big) + \theta\hat{\phi}_{,\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta)\cdot\Big(-\frac{1}{\theta^2}\Big) \\
&= \hat{\phi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) - \vartheta\hat{\phi}_{,\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) \\
&= \hat{\phi}(\boldsymbol{F},\chi,\boldsymbol{D},\chi,\vartheta) - \vartheta\hat{\bar{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) && \text{(by } (2.3)_2) \\
&= -\hat{\bar{\eta}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) && \text{(by } (2.3_1)) \\
&= -\hat{\eta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) && \text{(by } (2.4)_2)
\end{aligned}$$

prove that (2.3) implies $(2.2)_2$. This completes the proof. ∎

3.3. The specific heat (heat capacity). According to the terminology of Şilhavý [133], Sect. 10.8, the specific heat (heat capacity) at constant deformation, associated with free energy (3.1) is defined by

$$c_{\boldsymbol{F}} = \hat{c}_{\boldsymbol{F}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) := \hat{e}_{,\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta). \tag{3.1}$$

On account of thermodynamic relations (2.2), $c_{\boldsymbol{F}}$ admits the following equivalent forms:

$$\begin{aligned}
c_{\boldsymbol{F}} = \hat{c}_{\boldsymbol{F}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) &= \hat{e}_{,\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) \\
&= (\hat{f}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) + \theta\hat{\eta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta))_{,\theta} && \text{(by } (2.2)_1) \\
&= \theta\hat{\eta}_{,\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) && \text{(by } (2.2)_2) \\
&= -\theta\hat{f}_{,\theta\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta). && \text{(by } (2.2)_2)
\end{aligned} \tag{3.2}$$

Further, let us dentoe

$$\bar{c}_{\boldsymbol{F}} = \hat{\bar{c}}_{\boldsymbol{F}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) := \hat{c}_{\boldsymbol{F}}\Big(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\frac{1}{\vartheta}\Big) \tag{3.3}$$

the specific heat expressed as a functions of the inverse temperature. With the use of thermodynamic relations (2.3) $\bar{c}_{\boldsymbol{F}}$ admits the following equaivalent forms:

$$\begin{aligned}
\bar{c}_{\boldsymbol{F}} = \hat{\bar{c}}_{\boldsymbol{F}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) &= \hat{c}_{\boldsymbol{F}}\Big(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\frac{1}{\vartheta}\Big) \\
&= \hat{e}_{,\theta}\Big(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\frac{1}{\vartheta}\Big) && \text{(by } (3.1)) \\
&= -\vartheta^2\hat{\bar{e}}_{,\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) && \text{(by } (2.4)_1) \\
&= -\vartheta^2\hat{\phi}_{,\vartheta\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) && \text{(by } (2.3_2) \\
&= -\vartheta(\vartheta\hat{\bar{e}}_{,\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta)) \\
&= -\vartheta(\hat{\phi}_{,\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) + \hat{\bar{\eta}}_{,\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) - \hat{\bar{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta)) && \text{(by } (2.3)_1) \\
&= -\vartheta\hat{\bar{\eta}}_{,\vartheta}(]\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) && \text{(by } (2.3_2)).
\end{aligned} \tag{3.4}$$

3.4. Thermal stability. As common in thermodynamics, we shall postulate that the specific heat is stricty positive

$$c_{\boldsymbol{F}} = \hat{c}_{\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) > 0 \quad \text{forallarguments } (\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta). \tag{4.1}$$

Such postulate is known as *thermal stability*, see e.g. Woods [151], Chap. 2.7, 2.10. It implies in particular the validity of the partial Legendre transformations which allow to use alternatively the absolute temperature $\theta > 0$, the entropy η or the internal energy e as independent thermal variables. Assuming (4.1) we derive in Section 3.6 the relations corresponding to the passages from θ to η and from $\vartheta = 1/\theta$ to e.

The lemma below provides the equivalent statements of the thermal stability condition (4.1).

LEMMA 3.2 (Thermal stability). *Assume that thermodynamic relations (2.2) (equivalently (2.3)) haold true, and $\theta > 0$. Then the following statements are equivalent:*

(i) $\hat{c}_{\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) > 0$,
(ii) $\hat{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ *is strictly increasing in* θ,
(iii) $\hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ *is strictly increasing in* θ,
(iv) $\hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ *is strictly concave in* θ,
(v) $\hat{\hat{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)$ *is strictly decreasing in* ϑ,
(vi) $\hat{\hat{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)$ *is strictly decreasing in* ϑ,
(vii) $\phi(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)$ *is strictly concave in* ϑ.

Proof. The equivalances between (i), (ii), (iii) and (iv) are direct consequences of the equalities $(3.2)_1$, $(3.2)_3$, $(3.2)_4$, and the fact that $\theta > 0$.
In turn, the equivalances between (i), (v), (vi) and (vii) follow from the euqalities $(3.3)_3$, $(3.3)_7$, $(3.3)_4$, and the fact that $\vartheta = 1/\theta > 0$. ■

3.5. Duality relations. Let us consider the free energy $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$, and assume thermal stability conditions(4.1), that is strict concavity of $\hat{f}$ with respect to θ. Under such conditon we derive the partial Legendre transform relations, referred to as the *duality relations*.

We remark that in modelling of phase transitions the Legendre transformations have been used by Donnelly [47] in case of volumetric (not involving gradients) thermodynamic potentials, and by Penrose-Fife [129] in case of volumetric internal energy and gradient-type entropy.

It follows from Lemma 3.2 (iv), (vii) that under thermal stability condition (4.1) the function

$$\theta \mapsto -\hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) \quad \text{isstrictlyconvex}, \tag{5.1}$$

and the function

$$\vartheta \mapsto \hat{\phi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) \quad \text{isstrictlyconcave}. \tag{5.2}$$

Therefore, the following conjugate functions are well-defined:

- the conjugate convex function

$$\infty\hat{\hat{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta) := \sup_{0<\bar{\theta}<+\infty} \{\bar{\theta}\eta + \hat{f}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{\theta})\} \le +\infty \tag{5.3}$$

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

$$\hat{\hat{\eta}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e}) := \inf_{9<\bar{\vartheta}<+\infty} \{\bar{\vartheta}\bar{e} - \hat{\phi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{\theta})\} \ge -\infty, \tag{5.4}$$

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

We underline that the distinction in the notation $\bar{e}$ and e, is meaningless if the internal energy is treated as a variable, not as a function. We write $\bar{e}$ to indicate the connection with thermodynamic relations (2.3).

LEMMA 3.3 (Duality relations). *Assume thermodynamic relations (2.2), (2.3) and thermal stability condition* $c_{\boldsymbol{F}} = c_{\boldsymbol{F}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) > 0$. *Let the conjugate functions* $\hat{\hat{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta)$ *and* $\hat{\hat{\eta}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e})$ *be defined by (5.3) and (5.4). Then:*

(i) *The unique supremum in (5.3) is attained at*

$$\theta = \hat{\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta) \tag{5.5}$$

and is characterized by the following relations

$$\begin{aligned} &\hat{\hat{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta) - \hat{f}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) = \theta\eta, \\ &\hat{\hat{e}}_{,\eta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta) = \theta. \end{aligned} \tag{5.6}$$

(ii) *The unique infimum in (5.4) is attained at*

$$\vartheta = \hat{\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e}), \tag{5.7}$$

and is characterized by the relations

$$\begin{aligned} &\hat{\hat{\eta}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e}) + \hat{\phi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta) = \vartheta\bar{e}, \\ &\hat{\hat{\eta}}_{,\bar{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e}) = \vartheta. \end{aligned} \tag{5.8}$$

Proof. (i) By Lemma 3.2 (iii), the map $\theta \mapsto \hat{\eta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)$ is strictly increasing. Therefore, there exists the inverse map

$$\eta \mapsto \hat{\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta), \tag{5.9}$$

and the property $0 < \theta < +\infty$ is equivalent to $\eta_* < \eta < \eta^*$ with $\eta_* = \hat{\eta}_*(\boldsymbol{F},\chi,\boldsymbol{D}\chi) \ge -\infty$ and $\eta^* = \hat{\eta}^*(\boldsymbol{F},\chi,\boldsymbol{D}\chi) \le +\infty$. If $\eta_* < \eta < \eta^*$ then the supremum in (5.3) is uniquely attained at $\theta = \hat{\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta)$, and then

$$\hat{\hat{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta) = \theta\eta + \hat{f}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta). \tag{5.10}$$

This proves (5.5) and $(5.6)_1$. To get $(5.6)_2$ let us nde that the supremum in (5.3) implies the condition

$$\eta = -f_{,\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta). \tag{5.11}$$

Hence, from $(5.6)_1$ and (5.9), (5.11) it follows that

$$\hat{\hat{e}}_{,\eta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta)+\eta\hat{\theta}_{,\eta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta)=\theta+\eta\hat{\theta}_{,\eta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta),$$

which actually proves $(5.6)_2$.
(ii) By Lemma 3.2 (v), the map $\vartheta\mapsto\hat{e}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta)$ is strictly decreasing. Therefore there exists the inverse map

$$\bar{e}\mapsto\hat{\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e}), \tag{5.12}$$

and the property $9<\vartheta<+\infty$ is equivalent to $e_*<\bar{e}<e^*$ with $e_*=\hat{e}_*(\boldsymbol{F},\chi,\boldsymbol{D}\chi)\geq-\infty$ and $e^*=\hat{e}^*(\boldsymbol{F},\chi,\boldsymbol{D}\chi)\leq+\infty$. If $e_*<\bar{e}<e^*$ then the infimum in (5.4) is uniquely attained at $\vartheta=\hat{\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e})$, and then

$$\hat{\hat{\eta}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e})=\vartheta\bar{e}-\hat{\phi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta). \tag{5.13}$$

This proves (5.7) and $(5.8)_1$. To conclude $(5.8)_2$ we note that the infimum in (5.4) is characterized by

$$\bar{e}=\hat{\phi}_{,\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta). \tag{5.14}$$

Hence, $(5.8)_1$ and (5.12), (5.14) imply that

$$\hat{\hat{\eta}}_{,\bar{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e})+\bar{e}\hat{\vartheta}_{,\bar{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e})=\vartheta+\bar{e}\hat{\vartheta}_{,\bar{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e}).$$

This provides $(5.78)_2$ and thereby completes the proof. ∎

We shall refer to (5.6) and (5.8) as the *duality relations* expressed respectively in terms of entropy and energy as independent variables.

Our goal now is to prove that under thermal stability condition (4.1) all forms of thermodynamical relations (2.2), (2.3), (5.6) and (5.8) are equivalent. Moreover, we shall show that the convex function $\hat{\hat{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta)$ represents in fact the internal energy expressed as a function of entropy η, and that the concave function $\hat{\hat{\eta}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e})$ represents the entropy expressed as a function of the internal energy $\bar{e}$.

LEMMA 3.4 (Equivalance between primary and dual relations). *Assume thermal stability condition $c_{\boldsymbol{F}}=\hat{c}_{\boldsymbol{F}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)>0$. Then:*

(i) *The dual relation (5.6), i.e.,*

$$\begin{aligned}&\hat{\hat{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta)-\hat{f}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)=\theta\eta,\\&\hat{\hat{e}}_{,\eta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta)=\theta\end{aligned}$$

are equivalent to the primary ones (2.2), i.e.,

$$\begin{aligned}&\hat{e}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)-\hat{f}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)=\theta\eta,\\&-\hat{f}_{,\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)=\eta\end{aligned}$$

with

$$\hat{e}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)\equiv\hat{\hat{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\hat{\eta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)). \tag{5.15}$$

(ii) *The dual relations (5.8), i.e.,*

$$\begin{aligned}&\hat{\hat{\eta}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e})+\hat{\phi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta)=\vartheta\bar{e},\\&\hat{\hat{\eta}}_{,\bar{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e})=\vartheta\end{aligned}$$

are equivalent to the primary ones (2.3), i.e.,

$$\hat{\phi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) + \tilde{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) = \vartheta \bar{e},$$
$$\hat{\phi}_{,\vartheta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) = \bar{e}$$

with

$$\tilde{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) \equiv \hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \hat{\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)). \tag{5.16}$$

Moreover, the identities (5.15), (5.16) indicate that the conjugate convex function $\tilde{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$, defined by (5.3), is the internal energy expressed as a function of the entropy η, whereas the conjugate concave function $\hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})$, defined by (5.4), is the entropy exprssed as a function of the internal energy $\bar{e}$.

Proof. The implications (2.2) $\Rightarrow$ (5.6) and (2.3) $\rightarrow$ (5.8) result from Lemma 3.3 conversely, to prove the implication (5.6) $\Rightarrow$ (2.2) let us note that setting $\eta = \hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ into $(5.6)_1$ we get

$$\hat{\tilde{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)) - \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) = \theta \hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta). \tag{5.17}$$

this provides relation $(2.2)_1$ with

$$\hat{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) \equiv \hat{\tilde{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)),$$

and simulttaneously demonstrates that $\tilde{e}$ is the internal energy expressed as a function of the entropy η. Futher, differentiating the equality (5.17) with respect to θ gives

$$\begin{aligned} &\hat{\tilde{e}}_{,\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)\hat{\eta}_{,\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) - \hat{f}_{,\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) \\ &= \hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) + \theta \hat{\eta}_{,\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta). \end{aligned} \tag{5.18}$$

Hence, on account of $(5.6)_2$, it follows that

$$\hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) = -\hat{f}_{,\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta), \tag{5.19}$$

which is just relation $(2.2)_2$. Hence, the implication (5.6) $\Rightarrow$ (2.2) is proved.

Similarly, to check the implication (5.8) $\Rightarrow$ (2.3) notice that setting $\bar{e} = \hat{\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)$ in $(5.8)_1$ leads to

$$\hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \hat{\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)) + \hat{\phi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) = \vartheta \hat{\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta). \tag{5.20}$$

This yields relatoin $(2.3)_1$ with

$$\tilde{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) \equiv \hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \hat{\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)),$$

and simultaneously indicates that $\tilde{\eta}$ is the entropy expressed as a function of the internal energy $\bar{e}$. Further, differentiating the equality (5.20) with respect to ϑ gives

$$\hat{\tilde{\eta}}_{,\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})\hat{\bar{e}}_{,\vartheta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) + \hat{\phi}_{,\vartheta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta). \tag{5.30}$$

hence, in view of $(5.8)_2$ it follows that

$$\hat{\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) = \hat{\phi}_{,\vartheta}(\boldsymbol{D}, \chi, \boldsymbol{D}\chi, \vartheta). \tag{5.31}$$

which proves the relation $(2.3)_2$ and thereby the implication (5.8) $\rightarrow$ (2.3). The proof is now completed. ■

COROLLARY 3.5 (Equivalance of thermodynamic relations). *Lemma 3.1 assures the equivalence of thermodynamic relations (2.2) and (2.3). Combining this facrt with Lemma 3.4* *we conclude that under thermal stability condition all thermodynamic relations, the primary (2.2), (2.3) and the dual (5.6), (5.8), are equivalent.*

3.6. Change of independent thermal variables. The duality relations (5.6) and (5.8) allow for changes of independent thermal variables from θ to η and from $\vartheta = 1/\theta$ to $\bar{e} = e$. We remind that the distinction in the notation $\bar{e}$ and e is meaningless if the internal energy is tieated as a variable.

As it will be proved in Chapters 4 and 5, the constitutive relations in phase-field models with free energy $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ include the first variations

$$\frac{\delta f}{\delta \chi} = f_{,\chi} - \nabla \cdot f_{,\boldsymbol{D}\chi} \quad \text{and}$$
$$\frac{\delta \phi}{\delta \chi} = \phi_{,\chi} - \nabla \cdot \phi_{,\boldsymbol{D}\chi}.$$

These relations, among the others, involve the first order space derivatives $\boldsymbol{D}\theta$ or $\boldsymbol{D}\vartheta$. Therefore, in case of change of independent variable from θ to η one has to insert into all consitutive relations the equation

$$\theta = \hat{\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) \tag{6.1}$$

together with the corresponding first order space derivatives

$$\begin{aligned} \theta_{,i}\hat{\theta}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) \cdot F_{,i} + \hat{\theta}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)\chi_{,i} + \hat{\theta}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) \cdot \boldsymbol{D}\chi \\ + \hat{\theta}_{,\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)\eta_{,i}, \quad i = 1, 2, 3. \end{aligned} \tag{6.2}$$

Let us notice that due to the invertitility of the map $\eta \mapsto \hat{\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$ the equality (6.2) is equivalent to

$$\begin{aligned} \eta_{,i} = \hat{\eta}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) \cdot \boldsymbol{F}_{,i} + \hat{\eta}_{,\chi}(\boldsymbol{F}\chi, \boldsymbol{D}\chi, \theta)\chi_{,i} + \hat{\eta}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) \cdot \boldsymbol{D}\chi_{,i} \\ + \hat{\eta}_{,\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)\theta_{,i}. \end{aligned} \tag{6.3}$$

Similarly, choosing $\bar{e} = e$ as the independent variable one has to insert into the constitutive relations the equation

$$\vartheta = \hat{\vartheta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) \tag{6.4}$$

together with the corresponding first order space derivatives

$$\begin{aligned} \vartheta_{,i} = \hat{\vartheta}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) \cdot \boldsymbol{F}_{,i} + \hat{\vartheta}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})\chi_{,i} + \hat{\vartheta}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) \cdot \boldsymbol{D}\chi_{,i} \\ + \hat{\vartheta}_{,\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})\bar{e}_{,i}. \end{aligned} \tag{6.5}$$

In view of the invertibility of the map $\bar{e} \mapsto \hat{\vartheta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})$ the latter expression is equivalent to

$$\begin{aligned} \bar{e}_{,i} = \hat{\bar{e}}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) \cdot \boldsymbol{F}_{,i} + \hat{\bar{e}}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)\chi_{,i} + \hat{\bar{e}}_{\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) \cdot \boldsymbol{D}\chi_{,i} \\ + \hat{\bar{e}}_{,\vartheta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)\vartheta_{,i}. \end{aligned} \tag{6.6}$$

It os of interest to notice some important implications of the transformations (6.1), (6.2) and (6.4), (6.5).

If the entropy

$$\eta = \hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) = -\hat{f}_{,\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$$

does not depent on $\boldsymbol{D}\chi$, i.e., $\eta_{,\boldsymbol{D}\chi} = -f_{,\theta\boldsymbol{D}\chi} = \mathbf{0}$, then the transformation between η and θ doew not involve $\boldsymbol{D}\chi$, and the transformation between $\boldsymbol{D}\eta$ and $\boldsymbol{D}\theta$ does not involve second space derivaives $\boldsymbol{D}^2\chi$.

In subsequent chapters we shall refer to such gradient-type *free energy* f as being of *energetic type*, since then

$$f_{,\boldsymbol{D}\chi} = e_{,\boldsymbol{D}\chi} - \theta\eta_{,\boldsymbol{D}\chi} = e_{,\boldsymbol{D}\chi}, \tag{6.7}$$

that is the gradient $\boldsymbol{D}\chi$ contained in f fully contributes to the energy $e = \hat{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$.

Similarly, if the internal energy

$$\bar{e} = \hat{\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) = \hat{\phi}_{,\vartheta}(\boldsymbol{F}, \chi, D\chi, \vartheta)$$

does not depend on $\boldsymbol{D}\chi$, i.e., $\bar{e}_{,\boldsymbol{D}\chi} = \phi_{,\vartheta\boldsymbol{D}\chi} = \mathbf{0}$, then the transformation between $\bar{e}$ and ϑ does not involve $\boldsymbol{D}\chi$, and the transformation between $\boldsymbol{D}\bar{e}$ and $\boldsymbol{D}\vartheta$ does not involve $\boldsymbol{d}^2\chi$. We shall refer to such gradient-type free energy $\phi = f/\theta$ as being of *entropic type*, since then

$$\bar{\eta}_{,\boldsymbol{D}\chi} = \vartheta\bar{e}_{,\boldsymbol{D}\chi} - \phi_{,\boldsymbol{D}\chi} = -\phi_{,\boldsymbol{D}\chi}, \tag{6.8}$$

that is the gradient term contained in $\phi = f/\theta$ fully contributes to the entropy $\bar{\eta} = \hat{\bar{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)$.

3.7. Dual forms of the specific heat. For further use we collect the expressions of the specific heat $c_{\boldsymbol{F}}$ in terms of entropy and internal energy as independent variables.

LEMMA 3.6 (Dual forms of the specific heat). *Assume tharmodynamic relation (2.2), (2.3) and the thermal stability condition* $c_{\boldsymbol{F}} = \hat{c}_{\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) > 0$. *Then the specific heat* $c_{\boldsymbol{F}}$ *admits the following forms:*

(i) *in terms of the independent variable* η

$$\begin{aligned}\check{c}_{\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) &:= \hat{c}_{\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)\big|_{\theta=\hat{\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta)} \\ &= -\theta\hat{f}_{,\theta\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)\big|_{\theta=\hat{\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta)} \\ &= \hat{\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)\frac{1}{\hat{\hat{e}}_{,\eta\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)},\end{aligned} \tag{7.1}$$

(ii) *in terms of the independent variable* $\bar{e} = e$

$$\begin{aligned}\hat{\bar{c}}_{\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) &:= \hat{\bar{c}}_{\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)\big|_{\vartheta=\hat{\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e})} \\ &= -\vartheta^2\phi_{,\vartheta\vartheta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)\big|_{\vartheta=\bar{\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e})} \\ &= -\hat{\vartheta}^2(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})\frac{1}{\hat{\hat{\bar{\eta}}}_{,\bar{e}\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})}.\end{aligned} \tag{7.2}$$

Proof. (i) In view of euqalines in (3.2), taking into account the strict monotonicity of the map $\theta \mapsto \hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ and the dual relation $(5.6)_2$ we infer that

$$
\begin{aligned}
&\hat{c}_{\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)\big|_{\theta=\hat{\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta)} \\
&= -\theta \hat{f}_{,\theta\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)\big|_{\theta=\hat{\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta)} && \text{(by } (3.2)_4) \\
&= \theta \hat{\eta}_{,\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)\big|_{\theta=\hat{\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta)} && \text{(by } (3.2)_3) \\
&= \hat{\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) \frac{1}{\hat{\theta}_{,\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)} && \text{(bythemonotonicityof } \hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) \text{ in } \theta) \\
&= \hat{\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) \frac{1}{\hat{\hat{e}}_{,\eta\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)} && \text{(by } (5.6)_2),
\end{aligned}
$$

which proves (7.1).

(ii) Similarly, by equalities in (3.3), the strict monotonicity of the map $\vartheta \mapsto \hat{\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)$, and the dual relation $(5.8)_2$, we have

$$
\begin{aligned}
&\hat{\bar{c}}_{\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)\big|_{\vartheta=\hat{\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e})} \\
&= -\vartheta^2 \phi_{,\vartheta\vartheta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)\big|_{\vartheta=\hat{\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e})} && \text{(by } (3.3)_4) \\
&= -\vartheta^2 \hat{\bar{e}}_{,\vartheta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)\big|_{\vartheta=\hat{\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e})} && \text{(by } (3.3)_3) \\
&= -\hat{\vartheta}^2(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) \frac{1}{\hat{\vartheta}_{,\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})} && \text{(bythemonotonicityof } \hat{\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) \text{ in } \vartheta) \\
&= -\hat{\vartheta}^2(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) \frac{1}{\hat{\hat{\eta}}_{,\bar{e}\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})} && \text{(by } (5.8)_2).
\end{aligned}
$$

This demonstrates (7.2) and thereby completes the proof. ∎

COROLLARY 3.7. *In view of the dual forms of the specific heat in (7.1) and (7.2), the thermal stability statements (i)–(vii) in Lemma 3.2 are equivalent to the following ones:*

(viii) $\hat{\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$ *is strictly increasing in* η,
(ix) $\hat{\hat{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$ *is strictly convex in* η,
(x) $\hat{\vartheta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})$ *is strictly decreasing in* $\bar{e}$,
(xi) $\hat{\hat{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})$ *is strictly concave in* $\bar{e}$.

3.8. Relations between derivatives of thermodynamic potentials with respect to parameters. In changing thermodynamic variables one needs formulas relating derivatives of the thermodynamic potentials $\hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$, $\hat{\phi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)$, $\hat{\hat{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$, $\hat{\hat{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})$ with respect to the parameters $\boldsymbol{F}, \chi, \boldsymbol{D}\chi$. In particular, one needs formulas linking the first variations of the above gradient-type potentials with respect to χ. We have

LEMMA 3.8 (Derivatives of thermodynamic potentials with respect to parameters). *Assume thermodynamic relations (2.2), (2.3) and the thermal stability conditions* $c_{\boldsymbol{F}} = \hat{c}_{\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) > 0$. *Then the following relations are satisfied*

$$
\begin{aligned}
&\hat{f}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) = \hat{\hat{e}}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta),\\
&\hat{f}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) = \hat{\hat{e}}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta),\\
&\hat{f}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) = \tilde{e}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta),\\
&\frac{\delta \hat{f}}{\delta \chi}(\boldsymbol{F}, \boldsymbol{D}\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta, \boldsymbol{D}\theta) = \frac{\delta \hat{\hat{e}}}{\delta \chi}(\boldsymbol{F}\boldsymbol{D}\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \eta, \boldsymbol{D}\eta),
\end{aligned}
\tag{8.1}
$$

and

$$
\begin{aligned}
&\hat{\phi}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) = -\hat{\bar{\eta}}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}),\\
&\hat{\phi}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) = -\hat{\bar{\eta}}_{,\chi}(\boldsymbol{F}, \chi, chi, \bar{e}),\\
&\hat{\phi}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) = -\hat{\bar{\eta}}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}),\\
&\frac{\delta \hat{\phi}}{\delta \chi}(\boldsymbol{F}, \boldsymbol{D}\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \vartheta, \boldsymbol{D}\vartheta) = -\frac{\delta \hat{\bar{\eta}}}{\delta \chi}(\boldsymbol{F}, \boldsymbol{D}\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \bar{e}, \boldsymbol{D}\bar{e}),
\end{aligned}
\tag{8.2}
$$

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

$$
\begin{aligned}
\eta &= \hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta),\\
\eta_{,i} &= \hat{\eta}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) \cdot \boldsymbol{F}_{,i} + \hat{\eta}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)\chi_{,i}\\
&\quad + \hat{\eta}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) \cdot \boldsymbol{D}\chi_{,i} + \hat{\eta}_{,\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)\theta_{,i},
\end{aligned}
\tag{8.3}
$$

while $\bar{e}$, $\boldsymbol{D}\bar{e}$ *and* ϑ, $\boldsymbol{D}\vartheta$ *by*

$$
\begin{aligned}
\bar{e} &= \hat{\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta),\\
\bar{e}_{,i} &= \hat{\bar{e}}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) \cdot \boldsymbol{F}_{,i} + \hat{\bar{e}}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)\chi_{,i}\\
&\quad + \hat{\bar{e}}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) \cdot \boldsymbol{D}\chi_{,i} + \hat{\bar{e}}_{,\vartheta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)\vartheta_{,i}.
\end{aligned}
\tag{8.4}
$$

Proof. By Lemma 3.3 the duality relations (5.6) and (5.8) hold true. From $(5.6)_1$ it follows that

$$
\hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) - \theta\hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) + \hat{\hat{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)).
$$

Hence, using $(5.6)_2$, we deduce the relations

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

where $\eta = \hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$. This proves equalities $(8.1)_{1-3}$. Further, by the definition of the first variation we deduce from $(8.1)_{2,3}$ that

$$\frac{\delta \hat{f}}{\delta \chi}(\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta, \boldsymbol{D}\theta) = \hat{f}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) + \nabla \cdot \hat{f}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$$

$$= \hat{\hat{e}}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) + \nabla \cdot \hat{\hat{e}}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$$

$$= \frac{\delta \hat{\hat{e}}}{\delta \chi}(\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \eta, \boldsymbol{D}\eta),$$

where η, $\boldsymbol{D}\eta$ and θ, $\boldsymbol{D}\theta$ are related by (8.3). This proves the equality $(8.1)_4$.

Similarly, from the duality relation $(5.8)_1$ it follows that

$$\hat{\phi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) = \vartheta \hat{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) - \hat{\hat{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \hat{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)).$$

Hence, by $(5.8)_2$ we have

$$\begin{aligned}
\hat{\phi}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) &= \vartheta \hat{\hat{e}}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) - \hat{\hat{\eta}}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) \\
&\quad - \hat{\hat{\eta}}_{,\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) \hat{\hat{e}}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) = -\hat{\hat{\eta}}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}), \\
\hat{\phi}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) &= \vartheta \hat{\hat{e}}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) - \hat{\hat{\eta}}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) \\
&\quad - \hat{\hat{\eta}}_{,\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) \hat{\hat{e}}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) = -\hat{\hat{\eta}}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}), \\
\hat{\phi}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) &= \vartheta \hat{\hat{e}}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) - \hat{\hat{\eta}}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) \\
&\quad - \hat{\hat{\eta}}_{,\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) \hat{\hat{e}}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) = -\hat{\hat{\eta}}_{,\boldsymbol{D}\chi}(\boldsymbol{F}\chi, \boldsymbol{D}\chi, \bar{e}),
\end{aligned}$$

where $\bar{e} = \hat{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)$. This proves equalities $(8.2)_{1-3}$. From $(8.2)_{2,3}$ it follows that

$$\frac{\delta \hat{\phi}}{\delta \chi}(\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \vartheta, \boldsymbol{D}^2\vartheta) = \hat{\phi}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) + \nabla \cdot \cdot \hat{\phi}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)$$

$$= -]\hat{\hat{\eta}}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) - \nabla \cdot \hat{\hat{\eta}}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})$$

$$= -\frac{\delta \hat{\hat{\eta}}}{\delta \chi}(\boldsymbol{F}, \boldsymbol{DF}, \chi, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \bar{e}, \boldsymbol{D}\bar{e}),$$

where $\bar{e}$, $\boldsymbol{D}\bar{e}$ and ϑ, $\boldsymbol{D}\vartheta$ are related by (8.4). This yields the relation $(8.2)_4$ and thereby completes the proof. ■

4. Representation of solutions to a residual dissipation inequality

4.1. Residual dissipation inequality. The exploitation of the second law of thermodynamics always leads to an inequality type condition on the constitutive functions. Such condition is called the *residual dissipation inequality*. It has the fundamental form

$$\sigma(\mathcal{X};\omega) := \mathcal{X} \cdot \mathcal{J}(\mathcal{X};\omega) \geq 0 \quad \text{for all} \quad \{\mathcal{X};\omega\}, \tag{1.1}$$

where $\mathcal{X}$, ω and $\mathcal{J}$ are elements of finite dimensional vector spaces. The form (1.1) is standard in irreversible thermodynamics where $\mathcal{J}$ is identified with thermodynamic fluxes, $\mathcal{X}$ their conjugate forces, ω corresponds to a set of state variables, and the scalar σ, called *dissipation scalar*, denotes the rate of entropy production in the state ω with forces $\mathcal{X}$, see, e.g., de Groot-Mazur [45].

We record two results known in the literature on the representation of solutions of thermodynamical inequality (1.1).

The first one is the decomposition theorem due to Edelen [50] which represents a special case of the Helmholtz theorem in vector analysis. This theorem asserts a splitting of the solution to the dissipation inequality into a dissipative and a nondissipative part.

The second result by Gurtin [83] gives a representation of the solution to the dissipation inequality in terms of a linear transformation which satisfies in a certain sense the semi-definiteness condition.

In our further considerations we shall repeatedly apply these representation results. We point out that the application of the Edelen decomposition theorem for the phase-field systems we are dealing with leads to interesting conclusions on the structure of the constitutive quantities. It turns out that the nonstationary parts of some constitutive quantities may in general contribute to nondissipative thermodynamic fluxes. In other words, if not excluded by other arguments, such anomaly fluxes are not restricted by the second law of thermodynamics. In the class of models with gradient-type free energy the key role plays the nondissipative energy flux.

The free choice of the nondissipative energy flux together with a special relation between energy and entropy fluxes (see eq. (7.1.9)) allows to enlighten a question of particular interest in phase-field modelling whether to modify the energy or the entropy equation, see, e.g., discussion in Fabrizio-Giorgi-Morro [53]. From the point of view of the Edelen theorem both variants are admissible and arise due to particular choices of the nonstationary energy flux.

4.2. The Edelen decomposition theorem.

LEMMA 4.1 (Edelen's decomposition). , *Edelen [50, Corollary p.220] Let $\mathcal{X}$ stand for elements of an N-dimensional vector space E^N with inner product $\mathcal{X} \cdot \mathcal{Y}$, let ω stand for an element of a p-dimensional vector space E^p, and let $\mathcal{J}(\mathcal{X};\omega) : E^N \times E^p \to E^N$ be a mapping which is continuous in ω and of class C^1 in $\mathcal{X}$. There exists a scalar-valued function $\mathcal{D}(\mathcal{X};\omega)$ that is unique to within an added function of ω, and a unique vector-valued function $\mathcal{U}(\mathcal{X};\omega)$ such that*

$$\begin{aligned} &\mathcal{J}(\mathcal{X};\omega) = \nabla_{\mathcal{X}}\mathcal{D}(\mathcal{X};\omega) + \mathcal{U}(\mathcal{X};\omega), \\ &\mathcal{X} \cdot \mathcal{U}(\mathcal{X};\omega) = 0, \quad \mathcal{U}(\mathbf{0};\omega) = \mathbf{0}, \end{aligned} \tag{2.1}$$

where $\nabla_{\mathcal{X}}$ denotes the gradient with respect to $\mathcal{X}$.
The mappings $\mathcal{D}(\mathcal{X};\omega)$ and $\mathcal{U}(\mathcal{X};\omega)$ are given by

$$\begin{aligned} \mathcal{D}(\mathcal{X};\omega) &= \int_0^1 \mathcal{X} \cdot \mathcal{J}(\tau\mathcal{X};\omega) d\tau, \\ U_i(\mathcal{X};\omega) &= \int_0^1 \tau\mathcal{X}_j \left\{ \frac{\partial J_i(\tau\mathcal{X};\omega)}{\partial(\tau\mathcal{X}_j)} - \frac{\partial J_j(\tau\mathcal{X};\omega)}{\partial(\tau\mathcal{X}_i)} \right\} d\tau. \end{aligned} \tag{2.2}$$

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

$$\nabla_{\mathcal{X}} \wedge (\mathcal{J}(\mathcal{X};\omega) - \mathcal{U}(\mathcal{X};\omega)) = \mathbf{0}, \tag{2.3}$$

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

This lemma is a special case of a more general decomposition theorem proved by Edelen [50]. For clarity we present here a direct, simplified proof of this special case.

Proof. Let $\mathcal{D}(\mathcal{X};\omega)$ be defined by $(2.2)_1$. Since $J(\mathcal{X};\omega)$ is of class C^1 in $\mathcal{X}$, $\mathcal{D}(\mathcal{X};\omega)$ is of class C^1 in $\mathcal{X}$ as well. Further, let

$$\tilde{\mathcal{J}} = \mathcal{J}(\tau\mathcal{X};\omega).$$

Then

$$\begin{aligned} \frac{\partial \mathcal{D}}{\partial \mathcal{X}_i} &= \int_0^1 \left\{ \tilde{J}_i + \tau\mathcal{X}_j \frac{\partial \tilde{J}_j}{\partial(\tau\mathcal{X}_i)} \right\} d\tau \\ &= \int_0^1 \left\{ \tilde{J}_i + \tau\mathcal{X}_j \frac{\partial \tilde{J}_i}{\partial(\tau\mathcal{X}_j)} \right\} d\tau \\ &\quad + \int_0^1 \tau\mathcal{X}_j \left\{ \frac{\partial \tilde{J}_j}{\partial(\tau\mathcal{X}_i)} - \frac{\partial \tilde{J}_i}{\partial(\tau\mathcal{X}_j)} \right\} d\tau \\ &= I_1 + I_2. \end{aligned} \tag{2.4}$$

Since

$$\frac{d}{d\tau}\tilde{J}_i = \frac{\partial \tilde{J}_i}{\partial(\tau\mathcal{X}_j)} \mathcal{X}_j,$$

the integration by parts in I_1 gives

$$I_1 = \int_0^1 \left\{ \tilde{J}_i + \tau \frac{d}{d\tau} \tilde{J}_i \right\} d\tau = \tau \tilde{J}_i \Big|_0^1 = J_i(\mathcal{X}; \omega). \tag{2.5}$$

Thus, from (2.4) and (2.5) it follows that

$$\begin{aligned} J_i(\mathcal{X}; \omega) &= \frac{\partial \mathcal{D}}{\partial \mathcal{X}_i} - I_2 \\ &= \frac{\partial \mathcal{D}}{\partial \mathcal{X}_i} + \int_0^1 \tau \mathcal{X}_j \left\{ \frac{\partial \tilde{J}_i}{\partial(\tau \mathcal{X}_j)} - \frac{\partial \tilde{J}_j}{\partial(\tau \mathcal{X}_i)} \right\} d\tau. \end{aligned}$$

When substitution $(2.2)_2$ is used, we obtain

$$J_i(\mathcal{X}; \omega) = \frac{\partial \mathcal{D}}{\partial \mathcal{X}_i} + U_i(\mathcal{X}; \omega)$$

which yields decomposition $(2.1)_1$.

It now follows directly from $(2.2)_2$ that $(2.1)_2$ is satisfied:

$$\mathcal{X} \cdot \mathcal{U}(\mathcal{X}; \omega) = \int_0^1 \tau \mathcal{X}_i \mathcal{X}_j \left\{ \frac{\partial J_i(\tau \mathcal{X}; \omega)}{\partial(\tau \mathcal{X}_j)} - \frac{\partial J_j(\tau \mathcal{X}; \omega)}{\partial(\tau \mathcal{X}_i)} \right\} d\tau = 0,$$

and

$$\mathcal{U}(\mathbf{0}; \omega) = \mathbf{0}.$$

It remains to show the uniqueness of the decompostion. Clearly,

$$\mathcal{J} = \nabla_{\mathcal{X}} \mathcal{D}_1 + \mathcal{U}_1 = \nabla_{\mathcal{X}} \mathcal{D}_2 + \mathcal{U}_2$$

with

$$\mathcal{X} \cdot \mathcal{U}_1 = \mathcal{X} \cdot \mathcal{U}_2 = 0,$$

imply that

$$\mathcal{U}_1 - \mathcal{U}_2 = \nabla_{\mathcal{X}}(\mathcal{D}_2 - \mathcal{D}_1) \tag{2.6}$$

and

$$\mathcal{X} \cdot (\mathcal{U}_1 - \mathcal{U}_2) = \mathcal{X} \cdot \nabla_{\mathcal{X}}(\mathcal{D}_2 - \mathcal{D}_1) = 0. \tag{2.7}$$

Since $\mathcal{D}_1$ and $\mathcal{D}_2$ are C^1 functions of $\mathcal{X}$, the difference $\mathcal{D} = \mathcal{D}_2 - \mathcal{D}_1$ is a C^1 function of $\mathcal{X}$. However, the only C^1 solution of (2.7) is given by

$$\mathcal{D}_2 = \mathcal{D}_1 + \mathcal{D}(\mathbf{0}; \omega). \tag{2.8}$$

Hence, $\mathcal{D}$ is unique to within an additive function of ω. When (2.8) is substituted into (2.6), we obtain

$$\mathcal{U}_1 = \mathcal{U}_2. \tag{2.9}$$

This establishes the uniqueness of the decomposition $(2.1)_1$.

Finally, if $\mathcal{J}(\mathcal{X}; \omega)$ is of class C^2 in $\mathcal{X}$, then $\mathcal{D}(\mathcal{X}; \omega)$ is of class C^2 in $\mathcal{X}$ as well. Then exterior differentiation of $(2.1)_1$ with respect to $\mathcal{X}$ gives (2.3). This completes the proof. ∎

4.3. The dissipation potential. We note important implications and interpretations of Edelen's decomposition theorem in regard to the dissipation inequality. It is seen that on account of $(2.1)_2$, inequality (1.1) reduces to

$$\sigma(\mathcal{X};\omega) = \mathcal{X} \cdot \mathcal{J}(\mathcal{X};\omega) = \mathcal{X} \cdot \nabla_{\mathcal{X}} \mathcal{D}(\mathcal{X};\omega) \geq 0 \quad \text{for all} \quad \{\mathcal{X};\omega\}. \tag{3.1}$$

It is thus only the part $\nabla_{\mathcal{X}} \mathcal{D}(\mathcal{X};\omega)$ of the thermodynamic fluxes $\mathcal{J}(\mathcal{X};\omega)$ that contributes to the rate of entropy production. The function $\mathcal{D}(\mathcal{X};\omega)$ can thus be interpreted as a *dissipation potential.*

In other words, Edelen's theorem asserts that there exists a dissipation potential $\mathcal{D}(\mathcal{X};\omega)$ for every system of constitutive relations that satisfies the dissipation inequality. In fact, it follows directly from $(2.2)_1$ and (3.1) that $\sigma(\mathcal{X};\omega)$ and $\mathcal{D}(\mathcal{X};\omega)$ stay in the relation

$$\mathcal{D}(\mathcal{X};\omega) = \int_0^1 \sigma(\tau\mathcal{X};\omega)\frac{d\tau}{\tau}. \tag{3.2}$$

Thus, (3.1) and (3.2) imply that $\mathcal{D}(\mathcal{X};\omega)$ is nonnegative, convex in $\mathcal{X}$ and achieves its absolute minimum of zero at $\mathcal{X} = \mathbf{0}$.

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

The symmetry relations (2.3) assert that reciprocity relations are always satisfied by any solution of the dissipation inequality, although it is $\mathcal{J} - \mathcal{U}$ rather than just $\mathcal{J}$ that satisfies them. In this sense (2.3) generalize the Onsager reciprocity relations of linear theory of irreversible processes to the nonlinear case. More precisely, it follows from (2.3) that

$$\nabla_{\mathcal{X}} \wedge \mathcal{J} = \mathbf{0}, \quad \text{i.e.} \quad \partial \mathcal{J}_i / \partial_{\mathcal{X}_j} = \partial \mathcal{J}_j / \partial_{\mathcal{X}_i}, \quad i,j = 1,\ldots,N,$$

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

REMARK 4.2. If it worth to remark that the notion of the dissipation potential has been firstly introduced by Lord Rayleigh in 1873, see [152], in description of wave phenomena with friction.

REMARK 4.3. The potential $\mathcal{D}(\mathcal{X};\omega)$ in the statement of Edelen's decompositon theorem represents a smooth version of a more general notion called *pseudopotential of dissipation.* Such object has been introduced by Moreau [108] and advanced in the theory of non-smooth thermomechanics and phase transitions by Frémond [70] and co-workers Bonfanti-Frémond-Luterotti [17], [18], Luterotti-Schimperna-Stefanelli [99], Colli-Luterotti-Schimperna-Stefanelli [41], Bonetti [14], Bonetti-Bonfanti [15].

The pseudopotential of dissipation has the same properties as $\mathcal{D}(\mathcal{X};\omega)$ of being nonnegative, convex with respect to dissipative variables $\mathcal{X}$, and achieving value of zero at $\mathcal{X} = \mathbf{0}$ but, more generally, is only required to be subdifferentiable, see Frémond [70, Chap. 4].

4.4. The Gurtin representation lemma.

LEMMA 4.4 (Gurtin's representation, Gurtin). *[83, Appendix B] Let $\mathcal{X}$ be a generic element of an N-dimensional vector space E^N with inner product $\mathcal{X} \cdot \mathcal{Y}$, let ω be a generic element of a p-dimensional vector space E^p, and let $\mathcal{J}(\mathcal{X};\omega)$: $E^N \times E^p \to E^N$ be a smooth function satisfying the inequality*

$$\mathcal{X} \cdot \mathcal{J}(\mathcal{X};\omega) \geq 0 \quad \text{for all} \ (\mathcal{X};\omega) \in E^N \times E^p. \tag{4.1}$$

Then $\mathcal{J}$ is given by

$$\mathcal{J}(\mathcal{X};\omega) = \boldsymbol{B}(\mathcal{X};\omega)\mathcal{X}, \tag{4.2}$$

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

$$\mathcal{X} \cdot \boldsymbol{B}(\mathcal{X};\omega)\mathcal{X} \geq 0 \quad \text{for all} \ (\mathcal{X};\omega) \in E^N \times E^p. \tag{4.3}$$

The mapping $\boldsymbol{B}(\mathcal{X};\omega)$ is given by

$$\boldsymbol{B}(\mathcal{X};\omega) = \int_0^1 \nabla_{(\tau\mathcal{X})}\mathcal{J}(\tau\mathcal{X};\omega)d\tau, \tag{4.4}$$

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

For reader's convenience we record the proof of the above lemma.

Proof. According to (4.1), for $\lambda > 0$ it holds

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

and hence

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

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

$$\mathcal{J}(\mathbf{0};\omega) = \mathbf{0}. \tag{4.5}$$

In view of (4.5), denoting

$$\tilde{\mathcal{J}} = \mathcal{J}(\tau\mathcal{X};\omega),$$

it follows that

$$\mathcal{J}(\mathcal{X};\omega) = \mathcal{J}(\mathcal{X};\omega) - \mathcal{J}(\mathbf{0};\omega) = \int_0^1 \frac{d}{d\tau}\tilde{\mathcal{J}}d\tau$$

$$= \int_0^1 \frac{\partial\tilde{\mathcal{J}}}{\partial(\tau\mathcal{X}_j)}\mathcal{X}_j d\tau = \left\{\int_0^1 \nabla_{(\tau\mathcal{X})}\mathcal{J}(\tau\mathcal{X};\omega)d\tau\right\}\mathcal{X}.$$

Hence, denoting

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

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

$$\mathcal{J}(\mathcal{X};\omega) = \boldsymbol{B}(\mathcal{X};\omega)\mathcal{X} \quad \text{for all} \ (\mathcal{X};\omega). \tag{4.6}$$

A general solution $\mathcal{J}$ of inequality (4.1) is therefore given by (4.6) with $\boldsymbol{B}(\mathcal{X};\omega)$, for each $(\mathcal{X};\omega)$, a linear transformation from E^N into E^N, consistent with the inequality (4.3). This proves the lemma. ∎

REMARK 4.5. Because of the dependence of $\boldsymbol{B}(\mathcal{X};\omega)$ on $\mathcal{X}$, the inequality (4.3) is weaker than positive definiteness of $\boldsymbol{B}(\mathcal{X};\omega)$. However, when $\mathcal{J}(\mathcal{X};\omega)$ is linear in $\mathcal{X}$ for each ω, then

$$\mathcal{J}(\mathcal{X};\omega) = \boldsymbol{B}(\omega)\mathcal{X} \quad \text{for all} \quad (\mathcal{X};\omega) \in E^N \times E^P,$$

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

5. Constitutive relations for conserved and nonconserved phase-field models via the evaluation of the entropy inequality

To illustrate the role of the duality relations we present two alternative approaches of evaluating the entropy inequality which use either the entropy or the internal energy as the independent thermal variable.

5.1. Evaluation of the entropy inequality. Dual approach with entropy as independent variable. In this section we use entropy as the independent thermal variable. In such a case, by the duality relations, the internal energy $\tilde{e} = \hat{\tilde{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$ expressed as a function of the entropy η represents the correspondign thermodynamic potential.

5.1.1. System of equations and the entropy inequality. Let us consider system of balance equations (2.2.6) with constitutive relations (2.2.7) and the state space Y_η with the entropy as the independent variable, viz.

$$\begin{aligned} &\varrho_0 \ddot{\boldsymbol{u}} - \nabla \cdot \boldsymbol{S} = \varrho_0 \boldsymbol{b}, \\ &\boldsymbol{S}\boldsymbol{F}^T = \boldsymbol{F}\boldsymbol{S}^T, \\ &\varrho_0 \dot{\chi} + \nabla \cdot \boldsymbol{j} - \varrho_0 r = \varrho_0 \tau, \\ &\varrho_0 \dot{\tilde{e}} + \nabla \cdot \boldsymbol{q} - \boldsymbol{S} \cdot \dot{\boldsymbol{F}} = \varrho_0 g, \end{aligned} \tag{1.1}$$

where

$$\boldsymbol{S} = \hat{\boldsymbol{S}}(Y_\eta), \quad \boldsymbol{j} = \hat{\boldsymbol{j}}(Y_\eta), \quad r = \hat{r}(Y_\eta), \quad \tilde{e} = \hat{\tilde{e}}(Y_\eta), \quad \boldsymbol{q} = \hat{\boldsymbol{q}}(Y_\eta) \tag{1.2}$$

and

$$Y_\eta := \{\boldsymbol{F}, \boldsymbol{D}\boldsymbol{F}, \dots, \boldsymbol{D}^M \boldsymbol{F}, \chi, \boldsymbol{D}\chi, \dots, \boldsymbol{D}^K \chi, \eta, \boldsymbol{D}\eta, \dots, \boldsymbol{D}^L \eta, \chi_{,t}\} \tag{1.3}$$

with integers $M, L \geq 1$, $K \geq 2$, and $\hat{\boldsymbol{S}}$, $\hat{\boldsymbol{j}}$, $\hat{r}$, $\hat{\tilde{e}}$, $\tilde{\boldsymbol{q}}$ being smooth functions of their arguments.

We remind that by assumption (2.2.5), $\varrho_0 = \varrho_0(\boldsymbol{X}) > 0$ is a given referential mass density.

For later purposes we split the state space

$$Y_\eta = \{Y^0, Y^1\} \tag{1.4}$$

into two subsets

$$Y^0 := \{\boldsymbol{F}, \boldsymbol{D}\boldsymbol{F}, \dots, \boldsymbol{D}^M \boldsymbol{F}, \chi, \boldsymbol{D}\chi, \dots, \boldsymbol{D}^K \chi, \eta, \boldsymbol{D}\eta, \dots, \boldsymbol{D}^L \eta\} \tag{1.5}$$

and

$$Y^1 := \{\chi_{,t}\}, \tag{1.6}$$

which distinguish between stationary variables and the nonstationary one vanishing at equilibrium.

Because of the presence of tensors of order higher than one we supplement (1.4) by the following convention:

Any constitutive function defined on the set Y_η, say $\hat{\jmath}(Y_\eta)$, is understood in the sense of the following extension:

$$\begin{aligned}
&\hat{\jmath}(F_{ij},\ldots,\boldsymbol{A}^m_{ij}+(\boldsymbol{A}^m_{ij})^{skew},\ldots,\chi,\ldots,\\
&\quad \boldsymbol{B}^k+(\boldsymbol{B}^k)^{skew},\ldots,\eta,\ldots,\boldsymbol{C}^l+(\boldsymbol{C}^l)^{skew},\ldots)\\
&=\hat{\jmath}(F_{ij},\ldots,\boldsymbol{A}^m_{ij},\ldots,\chi,\ldots,\boldsymbol{B}^k,\ldots,\eta,\ldots,\boldsymbol{C}^l,\ldots),
\end{aligned} \tag{1.7}$$

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

Such extension is used for all other constitutive functions. Consequently, for instance in the case of $\boldsymbol{D}^2\chi$, 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 all further considerations.

To select a class of admissible constitutive relations we impose the entropy inequality with multipliers (2.6.2) which in case of state space Y_η reads as follows.

There exists the entropy η, considered as the independent thermal variable, and the entropy flux $\boldsymbol{\Psi}$ given by the constitutive relation

$$\boldsymbol{\Psi} = \hat{\boldsymbol{\Psi}}(Y_\eta), \tag{1.8}$$

as well as the multipliers

$$\boldsymbol{\lambda}_u = \hat{\boldsymbol{\lambda}}_u(Y_\eta), \quad \lambda_\chi = \hat{\lambda}(Y_\eta), \quad \lambda_e = \hat{\lambda}_e(Y_\eta), \tag{1.9}$$

conjugated respectively with balance equations $(1.1)_1$, $(1.1)_3$ and $(1.1)_4$, such that the inequality

$$\begin{aligned}
&\varrho_0\dot{\eta} + \nabla\cdot\boldsymbol{\Psi} - \boldsymbol{\lambda}_u\cdot(\varrho_0\ddot{\boldsymbol{u}} - \nabla\cdot\boldsymbol{S}) - \lambda_\chi(\varrho_0\dot{\chi} + \nabla\cdot\boldsymbol{j} - \varrho_0 r)\\
&\quad - \lambda_e(\varrho_0\dot{e} + \nabla\cdot\boldsymbol{q} - \boldsymbol{S}\cdot\dot{\boldsymbol{F}}) \ge 0
\end{aligned} \tag{1.10}$$

is satisfied for all fields $\boldsymbol{u}$, χ and η.

5.1.2. Algebraic preliminaries. We prepare some simplifying notation. For $f = \hat{f}(Y_\eta)$ a smooth function of its arguments, we denote by $\partial_i^{Y^0} f$, $i = 1,2,3$, the algebraic version of the spatial derivative $\partial f/\partial x_i$ contracted to the set of variables Y^0 (applying differentiation by the chain rule):

$$\partial_i^{Y^0} f := \sum_{m=0}^{M} f_{,\boldsymbol{D}^m\boldsymbol{F}}\cdot\boldsymbol{D}^m\boldsymbol{F}_{,i} + \sum_{k=0}^{K} f_{,\boldsymbol{D}^k\chi}\cdot\boldsymbol{D}^k\chi_{,i} + \sum_{l=0}^{L} f_{,\boldsymbol{D}^l\eta}\cdot\boldsymbol{D}^l\eta_{,i}, \tag{1.11}$$

and by $\nabla^{Y^0} f = (\partial_i^{Y^0} f)_{i=1,2,3}$ the corresponding gradient ∇f contracted to the set Y^0. The convention $\boldsymbol{D}^0\varphi = \varphi$ is used.

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

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

Moreover, to separate the highest order space derivatives $\{\boldsymbol{D}^M \boldsymbol{F}, \boldsymbol{D}^K \chi, \boldsymbol{D}^L \eta\}$ we introduce the following subset of Y^0:

$$\begin{aligned} \tilde{Y}^0 &:= Y^0 \setminus \{\boldsymbol{D}^m \boldsymbol{F}, \boldsymbol{D}^K \chi, \boldsymbol{D}^L \eta\} \\ &= \{\boldsymbol{F}, \boldsymbol{D}\boldsymbol{F}, \dots, \boldsymbol{D}^{M-1}\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \dots, \boldsymbol{D}^{K-1}\chi, \eta, \boldsymbol{D}\eta, \dots, \boldsymbol{D}^{L-1}\eta\}. \end{aligned} \tag{1.12}$$

Then, in particular, for a function $\boldsymbol{\Phi} = \hat{\boldsymbol{\Phi}}(Y_\eta)$, the expression

$$\nabla^{\tilde{Y}^0} \cdot \boldsymbol{\Phi} = \sum_{i=1}^{3} \Big[\sum_{m=0}^{M-1} \Phi_{i,\boldsymbol{D}^m \boldsymbol{F}} \cdot \boldsymbol{D}^m \boldsymbol{F}_{,i} + \sum_{k=0}^{K-1} \Phi_{i,\boldsymbol{D}^k \chi} \cdot \boldsymbol{D}^k \chi_{,i} + \sum_{l=0}^{L-1} \Phi_{i,\boldsymbol{D}^l \eta} \cdot \boldsymbol{D}^l \eta_{,i} \Big]$$

does not exceed the set of variables Y_η.

For a function $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$ we introduce the algebraic version of the first variation $\delta f / \delta \chi = f_{,\chi} - \nabla \cdot f_{,\boldsymbol{D}\chi}$ contracted to the subset $\tilde{Y}^0$, i.e.,

$$\begin{aligned} \frac{\delta^{\tilde{Y}^0} f}{\delta \chi} &:= f_{,\chi} - \nabla^{\tilde{Y}^0} \cdot f_{,\boldsymbol{D}\chi} \\ &= f_{,\chi} - \sum_{i=1}^{3} \Big[f_{,\chi_{,i}\boldsymbol{F}} \cdot \boldsymbol{F}_{,i} + \sum_{j=1}^{3} f_{,\chi_{,i}\chi_{,j}} \chi_{,ji} + f_{,\chi_{,i}\eta} \eta_{,i} \Big]. \end{aligned} \tag{1.13}$$

Note that since $M, L \geq 1$ and $K \geq 2$, the above expression coincides with the algebraic version of the first variation (in this case the contraction to $\tilde{Y}^0$ is meaningless). Thus, we shall simply write

$$\frac{\delta^{\tilde{Y}^0} f}{\delta \chi} = \frac{\delta f}{\delta \chi}. \tag{1.14}$$

Similarly, in this case, we write

$$\nabla^{\tilde{Y}^0} f = \nabla f. \tag{1.15}$$

5.1.3. The implications of the entropy inequality. To evaluate the entropy inequality (1.10) we impose three structural assumptions.

- The nondegeneracy condition for the internal energy

$$\tilde{e}_{,\eta}(Y_\eta) > 0 \quad \text{for all variables } Y_\eta. \tag{1.16}$$

- The relation between stationary entropy, energy and phase variable fluxes

$$\boldsymbol{\Psi}^0 = \lambda_\chi^0 \boldsymbol{j}^0 + \lambda_e^0 \boldsymbol{q}^0, \tag{1.17}$$

  where $\boldsymbol{\Psi}^0$, $\boldsymbol{j}^0$, $\boldsymbol{q}^0$, λ_χ^0 and λ_e^0 denote stationary quantities defined by setting $\chi_{,t} = 0$ in the set Y_η, i.e.,

$$\boldsymbol{\Psi}^0 := \hat{\Psi}(Y^0, Y^1)|_{Y^1 = \{0\}},$$

  and similarly for other quantities. goodbreak

- In addition, without loss of generality, we assume the following splitting of the energy flux vector
$$\boldsymbol{q} = \boldsymbol{q}^0 - \chi_{,t}\boldsymbol{h}^e, \tag{1.18}$$
where $\boldsymbol{q}^0 = \hat{\boldsymbol{q}}^0(Y^0)$ is a stationary heat flux, and $-\chi_{,t}\boldsymbol{h}^e$ is a nonstationary energy flux with $\boldsymbol{h}^e = \hat{\boldsymbol{h}}^e(Y_\eta)$ some constitutive vector quantity.

We remark that in view of the duality relations (cf. $(3.5.6)_2$) assumption (1.16) expresses the strict positivity of the absolute temperature θ. The relation (1.17) is standard in the classical thermodynamics theory where potentials do not involve gradients, see e.g., Müller [116].

We prove the following

THEOREM 5.1 (Consistency with the entropy inequality). *Let us consider balance laws (1.1) with constitutive relations (1.2). Suppose that the entropy inequality (1.8)–(1.10) is satisfied and assumptions (1.16)–(1.18) hold true. Then the following relations are satisfied:*

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

(ii) *internal energy* $\tilde{e} = \hat{\tilde{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$;

(iii) *multiplier of the energy equation*
$$\lambda_e = \hat{\lambda}_e(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) = \frac{1}{\tilde{e}_{,\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)} > 0; \tag{1.19}$$

(iv) *stress tensor*
$$\boldsymbol{S} = \hat{\boldsymbol{S}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) = \varrho_0 \tilde{e}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta); \tag{1.20}$$

(v) *entropy flux*
$$\boldsymbol{\Psi} = \lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q} + \chi_{,t}\left[\lambda_e \varrho_0 \tilde{e}_{,\boldsymbol{D}\chi} - \int_0^1 (\lambda_{\chi,\chi_{,t}} \boldsymbol{j})(Y^0, \tau\chi_{,t})d\tau\right]; \tag{1.21}$$

(vi) *compatibility conditions*
$$\begin{aligned}
&\chi_{,t}\left[-\int_0^1 (\lambda_{\chi,\chi_{,t}} j_i)(Y^0, \tau\chi_{,t})d\tau\right]_{,\boldsymbol{D}^M\boldsymbol{F}} + \lambda_{\chi,\boldsymbol{D}^M\boldsymbol{F}} j_i = \boldsymbol{0},\\
&\chi_{,t}\left[-\int_0^1 (\lambda_{\chi,\chi_{,t}} j_i)(Y^0, \tau\chi_{,t})d\tau\right]_{,\boldsymbol{D}^K\chi} + \lambda_{\chi,\boldsymbol{D}^K\chi} j_i = \boldsymbol{0},\\
&\chi_{,t}\left[-\int_0^1 (\lambda_{\chi,\chi_{,t}} j_i)(Y^0, \tau\chi_{,t})d\tau\right]_{,\boldsymbol{D}^L\eta} + \lambda_{\chi,\boldsymbol{D}^L\eta} j_i = \boldsymbol{0}
\end{aligned} \tag{1.22}$$

for $i = 1, 2, 3$.

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

(vii) *multiplier* $\lambda_\chi = \hat{\lambda}_\chi(Y_\eta)$ *satisfies the equation*

$$-\varrho_0\lambda_\chi = \lambda_e\frac{\delta(\varrho_0\tilde{e})}{\delta\chi} - \varrho_0\nabla\lambda_e\cdot\tilde{e}_{,D\chi} + \nabla^{\tilde{Y}^0}\cdot\int_0^1(\lambda_{\chi,\chi,_t}\boldsymbol{j})(Y^0,\tau\chi_{,t})d\tau + \nabla\lambda_e\cdot\boldsymbol{h}^e + a; \tag{1.23}$$

(viii) *the quantities* $r = \hat{r}(Y_\eta)$, $\boldsymbol{j} = \hat{\boldsymbol{j}}(Y_\eta)$, $\boldsymbol{q}^0 = \hat{\boldsymbol{q}}^0(Y^0)$ *and* $a = \hat{a}(Y_\eta)$ *satisfy the residual dissipation inequality*

$$\lambda_\chi\varrho_0 r + \nabla^{\tilde{Y}^0}\lambda_\chi\cdot\boldsymbol{j} + \nabla\lambda_e\cdot\boldsymbol{q}^0 + \chi_{,t}a \geq 0 \tag{1.24}$$

for all variables Y_η.

REMARK 5.2. By assertion (ii), the first variation $\delta\tilde{e}/\delta\chi$ depends on the variables $\{\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \eta, \boldsymbol{D}\eta\}$. For that reason we have allowed for the higher gradient dependence $M, L \geq 1$, $K \geq 2$ in the state space Y_η.

REMARK 5.3. In view of thermodynamic relation $(3.5.6)_2$ assertion (iii) 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 thermodynamic relation $(3.8.1)_4$, equation (1.23) for $-\lambda_\chi$ resembles the expression for the chemical potential in the classical Cahn-Hilliard theory which for $\theta =$ const, $\varrho_0 =$ const is given by $\mu = \delta f/\delta\chi$. Thus, the form (1.23) suggests that the quantity $-\lambda_\chi$ may be identified with a rescaled chemical potential

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

The above correspondences will be established rigorously in Subsection 6.2.1.

Proof. of Theorem 5.1. By inserting constitutive equations (1.2), (1.8) and (1.9) into entropy inequality (1.10) and applying the chain rule we arrive at the following algebraic inequality

$$\begin{aligned}
&\varrho_0\eta_{,t} + \boldsymbol{\Psi}_{,\chi,_t}\cdot\boldsymbol{D}\chi_{,t} + \nabla^{Y^0}\cdot\boldsymbol{\Psi} - \varrho_0\boldsymbol{\lambda_u}\cdot\boldsymbol{u}_{,tt} + \boldsymbol{\lambda_u}\cdot(\boldsymbol{S}_{,\chi,_t}\boldsymbol{D}\chi_{,t})\\
&\quad + \boldsymbol{\lambda_u}\cdot(\nabla^{Y^0}\cdot\boldsymbol{S}) - \lambda_\chi\varrho_0\chi_{,t} - \lambda_\chi\boldsymbol{j}_{,\chi,_t}\cdot\boldsymbol{D}\chi_{,t} - \lambda_\chi\nabla^{Y^0}\cdot\boldsymbol{j} + \lambda_\chi\varrho_0 r\\
&\quad - \lambda_e\sum_{m=0}^{M}\varrho_0\tilde{e}_{,\boldsymbol{D}^m\boldsymbol{F}}\cdot\boldsymbol{D}^m\boldsymbol{F}_{,t} - \lambda_e\sum_{k=0}^{K}\varrho_0\tilde{e}_{,\boldsymbol{D}^k\chi}\cdot\boldsymbol{D}^k\chi_{,t} - \lambda_e\sum_{l=0}^{L}\varrho_0\tilde{e}_{,\boldsymbol{D}^l\eta}\cdot\boldsymbol{D}^l\eta_{,t}\\
&\quad - \lambda_e\varrho_0\tilde{e}_{,\chi,_t}\chi_{,tt} - \lambda_e\boldsymbol{q}_{,\chi,_t}\cdot\boldsymbol{D}\chi_{,t} - \lambda_e\nabla^{Y^0}\cdot\boldsymbol{q} + \lambda_e\boldsymbol{S}\cdot\boldsymbol{F}_{,t} \geq 0
\end{aligned} \tag{1.25}$$

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

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

denotes the set of variables (called higher derivatives) in which the left-hand side of (1.25) is linear. The evaluation of (1.25) 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. The proof will be divided into steps $1^\circ - 7^\circ$.

1° By the linearity of the left-hand side of (1.25) in $\boldsymbol{u}_{,tt}$ it follows that the corresponding coefficient has to vanish, that is $\boldsymbol{\lambda}_u = \boldsymbol{0}$. This proves (i).

2° The linearity in $\eta_{,t}$ implies that

$$\varrho_0(1 - \lambda_e \tilde{e}_{,\eta}) = 0,$$

so in view of assumption (1.16) and the fact that $\varrho_0 > 0$, we infer that

$$\lambda_e = \frac{1}{\tilde{e}_{,\eta}} > 0. \tag{1.26}$$

3° By the linearity in the variables

$$(\boldsymbol{D}^m \boldsymbol{F}_{,t})_{1\le m\le M}, \quad (\boldsymbol{D}^k \chi_{,t})_{2\le k\le K}, \quad (\boldsymbol{D}^l \eta_{,t})_{1\le l\le L}, \chi_{,tt},$$

bearing in mind that λ_e, $\varrho_0 > 0$, we read off that

$$\begin{aligned} &\tilde{e}_{,\boldsymbol{D}^m \boldsymbol{F}} = \boldsymbol{0} \text{ for } 1 \le m \le M, \quad && \tilde{e}_{,\boldsymbol{D}^k \chi} = \boldsymbol{0} \text{ for } 2 \le k \le K, \\ &\tilde{e}_{,\boldsymbol{D}^l \eta} = \boldsymbol{0} \text{ for } 1 \le l \le L, && \tilde{e}_{,\chi_{,t}} = 0. \end{aligned}$$

Hence, the constitutive dependence of $\tilde{e}$ is restricted to $\tilde{e} = \hat{\tilde{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$ which proves (ii).
Simultaneously, from the relation (1.26) it follows that the constitutive dependence of λ_e is restricted to $\lambda_e = \hat{\lambda}_e(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$ which proves (iii).

4° By the linearity in $\boldsymbol{F}_{,t}$,

$$\lambda_e \boldsymbol{S} - \lambda_e \varrho_0 \tilde{e}_{,\boldsymbol{F}} = \boldsymbol{0}.$$

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

5° From the linearity in $\boldsymbol{D}\chi_{,t}$ we deduce that

$$\boldsymbol{\Psi}_{,\chi_{,t}} - \lambda_\chi \boldsymbol{j}_{,\chi_{,t}} - \lambda_e \varrho_0 \tilde{e}_{,\boldsymbol{D}\chi} - \lambda_e \boldsymbol{q}_{,\chi_{,t}} = \boldsymbol{0}. \tag{1.27}$$

Let us define the vector

$$\tilde{\boldsymbol{\Psi}} := \boldsymbol{\Psi} - \lambda_\chi \boldsymbol{j} - \lambda_e \boldsymbol{q}. \tag{1.28}$$

By virtue of assumption (1.17), we have

$$\tilde{\boldsymbol{\Psi}}^0 = \boldsymbol{0}. \tag{1.29}$$

From (1.28), using (1.27) and (iii), we get

$$\begin{aligned} \tilde{\boldsymbol{\Psi}}_{,\chi_{,t}} &= \boldsymbol{\Psi}_{,\chi_{,t}} - \lambda_{\chi,\chi_{,t}} \boldsymbol{j} - \lambda_\chi \boldsymbol{j}_{,\chi_{,t}} - \lambda_e \boldsymbol{q}_{,\chi_{,t}} \\ &= \lambda_e \varrho_0 \tilde{e}_{,\boldsymbol{D}\chi} - \lambda_{\chi,\chi_{,t}} \boldsymbol{j}. \end{aligned} \tag{1.30}$$

Hence, in view of (1.29) and (ii), (iii), it follows that

$$\begin{aligned} \tilde{\boldsymbol{\Psi}} &= \lambda_e \varrho_0 \tilde{e}_{,\boldsymbol{D}\chi} \chi_{,t} - \int_0^{\chi_{,t}} (\lambda_{\chi,\chi_{,t}} \boldsymbol{j})(Y^0, \xi)\, d\xi \\ &= \chi_{,t} \left[\lambda_e \varrho_0 \tilde{e}_{,\boldsymbol{D}\chi} - \int_0^1 (\lambda_{\chi,\chi_{,t}} \boldsymbol{j})(Y^0, \tau\chi_{,t})\, d\tau \right]. \end{aligned} \tag{1.31}$$

From (1.28) and (1.31) we conclude (v).

6° It remains to examine the linearity in the variables $\boldsymbol{D}^{M+1}\boldsymbol{F}, \boldsymbol{D}^{K+1}\chi, \boldsymbol{D}^{L+1}\eta$. In view of the results obtained in the previous steps inequality (1.25) is reduced to

$$-\varrho_0(\lambda_\chi + \lambda_e \tilde{e}_{,\chi})\chi_{,t} + \lambda_\chi \varrho_0 r + \nabla^{Y^0} \cdot \boldsymbol{\Psi} - \lambda_\chi \nabla^{Y^0} \cdot \boldsymbol{j} - \lambda_e \nabla^{Y^0} \cdot \boldsymbol{q} \geq 0 \qquad (1.32)$$

to be satisfied for all variables $\{\boldsymbol{D}^{M+1}\boldsymbol{F}, \boldsymbol{D}^{K+1}\chi, \boldsymbol{D}^{L+1}\eta, Y_\eta\}$.
We rearrange now the sum of the last three terms on the left-hand side of (1.32) to the form

$$\begin{aligned}
&\nabla^{Y^0} \cdot \boldsymbol{\Psi} - \lambda_\chi \nabla^{Y^0} \cdot \boldsymbol{j} - \lambda_e \nabla^{Y^0} \cdot \boldsymbol{q} \\
&= \nabla^{Y^0} \cdot (\boldsymbol{\Psi} - \lambda_\chi \boldsymbol{j} - \lambda_e \boldsymbol{q}) + \nabla^{Y^0}\lambda_\chi \cdot \boldsymbol{j} + \nabla^{Y^0}\lambda_e \cdot \boldsymbol{q} \\
&= \nabla^{Y^0} \cdot \tilde{\boldsymbol{\Psi}} + \nabla^{Y^0}\lambda_\chi \cdot \boldsymbol{j} + \nabla^{Y^0}\lambda_e \cdot \boldsymbol{q}.
\end{aligned} \qquad (1.33)$$

Further, using (1.31) and the definition of the contracted divergence $\nabla^{Y^0}\cdot$ (see notation in Subsection 5.1.2), we obtain

$$\nabla^{Y^0} \cdot \tilde{\boldsymbol{\Psi}} = \chi_{,t}\left[\nabla^{Y^0} \cdot (\lambda_e \varrho_0 \tilde{e}_{,\boldsymbol{D}\chi}) - \nabla^{Y^0} \cdot \int_0^1 (\lambda_{\chi,\chi_{,t}} \boldsymbol{j})(Y^0, \tau\chi_{,t}) d\tau\right]. \qquad (1.34)$$

By combining (1.33), (1.34), and using assumption (1.18) on $\boldsymbol{q}$, inequality (1.32) is transformed to the form

$$\begin{aligned}
&\chi_{,t}\Big[-\varrho_0\lambda_\chi - \lambda_e\varrho_0\tilde{e}_{,\chi} + \nabla^{Y^0} \cdot (\lambda_e \varrho_0 \tilde{e}_{,\boldsymbol{D}\chi}) \\
&\quad - \nabla^{Y^0} \cdot \int_0^1 (\lambda_{\chi,\chi_{,t}} \boldsymbol{j})(Y^0, \tau\chi_{,t}) d\tau - \nabla^{Y^0}\lambda_e \cdot \boldsymbol{h}^e\Big] \\
&\quad + \lambda_\chi \varrho_0 r + \nabla^{Y^0}\lambda_\chi \cdot \boldsymbol{j} + \nabla^{Y^0}\lambda_e \cdot \boldsymbol{q}^0 \geq 0
\end{aligned} \qquad (1.35)$$

for all variables $\{\boldsymbol{D}^{M+1}\boldsymbol{F}, \boldsymbol{D}^{K+1}\chi, \boldsymbol{D}^{L+1}\eta, Y_\eta\}$.
From (1.35), performing differentiation by the chain rule in terms involving divergence ∇^{Y^0} and gradient ∇^{Y^0} (contracting now to the subset $\tilde{Y}^0$), the linearity in the variables $\boldsymbol{D}^{M+1}\boldsymbol{F}$, $\boldsymbol{D}^{K+1}\chi$ and $\boldsymbol{D}^{L+1}\eta$ implies that the coefficients preceding these variables have to vanish. Hence, recalling assertions (ii) and (iii), we conclude (vi).

7° We shall derive conclusions from inequality (1.35) which remains after taking into account (vi). It reads

$$\begin{aligned}
&\chi_{,t}\Big[-\varrho_0\lambda_\chi - \lambda_e\varrho_0\tilde{e}_{,\chi} + \nabla^{\tilde{Y}^0} \cdot (\lambda_e \varrho_0 \tilde{e}_{,\boldsymbol{D}\chi}) \\
&\quad - \nabla^{\tilde{Y}^0} \cdot \int_0^1 (\lambda_{\chi,\chi_{,t}} \boldsymbol{j})(Y^0, \tau\chi_{,t}) d\tau - \nabla^{\tilde{Y}^0}\lambda_e : \boldsymbol{h}^e\Big] \\
&\quad + \lambda_\chi \varrho_0 r + \nabla^{\tilde{Y}^0}\lambda_\chi \cdot \boldsymbol{j} + \nabla^{\tilde{Y}^0}\lambda_e \cdot \boldsymbol{q}^0 \geq 0
\end{aligned} \qquad (1.36)$$

for all variables Y_η.
Let us define now the scalar quantity $a = \hat{a}(Y_\eta)$ given by the squared parenthesis

in (1.36), i.e.,

$$\begin{aligned} a := & -\varrho_0\lambda_\chi - \lambda_e\varrho_0\tilde{e}_{,\chi} + \nabla^{\tilde{Y}_0}\cdot(\lambda_e\varrho_0\tilde{e}_{,\boldsymbol{D}\chi}) \\ & - \nabla^{\tilde{Y}_0}\cdot\int_0^1 (\lambda_{\chi,\chi,t}\boldsymbol{j})(Y^0,\tau\chi_{,t})d\tau - \nabla^{\tilde{Y}^0}\lambda_e\cdot\boldsymbol{h}^e \\ = & \ \varrho_0\lambda_\chi - \lambda_e[\varrho_0\tilde{e}_{,\chi} - \nabla^{\tilde{Y}^0}\cdot(\varrho_0\tilde{e}_{,\boldsymbol{D}\chi})] \\ & + \varrho_0\nabla^{\tilde{Y}^0}\lambda_e\cdot\tilde{e}_{,\boldsymbol{D}\chi} - \nabla^{\tilde{Y}^0}\cdot\int_0^1(\lambda_{\chi,\chi,t}\boldsymbol{j})(Y^0,\tau\chi_{,t})d\tau - \nabla^{\tilde{Y}^0}\lambda_e\cdot\boldsymbol{h}^e. \end{aligned} \tag{1.37}$$

Bearing in mind that $\tilde{e} = \hat{\tilde{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta)$ and $\tilde{\lambda}_e = \hat{\lambda}_e(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta)$, recalling notational convention (1.12)–(1.15), we have

$$\nabla^{\tilde{Y}^0}\cdot(\varrho_0\tilde{e}_{,\boldsymbol{D}\chi}) = \nabla\cdot(\varrho_0\tilde{e}_{,\boldsymbol{D}\chi}), \quad \nabla^{\tilde{Y}^0}\lambda_e = \nabla\lambda_e, \tag{1.38}$$

$$\frac{\delta^{\tilde{Y}^0}(\varrho_0\tilde{e})}{\delta\chi} = \varrho_0\tilde{e}_{,\chi} - \nabla^{\tilde{Y}^0}\cdot(\varrho_0\tilde{e}_{,\boldsymbol{D}\chi}) = \varrho_0\tilde{e}_{,\chi} - \nabla\cdot(\varrho_0\tilde{e}_{,\boldsymbol{D}\chi}) = \frac{\delta(\varrho_0\tilde{e})}{\delta\chi}.$$

Thus, (1.37) takes the form

$$\begin{aligned} a = & -\varrho_0\lambda_\chi - \lambda_e\frac{\delta(\varrho_0\tilde{e})}{\delta\chi} + \varrho_0\nabla\lambda_e\cdot\tilde{e}_{,\boldsymbol{D}\chi} \\ & - \nabla^{\tilde{Y}^0}\cdot\int_0^1(\lambda_{\chi,\chi,t}\boldsymbol{j})(Y^0,\tau\chi_{,t})d\tau - \nabla\lambda_e\cdot\boldsymbol{h}^e, \end{aligned} \tag{1.39}$$

which yields equality (1.23) in assertion (vii).

Finally, owing to (1.39), inequality (1.36) takes the form of the residual inequality (1.24). This yields assertion (viii), which completes the proof. ∎

5.1.4. The implications in the nonconserved case. Theorem 5.1 simplifies in the case of the nonconserved dynamics of the phase variable, i.e., $\boldsymbol{j} \equiv \boldsymbol{0}$, $r \neq 0$. Then, assumption (1.17) is replaced by

$$\boldsymbol{\Psi}^0 = \lambda_e^0\boldsymbol{q}^0, \tag{1.40}$$

and we have

THEOREM 5.4 (Consistency with the entropy inequality in the nonconserved case). *Let us consider balance laws (1.1) with constitutive equations (1.2) in the nonconserved case* $\boldsymbol{j} \equiv \boldsymbol{0}$, $r \neq 0$. *Suppose that the entropy inequality (1.8)–(1.10) is satisfied and assumptions (1.16), (1.18), (1.40) hold true. Then the following relations are satisfied:*

(i) *multiplier of the linear mamentum* $\boldsymbol{\lambda_u} = \boldsymbol{0}|$;
(ii) *internal energy* $\tilde{e} = \hat{\tilde{e}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta)$;
(iii) *multiplier of the energy equation*

$$\lambda_e = \hat{\lambda}_e(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta) = \frac{1}{\tilde{e}_{,\eta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\eta)} > 0; \tag{1.41}$$

(iv) *stress tensor*

$$\boldsymbol{S} = \hat{\boldsymbol{S}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) = \varrho_0 \tilde{e}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta); \tag{1.42}$$

(v) *entropy flux*

$$\boldsymbol{\Psi} = \lambda_e \boldsymbol{q} + \chi_{,t} \lambda_e \varrho_0 \tilde{e}_{,\boldsymbol{D}\chi}. \tag{1.43}$$

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

(vi) *multiplier* $\lambda_\chi = \hat{\lambda}_\chi(Y_\eta)$ *satisfies the equation*

$$-\varrho_0 \lambda_\chi = \lambda_e \frac{\delta(\varrho_0 \tilde{e})}{\delta \chi} - \varrho_0 \nabla \lambda_e \cdot \tilde{e}_{,\boldsymbol{D}\chi} + \nabla \lambda_e \cdot \boldsymbol{h}^e + a; \tag{1.44}$$

(vii) *the quantities* $r = \hat{r}(Y_\eta)$, $\boldsymbol{q}^0 = \hat{\boldsymbol{q}}^0(Y^0)$ *and* $a = \hat{a}(Y_\eta)$ *satisfy the residual dissipation inequality*

$$\lambda_\chi \varrho_0 r + \nabla \lambda_e \cdot \boldsymbol{q}^0 + \chi_{,t} a \geq 0 \tag{1.45}$$

for all variables Y_η.

Proof. Setting $\boldsymbol{j} = \boldsymbol{0}$ the assertions result immediately from the proof of Theorem 5.1. ∎

5.2. Evaluation of the entropy inequality. Dual approach with internal energy as independent variable. Here we use internal energy as an independent thermal variable. In such a case the entropy $\tilde{\eta} = \hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e)$ expressed as a function of the internal energy e represents the corresponding thermodynamic potential. The considerations parallel those presented in Section 5.1.

5.2.1. System of equations and the entropy inequality. Let us consider system of balance equations (2.2.6) with constitutive relations (2.2.7) and the state space Y_e with the internal energy as independent variable, viz.

$$\begin{aligned} &\varrho_0 \ddot{\boldsymbol{u}} - \nabla \cdot \boldsymbol{S} = \varrho_0 \boldsymbol{b}, \\ &\boldsymbol{S}\boldsymbol{F}^T = \boldsymbol{F}\boldsymbol{S}^T, \\ &\varrho_0 \dot{\chi} + \nabla \cdot \boldsymbol{j} - \varrho_0 r = \varrho_0 \tau, \\ &\varrho_0 \dot{e} + \nabla \cdot \boldsymbol{q} - \boldsymbol{S} \cdot \dot{\boldsymbol{F}} = \varrho_0 g, \end{aligned} \tag{2.1}$$

where $\varrho_0 = \varrho(\boldsymbol{X}) > 0$ is a given referential mass density,

$$\boldsymbol{S} = \hat{\boldsymbol{S}}(Y_e), \quad \boldsymbol{j} = \hat{\boldsymbol{j}}(Y_e), \quad r = \hat{r}(Y_e), \quad \boldsymbol{q} = \hat{\boldsymbol{q}}(Y_e) \tag{2.2}$$

with smooth functions $\hat{\boldsymbol{S}}$, $\hat{\boldsymbol{j}}$, $\hat{r}$, $\hat{\boldsymbol{q}}$, and

$$Y_e := \{\boldsymbol{F}, \boldsymbol{D}\boldsymbol{F}, \ldots, \boldsymbol{D}^M \boldsymbol{F}, \chi, \boldsymbol{D}\chi, \ldots, \boldsymbol{D}^K \chi, e, \boldsymbol{D}e, \ldots, \boldsymbol{D}^L e, \chi_{,t}\} \tag{2.3}$$

with integers M, K, L such that $M, L \geq 1$ and $K \geq 2$.

As in (1.4) we split the state space

$$Y_e = \{Y^0, Y^1\} \tag{2.4}$$

into two subsets:

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

and

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

which distinguish between stationary variables and the nonstationary one.

To select a class of thermodynamically admissible constitutive relations we impose the entropy inequality with multipliers (2.6.2) which in the case of state space Y_e reads as follows:

There exists the entropy $\eta = \tilde{\eta}$ and the entropy flux $\boldsymbol{\Psi}$ given by the constitutive relations

$$\tilde{\eta} = \hat{\tilde{\eta}}(Y_e), \quad \boldsymbol{\Psi} = \hat{\boldsymbol{\Psi}}(Y_e), \tag{2.5}$$

as well as the multipliers

$$\boldsymbol{\lambda_u} = \hat{\boldsymbol{\lambda}}_{\boldsymbol{u}}(Y_e), \quad \lambda_\chi = \hat{\lambda}_\chi(Y_e), \quad \lambda_e = \hat{\lambda}_e(Y_e), \tag{2.6}$$

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

$$\begin{aligned} &\varrho_0\dot{\tilde{\eta}} + \nabla\cdot\boldsymbol{\Psi} - \boldsymbol{\lambda_u}\cdot(\varrho_0\ddot{\boldsymbol{u}} - \nabla\cdot\boldsymbol{S}) - \lambda_\chi(\varrho_0\dot{\chi} + \nabla\cdot\boldsymbol{j} - \varrho_0\tau) \\ &\quad - \lambda_e(\varrho_0\dot{e} + \nabla\cdot\boldsymbol{q} - \boldsymbol{S}\cdot\dot{\boldsymbol{F}}) \geq 0 \end{aligned} \tag{2.7}$$

is satisfied for all fields $\boldsymbol{u}$, χ and e. We remind that the notation $\tilde{\eta}$ instead of η indicates that the entropy is considered as a function of the internal energy e.

5.2.2. The implications of the entropy inequality. To evaluate the entropy inequallity (2.7) we impose three structural assumptions that parallel those in Subsection 5.1.3:

- The nondegeneracy condition for the entropy

$$\tilde{\eta}_{,e}(Y_e) > 0 \quad \text{for all variables } Y_e. \tag{2.8}$$

- The relation between stationary entropy, energy and phase variable fluxes

$$\boldsymbol{\Psi}^0 = \lambda_\chi^0 \boldsymbol{j}^0 + \lambda_e^0 \boldsymbol{q}^0, \tag{2.9}$$

  where $\boldsymbol{\Psi}^0$, $\boldsymbol{j}^0$, $\boldsymbol{q}^0$, λ_χ^0 and λ_e^0 denote stationary quantities defined by setting $\chi_{,t} = 0$ in the set Y_e, i.e.,

$$\boldsymbol{\Psi}^0 := \boldsymbol{\Psi}(Y^0, Y^1)|_{Y^1=\{0\}},$$

  and similarly for other quantities.
- Without loss of generality, we assume the splitting of the energy flux vector

$$\boldsymbol{q} = \boldsymbol{q}^0 - \chi_{,t}\boldsymbol{h}^e, \tag{2.10}$$

  where $\boldsymbol{q}^0 = \hat{\boldsymbol{q}}^0(Y^0)$ is a stationary heat flux, and $-\chi_{,t}\boldsymbol{h}^e$ is a nonstationary energy flux with $\boldsymbol{h}^e = \hat{\boldsymbol{h}}^e(Y_e)$ some constitutive vector quantity.

We remark that in view of the duality relations (cf., (3.5.8)) assumption (2.8) expresses the strict positivity of the inverse temperature $\vartheta = 1/\theta$. As already mentioned in Subsection 5.1.3 the relation (2.9) between stationary fluxes $\boldsymbol{\Psi}^0$, $\boldsymbol{j}^0$, and $\boldsymbol{q}^0$ is standard in the classical thermodynamics.

We prove the following

THEOREM 5.5 (Consistency with the entropy inequality). *Let us consider balance laws (2.1) with constitutive equations (2.2). Suppose that entropy inequality (2.5)–(2.7) is satisfied and assumptions (2.8)–(2.10) hold true. Then the following relations are satisfied:*

(i) *multiplier of the linear momentum* $\boldsymbol{\lambda_u} = \mathbf{0}$;

(ii) *entropy* $\tilde{\eta} = \hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e)$;

(iii) *multiplier of the energy equation*

$$\lambda_e = \hat{\lambda}_e(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e) = \tilde{\eta}_{,e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e) > 0; \tag{2.11}$$

(iv) *stress tensor*

$$\boldsymbol{S} = \hat{\boldsymbol{S}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e) = -\frac{1}{\lambda_e(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e)} \varrho_0 \tilde{\eta}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e); \tag{2.12}$$

(v) *entropy flux*

$$\boldsymbol{\Psi} = \lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q} - \chi_{,t} \left[\varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi} + \int_0^1 (\lambda_{\chi,\chi_{,t}} \boldsymbol{j})(Y^0, \tau\chi_{,t}) d\tau \right]; \tag{2.13}$$

(vi) *compatibility conditions*

$$\begin{aligned}
&\chi_{,t} \left[- \int_0^1 (\lambda_{\chi,\chi_{,t}} j_i)(Y^0, \tau\chi_{,t}) d\tau \right]_{,\boldsymbol{D}^M \boldsymbol{F}} + \lambda_{\chi,\boldsymbol{D}^M \boldsymbol{F}} j_i = \mathbf{0},\\
&\chi_{,t} \left[- \int_0^1 (\lambda_{\chi,\chi_{,t}} j_i)(Y^0, \tau\chi_{,t}) d\tau \right]_{,\boldsymbol{D}^K \chi} + \lambda_{\chi,\boldsymbol{D}^K \chi} j_i = \mathbf{0},\\
&\chi_{,t} \left[- \int_0^1 (\lambda_{\chi,\chi_{,t}} j_i)(Y^0, \tau\chi_{,t}) d\tau \right]_{,\boldsymbol{D}^L e} + \lambda_{\chi,\boldsymbol{D}^L e} j_i = \mathbf{0}
\end{aligned} \tag{2.14}$$

for $i = 1, 2, 3$.

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

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

$$-\varrho_0 \lambda_\chi = -\frac{\delta(\varrho_0 \tilde{\eta})}{\delta\chi} + \nabla^{\tilde{Y}^0} \cdot \int_0^1 (\lambda_{\chi,\chi_{,t}} \boldsymbol{j})(Y^0, \tau\chi_{,t}) d\tau + \nabla\lambda_e \cdot \boldsymbol{h}^e + a, \tag{2.15}$$

where, according to notation in Subsection 5.1.2,

$$\begin{aligned}
\tilde{Y}^0 &:= Y^0 \setminus \{\boldsymbol{D}^M \boldsymbol{F}, \boldsymbol{D}^K \chi, \boldsymbol{D}^L e\}\\
&= \{\boldsymbol{F}, \boldsymbol{DF}, \ldots, \boldsymbol{D}^{M-1}\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \ldots, \boldsymbol{D}^{K-1}\chi, e, \boldsymbol{D}e, \ldots, \boldsymbol{D}^{L-1}e\},\\
\frac{\delta(\varrho_0 \tilde{\eta})}{\delta\chi} &= \varrho_0 \tilde{\eta}_{,\chi} - \nabla \cdot (\varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi});
\end{aligned}$$

(viii) *the quantities* $r = \hat{r}(Y_e)$, $\boldsymbol{j} = \hat{\boldsymbol{j}}(Y_e)$, $\boldsymbol{q}^0 = \hat{\boldsymbol{q}}^0(Y^0)$ *and* $a = \hat{a}(Y_e)$ *satisfy the residual dissipation inequality*

$$\lambda_\chi \varrho_0 r + \nabla^{\tilde{Y}^0} \lambda_\chi \cdot \boldsymbol{j} + \nabla\lambda_e \cdot \boldsymbol{q}^0 + \chi_{,t} a \geq 0 \tag{2.16}$$

for all variables Y_e.

Proof. We use the same algebraic notation as in Subsection 5.1.2. By inserting constitutive equations (2.2), (2.5), (2.6) into entropy inequality (2.7) and applying the chain rule we arrive at the algebraic inequality:

$$\begin{aligned}&\sum_{m=0}^{M}\varrho_0\tilde{\eta}_{,\boldsymbol{D}^m\boldsymbol{F}}\cdot\boldsymbol{D}^m\boldsymbol{F}_{,t}+\sum_{k=0}^{K}\varrho_0\tilde{\eta}_{,\boldsymbol{D}^k\chi}\cdot\boldsymbol{D}^k\chi_{,t}+\sum_{l=0}^{L}\varrho_0\tilde{\eta}_{,\boldsymbol{D}^l e}\cdot\boldsymbol{D}^l e_{,t}\\&\quad+\varrho_0\tilde{\eta}_{,\chi_{,t}}\chi_{,tt}+\boldsymbol{\Psi}_{,\chi_{,t}}\cdot\boldsymbol{D}\chi_{,t}+\nabla^{Y^0}\cdot\boldsymbol{\Psi}-\varrho_0\boldsymbol{\lambda}_{\boldsymbol{u}}\cdot\boldsymbol{u}_{,tt}\\&\quad+\lambda_{\boldsymbol{u}}\cdot(\boldsymbol{S}_{,\chi_{,t}}\boldsymbol{D}\chi_{,t})+\lambda_{\boldsymbol{u}}\cdot(\nabla^{Y^0}\cdot\boldsymbol{S})-\lambda_\chi\varrho_0\chi_{,t}-\lambda_\chi\boldsymbol{j}_{,\chi_{,t}}\cdot\boldsymbol{D}\chi_{,t}\\&\quad-\lambda_\chi\nabla^{Y^0}\cdot\boldsymbol{j}+\lambda_\chi\varrho_0 r-\lambda_e\varrho_0 e_{,t}-\lambda_e\boldsymbol{q}_{,\chi_{,t}}\cdot\boldsymbol{D}\chi_{,t}-\lambda_e\nabla^{Y^0}\cdot\boldsymbol{q}+\lambda_e\boldsymbol{S}\cdot\boldsymbol{F}_{,t}\geq 0\end{aligned}\tag{2.17}$$

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

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

denotes the set of variables in which the left-hand side of (2.17) is linear. Further proof consists in deriving consequences from the linearity in the variables belonging to the set W. The proof will be divided into steps $1^\circ - 7^\circ$.

1° By the linearity of the left-hand side of (2.17) in $\boldsymbol{u}_{,tt}$ it follows that the coefficient preceding this variable has to vanish, i.e., $\boldsymbol{\lambda}_{\boldsymbol{u}} = \boldsymbol{0}$. This yields (i).

2° By the linearity in the variables $(\boldsymbol{D}^m\boldsymbol{F}_{,t})_{1\leq m\leq M}$, $(\boldsymbol{D}^k\chi_{,t})_{2\leq k\leq K}$, $(\boldsymbol{D}^l e_{,t})_{1\leq l\leq L}$, $\chi_{,tt}$ we read off that

$$\tilde{\eta}_{,\boldsymbol{D}^m\boldsymbol{F}}=\boldsymbol{0}\ \text{for}\ 1\leq m\leq M,\quad \tilde{\eta}_{,\boldsymbol{D}^k\chi}=\boldsymbol{0}\ \text{for}\ 2\leq k\leq K,\quad \tilde{\eta}_{,\boldsymbol{D}^l e}=\boldsymbol{0}\ \text{for}\ 1\leq l\leq L,$$

and $\tilde{\eta}_{,\chi_{,t}} = 0$.
Hence, the constitutive dependence of $\tilde{\eta}$ is restricted to $\tilde{\eta} = \hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e)$ which proves (ii).

3° Since $\varrho_0 > 0$, the linearity in $e_{,t}$ implies that

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

Hence, in view of (ii) and assumption (2.8) we conclude (iii).

4° By the linearity in $\boldsymbol{F}_{,t}$,

$$\varrho_0\tilde{\eta}_{,\boldsymbol{F}} + \lambda_e\boldsymbol{S} = \boldsymbol{0},$$

so, by virtue of (ii) and (iii) we infer (iv).

5° From the linearity in $\boldsymbol{D}\chi_{,t}$ we deduce that

$$\varrho_0\tilde{\eta}_{,\boldsymbol{D}\chi} + \boldsymbol{\Psi}_{,\chi_{,t}} - \lambda_\chi\boldsymbol{j}_{,\chi_{,t}} - \lambda_e\boldsymbol{q}_{,\chi_{,t}} = \boldsymbol{0}. \tag{2.18}$$

Next, let us define the vector

$$\tilde{\boldsymbol{\Psi}} := \boldsymbol{\Psi} - \lambda_\chi\boldsymbol{j} - \lambda_e\boldsymbol{q}. \tag{2.19}$$

By virtue of assumption (2.9),

$$\tilde{\boldsymbol{\Psi}}^0 = \boldsymbol{0}. \tag{2.20}$$

From (2.19), using (2.18) and (iii), we get

$$\begin{aligned}\tilde{\boldsymbol{\Psi}}_{,\chi,t} &= \boldsymbol{\Psi}_{,\chi,t} - \lambda_{\chi,\chi,t}\boldsymbol{j} - \lambda_\chi \boldsymbol{j}_{,\chi,t} - \lambda_e \boldsymbol{q}_{,\chi,t} \\ &= -\varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi} - \lambda_{\chi,\chi,t}\boldsymbol{j}.\end{aligned} \tag{2.21}$$

Hence, in view of (2.20), (ii) and (iii), it follows that

$$\begin{aligned}\tilde{\boldsymbol{\Psi}} &= -\varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi}\chi_{,t} - \int_0^{\chi_{,t}} (\lambda_{\chi,\chi,t}\boldsymbol{j})(Y^0, \xi)d\xi \\ &= -\chi_{,t}\left[\varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi} + \int_0^1 (\lambda_{\chi,\chi,t}\boldsymbol{j})(Y^0, \tau\chi_{,t})d\tau\right].\end{aligned} \tag{2.22}$$

From (2.19) and (2.22) we conclude (v).

6° It remains to examine the linearity in the variables $\boldsymbol{D}^{M+1}\boldsymbol{F}$, $\boldsymbol{D}^{K+1}\chi$ and $\boldsymbol{D}^{L+1}e$. On account of the results obtained in the previous steps, inequality (2.17) is reduced to

$$\varrho_0(\tilde{\eta}_{,\chi} - \lambda_\chi)\chi_{,t} + \lambda_\chi \varrho_0 r + \nabla^{Y^0} \cdot \boldsymbol{\Psi} - \lambda_\chi \nabla^{Y^0} \cdot \boldsymbol{j} - \lambda_e \nabla^{Y^0} \cdot \boldsymbol{q} \geq 0 \tag{2.23}$$

for all variables $\{\boldsymbol{D}^{M+1}\boldsymbol{F}, \boldsymbol{D}^{K+1}\chi, \boldsymbol{D}^{L+1}e, Y_e\}$. We rearrange now the sum of the last three terms on the left-hand side of (2.23) to the form

$$\begin{aligned}&\nabla^{Y^0} \cdot \boldsymbol{\Psi} - \lambda_\chi \nabla^{Y^0} \cdot \boldsymbol{j} - \lambda_e \nabla^{Y^0} \cdot \boldsymbol{q} \\ &= \nabla^{Y^0} \cdot (\boldsymbol{\Psi} - \lambda_\chi \boldsymbol{j} - \lambda_e \boldsymbol{q}) + \nabla^{Y^0}\lambda_\chi \cdot \boldsymbol{j} + \nabla^{Y^0}\lambda_e \cdot \boldsymbol{q} \\ &= \nabla^{Y^0} \cdot \tilde{\boldsymbol{\Psi}} + \nabla^{Y^0}\lambda_\chi \cdot \boldsymbol{j} + \nabla^{Y^0}\lambda_e \cdot \boldsymbol{q}.\end{aligned} \tag{2.24}$$

Next, using (2.22), recalling the definition of $\nabla^{Y^0}\cdot$ (see Subsection 5.1.2), it follows that

$$\nabla^{Y^0} \cdot \tilde{\boldsymbol{\Psi}} = -\chi_{,t}\left[\nabla^{Y^0} \cdot (\varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi}) + \nabla^{Y^0} \cdot \int_0^1 (\lambda_{\chi,\chi,t}\boldsymbol{j})(Y^0, \tau\chi_{,t})d\tau\right]. \tag{2.25}$$

By combining (2.24), (2.25), and using assumption (2.10) on $\boldsymbol{q}$, inequality (2.23) is transformed to the form

$$\begin{aligned}&\chi_{,t}\left[-\varrho_0\lambda_\chi + \varrho_0\tilde{\eta}_{,\chi} - \nabla^{Y^0} \cdot (\varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi}) - \nabla^{Y^0} \cdot \int_0^1 (\lambda_{\chi,\chi,t}\boldsymbol{j})(Y^0, \tau\chi_{,t})d\tau - \nabla^{Y^0}\lambda_e \cdot \boldsymbol{h}^e\right] \\ &\quad + \lambda_\chi \varrho_0 r + \nabla^{Y^0}\lambda_\chi \cdot \boldsymbol{j} + \nabla^{Y^0}\lambda_e \cdot \boldsymbol{q}^0 \geq 0\end{aligned} \tag{2.26}$$

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

From (2.26), performing differentiation by the chain rule in terms involving $\nabla^{Y^0}\cdot$ and ∇^{Y^0} (contracting now to the subset $\tilde{Y}^0$), the lineartiy in the variables $\boldsymbol{D}^{M+1}\boldsymbol{F}$, $\boldsymbol{D}^{K+1}\chi$ and $\boldsymbol{D}^{L+1}e$ implies that the coefficients preceding these variables have to vanish. Hence, recalling (ii) and (iii), we conclude (vi).

7° On account of (vi) inequality (2.26) becomes

$$\chi_{,t}\Big[-\varrho_0\lambda_\chi+\varrho_0\tilde{\eta}_{,\chi}-\nabla^{\tilde{Y}^0}\cdot(\varrho_0\tilde{\eta}_{,\boldsymbol{D}\chi})-\nabla^{\tilde{Y}^0}\cdot\int_0^1(\lambda_{\chi,\chi,_t}\boldsymbol{j})(Y^0,\tau\chi_{,t})d\tau-\nabla^{\tilde{Y}^0}\lambda_e\cdot\boldsymbol{h}^e\Big]$$
$$+\lambda_\chi\varrho_0 r+\nabla^{\tilde{Y}^0}\lambda_\chi\cdot\boldsymbol{j}+\nabla^{\tilde{Y}^0}\lambda_e\cdot\boldsymbol{q}^0\geq 0 \tag{2.27}$$

for all variables Y_e.

Now, let us define the scalar quantity $a=\hat{a}(Y_e)$ given by the squared parenthesis in (2.27), viz.

$$a:=-\varrho_0\lambda_\chi+\varrho_0\tilde{\eta}_{,\chi}-\nabla^{\tilde{Y}^0}\cdot(\varrho_0\tilde{\eta}_{,\boldsymbol{D}\chi})$$
$$-\nabla^{\tilde{Y}^0}\cdot\int_0^1(\lambda_{\chi,\chi,_t}\boldsymbol{j})(Y^0,\tau\chi_{,t})d\tau-\nabla^{\tilde{Y}^0}\lambda_e\cdot\boldsymbol{h}^e. \tag{2.28}$$

Let us note that on account of (ii) and (iii), recalling notation (1.12)–(1.15), we have

$$\nabla^{\tilde{Y}^0}\cdot(\varrho_0\tilde{\eta}_{,\boldsymbol{D}\chi})=\nabla\cdot(\varrho_0\tilde{\eta}_{,\boldsymbol{D}\chi}),\quad \nabla^{\tilde{Y}^0}\lambda_e=\nabla\lambda_e,$$
$$\frac{\delta^{\tilde{Y}^0}(\varrho_0\tilde{\eta})}{\delta\chi}=\varrho_0\tilde{\eta}_{,\chi}-\nabla\cdot(\varrho_0\tilde{\eta}_{,\boldsymbol{D}\chi})=\frac{\delta(\varrho_0\tilde{\eta})}{\delta\chi}.$$

Consequently, (2.28) becomes

$$a=-\varrho_0\lambda_\chi+\frac{\delta(\varrho_0\tilde{\eta})}{\delta\chi}-\nabla^{\tilde{Y}^0}\cdot\int_0^1(\lambda_{\chi,\chi,_t}\boldsymbol{j})(Y^0,\tau\chi_{,t})d\tau-\nabla\lambda_e\cdot\boldsymbol{h}^e. \tag{2.29}$$

This yields assertion (vii). Finally, by (2.29), inequality (2.27) takes the form of the residual inequality (2.16). This implies (viii) and thereby completes the proof. ∎

5.2.3. The implications in the nonconserved case. As in Subsection 5.1.4 it is of interest to distinguish thermodynamic restrictions in the nonconserved case $\boldsymbol{j}\equiv\boldsymbol{0}$. Then assumption (2.9) reduces to

$$\boldsymbol{\Psi}^0=\lambda_e^0\boldsymbol{q}^0, \tag{2.30}$$

and Theorem 5.5 specializes to

THEOREM 5.6 (Consistency with the entropy inequality in the nonconserved case). *Let us consider balance laws (2.1) with constitutive equations (2.2) in the nonconserved case* $\boldsymbol{j}\equiv\boldsymbol{0}$, $r\neq 0$. *Suppose that the entropy inequality (2.5)–(2.7) is satisfied and assumptions (2.8), (2.10), (2.30) hold true. Then the following relations are satisfied:*

(i) *multiplier of the linear momentum* $\boldsymbol{\lambda_u}=\boldsymbol{0}$;
(ii) *entropy* $\tilde{\eta}=\hat{\tilde{\eta}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,e)$;
(iii) *multiplier of the energy equation*

$$\lambda_e=\hat{\lambda}_e(\boldsymbol{F},\chi,\boldsymbol{D}\chi,e)=\tilde{\eta}_{,e}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,e)>0; \tag{2.31}$$

(iv) *stress tensor*

$$\boldsymbol{S} = \hat{\boldsymbol{S}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e) = -\frac{1}{\lambda_e(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e)} \varrho_0 \tilde{\eta}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e); \tag{2.32}$$

(v) *entropy flux*

$$\boldsymbol{\Psi} = \lambda_e \boldsymbol{q} - \chi_{,t} \varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi}. \tag{2.33}$$

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

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

$$-\varrho_0 \lambda_\chi = -\frac{\delta(\varrho_0 \tilde{\eta})}{\delta \chi} + \nabla \lambda_e \cdot \boldsymbol{h}^e + a; \tag{2.34}$$

(vii) *the quantities* $r = \hat{r}(Y_e)$, $\boldsymbol{q}^0 = \hat{\boldsymbol{q}}^0(Y^0)$ *and* $a = \hat{a}(Y_e)$ *satisfy the residual dissipation inequality*

$$\lambda_\chi \varrho_0 r + \nabla \lambda_e \cdot \boldsymbol{q}^0 + \chi_{,t} a \geq 0 \tag{2.35}$$

for all variables Y_e.

Proof. The assertions follow immediately from the proof Theorem 5.5 by setting $\boldsymbol{j} = \boldsymbol{0}$. ∎

6. Extended conserved and nonconserved phase-field models with multipliers as independent variables

On the basis of Theorems 5.1 and 5.5 we introduce two classes of extended phase-field models, $(PF)_\eta$ and $(PF)_e$, in which the multipliers λ_χ and λ_e are in addition to $\boldsymbol{u}$, χ, η, and to $\boldsymbol{u}$, χ and e, respectively, treated as independent variables. Then, due to the duality relations, we give equivalent formulations, $(PF)_\theta$ and $(PF)_\vartheta$, of models $(PF)_\eta$ and $(PF)_e$, with absolute temperature θ and inverse temperature $\vartheta = 1/\theta$ in place of η and e, respectively.

6.1. Phase-field model $(PF)_\eta$ with multipliers and entropy as independent variables.

6.1.1. Structural postulates. Regarding Theorem 5.1 (and Theorem 5.4 in the nonconserved case) we introduce the extended model in which the multipliers λ_χ and λ_e are in addition to $\boldsymbol{u}$, χ 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 two modifications of the statements of Theorem 5.1:

- We replace the state space Y_η in (5.1.3) by
$$\mathcal{Z}_\eta := \{\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \eta, D\eta, \lambda_\chi, \boldsymbol{D}\lambda_\chi, \lambda_e, \boldsymbol{D}\lambda_e, \chi_{,t}\}. \tag{1.1}$$
This set includes all variables which will appear in the extended model. In fact, since $\tilde{e} = \hat{\tilde{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$, the first variation $\delta(\varrho_0\tilde{e})/\delta\chi$ depends only on $\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \eta, D\eta$. Thus, the higher derivatives $\boldsymbol{D}^m\boldsymbol{F}, \boldsymbol{D}^k\chi, \boldsymbol{D}^l\eta$ for $m, l \geq 2$, $k \geq 3$ become irrelevant.
As for Y_η, we introduce the splitting
$$\mathcal{Z}_\eta = \{\mathcal{Z}^0_\eta, \mathcal{Z}^1_\eta\}$$
into the stationary part
$$\mathcal{Z}^0_\eta := \{\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \eta, D\eta, \lambda_\chi, \boldsymbol{D}\lambda_\chi, \lambda_e, \boldsymbol{D}\lambda_e\},$$
and the nonstationary one
$$\mathcal{Z}^1 := \{\chi_{,t}\}.$$
- Regarding λ_χ as an independent variable we set all expressions involving its derivatives with respect to $\chi_{,t}, \boldsymbol{D}^M\boldsymbol{F}, \boldsymbol{D}^K\chi, \boldsymbol{D}^L\eta$ identically equal zero and consequently replace the gradient $\nabla^{\tilde{Y}^0}\lambda_\chi$ contracted to variables $\tilde{Y}^0$ by the gradient $\nabla\lambda_\chi$.

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

($\tilde{v}$) $\boldsymbol{\Psi} = \lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q} + \chi_{,t}\varrho_0\lambda_e\tilde{e}_{,\boldsymbol{D}\chi}$;

($\widetilde{vii}$) $-\varrho_0\lambda_\chi = \lambda_e \frac{\delta(\varrho_0\tilde{e})}{\delta\chi} - \varrho_0\nabla\lambda_e\cdot\tilde{e}_{,\boldsymbol{D}\chi} + \nabla\lambda_e\cdot\boldsymbol{h}^e + a$;

($\widetilde{viii}$) the quantities $r = \hat{r}(\mathcal{Z}_\eta)$, $\boldsymbol{j} = \hat{\boldsymbol{j}}(\mathcal{Z}_\eta)$, $\boldsymbol{q}^0 = \hat{\boldsymbol{q}}^0(\mathcal{Z}^0_\eta)$ and $a = (\mathcal{Z}_\eta)$ satisfy the residual dissipation inequality

$$\lambda_\chi\varrho_0 r + \boldsymbol{D}\lambda_\chi\cdot\boldsymbol{j} + \boldsymbol{D}\lambda_e\cdot\boldsymbol{q}^0 + \chi_{,t}a \geq 0$$

for all variables $\mathcal{Z}_\eta$ in (1.1).

In Subsection 6.1.3 it will be proved that the above mentioned modifications lead to a model which is consistent with the second law of thermodynamics.

6.1.2. Formulation $(PF)_\eta$**.** The extended phase-field model, further referred to as $(PF)_\eta$, is based on the following postulates (i)–(iv):

$(PF)_\eta$ (i) The unknowns are the fields $\boldsymbol{u}$, χ, η, λ_χ and $\lambda_e > 0$.
$(PF)_\eta$ (ii) The state space is given by (1.1), i.e., $\mathcal{Z}_\eta = \{\mathcal{Z}^0_\eta, \mathcal{Z}^1_\eta\}$.
A thermodynamic potential is the internal energy

$$\tilde{e} = \hat{\tilde{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) \tag{1.2}$$

satisfying (in consistency with assumption (5.1.16)) the nondegeneracy condition

$$\tilde{e}_{,\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) > 0 \quad \text{for all arguments} \quad (\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta). \tag{1.3}$$

$(PF)_\eta$ (iii) The fields $\boldsymbol{u}$, χ, η, λ_χ and λ_e satisfy the system of differential equations

$$\begin{aligned}
&\varrho_0\ddot{\boldsymbol{u}} - \nabla\cdot\boldsymbol{S} = \varrho_0\boldsymbol{b},\\
&\varrho_0\dot{\chi} + \nabla\cdot\boldsymbol{j} - \varrho_0 r = \varrho_0\tau,\\
&-\varrho_0\lambda_\chi = \lambda_e\frac{\delta(\varrho_0\tilde{e})}{\delta\chi} - \nabla\lambda_e\cdot(\varrho_0\tilde{e}_{,\boldsymbol{D}\chi}) + \nabla\lambda_e\cdot\boldsymbol{h}^e + a\\
&\quad= \frac{\delta(\lambda_e\varrho_0\tilde{e})}{\delta\chi} + \nabla\lambda_e\cdot\boldsymbol{h}^e + a,\\
&\varrho_0\dot{\tilde{e}} + \nabla\cdot(\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S}\cdot\dot{\boldsymbol{F}} = \varrho_0 g,\\
&\lambda_e\tilde{e}_{,\eta} = 1,
\end{aligned} \tag{1.4}$$

where $\boldsymbol{S}$ is given by

$$\boldsymbol{S} = \varrho_0\tilde{e}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta), \tag{1.5}$$

consistent with the condition

$$\boldsymbol{S}\boldsymbol{F}^T = \boldsymbol{F}\boldsymbol{S}^T. \tag{1.6}$$

Moreover, the quantities $r = \hat{r}(\mathcal{Z}_\eta)$, $\boldsymbol{j} = \hat{\boldsymbol{j}}(\mathcal{Z}_\eta)$, $\boldsymbol{q}^0 = \hat{\boldsymbol{q}}^0(\mathcal{Z}^0_\eta)$ and $a = \hat{a}(\mathcal{Z}_\eta)$, with the state space $\mathcal{Z}_\eta$ given by (1.1), are subject to the residual dissipation inequality

$$\lambda_\chi\varrho_0 r + \boldsymbol{D}\lambda_\chi\cdot\boldsymbol{j} + \boldsymbol{D}\lambda_e\cdot\boldsymbol{q}^0 + \chi_{,t}a \geq 0 \tag{1.7}$$

to be satisfied for all variables $\mathcal{Z}_\eta$, of equivalently for all fields $\boldsymbol{u}$, χ, η, λ_χ and λ_e. The vector $\boldsymbol{h}^e = \hat{\boldsymbol{h}}^e(\mathcal{Z}_\eta)$ is an arbitrary quantity.

$(PF)_\eta$ (iv) In addition, according to the principle of frame invariance, the constitutive equations

$$\begin{aligned}
&\tilde{e} = \hat{\tilde{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta), \quad \boldsymbol{S} = \hat{\boldsymbol{S}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta),\\
&\xi = \hat{\xi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) := \tilde{e}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta),\\
&\boldsymbol{j} = \hat{\boldsymbol{j}}(\mathcal{Z}_\eta), \quad \boldsymbol{q}^0 = \hat{\boldsymbol{q}}^0(\mathcal{Z}^0_\eta), \quad \boldsymbol{h}^e = \hat{\boldsymbol{h}}^e(\mathcal{Z}_\eta) \quad r = \hat{r}(\mathcal{Z}_\eta), \quad a = \hat{a}(\mathcal{Z}_\eta)
\end{aligned}$$

are assumed to be invariant under changes in observer, i.e., under transformations

$$\begin{aligned}
&\tilde{e} \to \tilde{e}, \quad \boldsymbol{S} \to \boldsymbol{R}\boldsymbol{S}, \quad \boldsymbol{\xi} \to \boldsymbol{\xi}, \quad \boldsymbol{j} \to \boldsymbol{j}, \quad \boldsymbol{q}^0 \to \boldsymbol{q}^0, \quad \boldsymbol{h}^e \to \boldsymbol{h}^e, \quad r \to r, \quad a \to a,\\
&\{\boldsymbol{F}, \boldsymbol{D}\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \eta, \boldsymbol{D}\eta, \lambda_\chi, \boldsymbol{D}\lambda_\chi, \lambda_e, \boldsymbol{D}\lambda_e, \chi_{,t}\}\\
&\quad \to \{\boldsymbol{R}\boldsymbol{F}, \boldsymbol{D}(\boldsymbol{R}\boldsymbol{F}), \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \eta, \boldsymbol{D}\eta, \lambda_\chi, \boldsymbol{D}\lambda_\chi, \lambda_e, \boldsymbol{D}\lambda_e, \chi_{,t}\}
\end{aligned}$$

for all proper orthogonal tensors $\boldsymbol{R}$ ($\boldsymbol{R}\boldsymbol{R}^T = \boldsymbol{R}^T\boldsymbol{R} = \boldsymbol{I}$ with det $\boldsymbol{R} > 0$). This leads to the following restrictions (see, e.g., Gurtin [83, Sec. 4.2], Šilhavý [133, Chap. III. 9]):

$$\begin{aligned}
&\hat{\tilde{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) = \hat{\hat{\tilde{e}}}(\boldsymbol{C}, \chi, \boldsymbol{D}\chi, \eta),\\
&\hat{\boldsymbol{S}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) = \boldsymbol{F}\hat{\hat{\boldsymbol{S}}}(\boldsymbol{C}, \chi, \boldsymbol{D}\chi, \eta),\\
&\hat{\boldsymbol{\xi}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) = \hat{\hat{\boldsymbol{\xi}}}(\boldsymbol{C}, \chi, \boldsymbol{D}\chi, \eta),\\
&\hat{\boldsymbol{j}}(\mathcal{Z}_\eta) = \hat{\hat{\boldsymbol{j}}}(\bar{\mathcal{Z}}_\eta), \quad \hat{\boldsymbol{q}}^0(\mathcal{Z}^0_\eta) = \hat{\hat{\boldsymbol{q}}}^0(\bar{\mathcal{Z}}^0_\eta), \quad \hat{\boldsymbol{h}}^e(\mathcal{Z}_\eta) = \hat{\hat{\boldsymbol{h}}}^e(\bar{\mathcal{Z}}_\eta),\\
&\hat{r}(\mathcal{Z}_\eta) = \hat{\hat{r}}(\bar{\mathcal{Z}}_\eta), \quad \hat{a}(\mathcal{Z}_\eta) = \hat{\hat{a}}(\bar{\mathcal{Z}}_\eta),
\end{aligned} \tag{1.8}$$

where

$$\bar{\mathcal{Z}}_\eta := \{\boldsymbol{C}, \boldsymbol{D}\boldsymbol{C}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \eta, \boldsymbol{D}\eta, \lambda_\chi, \boldsymbol{D}\lambda_\chi, \lambda_e, \boldsymbol{D}\lambda_e, \chi_{,t}\} \equiv \bar{\mathcal{Z}}^0_\eta \cup \{\chi_{,t}\},$$

with $\boldsymbol{C} = \boldsymbol{F}^T\boldsymbol{F}$ the right Cauchy-Green strain tensor. We note that by virtue of $(1.8)_2$ condition (1.6) is automatically satisfied (see, Gurtin [83]).

6.1.3. Thermodynamical consistency. We shall prove that the phase-field model $(PF)_\eta$ is consistent with the second law of thermodynamics. More precisely, we shall prove that it satisfies the Müller-Liu entropy inequality with multipliers.

THEOREM 6.1. *System (1.4)–(1.6) with inequality constraint (1.7) satisfies the following entropy inequality with multipliers*

$$\begin{aligned}
&\varrho_0\dot{\eta} + \nabla\cdot\boldsymbol{\Psi} - \Lambda_u\cdot(\varrho_0\ddot{\boldsymbol{u}} - \nabla\cdot\boldsymbol{S}) - \Lambda_\chi(\varrho_0\dot{\chi} + \nabla\cdot\boldsymbol{j} - \varrho_0 r)\\
&\quad - \Lambda_{\lambda_\chi}[\varrho_0\lambda_\chi + \lambda_e\varrho_0\tilde{e}_{,\chi} - \nabla\cdot(\lambda_e\varrho_0\tilde{e}_{,\boldsymbol{D}\chi}) + \nabla\lambda_e\cdot\boldsymbol{h}^e + a]\\
&\quad\quad - \Lambda_e[\varrho_0\dot{\tilde{e}} + \nabla\cdot(\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S}\cdot\dot{\boldsymbol{F}}] - \Lambda_{\lambda_e}(\lambda_e\tilde{e}_{,\eta} - 1) - \Lambda_{\boldsymbol{S}}\cdot(\boldsymbol{S} - \varrho_0\tilde{e}_{,\boldsymbol{F}})\\
&\quad = \lambda_\chi\varrho_0 r + \nabla\lambda_\chi\cdot\boldsymbol{j} + \nabla\lambda_e\cdot\boldsymbol{q}^0 + \dot{\chi}a \geq 0
\end{aligned} \tag{1.9}$$

for all fields $\boldsymbol{u}$, χ, η, λ_χ, λ_e. The corresponding multipliers are given by

$$\begin{aligned}
&\Lambda_u = \boldsymbol{0}, \quad \Lambda_\chi = \lambda_\chi, \quad \Lambda_{\lambda_\chi} = -\dot{\chi},\\
&\Lambda_e = \lambda_e, \quad \Lambda_{\lambda_e} = -\varrho_0\dot{\eta}, \quad \Lambda_{\boldsymbol{S}} = \lambda_e\dot{\boldsymbol{F}},
\end{aligned} \tag{1.10}$$

and the entropy flux is

$$\begin{aligned}\boldsymbol{\Psi} &= \lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q} + \dot{\chi}\lambda_e \varrho_0 \tilde{e}_{,\boldsymbol{D}\chi} \\ &= \lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q}^0 + \dot{\chi}\lambda_e(\varrho_0 \tilde{e}_{,\boldsymbol{D}\chi} - \boldsymbol{h}^e).\end{aligned} \tag{1.11}$$

Proof. Let $\boldsymbol{u}$, χ, η, λ_χ, λ_e be any fields and Λ_u, Λ_χ, Λ_{λ_χ}, Λ_e, Λ_{λ_e}, $\Lambda_{\boldsymbol{S}}$ be defined by (1.10). Then, after simple rearrangements, one arrives at the following identities:

$$\begin{aligned}&\Lambda_u \cdot (\varrho_0 \ddot{\boldsymbol{u}} - \nabla \cdot \boldsymbol{S}) + \Lambda_\chi(\varrho_0 \dot{\chi} + \nabla \cdot \boldsymbol{j} - \varrho_0 r) \\ &\quad + \Lambda_{\lambda_\chi}[\varrho_0 \lambda_\chi + \lambda_e \varrho_0 \tilde{e}_{,\chi} - \nabla \cdot (\lambda_e \varrho_0 \tilde{e}_{,\boldsymbol{D}\chi}) + \nabla \lambda_e \cdot \boldsymbol{h}^e + a] \\ &\quad + \Lambda_e[\varrho_0 \dot{\tilde{e}} + \nabla \cdot (\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S} \cdot \boldsymbol{F}] + \Lambda_{\lambda_e}(\lambda_e \tilde{e}_{,\eta} - 1) \\ &\quad + \Lambda_{\boldsymbol{S}} \cdot (\boldsymbol{S} - \varrho_0 \tilde{e}_{,\boldsymbol{F}}) \\ &= \lambda_\chi(\varrho_0 \dot{\chi} + \nabla \cdot \boldsymbol{j} - \varrho_0 r) \\ &\quad - \dot{\chi}[\varrho_0 \lambda_\chi + \lambda_e \varrho_0 \tilde{e}_{,\chi} - \nabla \cdot (\lambda_e \varrho_0 \tilde{e}_{,\boldsymbol{D}\chi}) + \nabla \lambda_e \cdot \boldsymbol{h}^e + a] \\ &\quad + \lambda_e[\varrho_0 \tilde{e}_{,\boldsymbol{F}} \cdot \dot{\boldsymbol{F}} + \varrho_0 \tilde{e}_{,\chi}\dot{\chi} + \varrho_0 \tilde{e}_{,\boldsymbol{D}\chi} \cdot \nabla \dot{\chi} + \varrho_0 \tilde{e}_{,\eta}\dot{\eta} + \nabla \cdot (\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S} \cdot \dot{\boldsymbol{F}}] \\ &\quad - \varrho_0 \dot{\eta}(\lambda_e \tilde{e}_{,\eta} - 1) + \lambda_e \dot{\boldsymbol{F}} \cdot (\boldsymbol{S} - \varrho_0 \tilde{e}_{,\boldsymbol{F}}) \\ &= \varrho_0 \dot{\eta} + \nabla \cdot [\lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q}^0 + \dot{\chi}\lambda_e(\varrho_0 \tilde{e}_{,\boldsymbol{D}\chi} - \boldsymbol{h}^e)] \\ &\quad - \lambda_\chi \varrho_0 r - \nabla \lambda_\chi \cdot \boldsymbol{j} - \nabla \lambda_e \cdot \boldsymbol{q}^0 - \dot{\chi} a.\end{aligned}$$

This proves the equality in (1.9). The inequality in (1.9) results on account of the residual dissipation inequality (1.7). The proof is completed. ■

COROLLARY 6.2. *From (1.9) it follows that the solutions of system (1.4)–(1.6) with inequality constraint (1.7) (called thermodynamic processes) satisfy the following entropy equation and inequality*

$$\begin{aligned}\varrho_0 \dot{\eta} + \nabla \cdot \boldsymbol{\Psi} &= \lambda_\chi \varrho_0 r + \nabla \lambda_\chi \cdot \boldsymbol{j} + \nabla \lambda_e \cdot \boldsymbol{q}^0 + \dot{\chi} a + \lambda_\chi \varrho_0 \tau + \lambda_e \varrho_0 g \\ &\geq \lambda_\chi \varrho_0 \tau + \lambda_e \varrho_0 g\end{aligned} \tag{1.12}$$

with the entropy flux $\boldsymbol{\Psi}$ given by (1.11).
We point out that the structure of $\boldsymbol{\Psi}$ remains in compatibility with assumption (5.1.17) postulated in Theorem 5.1.

6.2. Phase-field model $(PF)_\theta$ with multipliers and absolute temperature as independent variables. In this section we shall express model $(PF)_\eta$ in terms of absolute temperature $\theta > 0$ as independent thermal variable and the Helmholtz free energy $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ as a thermodynamical potential. To this purpose, under an additional assumption on the internal energy $\tilde{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$, we apply the duality relations (3.5.6).

6.2.1. Transformation relations between entropy and absolute temperature. To apply the duality relations we assume the thermal stability condition, that is the strict positivity of the specific heat $c_{\boldsymbol{F}} = \hat{c}_{\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) > 0$ for all arguments $(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$. Then, by virtue of Lemma 3.6 on dual forms of the specific heat,

$$\begin{aligned}c_{\boldsymbol{F}} &= \hat{c}_{\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) = -\theta \hat{f}_{,\theta\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)|_{\theta = \hat{\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)} \\ &= \hat{\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) \frac{1}{\hat{\tilde{e}}_{,\eta\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)} > 0\end{aligned} \tag{2.1}$$

for all arguments $(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$. This shows explicitly that

$$\begin{aligned}&\text{the map } \eta \mapsto \hat{\tilde{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) \text{ is strictly convex,}\\ &\text{so the map } \eta \mapsto \hat{\tilde{e}}_{,\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) \text{ is strictly increasing.}\end{aligned} \tag{2.2}$$

Thus, from now on we shall assume that the internal energy $\tilde{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$ satisfies (2.2) in addition to the requirement (1.3), that is

$$\begin{aligned}&\tilde{e} = \hat{\tilde{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) \text{ is strictly convex as a function of } \eta,\\ &\text{and such that } \hat{\tilde{e}}_{,\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) > 0 \text{ for all arguments } (\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta).\end{aligned} \tag{2.3}$$

Under such assumption Lemma 3.3 yields the duality relations

$$\begin{aligned}&\hat{\tilde{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) - \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) = \theta\eta,\\ &\hat{\tilde{e}}_{,\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) = \theta.\end{aligned} \tag{2.4}$$

Hence, $(2.4)_2$ together with equality $(1.4)_5$ imply that

$$\lambda_e = \frac{1}{\tilde{e}_{,\eta}} = \frac{1}{\theta}, \tag{2.5}$$

which means that the energy multiplier can be identified with the inverse temperature. Clearly, the assumption $\hat{\tilde{e}}_{,\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) > 0$ is equivalent to $\theta > 0$.

Moreover, the requirement (2.2) means that

$$\begin{aligned}&\text{the map } \eta \mapsto \hat{\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) \text{ is strictly increasing,}\\ &\text{so there exists a well–defined inverse map } \theta \mapsto \hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta).\end{aligned} \tag{2.6}$$

Further, in view of equalities (2.1), the strict convexity of $\tilde{e} = \hat{\tilde{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$ with respect to η is equivalent to the strict concavity of $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ with respect to θ. Hence, the assumption (2.3) expressed in terms of the free energy f reads:

$$f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) \text{ is strictly concave with respect to } \theta > 0. \tag{2.7}$$

By virtue of Lemma 3.4, duality relations (2.4) are equivalent to

$$\begin{aligned}&\hat{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) - \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) = \theta\eta,\\ &\eta = \hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) = -\hat{f}_{,\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)\end{aligned} \tag{2.8}$$

with

$$\hat{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) = \hat{\tilde{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)).$$

Further, due to Lemma 3.8, the following equalities hold true:

$$\begin{aligned}&\hat{\tilde{e}}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) = \hat{f}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta),\\ &\hat{\tilde{e}}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) = \hat{f}_{,\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta),\\ &\hat{\tilde{e}}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) = \hat{f}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta),\\ &\frac{\delta\hat{\tilde{e}}}{\delta\chi}(\boldsymbol{F}, \boldsymbol{D}\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \eta, \boldsymbol{D}\eta) = \frac{\delta\hat{f}}{\delta\chi}(\boldsymbol{F}, \boldsymbol{D}\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta, \boldsymbol{D}\theta),\end{aligned} \tag{2.9}$$

where η, $\boldsymbol{D}\eta$ and θ, $\boldsymbol{D}\theta$ are related by the formulas

$$\begin{aligned}&\eta = \hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta),\\ &\eta_{,i} = \hat{\eta}_{,\boldsymbol{F}} \cdot \boldsymbol{F}_{,i} + \hat{\eta}_{,\chi}\chi_{,i} + \hat{\eta}_{,\boldsymbol{D}\chi} \cdot \boldsymbol{D}\chi_{,i} + \hat{\eta}_{,\theta}\theta_{,i}, \quad i = 1, 2, 3.\end{aligned} \tag{2.10}$$

Hence, the stress relation (1.5) transforms to

$$\boldsymbol{S} = \varrho_0 \hat{f}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta). \tag{2.11}$$

Let us transform now equation $(1.4)_3$ for the multiplier λ_χ. As already mentioned in Remark 5.3, we shall identify $-\lambda_\chi$ with the quantity $\bar{\mu}$, defined as a quotient of the chemical potential μ over absolute temperature θ:

$$-\lambda_\chi \equiv \bar{\mu} := \frac{\mu}{\theta}. \tag{2.12}$$

We call $\bar{\mu}$ the *rescaled chemical potential.*

Then, in view of (2.5) and (2.9), equation $(1.4)_3$ transforms to

$$\begin{aligned}
\varrho_0 \bar{\mu} &= \frac{1}{\theta}\frac{\delta(\varrho_0 f)}{\delta\chi} - \varrho_0 f_{,\boldsymbol{D}\chi} \cdot \nabla\frac{1}{\theta} + \nabla\frac{1}{\theta} \cdot \boldsymbol{h}^e + a \\
&= \frac{1}{\theta}[\varrho_0 f_{,\chi} - \nabla \cdot (\varrho_0 f_{,\boldsymbol{D}\chi})] - \varrho_0 f_{,\boldsymbol{D}\chi} \cdot \nabla\frac{1}{\theta} + \nabla\frac{1}{\theta} \cdot \boldsymbol{h}^e + a \\
&= \frac{\delta(\varrho_0 f/\theta)}{\delta\chi} + \nabla\frac{1}{\theta} \cdot \boldsymbol{h}^e + a.
\end{aligned} \tag{2.13}$$

Finally, let us note that on account of relations (2.5), (2.6), $(2.10)_2$ and (2.12), the state space

$$\mathscr{Z}_\eta = \{\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \eta, \boldsymbol{D}\eta, \lambda_\chi, \boldsymbol{D}\lambda_\chi, \lambda_e, \boldsymbol{D}\lambda_e, \chi_{,t}\}$$

in model $(PF)_\eta$ transforms to

$$\mathscr{Z}_\theta := \left\{\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta, \boldsymbol{D}\frac{1}{\theta}, \bar{\mu}, \boldsymbol{D}\bar{\mu}, \chi_{,t}\right\}, \quad \bar{\mu} = \frac{\mu}{\theta},$$

in model $(PF)_\theta$ expressed in terms of absolute temperature θ in place of entropy η.

6.2.2. Formulation $(PF)_\theta$**.** The presented relations allow to transform the phase-field model $(PF)_\eta$ into the following form $(PF)_\theta$ expressed in terms of θ as independent thermal variable:

$(PF)_\theta$ (i) The unknowns are the fields $\boldsymbol{u}$, χ, $\bar{\mu} = \mu/\theta$ and $\theta > 0$.

$(PF)_\theta$ (ii) The state space is given by

$$\mathscr{Z}_\theta = \left\{\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta, \boldsymbol{D}\frac{1}{\theta}, \bar{\mu}, \boldsymbol{D}\bar{\mu}, \chi_{,t}\right\} \equiv \mathscr{Z}^0_\theta \cup \{\chi_{,t}\}. \tag{2.14}$$

A thermodynamic potential is the free energy $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ which is strictly concave with respect to $\theta > 0$.

$(PF)_\theta$ (iii) The fields $\boldsymbol{u}$, χ, $\bar{\mu} = \mu/\theta$ and θ satisfy the system of differential equations

$$\begin{aligned}
&\varrho_0 \ddot{\boldsymbol{u}} - \nabla \cdot \boldsymbol{S} = \varrho_0 \boldsymbol{b}, \\
&\varrho_0 \dot{\chi} + \nabla \cdot \boldsymbol{j} - \varrho_0 r = \varrho_0 \tau, \\
&\varrho_0 \bar{\mu} = \frac{\delta(\varrho_0 f/\theta)}{\delta\chi} + \nabla\frac{1}{\theta} \cdot \boldsymbol{h}^e + a, \\
&\varrho_0 \dot{e} + \nabla \cdot (\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S} \cdot \dot{\boldsymbol{F}} = \varrho_0 g,
\end{aligned} \tag{2.15}$$

where

$$
\begin{aligned}
&e = \hat{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) + \theta\hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta),\\
&\eta = \hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) = -f_{,\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta),\\
&\frac{\delta(\varrho_0 f/\theta)}{\delta\chi} = \frac{\varrho_0 f_{,\chi}}{\theta} - \nabla\cdot\left(\frac{\varrho_0 f_{,\boldsymbol{D}\chi}}{\theta}\right),
\end{aligned}
\tag{2.16}
$$

and $\boldsymbol{S}$ is given by

$$
\boldsymbol{S} = \varrho_0 f_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta), \tag{2.17}
$$

consistent with the condition

$$
\boldsymbol{S}\boldsymbol{F}^T = \boldsymbol{F}\boldsymbol{S}^T. \tag{2.18}
$$

The functions $\varrho_0 = \varrho_0(\boldsymbol{X}) > 0$ and $\boldsymbol{b} = \boldsymbol{b}(\boldsymbol{X}, t)$, $\tau = \tau(\boldsymbol{X}, t)$, $g = g(\boldsymbol{X}, t)$, representing referential mass density and specific external sources, are given.

Moreover, the quantities $r = \hat{r}(\mathcal{Z}_\theta)$, $\boldsymbol{j} = \hat{\boldsymbol{j}}(\mathcal{Z}_\theta)$, $\boldsymbol{q}^0 = \hat{\boldsymbol{q}}^0(\mathcal{Z}_\theta^0)$ and $a = \hat{a}(\mathcal{Z}_\theta)$ are subject to the residual dissipation inequality

$$
-\bar{\mu}\varrho_0 r - \boldsymbol{D}\bar{\mu}\cdot\boldsymbol{j} + \boldsymbol{D}\frac{1}{\theta}\cdot\boldsymbol{q}^0 + \chi_{,t}a \equiv \varrho_0\sigma \geq 0 \tag{2.19}
$$

for all variables $\mathcal{Z}_\theta$, or equivalently, for all fields $\boldsymbol{u}$, χ, $\bar{\mu}$ and $\theta > 0$. The vector $\boldsymbol{h}^e = \hat{\boldsymbol{h}}^e(\mathcal{Z}_\theta)$ is an arbitrary quantity.

$(PF)_\theta$ (iv) The constitutive equations have to be invariant under changes in observer, as in (1.8).

REMARK 6.3. The characteristic feature of both models $(PF)_\eta$ and $(PF)_\theta$ is the presence of an "extra" nondissipative vector field $\boldsymbol{h}^e$ which contributes to the equations for the chemical potential and the energy balance but not to the residual dissipation inequality. In other words, the presence of such vector field does not change the entropy production but influences the structure of the model equations. In Chapter 7 we introduce some physically realistic examples of such vector field. These examples will be used in Part II to discuss relations of the presented models to other phase-field models well-known in the literature.

REMARK 6.4. It is seen that in both presented phase-field models $(PF)_\eta$ and $(PF)_\theta$ the fundamental problem is that of obtaining all solutions to the residual dissipation inequalities (1.7) and (2.19) and thereby all possible constitutive relations for the quantities r, $\boldsymbol{j}$, $\boldsymbol{q}^0$ and a. In particular, in the case of inequality (2.19) let us define the thermodynamic forces $\mathcal{X}$ and the thermodynamic fluxes $\mathcal{J}$ by

$$
\mathcal{X} := \left(\bar{\mu}, \boldsymbol{D}\bar{\mu}, \boldsymbol{D}\frac{1}{\theta}, \chi_{,t}\right), \quad \mathcal{J} := (-\varrho_0 r, -\boldsymbol{j}, \boldsymbol{q}^0, a), \tag{2.20}
$$

and identify the remaining variables from the set $\mathcal{Z}_\theta$, not belonging to $\mathcal{X}$, with the state variables

$$
\omega := (\boldsymbol{F}, \boldsymbol{D}\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta), \quad \text{so that } \{\mathcal{X}; \omega\} = \mathcal{Z}_\theta. \tag{2.21}
$$

Then (2.19) takes on the form of the standard thermodynamical inequality

$$
\begin{aligned}
\varrho_0\sigma &:= -\bar{\mu}\varrho_0 r - \boldsymbol{D}\bar{\mu}\cdot\boldsymbol{j} + \boldsymbol{D}\frac{1}{\theta}\cdot\boldsymbol{q}^0 + \chi_{,t}a\\
&= \mathcal{X}\cdot\mathcal{J}(\mathcal{X}; \omega) \geq 0
\end{aligned}
\tag{2.22}
$$

for all variables $\{\mathcal{X};\omega\} = \mathcal{Z}_\theta$, or equivalently, for all fields $\boldsymbol{u}$, χ, $\bar{\mu}$ and $\theta > 0$; σ is the specific entropy production.

The question of solving inequalities like (2.22) is addressed in Chapter 4 (see also Remark 6.6 below).

REMARK 6.5. The vector field $\boldsymbol{q}^0$ in dissipation inequalities (1.7) and (2.19) depends only on stationary variables $\mathcal{Z}_\eta^0$ and $\mathcal{Z}_\theta^0$, respectively, but not on $\chi_{,t}$. By the Curie's principle (see, e.g., De Groot [45, Chap 6]), for isotropic media tensors of rank differing by an odd integer cannot be coupled. Therefore, inequalities (1.7) and (2.19) exclude the case of anisotropic systems. It should be pointed out, however, that the presented models $(PF)_\eta$ and $(PF)_\theta$ can be generalized to the anisotropic case where the above mentioned coupling is allowed, that is vector $\boldsymbol{q}^0$ is replaced by $\boldsymbol{q}^d = \hat{\boldsymbol{q}}^d(\mathcal{Z}_\eta)$ in $(PF)_\eta$ and $\boldsymbol{q}^d = \hat{\boldsymbol{q}}^d(\mathcal{Z}_\theta)$ in $(PF)_\theta$. The superscript d means that the quantity is dissipative.

To be specific, we explain this for model $(PF)_\theta$. Let us assume that $\boldsymbol{h}^e = \boldsymbol{h}_1^e + \boldsymbol{h}_2^e$, where $\boldsymbol{h}_i = \hat{\boldsymbol{h}}_i(\mathcal{Z}_\theta)$, $i = 1, 2$, are arbitrary vector fields. Now let us define the quantities

$$\begin{aligned} r^d &:= \hat{r}(\mathcal{Z}_\theta), \quad \boldsymbol{j}^d := \hat{\boldsymbol{j}}(\mathcal{Z}_\theta), \quad \boldsymbol{q}^d = \hat{\boldsymbol{q}}^d(\mathcal{Z}_\theta) := \boldsymbol{q}^0 - \chi_{,t}\boldsymbol{h}_1^e, \\ a^d &= \hat{a}^d(\mathcal{Z}_\theta) := a + \boldsymbol{h}_1^e \cdot \boldsymbol{D}\frac{1}{\theta}. \end{aligned} \tag{2.23}$$

With the use of (2.23) system (2.15) reads as follows

$$\begin{aligned} &\varrho_0\ddot{\boldsymbol{u}} - \nabla\cdot\boldsymbol{S} = \varrho_0\boldsymbol{b}, \\ &\varrho_0\dot{\chi} + \nabla\cdot\boldsymbol{j}^d - \varrho_0 r^d = \varrho_0\tau, \\ &\varrho_0\bar{\mu} = \frac{\delta(\varrho_0 f/\theta)}{\delta\chi} + \nabla\frac{1}{\theta}\cdot\boldsymbol{h}_2^e + a^d, \\ &\varrho_0\dot{e} + \nabla\cdot(\boldsymbol{q}^d - \dot{\chi}\boldsymbol{h}_2^e) - \boldsymbol{S}\cdot\dot{\boldsymbol{F}} = \varrho_0 g. \end{aligned} \tag{2.24}$$

We see that (2.24) has the same structure as (2.15) except that now the quantities j^d, r^d and a^d can depend on the variables $\mathcal{Z}_\theta$ that admits anisotropic situation. Moreover, the dissipation inequality (2.19) remains unchanged, since

$$\begin{aligned} \varrho_0\sigma &:= -\bar{\mu}\varrho_0 r - \boldsymbol{D}\bar{\mu}\cdot\boldsymbol{j} + \boldsymbol{D}\frac{1}{\theta}\cdot\boldsymbol{q}^0 + \chi_{,t}a \\ &= -\bar{\mu}\varrho_0 r^d - \boldsymbol{D}\bar{\mu}\cdot\boldsymbol{j}^d + \boldsymbol{D}\frac{1}{\theta}\cdot\boldsymbol{q}^d + \chi_{,t}a^d \\ &\quad + \left[\boldsymbol{D}\frac{1}{\theta}\cdot(-\chi_{,t}\boldsymbol{h}_1^e) + \chi_{,t}\left(\boldsymbol{h}_1^e\cdot\boldsymbol{D}\frac{1}{\theta}\right)\right] \\ &= -\bar{\mu}\varrho_0 r^d - \boldsymbol{D}\bar{\mu}\cdot\boldsymbol{j}^d + \boldsymbol{D}\frac{1}{\theta}\cdot\boldsymbol{q}^d + \chi_{,t}a^d \geq 0. \end{aligned} \tag{2.25}$$

In conclusion, since $\boldsymbol{h}_2^e = \hat{\boldsymbol{h}}_2^e(\mathcal{Z}_\theta)$ is arbitrary, (2.24) and (2.25) prove the claim.

REMARK 6.6. It is of interest to relate the equalities in (2.25) to the Edelen decomposition theorem (see Lemma 4.1). Recalling (2.22), we have

$$\varrho_0\sigma = \mathcal{X}\cdot\mathcal{J}(\mathcal{X};\omega) \geq 0, \tag{2.26}$$

where $\mathcal{X}$ and $\mathcal{J}$ are defined by (2.20). By Edelen's decomposition theorem it is possible to substract from a vector field $\mathcal{J}$ a vector field $\mathcal{U}$ which does not contribute to the scalar product $\mathcal{X} \cdot \mathcal{J}$ in such a way that the resulting vector field $\mathcal{J}^d = \mathcal{J} - \mathcal{U}$ has a potential.

In the case of inequality (2.26) this implies that one may decompose each of the constitutive functions $\hat{r}$, $\hat{\boldsymbol{j}}$, $\hat{\boldsymbol{q}}$ and $\hat{a}$ into two parts

$$\begin{aligned} \hat{r}(\mathcal{Z}_\theta) &= \hat{r}^d(\mathcal{Z}_\theta) + \hat{r}^{nd}(\mathcal{Z}_\theta), \\ \hat{\boldsymbol{j}}(\mathcal{Z}_\theta) &= \hat{\boldsymbol{j}}^d(\mathcal{Z}_\theta) + \hat{\boldsymbol{j}}^{nd}(\mathcal{Z}_\theta), \\ \hat{\boldsymbol{q}}(\mathcal{Z}_\theta) &= \hat{\boldsymbol{q}}^d(\mathcal{Z}_\theta) + \hat{\boldsymbol{q}}^{nd}(\mathcal{Z}_\theta), \\ \hat{a}(\mathcal{Z}_\theta) &= \hat{a}^d(\mathcal{Z}_\theta) + \hat{a}^{nd}(\mathcal{Z}_\theta) \end{aligned} \tag{2.27}$$

in such a way that the quantities $\hat{r}^d$, $\hat{\boldsymbol{j}}^d$, $\hat{\boldsymbol{q}}^d$, $\hat{a}^d$, referred to as dissipative, have a dissipation potential while $\hat{r}^{nd}$, $\hat{\boldsymbol{j}}^{nd}$, $\hat{\boldsymbol{q}}^{nd}$, $\hat{a}^{nd}$, referred to as nondissipative ones, do not contribute to the entropy production. In particular, in (2.23) we set

$$r^{nd} = 0, \quad \boldsymbol{j}^{nd} = \boldsymbol{0}, \quad \boldsymbol{q}^{nd} = -\chi_{,t}\boldsymbol{h}_1^e, \quad a^{nd} = \boldsymbol{h}_1^e \cdot \boldsymbol{D}\frac{1}{\theta}. \tag{2.28}$$

Consequently, the dissipation inequality (2.26) is transformed to the following decomposed form

$$\begin{aligned} \varrho_0\sigma &= \mathcal{X} \cdot \mathcal{J}(\mathcal{X};\omega) \\ &= -\bar{\mu}\varrho_0 r^d - \boldsymbol{D}\bar{\mu} \cdot \boldsymbol{j}^d + \boldsymbol{D}\frac{1}{\theta} \cdot \boldsymbol{q}^d + \chi_{,t}a^d \\ &\quad + \left[\boldsymbol{D}\frac{1}{\theta} \cdot (-\chi_{,t}\boldsymbol{h}_1^e) + \chi_{,t}\left(\boldsymbol{h}_1^e \cdot \boldsymbol{D}\frac{1}{\theta}\right)\right] \\ &= \mathcal{X} \cdot (\mathcal{J}^d(\mathcal{X};\omega) + \mathcal{U}(\mathcal{X};\omega)) \\ &= \mathcal{X} \cdot \mathcal{J}^d(\mathcal{X};\omega), \end{aligned} \tag{2.29}$$

where

$$\mathcal{J}^d := (-\varrho_0 r^d, -\boldsymbol{j}^d, \boldsymbol{q}^d, a^d)$$

is the dissipative part of the thermodynamic fluxes $\mathcal{J}$, and

$$\mathcal{U} := \left(0, \boldsymbol{0}, -\chi_{,t}\boldsymbol{h}_1^e, \boldsymbol{h}_1^e \cdot \boldsymbol{D}\frac{1}{\theta}\right), \tag{2.30}$$

satisfying

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

is the nondissipative part. By Edelen's decomposition theorem $\mathcal{J}^d$ is characterized by

$$J^d(\mathcal{X};\omega) = \nabla_{\mathcal{X}}\mathcal{D}(\mathcal{X};\omega), \tag{2.31}$$

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

6.2.3. Thermodynamical consistency. Thermodynamical consistency (compatibility with the second law of thermodynamics) of model $(PF)_\theta$ can be deduced from the thermodynamical consistency of model $(PF)_\eta$, proved in Theorem 6.1.

For clarity we prove this fact directly.

THEOREM 6.7. *System (2.15)–(2.18) with inequality constraint (2.19) satisfies the following entropy inequality with multipliers*

$$\begin{aligned}
&\varrho_0\dot{\eta} + \nabla\cdot\boldsymbol{\Psi} - \Lambda_u\cdot(\varrho_0\ddot{\boldsymbol{u}} - \nabla\cdot\boldsymbol{S})\\
&\quad - \Lambda_\chi(\varrho_0\dot{\chi} + \nabla\cdot\boldsymbol{j} - \varrho_0 r)\\
&\quad - \Lambda_{\bar\mu}\Big(- \varrho_0\bar{\mu} + \frac{\varrho_0 f_{,\chi}}{\theta} - \nabla\cdot\Big(\frac{\varrho_0 f_{,\boldsymbol{D}\chi}}{\theta}\Big) + \nabla\frac{1}{\theta}\cdot\boldsymbol{h}^e + a\Big)\\
&\quad - \Lambda_e[\varrho_0\dot{e} + \nabla\cdot(\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S}\cdot\dot{\boldsymbol{F}}] - \Lambda_{\boldsymbol{S}}\cdot(\boldsymbol{S} - \varrho_0 f_{,\boldsymbol{F}})\\
&= -\bar{\mu}\varrho_0 r - \nabla\bar{\mu}\cdot\boldsymbol{j} + \nabla\frac{1}{\theta}\cdot\boldsymbol{q}^0 + \dot{\chi}a \geq 0
\end{aligned} \tag{2.32}$$

for all fields $\boldsymbol{u}$, χ, $\bar{\mu} = \mu/\theta$ *and* θ. *The multipliers are given by*

$$\Lambda_{\boldsymbol{u}} = \boldsymbol{0},\quad \Lambda_\chi = -\bar{\mu},\quad \Lambda_{\bar\mu} = -\dot{\chi},\quad \Lambda_e = \frac{1}{\theta},\quad \Lambda_{\boldsymbol{S}} = \frac{\dot{\boldsymbol{F}}}{\theta}, \tag{2.33}$$

and the entropy flux is

$$\begin{aligned}
\boldsymbol{\Psi} &= -\bar{\mu}\boldsymbol{j} + \frac{1}{\theta}\boldsymbol{q} + \dot{\chi}\frac{\varrho_0 f_{,\boldsymbol{D}\chi}}{\theta}\\
&= -\bar{\mu}\boldsymbol{j} + \frac{1}{\theta}\boldsymbol{q}^0 + \frac{\dot{\chi}}{\theta}(\varrho_0 f_{,\boldsymbol{D}\chi} - \boldsymbol{h}^e).
\end{aligned} \tag{2.34}$$

Proof. Let $\boldsymbol{u}$, χ, $\bar{\mu}$ and θ be any fields and Λ_u, Λ_χ, $\Lambda_{\bar\mu}$, λ_e and $\Lambda_{\boldsymbol{S}}$ be defined by (2.33). Then

$$\begin{aligned}
&\Lambda_{\boldsymbol{u}}\cdot(\varrho_0\ddot{\boldsymbol{u}} - \nabla\cdot\boldsymbol{S}) + \Lambda_\chi(\varrho_0\dot{\chi} + \nabla\cdot\boldsymbol{j} - \varrho_0 r)\\
&\quad + \Lambda_{\bar\mu}\Big(- \varrho_0\bar{\mu} + \frac{\varrho_0 f_{,\chi}}{\theta} - \nabla\cdot\Big(\frac{\varrho_0 f_{,\boldsymbol{D}\chi}}{\theta}\Big) + \nabla\frac{1}{\theta}\cdot\boldsymbol{h}^e + a\Big)\\
&\quad + \Lambda_e[\varrho_0\dot{e} + \nabla\cdot(\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S}\cdot\dot{\boldsymbol{F}}] + \Lambda_{\boldsymbol{S}}\cdot(\boldsymbol{S} - \varrho_0 f_{,\boldsymbol{F}})\\
&= -\bar{\mu}(\varrho_0\dot{\chi} + \nabla\cdot\boldsymbol{j} - \varrho_0 r) - \dot{\chi}\Big(- \varrho_0\bar{\mu} + \frac{\varrho_0 f_{,\chi}}{\theta} - \nabla\cdot\Big(\frac{\varrho_0 f_{,\boldsymbol{D}\chi}}{\theta}\Big) + \nabla\frac{1}{\theta}\cdot\boldsymbol{h}^e + a\Big)\\
&\quad + \frac{1}{\theta}[\varrho_0\dot{e} + \nabla\cdot(\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S}\cdot\dot{\boldsymbol{F}}] + \frac{\dot{\boldsymbol{F}}}{\theta}\cdot(\boldsymbol{S} - \varrho_0 f_{,\boldsymbol{F}}) \equiv R.
\end{aligned} \tag{2.35}$$

Taking into account that by $(2.16)_{1,2}$,

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

the right-hand side of (2.35) is after simple rearrangements transformed to the form

$$\begin{aligned}
R &= -\bar{\mu}\nabla\cdot\boldsymbol{j} + \bar{\mu}\varrho_0 r + \dot{\chi}\nabla\cdot\Big(\frac{\varrho_0 f_{,\boldsymbol{D}\chi}}{\theta}\Big) - \dot{\chi}\nabla\frac{1}{\theta}\cdot\boldsymbol{h}^e - \dot{\chi}a + \varrho_0\dot{\eta} + \frac{\varrho_0 f_{,\boldsymbol{D}\chi}}{\theta}\cdot\nabla\dot{\chi}\\
&\quad + \frac{1}{\theta}\nabla\cdot(\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e)\\
&= \varrho_0\dot{\eta} + \nabla\cdot\Big[- \bar{\mu}\boldsymbol{j} + \frac{1}{\theta}\boldsymbol{q}^0 + \frac{\dot{\chi}}{\theta}(\varrho_0 f_{,\boldsymbol{D}\chi} - \boldsymbol{h}^e)\Big] + \bar{\mu}\varrho_0 r + \nabla\bar{\mu}\cdot\boldsymbol{j} - \nabla\frac{1}{\theta}\cdot\boldsymbol{q}^0 - \dot{\chi}a.
\end{aligned}$$

This proves the equality in (2.32). The inequality in (2.32) is a consequence of (2.19). ∎

Now we collect some important, immediate implications of the above thorem.

COROLLARY 6.8. *The solutions of system (2.15)–(2.19) satisfy the entropy equation and inequality*

$$\varrho_0\dot{\eta} + \nabla\cdot\boldsymbol{\Psi} = \varrho_0\sigma - \bar{\mu}\varrho_0\tau + \frac{\varrho_0 g}{\theta} \geq -\bar{\mu}\varrho_0\tau + \frac{\varrho_0 g}{\theta} \tag{2.36}$$

with the entropy flux

$$\boldsymbol{\Psi} = -\bar{\mu}\boldsymbol{j} + \frac{1}{\theta}\boldsymbol{q}^0 + \frac{\dot{\chi}}{\theta}(\varrho_0 f_{,\boldsymbol{D}\chi} - \boldsymbol{h}^e),$$

and the entropy production (dissipation scalar)

$$\varrho_0\sigma = -\bar{\mu}\varrho_0 r - \nabla\bar{\mu}\cdot\boldsymbol{j} + \nabla\frac{1}{\theta}\cdot\boldsymbol{q}^0 + \dot{\chi}a \geq 0.$$

COROLLARY 6.9. *The solutions of system (2.15)–(2.19) satisfy the following free energy equation and inequality*

$$\begin{aligned} &\varrho_0\dot{f} + \nabla\cdot(\mu\boldsymbol{j} - \dot{\chi}\varrho_0 f_{,\boldsymbol{D}\chi}) - \boldsymbol{S}\cdot\dot{\boldsymbol{F}} + \varrho_0\eta\dot{\theta} + \boldsymbol{\Psi}\cdot\nabla\theta \\ &= -\theta\varrho_0\sigma + \mu\varrho_0\tau \leq \mu\varrho_0\tau, \end{aligned} \tag{2.37}$$

where

$$f = e - \theta\eta, \quad \mu = \theta\bar{\mu}, \quad \boldsymbol{S} = \varrho_0 f_{,\boldsymbol{F}},$$

and $\boldsymbol{\Psi}$, σ *are as in (2.36).*

Proof. The equality results by summing up energy equation $(2.15)_4$ and entropy equation (2.36) multiplied by $-\theta$. ■

COROLLARY 6.10. *The solutions of system (2.15)–(2.19) satisfy the so-called availability identity*

$$\begin{aligned} &\varrho_0\Big(e + \frac{1}{2}|\dot{\boldsymbol{u}}|^2 - \bar{\theta}\eta\Big)^{\cdot} + \nabla\cdot[-\boldsymbol{S}^T\dot{\boldsymbol{u}} + \boldsymbol{q} - \bar{\theta}\boldsymbol{\Psi}] \\ &= -\bar{\theta}\Big(-\frac{\mu}{\theta}\varrho_0 r - \nabla\frac{\mu}{\theta}\cdot\boldsymbol{j} + \nabla\frac{1}{\theta}\cdot\boldsymbol{q}^0 + \dot{\chi}a\Big) + \varrho_0\dot{\boldsymbol{u}}\cdot\boldsymbol{b} + \varrho_0 g - \bar{\theta}\varrho_0\Big(-\frac{\mu}{\theta}\tau + \frac{g}{\theta}\Big), \end{aligned} \tag{2.38}$$

where $\bar{\theta} = \text{const} > 0$, $\boldsymbol{q} = \boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e$.

Proof. Multiplying $(2.15)_1$ by $\dot{\boldsymbol{u}}$ we obtain the balance equation for the kinetic energy

$$\varrho_0\Big(\frac{1}{2}|\dot{\boldsymbol{u}}|^2\Big)^{\cdot} - \nabla\cdot(\boldsymbol{S}^T\dot{\boldsymbol{u}}) + \boldsymbol{S}\cdot\dot{\boldsymbol{F}} = \varrho_0\dot{\boldsymbol{u}}\cdot\boldsymbol{b}. \tag{2.39}$$

Summing up (2.39), energy equation $(2.15)_4$ and entropy equation (2.36) multiplied by $-\bar{\theta}$ we obtain (2.38). ■

COROLLARY 6.11. *The solutions of system (2.15)–(2.19) satisfy the Lyapunov relation. Namely, integration of availability identity (2.38) over* Ω *gives*

$$\begin{aligned}
&\frac{d}{dt}\int_\Omega \varrho_0\Big(e+\frac{1}{2}|\dot{\boldsymbol{u}}|^2-\bar{\theta}\eta\Big)dx\\
&+\int_S\Big[-(\boldsymbol{Sn})\cdot\dot{\boldsymbol{u}}+\boldsymbol{n}\cdot\boldsymbol{q}-\bar{\theta}\boldsymbol{n}\cdot\Big(-\frac{\mu}{\theta}\boldsymbol{j}+\frac{1}{\theta}\boldsymbol{q}+\dot{\chi}\frac{\varrho_0 f_{,\boldsymbol{D}\chi}}{\theta}\Big)\Big]dS\\
&=-\int_\Omega\bar{\theta}\Big(-\frac{\mu}{\theta}\varrho_0 r-\nabla\frac{\mu}{\theta}\cdot\boldsymbol{j}+\nabla\frac{1}{\theta}\cdot\boldsymbol{q}^0+\dot{\chi}a\Big)dx\\
&+\int_\Omega\varrho_0\Big[\dot{\boldsymbol{u}}\cdot\boldsymbol{b}+g-\bar{\theta}\Big(-\frac{\mu}{\theta}\tau+\frac{g}{\theta}\Big)\Big]dx\\
&\le\int_\Omega\varrho_0\Big[\dot{\boldsymbol{u}}\cdot\boldsymbol{b}+g-\bar{\theta}\Big(-\frac{\mu}{\theta}\tau+\frac{g}{\theta}\Big)\Big]dx,
\end{aligned}\tag{2.40}$$

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

$$\boldsymbol{b}=\boldsymbol{0},\quad g=0,\quad \tau=0,$$

and if the boundary conditions on S *imply that*

$$(\boldsymbol{Sn})\cdot\dot{\boldsymbol{u}}=0,\quad \frac{\mu}{\theta}\boldsymbol{n}\cdot\boldsymbol{j}=0,\quad \Big(1-\frac{\bar{\theta}}{\theta}\Big)\boldsymbol{n}\cdot(\boldsymbol{q}^0-\dot{\chi}\boldsymbol{h}^e)=0,\quad \frac{\dot{\chi}}{\theta}\boldsymbol{n}\cdot f_{,\boldsymbol{D}\chi}=0,\tag{2.41}$$

then solutions of system (2.15)–(2.19) satisfy the inequality

$$\frac{d}{dt}\int_\Omega\varrho_0\Big(e(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)+\frac{1}{2}|\dot{\boldsymbol{u}}|^2-\bar{\theta}\eta(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)\Big)dx\le 0.\tag{2.42}$$

This is the Lyapunov relation asserting that the function $\int\varrho_0\big(e+\frac{1}{2}|\dot{\boldsymbol{u}}|^2-\bar{\theta}\eta\big)dx$, *called equilibrium free energy, is nonincreasing on solutions paths.*

6.3. Phase-field model $(PF)_e$ with multipliers and internal energy as independent variables.

6.3.1. Structural postulates. On the basis of Theorem 5.5, following the same procedure as in Section 6.1, we introduce an extended model in which the multipliers λ_χ and λ_e join $\boldsymbol{u}$, χ and e as independent variables. Such idea is admissible because theorem has been proved under no assumptions on λ_χ and λ_e.

The extended model is based on the following two modifications of the statements of Theorem 5.5:

- The state space Y_e in (5.2.3) is replaced by

$$\mathcal{Z}_e:=\{\boldsymbol{F},\boldsymbol{DF},\chi,\boldsymbol{D}\chi,\boldsymbol{D}^2\chi,e,\boldsymbol{D}e,\lambda_\chi,\boldsymbol{D}\lambda_\chi,\lambda_e,\boldsymbol{D}\lambda_e,\chi_{,t}\}.\tag{3.1}$$

  This set includes the relevant variables for the extended model. In fact, since $\tilde{\eta}=\hat{\tilde{\eta}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,e)$, the first variation $\delta(\varrho_0\tilde{\eta})/\delta\chi$ depends only on $\boldsymbol{F},\boldsymbol{DF},\chi,\boldsymbol{D}\chi,\boldsymbol{D}^2\chi,e,\boldsymbol{D}e$. Thus, the higher derivatives $\boldsymbol{D}^m\boldsymbol{F},\boldsymbol{D}^k\chi,\boldsymbol{D}^l e$ for $m,l\ge 2$, $k\ge 3$

are irrelevant. As for Y_e, we split $\mathcal{Z}_e = \{\mathcal{Z}_e^0, \mathcal{Z}^1\}$ into the stationary part $\mathcal{Z}_e^0 := \{\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, e, \boldsymbol{D}e, \lambda_\chi, \boldsymbol{D}\lambda_\chi, \lambda_e, \boldsymbol{D}\lambda_e\}$ and the nonstationary one $\mathcal{Z}^1 := \{\chi_{,t}\}$.

- Regarding λ_χ not as a function but an independent variable, all expressions involving its derivatives with respect to $\chi_{,t}, \boldsymbol{D}^M\boldsymbol{F}, \boldsymbol{D}^K\chi, \boldsymbol{D}^L e$ are set to be equal zero, and the gradient $\nabla^{\tilde{Y}^0}\lambda_\chi$ contracted to the variables $\tilde{Y}^0$ is replaced by the gradient $\nabla\lambda_\chi$.

Formally, with such modifications the statements (i)–(iv) of Theorem 5.5 remain unchanged, (vi) is automatically satisfied and (v), (vii), (viii) are respectively replaced by the following:

$(\tilde{v})$ $\Psi = \lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q} - \chi_{,t}\varrho_0\tilde{\eta}_{,\boldsymbol{D}\chi}$;

$(\widetilde{vii})$ $-\varrho_0\lambda_\chi = -\frac{\delta(\varrho_0\tilde{\eta})}{\delta\chi} + \nabla\lambda_e \cdot \boldsymbol{h}^e + a$;

$(\widetilde{viii})$ the quantities $r = \hat{r}(\mathcal{Z}_e)$, $\boldsymbol{j} = \hat{\boldsymbol{j}}(\mathcal{Z}_e)$, $\boldsymbol{q}^0 = \hat{\boldsymbol{q}}^0(\mathcal{Z}_e^0)$ and $a = \hat{a}(\mathcal{Z}_e)$ satisfy the residual dissipation inequality

$$\lambda_\chi\varrho_0 r + \boldsymbol{D}\lambda_\chi \cdot \boldsymbol{j} + \boldsymbol{D}\lambda_e \cdot \boldsymbol{q}^0 + \chi_{,t} a \geq 0$$

for all variables $\mathcal{Z}_e$ in (3.1).

In the next subsection we shall prove that such structural midifications lead to a model which is consistent with the second law of thermodynamics.

6.3.2. Formulation $(PF)_e$. The extended phase-field model, referred further to as $(PF)_e$, is based on the following postulates:

$(PF)_e$ (i) The unknowsns are the fields $\boldsymbol{u}$, χ, e, λ_χ and $\lambda_e > 0$.

$(PF)_e$ (ii) The state space is given by (3.1). A thermodynamic potential is the entropy

$$\tilde{\eta} = \hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e) \tag{3.2}$$

subject to the condition (in consistency with assumption (5.2.8))

$$\tilde{\eta}_{,e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e) > 0 \quad \text{for all arguments} \quad (\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e). \tag{3.3}$$

$(PF)_e$ (iii) The fields $\boldsymbol{u}$, χ, e, λ_χ and λ_e satisfy the differential equations

$$\begin{aligned}
&\varrho_0\ddot{\boldsymbol{u}} - \nabla \cdot \boldsymbol{S} = \varrho_0 \boldsymbol{b},\\
&\varrho_0\dot{\chi} + \nabla \cdot \boldsymbol{j} - \varrho_0 r = \varrho_0 \tau,\\
&-\varrho_0\lambda_\chi = -\frac{\delta(\varrho_0\tilde{\eta})}{\delta\chi} + \nabla\lambda_e \cdot \boldsymbol{h}^e + a,\\
&\varrho_0\dot{e} + \nabla \cdot (\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S} \cdot \dot{\boldsymbol{F}} = \varrho_0 g,\\
&\lambda_e = \tilde{\eta}_{,e},
\end{aligned} \tag{3.4}$$

where $\boldsymbol{S}$ is given by

$$\boldsymbol{S} = -\frac{1}{\lambda_e}\varrho_0\tilde{\eta}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e), \tag{3.5}$$

consistent with the condition

$$\boldsymbol{S}\boldsymbol{F}^T = \boldsymbol{F}\boldsymbol{S}^T. \tag{3.6}$$

Moreover, the quantities $r = \hat{r}(\mathcal{Z}_e)$, $\boldsymbol{j} = \hat{\boldsymbol{j}}(\mathcal{Z}_e)$, $\boldsymbol{q}^0 = \hat{\boldsymbol{q}}^0(\mathcal{Z}_e^0)$ and $a = \hat{a}(\mathcal{Z}_e)$ are subject to the residual dissipation inequality

$$\lambda_\chi \varrho_0 r + \boldsymbol{D}\lambda_\chi \cdot \boldsymbol{j} + \boldsymbol{D}\lambda_e \cdot \boldsymbol{q}^0 + \chi_{,t} a \geq 0 \tag{3.7}$$

to be satisfied for all variables $\mathcal{Z}_e$, or equivalently for all fields $\boldsymbol{u}$, χ, e, λ_χ and λ_e. The vector $\boldsymbol{h}^e = \hat{\boldsymbol{h}}^e(\mathcal{Z}_e)$ is an arbitrary quantity.

$(PF)_e$ (iv) In addition, according to the principle of frame invariance, the constitutive equations

$$\begin{aligned}
&\tilde{\eta} = \hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e), \quad \boldsymbol{S} = \hat{\boldsymbol{S}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e),\\
&\boldsymbol{\xi} = \hat{\boldsymbol{\xi}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e) := \tilde{\eta}_{,\boldsymbol{D}\chi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e),\\
&\boldsymbol{j} = \hat{\boldsymbol{j}}(\mathcal{Z}_e), \quad \boldsymbol{q}^0 = \hat{\boldsymbol{q}}^0(\mathcal{Z}_e^0), \quad \boldsymbol{h}^e = \hat{\boldsymbol{h}}^e(\mathcal{Z}_e), \quad r = \hat{r}(\mathcal{Z}_e), \quad a = \hat{a}(\mathcal{Z}_e)
\end{aligned}$$

are assumed to be invariant under changes in observer, similarly as in (1.8).

6.3.3. Thermodynamical consistency. We shall prove that phase-field model $(PF)_e$ is consistent with the second law of thermodynamics.

THEOREM 6.12. *System (3.4)–(3.6) with inequality constraint (3.7) satisfies the following entropy inequality with multipliers*

$$\begin{aligned}
&\varrho_0[\tilde{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e)]^{\cdot} + \nabla \cdot \Psi - \Lambda_u \cdot (\varrho_0 \ddot{\boldsymbol{u}} - \nabla \cdot \boldsymbol{S}) - \Lambda_\chi(\varrho_0 \dot{\chi} + \nabla \cdot \boldsymbol{j} - \varrho_0 r)\\
&\quad - \Lambda_{\lambda_\chi}[\varrho_0 \lambda_\chi - \varrho_0 \tilde{\eta}_{,\chi} + \nabla \cdot (\varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi}) + \nabla\lambda_e \cdot \boldsymbol{h}^e + a]\\
&\quad - \Lambda_e[\varrho_0 \dot{e} + \nabla \cdot (\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S} \cdot \dot{\boldsymbol{F}}] - \Lambda_{\lambda_e}(\lambda_e - \tilde{\eta}_{,e}) - \Lambda_{\boldsymbol{S}} \cdot \left(\boldsymbol{S} + \frac{1}{\lambda_e}\varrho_0 \tilde{\eta}_{,\boldsymbol{F}}\right)\\
&= \lambda_\chi \varrho_0 r + \nabla\lambda_\chi \cdot \boldsymbol{j} + \nabla\lambda_e \cdot \boldsymbol{q}^0 + \dot{\chi} a \geq 0
\end{aligned} \tag{3.8}$$

for all fields $\boldsymbol{u}$, χ, e, λ_χ, λ_e. The corresponding multipliers are given by

$$\begin{aligned}
&\Lambda_u = \boldsymbol{0}, \quad \Lambda_\chi = \lambda_\chi, \quad \Lambda_{\lambda_\chi} = -\dot{\chi},\\
&\Lambda_e = \lambda_e, \quad \Lambda_{\lambda_e} = -\varrho_0 \dot{e}, \quad \Lambda_{\boldsymbol{S}} = \lambda_e \dot{\boldsymbol{F}},
\end{aligned} \tag{3.9}$$

and the entropy flux is

$$\begin{aligned}
\boldsymbol{\Psi} &= \lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q} - \dot{\chi} \varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi}\\
&= \lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q}^0 - \dot{\chi}(\varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi} + \boldsymbol{h}^e).
\end{aligned} \tag{3.10}$$

Proof. Let $\boldsymbol{u}$, χ, e, λ_χ, λ_e be any fields and Λ_u, Λ_χ, Λ_{λ_χ}, Λ_e, $\Lambda_{\boldsymbol{S}}$ be defined by (3.9).

Then simple rearrangements lead to the following identities:

$$
\begin{aligned}
&\Lambda_u \cdot (\varrho_0 \ddot{\boldsymbol{u}} - \nabla \cdot \boldsymbol{S}) + \Lambda_\chi(\varrho_0 \dot{\chi} + \nabla \cdot \boldsymbol{j} - \varrho_0 r) \\
&\quad + \Lambda_{\lambda_\chi}[\varrho_0 \lambda_\chi - \varrho_0 \tilde{\eta}_{,\chi} + \nabla \cdot (\varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi}) + \nabla \lambda_e \cdot \boldsymbol{h}^e + a] \\
&\quad + \Lambda_e[\varrho_0 \dot{e} + \nabla \cdot (\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S} \cdot \dot{\boldsymbol{F}}] \\
&\quad + \Lambda_{\lambda_e}(\lambda_e - \tilde{\eta}_{,e}) + \Lambda_{\boldsymbol{S}} \cdot \left(\boldsymbol{S} + \frac{1}{\lambda_e}\varrho_0 \tilde{\eta}_{,\boldsymbol{F}}\right) \\
&= \lambda_\chi(\varrho_0 \dot{\chi} + \nabla \cdot \boldsymbol{j} - \varrho_0 r) \\
&\quad - \dot{\chi}[\varrho_0 \lambda_\chi - \varrho_0 \tilde{\eta}_{,\chi} + \nabla \cdot (\varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi}) + \nabla \lambda_e \cdot \boldsymbol{h}^e + a] \\
&\quad + \lambda_e[\varrho_0 \dot{e} + \nabla \cdot (\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S} \cdot \dot{\boldsymbol{F}}] \\
&\quad - \varrho_0 \dot{e}(\lambda_e - \tilde{\eta}_{,e}) \\
&\quad + \lambda_e \dot{\boldsymbol{F}} \cdot \left(\boldsymbol{S} + \frac{1}{\lambda_e}\varrho_0 \tilde{\eta}_{,\boldsymbol{F}}\right) \\
&= \varrho_0 \tilde{\eta}_{,\boldsymbol{F}} \cdot \dot{\boldsymbol{F}} + \varrho_0 \tilde{\eta}_{,\chi}\dot{\chi} + \varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi} \cdot \nabla\dot{\chi} + \varrho_0 \tilde{\eta}_{,e}\dot{e} \\
&\quad + \nabla \cdot (\lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q} - \dot{\chi}\varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi}) - \lambda_\chi \varrho_0 r - \nabla\lambda_\chi \cdot \boldsymbol{j} - \nabla \lambda_e \cdot \boldsymbol{q} - \dot{\chi} a \\
&= \varrho_0[\tilde{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e)]^{\cdot} + \nabla \cdot \boldsymbol{\Psi} - \lambda_\chi \varrho_0 r - \nabla \lambda_\chi \cdot \boldsymbol{j} - \nabla \lambda_e \cdot \boldsymbol{q}^0 - \dot{\chi} a.
\end{aligned}
$$

This establishes the equality in (3.8). The inequality in (3.8) is a consequence of residual dissipation inequality (3.7). The proof is completed. ∎

COROLLARY 6.13. *From (3.8) it follows that solutions of system (3.4)–(3.7) satisfy the following entropy equation and inequality*

$$
\begin{aligned}
\varrho_0[\tilde{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e)]^{\cdot} + \nabla \cdot \boldsymbol{\Psi} &= \lambda_\chi \varrho_0 r + \nabla \lambda_\chi \cdot \boldsymbol{j} + \nabla \lambda_e \cdot \boldsymbol{q}^0 + \dot{\chi} a + \lambda_\chi \varrho_0 \tau + \lambda_e \varrho_0 g \\
&\geq \lambda_\chi \varrho_0 \tau + \lambda_e \varrho_0 g,
\end{aligned} \tag{3.11}
$$

where the entropy flux $\boldsymbol{\Psi}$ *is given by (3.10).*

6.4. Phase-field model $(PF)_\vartheta$ with multipliers and inverse temperature as independent variables. In this section we shall express model $(PF)_e$ in terms of the inverse temperature $\vartheta = 1/\theta > 0$ as independent thermal variable and the rescaled free energy (see (3.1.3))

$$
\phi = \hat{\phi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) := \vartheta \hat{f}\left(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \frac{1}{\vartheta}\right)
$$

as a thermodynamical potential. This will be accomplished with the help of the duality relations (3.5.8) under additional assumption on the entropy potential $\tilde{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e)$.

6.4.1. Transformation relations between internal energy and inverse temperature. To apply the duality relations we shall assume the thermal stability condition, that is strict positivity of the specific heat

$$
\bar{c}_{\boldsymbol{F}} = \hat{c}_{\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) := \hat{c}_{\boldsymbol{F}}\left(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \frac{1}{\vartheta}\right) > 0
$$

for all arguments $(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)$. Then, due to Lemma 3.6, this condition admits the following form in terms of the internal energy $\bar{e} = e$ as independent variable (we remind that the distinction between $\bar{e}$ and e is meaningless if energy is treated as a variable; we use $\bar{e}$ in consistency with the notation in Chapter 3):

$$\begin{aligned}\hat{\bar{c}}_{\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) &= \hat{c}_{\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)|_{\vartheta=\hat{\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e})} \\ &= -\hat{\vartheta}^2 \hat{\phi}_{,\vartheta\vartheta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)|_{\vartheta=\hat{\vartheta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e})} \\ &= -\hat{\vartheta}^2(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) \frac{1}{\hat{\tilde{\eta}}_{,\bar{e}\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})} > 0\end{aligned} \tag{4.1}$$

for all $(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})$. This demonstrates explicitly that

$$\begin{aligned}&\text{the map} \quad \bar{e} \mapsto \hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) \quad \text{is strictly concave,} \\ &\text{so the map} \quad \bar{e} \mapsto \hat{\tilde{\eta}}_{,\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) \quad \text{is strictly decreasing.}\end{aligned} \tag{4.2}$$

For notational consistency with Chapter 3 let us set now $\bar{e}$ in place of e everywhere in the formulation of phase-field model $(PF)_e$.

Let us assume that the entropy $\tilde{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})$ satisfies (4.2) in addition to the requirement (3.3), viz.

$$\begin{aligned}&\tilde{\eta} = \hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) \quad \text{is strictly concave as a function of} \quad \bar{e}, \\ &\text{and such that} \quad \tilde{\eta}_{,\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) > 0 \quad \text{for all arguments} \quad (\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}).\end{aligned} \tag{4.3}$$

Under such assumption Lemma 3.3 yields the duality relations

$$\begin{aligned}\hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) + \hat{\phi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) &= \vartheta\bar{e}, \\ \hat{\tilde{\eta}}_{,\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) &= \vartheta.\end{aligned} \tag{4.4}$$

Hence, (4.4) together with equality $(3.4)_5$ imply that

$$\lambda_e = \tilde{\eta}_{,\bar{e}} = \vartheta, \tag{4.5}$$

which means that the energy multiplier can be identified with the inverse temperature. Clearly, then the assumption $\tilde{\eta}_{,\bar{e}} > 0$ is equivalent to $\vartheta > 0$.

Moreover, the requirement (4.2) means that

$$\begin{aligned}&\text{the map} \quad \bar{e} \mapsto \hat{\vartheta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e}) \quad \text{is strictly decreasing,} \\ &\text{so there exists a well–defined inverse map} \quad \vartheta \mapsto \hat{\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta).\end{aligned} \tag{4.6}$$

From the equalities (4.1) it follows that the strict concavity of $\tilde{\eta} = \hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \bar{e})$ with respect to $\bar{e}$ is equivalent to the strict concavity of $\phi = \hat{\phi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)$ with respect to ϑ. Hence, assumption (4.3) expressed in terms of the rescaled free energy ϕ reads as follows:

$$\phi = \hat{\phi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) \quad \text{is strictly concave with respect to} \quad \vartheta > 0. \tag{4.7}$$

By virtue of Lemma 3.4, duality relations (4.4) are equivalent to

$$\begin{aligned}\hat{\phi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) + \hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) &= \vartheta\bar{e}, \\ \bar{e} = \hat{\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) &= \hat{\phi}_{,\vartheta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)\end{aligned} \tag{4.8}$$

with

$$\hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) = \hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \hat{\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)).$$

Further, due to Lemma 3.8, the following equalities hold:

$$
\begin{aligned}
&-\hat{\bar{\eta}}_{,\boldsymbol{F}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e}) = \hat{\phi}_{,\boldsymbol{F}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta),\\
&-\hat{\bar{\eta}}_{,\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e}) = \hat{\phi}_{,\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta),\\
&-\hat{\bar{\eta}}_{,\boldsymbol{D}\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\bar{e}) = \hat{\phi}_{,\boldsymbol{D}\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta),\\
&-\frac{\delta\hat{\bar{\eta}}}{\delta\chi}(\boldsymbol{F},\boldsymbol{DF},\chi,\boldsymbol{D}\chi,\boldsymbol{D}^2\chi,\bar{e},\boldsymbol{D}\bar{e}) = \frac{\delta\hat{\phi}}{\delta\chi}(\boldsymbol{F},\boldsymbol{DF},\chi,\boldsymbol{D}\chi,\boldsymbol{D}^2\chi,\vartheta,\boldsymbol{D}\vartheta),
\end{aligned}
\tag{4.9}
$$

where $\bar{e}$, $\boldsymbol{D}\bar{e}$ and ϑ, $\boldsymbol{D}\vartheta$ are related by the formulas

$$
\begin{aligned}
&\bar{e} = \hat{e}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta),\\
&\bar{e}_{,i} = \hat{e}_{,\boldsymbol{F}}\cdot\boldsymbol{F}_{,i} + \hat{e}_{,\chi}\chi_{,i} + \hat{e}_{,\boldsymbol{D}\chi}\cdot\boldsymbol{D}\chi_{,i} + \hat{e}_{,\vartheta}\vartheta_{,i}, \quad i=1,2,3.
\end{aligned}
\tag{4.10}
$$

By (4.5) and $(4.9)_1$, stress tensor equation (3.5) transforms to

$$
\boldsymbol{S} = \frac{1}{\vartheta}\varrho_0\hat{\phi}_{,\boldsymbol{F}}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta). \tag{4.11}
$$

Let us turn now to equation $(3.4)_3$ for the multiplier λ_χ. Similarly as in Section 6.2 (see (2.12)) we shall identify $-\lambda_\chi$ with the rescaled chemical potential:

$$
-\lambda_\chi \equiv \bar{\mu} := \vartheta\mu. \tag{4.12}
$$

Then, on account of (4.9) and (4.5), equation $(3.4)_3$ transforms to

$$
\varrho_0\bar{\mu} = \frac{\delta(\varrho_0\phi)}{\delta\chi} + \nabla\vartheta\cdot\boldsymbol{h}^e + a. \tag{4.13}
$$

Finally, note that in view of relations (4.5), (4.6), $(4.10)_2$ and (4.12), the state space

$$
\mathcal{Z}_{\bar{e}} = \{\boldsymbol{F},\boldsymbol{DF},\chi,\boldsymbol{D}\chi,\boldsymbol{D}^2\chi,\bar{e},\boldsymbol{D}\bar{e},\lambda_\chi,\boldsymbol{D}\lambda_\chi,\lambda_e,\boldsymbol{D}\lambda_e,\chi_{,t}\}
$$

in phase-field model $(PF)_e$ transforms to

$$
\mathcal{Z}_\vartheta = \{\boldsymbol{F},\boldsymbol{DF},\chi,\boldsymbol{D}\chi,\boldsymbol{D}^2\chi,\vartheta,\boldsymbol{D}\vartheta,\bar{\mu},\boldsymbol{D}\bar{\mu},\chi_{,t}\}, \quad \bar{\mu}=\vartheta\mu,
$$

in model $(PF)_\vartheta$ expressed in terms of inverse temperature ϑ in place of energy $\bar{e}$.

6.4.2. Formulation $(PF)_\vartheta$. On account of the presented transformation relations phase-field model $(PF)_e$ takes on the following form $(PF)_\vartheta$ in terms of the inverse temperature ϑ as independent thermal variable:

$(PF)_\vartheta$ (i) The unknowns are the fields $\boldsymbol{u}$, χ, $\bar{\mu}=\vartheta\mu$ and $\vartheta>0$.
$(PF)_\vartheta$ (ii) The state space is given by

$$
\mathcal{Z}_\vartheta = \{\boldsymbol{FDF},\chi,\boldsymbol{D}\chi,\boldsymbol{D}^2\chi,\vartheta,\boldsymbol{D}\vartheta,\bar{\mu},\boldsymbol{D}\bar{\mu},\chi_{,t}\} \equiv \mathcal{Z}^0_\vartheta \cup \{\chi_{,t}\}. \tag{4.14}
$$

A thermodynamic potential is the rescaled free energy $\phi = \hat{\phi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\vartheta)$, which is strictly concave with respect to ϑ.
$(PF)_\vartheta$ (iii) The fields $\boldsymbol{u}$, χ, $\bar{\mu}=\vartheta\mu$ and ϑ satisfy the system of differential equations

$$
\begin{aligned}
&\varrho_0\ddot{\boldsymbol{u}} - \nabla\cdot\boldsymbol{S} = \varrho_0\boldsymbol{b},\\
&\varrho_0\dot{\chi} + \nabla\cdot\boldsymbol{j} - \varrho_0 r = \varrho_0\tau,\\
&\varrho_0\bar{\mu} = \frac{\delta(\varrho_0\phi)}{\delta\chi} + \nabla\vartheta\cdot\boldsymbol{h}^e + a,\\
&\varrho_0\dot{\bar{e}} + \nabla\cdot(\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S}\cdot\dot{\boldsymbol{F}} = \varrho_0 g,
\end{aligned}
\tag{4.15}
$$

where

$$
\begin{aligned}
&\bar e = \hat e(\boldsymbol F,\chi,\boldsymbol D\chi,\vartheta) = \hat\phi_{,\vartheta}(\boldsymbol F,\chi,\boldsymbol D\chi,\vartheta),\\
&\phi(\boldsymbol F,\chi,\boldsymbol D\chi,\vartheta) + \hat{\bar\eta}(\boldsymbol F,\chi,\boldsymbol D\chi,\vartheta) = \vartheta\hat{\bar e}(\boldsymbol F,\chi,\boldsymbol D\chi,\vartheta),\\
&\frac{\delta(\varrho_0\phi)}{\delta\chi} = \varrho_0\phi_{,\chi} - \nabla\cdot(\varrho_0\phi_{,\boldsymbol D\chi}),
\end{aligned}
\tag{4.16}
$$

and $\boldsymbol S$ is given by

$$
\boldsymbol S = \frac{1}{\vartheta}\varrho_0\phi_{,\boldsymbol F}(\boldsymbol F,\chi,\boldsymbol D\chi,\vartheta),
\tag{4.17}
$$

consistent with the condition

$$
\boldsymbol S\boldsymbol F^T = \boldsymbol F\boldsymbol S^T.
\tag{4.18}
$$

The functions $\varrho_0 = \varrho_0(\boldsymbol X) > 0$, $\boldsymbol b = \boldsymbol b(\boldsymbol X,t)$ and $\tau = \tau(\boldsymbol X,t)$ are given. Moreover, the quantities $r = \hat r(\mathcal Z_\vartheta)$, $\boldsymbol j = \hat{\boldsymbol j}(\mathcal Z_\vartheta)$, $\boldsymbol q^0 = \hat{\boldsymbol q}^0(\mathcal Z_\vartheta^0)$ and $a = \hat a(\mathcal Z_\vartheta)$ are subject to the residual dissipation inequality

$$
-\bar\mu\varrho_0 r - \boldsymbol D\bar\mu\cdot\boldsymbol j + \boldsymbol D\vartheta\cdot\boldsymbol q^0 + \chi_{,t}a \ge 0
\tag{4.19}
$$

for all variables $\mathcal Z_\vartheta$, or equvalently, for all fields $\boldsymbol u$, χ, $\bar\mu$ and $\vartheta > 0$. The vector $\boldsymbol h^e = \hat{\boldsymbol h}^e(\mathcal Z_\vartheta)$ is an arbitrary quantity.
$(PF)_\vartheta$ (iv) The constitutive equations have to be invariant under changes in observer, as in (1.8).

6.4.3. Thermodynamical consistency. In analogy to Theorem 6.7 we have

THEOREM 6.14. *System (4.15)–(4.19) with inequality constraint (4.19) satisfies the following entropy inequality with multipliers*

$$
\begin{aligned}
&\varrho_0\dot{\bar\eta} + \nabla\cdot\Psi - \Lambda_{\boldsymbol u}\cdot(\varrho_0\ddot{\boldsymbol u} - \nabla\cdot\boldsymbol S)\\
&\quad - \Lambda_\chi(\varrho_0\dot\chi + \nabla\cdot\boldsymbol j - \varrho_0 r)\\
&\quad - \Lambda_{\bar\mu}[-\varrho_0\bar\mu + \varrho_0\phi_{,\chi} - \nabla\cdot(\varrho_0\phi_{,\boldsymbol D\chi}) + \nabla\vartheta\cdot\boldsymbol h^e + a]\\
&\quad - \Lambda_e[\varrho_0\dot{\bar e} + \nabla\cdot(\boldsymbol q^0 - \dot\chi\boldsymbol h^e) - \boldsymbol S\cdot\dot{\boldsymbol F}]\\
&\quad - \Lambda_{\boldsymbol S}\cdot\left(\boldsymbol S - \frac{1}{\vartheta}\varrho_0\phi_{,\boldsymbol F}\right)\\
&= -\bar\mu\varrho_0 r - \nabla\bar\mu\cdot\boldsymbol j + \nabla\vartheta\cdot\boldsymbol q^0 + \dot\chi a \ge 0
\end{aligned}
\tag{4.20}
$$

for all fields $\boldsymbol u$, χ, $\bar\mu = \vartheta\mu$ and ϑ. The multipliers are given by

$$
\Lambda_{\boldsymbol u} = \boldsymbol 0,\quad \Lambda_\chi = -\bar\mu,\quad \Lambda_{\bar\mu} = -\dot\chi,\quad \Lambda_e = \vartheta,\quad \Lambda_{\boldsymbol S} = \vartheta\dot{\boldsymbol F},
\tag{4.21}
$$

and the entropy flux is

$$
\begin{aligned}
\Psi &= -\bar\mu\boldsymbol j + \vartheta\boldsymbol q + \dot\chi\varrho_0\phi_{,\boldsymbol D\chi}\\
&= -\bar\mu\boldsymbol j + \vartheta\boldsymbol q^0 + \dot\chi(\varrho_0\phi_{,\boldsymbol D\chi} - \vartheta\boldsymbol h^e).
\end{aligned}
\tag{4.22}
$$

Proof. Let u, χ, $\bar\mu$ and ϑ be any fields and $\Lambda_{\boldsymbol u}$, Λ_χ, $\Lambda_{\bar\mu}$, Λ_e and $\Lambda_{\boldsymbol S}$ be defined by (4.21).

Then

$$\begin{aligned}
&\Lambda_{\boldsymbol{u}} \cdot (\varrho_0 \ddot{\boldsymbol{u}} - \nabla \cdot \boldsymbol{S}) + \Lambda_\chi(\varrho_0 \dot{\chi} + \nabla \cdot \boldsymbol{j} - \varrho_0 r) + \Lambda_{\bar{\mu}}[-\varrho_0 \bar{\mu} + \varrho_0 \phi_{,\chi} - \nabla \cdot (\varrho_0 \phi_{,\boldsymbol{D}\chi}) \\
&\quad + \nabla\vartheta \cdot \boldsymbol{h}^e + a] + \Lambda_e[\varrho_0 \dot{\bar{e}} + \nabla \cdot (\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S} \cdot \dot{\boldsymbol{F}}] + \Lambda_{\boldsymbol{S}} \cdot \left(\boldsymbol{S} - \frac{1}{\vartheta}\varrho_0 \phi_{,\boldsymbol{F}}\right) \\
&= -\bar{\mu}(\varrho_0 \dot{\chi} + \nabla \cdot \boldsymbol{j} - \varrho_0 r) - \dot{\chi}[-\varrho_0 \bar{\mu} + \varrho_0 \phi_{,\chi} - \nabla \cdot (\varrho_0 \phi_{,\boldsymbol{D}\chi}) + \nabla\vartheta \cdot \boldsymbol{h}^e + a] \\
&\quad + \vartheta[\varrho_0 \dot{\bar{e}} + \nabla \cdot (\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S} \cdot \dot{\boldsymbol{F}}] + \vartheta \dot{\boldsymbol{F}} \cdot \left(\boldsymbol{S} - \frac{1}{\vartheta}\varrho_0 \phi_{,\boldsymbol{F}}\right) \equiv \mathcal{R}.
\end{aligned} \tag{4.23}$$

Taking into account that by relations $(4.16)_{1,2}$,

$$\begin{aligned}
\vartheta \dot{\bar{e}} &= \dot{\phi} + \dot{\bar{\eta}} - \bar{e}\dot{\vartheta} \\
&= \phi_{,\boldsymbol{F}} \cdot \dot{\boldsymbol{F}} + \phi_{,\chi}\dot{\chi} + \phi_{,\boldsymbol{D}\chi} \cdot \nabla\dot{\chi} + \phi_{,\vartheta}\dot{\vartheta} + \dot{\bar{\eta}} - \bar{e}\dot{\vartheta} \\
&= \dot{\bar{\eta}} + \phi_{,\boldsymbol{F}} \cdot \dot{\boldsymbol{F}} + \phi_{,\chi}\dot{\chi} + \phi_{,\boldsymbol{D}\chi} \cdot \nabla\dot{\chi},
\end{aligned}$$

the right-hand side (4.23) is transformed to the form

$$\begin{aligned}
\mathcal{R} &= -\bar{\mu}\nabla \cdot \boldsymbol{j} + \bar{\mu}\varrho_0 r + \dot{\chi}\nabla \cdot (\varrho_0 \phi_{,\boldsymbol{D}\chi}) - \dot{\chi}\nabla\vartheta \cdot \boldsymbol{h}^e - \dot{\chi}a + \varrho_0 \dot{\bar{\eta}} + \varrho_0 \phi_{,\boldsymbol{D}\chi} \cdot \nabla\dot{\chi} \\
&\quad + \vartheta\nabla \cdot (\boldsymbol{q}^0 - \dot{\chi}\boldsymbol{h}^e) \\
&= \varrho_0 \dot{\bar{\eta}} + \nabla \cdot [-\bar{\mu}\boldsymbol{j} + \vartheta \boldsymbol{q}^0 + \dot{\chi}(\varrho_0 \phi_{,\boldsymbol{D}\chi} - \vartheta \boldsymbol{h}^e)] + \bar{\mu}\varrho_0 r + \nabla\bar{\mu} \cdot \boldsymbol{j} - \nabla\vartheta \cdot \boldsymbol{q}^0 - \dot{\chi}a.
\end{aligned}$$

This proves the equality in (4.20). The inequality in (4.20) is a consequence of the residual dissipation inequality (4.19). ∎

6.4.4. Equivalance of models $(PF)_\vartheta$ and $(PF)_\theta$.

LEMMA 6.15. *Formulations $(PF)_\vartheta$ and $(PF)_\theta$ are equivalent.*

Proof. The equivalance results immediately on account of the following statements:
– the definitions of ϑ and ϕ

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

– the strict concavity of $\hat{\phi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)$ in ϑ is equivalent to the strict concavity of $\hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ in θ (by Lemma 3.2);
– the relations $(4.16)_{2,3}$ between $\hat{\bar{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)$, $\hat{\bar{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)$ and $\hat{\phi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)$ are equivalent to relations $(2.16)_{2,3}$ between $\hat{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$, $\hat{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ and $\hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ (by Lemma 3.1);
– the equalities

$$\begin{aligned}
&\frac{\delta(\varrho_0 \phi)}{\delta\chi} = \varrho_0 \phi_{,\chi} - \nabla \cdot (\varrho_0 \phi_{,\boldsymbol{D}\chi}) = \frac{\varrho_0 f_{,\chi}}{\theta} - \nabla \cdot \left(\frac{\varrho_0 f_{,\boldsymbol{D}\chi}}{\theta}\right) = \frac{\delta(\varrho_0 f/\theta)}{\delta\chi}, \\
&\boldsymbol{S} = \frac{1}{\vartheta}\phi_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) = f_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta), \\
&\bar{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) = e(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta), \quad \theta = 1/\vartheta.
\end{aligned}$$

∎

6.4.5. Concluding remarks.

1° We have presented four phase-field models, $(PF)_\eta$, $(PF)_e$, $(PF)_\theta$ and $(PF)_\vartheta$ expressed correspondignly in terms of entropy η, internal energy e, temperature θ and inverse temperature $\vartheta = 1/\theta$ as independent thermal variables.

The remaining independent variables in these models are the fields of displacement $\boldsymbol{u}$, phase variable χ, and the multipliers λ_e, λ_χ conjugated with equations of balance of energy and phase variable. In models $(PF)_\theta$ and $(PF)_\vartheta$ the multiplier λ_e is identified with the inverse temperature, $\lambda_e = 1/\theta = \vartheta$, and negative of the multiplier λ_χ with the rescaled chemical potential, $-\lambda_\chi \equiv \bar{\mu} = \mu/\theta = \vartheta\mu$, where μ is the chemical potential.

The thermodynamic potentials in models $(PF)_\eta$, $(PF)_e$, $(PF)_\theta$ and $(PF)_\vartheta$ are correspondingly the internal energy $\tilde{e} = \hat{\tilde{e}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$, the entropy $\tilde{\eta} = \hat{\tilde{\eta}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e)$, the free energy $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ and the rescaled free energy $\phi = \hat{\phi}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta)$.

2° Models $(PF)_\eta$ and $(PF)_e$ are more general than $(PF)_\theta$ and $(PF)_\vartheta$ in the sense of the imposed assumptions on the thermodynamic potentials.

The potentials in models $(PF)_\eta$ and $(PF)_e$ are required to satisfy the nondegeneracy conditions:

- in model $(PF)_\eta$

$$\hat{\tilde{e}}_{,\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) > 0 \quad \text{for all} \quad (\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta);$$

- in model $(PF)_e$

$$\hat{\tilde{\eta}}_{,e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e) > 0 \quad \text{for all} \quad (\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e).$$

The potentials in models $(PF)_\theta$ and $(PF)_\vartheta$ are required to satisfy in addition to the nondegeneracy conditions the concavity assumptions which ensure the validity of the duality relations, namely:

- in model $(PF)_\theta$

$$\hat{f}_{,\theta\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) < 0 \quad \text{for all} \quad (\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) \quad \text{and} \quad \theta > 0;$$

- in model $(PF)_\vartheta$

$$\hat{\phi}_{,\vartheta\vartheta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) < 0 \quad \text{for all} \quad (\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta) \quad \text{and} \quad \vartheta > 0.$$

Models $(PF)_\eta$ and $(PF)_e$ are equivalent to $(PF)_\theta$ and $(PF)_\vartheta$ provided the potentials $\tilde{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta)$ and $\tilde{\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e)$ satisfy the following conditions:

- in model $(PF)_\eta$

$$\hat{\tilde{e}}_{,\eta\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) > 0 \quad \text{and} \quad \hat{\tilde{e}}_{,\eta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta) > 0 \quad \text{for all} \quad (\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta);$$

- in model $(PF)_e$

$$\hat{\tilde{\eta}}_{,ee}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e) < 0 \quad \text{and} \quad \hat{\tilde{\eta}}_{,e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e) > 0 \quad \text{for all} \quad (\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e).$$

3° The presented models are thermodynamically consistent in the sense of satisfying the second law of thermodynamics. The characteristic feature of all models is the presence of an "extra" nondissipative vector field $\boldsymbol{h}^e$ which contributes to the nonstationary (depending on the time derivative of the phase variable) energy and entropy fluxes, $\boldsymbol{q}$ and $\boldsymbol{\Psi}$, as well as to the equation for the multiplier λ_χ (identified with the rescaled chemical potential). This vector field $\boldsymbol{h}^e$ is nondissipative, that is not restricted by the second law of thermodynamics. Thus, it can be selected arbitrarily in consistency with frame invariance and other physical requirements.

In all models the entropy flux $\boldsymbol{\Psi}$ contains an extra nonequilibrium term associated with the gradient part of the corresponding thermodynamic potential and the vector $\boldsymbol{h}^e$:

- in model $(PF)_\eta$

$$\begin{aligned}\boldsymbol{\Psi} &= \lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q} + \dot{\chi}\lambda_e \varrho_0 \tilde{e}_{,\boldsymbol{D}\chi} \\ &= \lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q}^0 + \dot{\chi}\lambda_e(\varrho_0 \tilde{e}_{,\boldsymbol{D}\chi} - \boldsymbol{h}^e),\end{aligned}$$

where λ_e and λ_χ are the multipliers conjugated with the equations of balance of energy and the phase variable, given by

$$\begin{aligned}\lambda_e &= \frac{1}{\tilde{e}_{,\eta}}, \\ -\varrho_0\lambda_\chi &= \lambda_e \frac{\delta(\varrho_0 \tilde{e})}{\delta\chi} - \nabla\lambda_e \cdot (\varrho_0 \tilde{e}_{,\boldsymbol{D}\chi}) + \nabla\lambda_e \cdot \boldsymbol{h}^e + a;\end{aligned}$$

- in model $(PF)_e$

$$\begin{aligned}\boldsymbol{\Psi} &= \lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q} - \dot{\chi}\varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi} \\ &= \lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q}^0 - \dot{\chi}(\varrho_0 \tilde{\eta}_{,\boldsymbol{D}\chi} + \boldsymbol{h}^e),\end{aligned}$$

where

$$\begin{aligned}\lambda_e &= \tilde{\eta}_{,e}, \\ -\varrho_0\lambda_\chi &= -\frac{\delta(\varrho_0 \tilde{\eta})}{\delta\chi} + \nabla\lambda_e \cdot \boldsymbol{h}^e + a;\end{aligned}$$

- in model $(PF)_\theta$

$$\begin{aligned}\boldsymbol{\Psi} &= \lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q} + \dot{\chi}\, \lambda_e \varrho_0 f_{,\boldsymbol{D}\chi} \\ &= \lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q}^0 + \dot{\chi}\lambda_e(\varrho_0 f_{,\boldsymbol{D}\chi} - \boldsymbol{h}^e),\end{aligned}$$

where the multipliers λ_e and λ_χ are identified with the inverse temperature and the rescaled chemical potential

$$\begin{aligned}\lambda_e &= \frac{1}{\theta}, \quad -\lambda_\chi \equiv \bar{\mu} = \frac{\mu}{\theta}, \\ \varrho_0\bar{\mu} &= \frac{\delta(\varrho_0 f/\theta)}{\delta\chi} + \nabla\frac{1}{\theta} \cdot \boldsymbol{h}^e + a;\end{aligned}$$

- in model $(PF)_\vartheta$

$$\begin{aligned}\boldsymbol{\Psi} &= \lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q} + \dot{\chi}\varrho_0 \phi_{,\boldsymbol{D}\chi} \\ &= \lambda_\chi \boldsymbol{j} + \lambda_e \boldsymbol{q}^0 + \dot{\chi}(\varrho_0 \phi_{,\boldsymbol{D}\chi} - \vartheta\boldsymbol{h}^e), \\ \lambda_e &= \vartheta, \quad -\lambda_\chi \equiv \bar{\mu} = \vartheta\mu, \\ \varrho_0\bar{\mu} &= \frac{\delta(\varrho_0 \phi)}{\delta\chi} + \nabla\vartheta \cdot \boldsymbol{h}^e + a.\end{aligned}$$

In all models the quantity a in the equations for the multiplier λ_χ (correspondingly for the rescaled chemical potential $\bar{\mu}$) represents an additive dissipative part, determined by the residual dissipation inequality

$$\lambda_\chi \varrho_0 r + \boldsymbol{D}\lambda_\chi \cdot \boldsymbol{j} + \boldsymbol{D}\lambda_e \cdot \boldsymbol{q}^0 + \chi_{,t} a \geq 0$$

to be satisfied for all corresponding independent variables.

4° According to the choice of the independent thermal variable the referential stress tensor $\boldsymbol{S}$ admits the following forms:

- in model $(PF)_\eta$

$$\boldsymbol{S} = \varrho_0 \tilde{e}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \eta);$$

- in model $(PF)_e$

$$\boldsymbol{S} = -\frac{1}{\tilde{\eta}_{,e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e)} \varrho_0 \tilde{\eta}_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, e);$$

- in model $(PF)_\theta$

$$\boldsymbol{S} = \varrho_0 f_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta);$$

- in model $(PF)_\vartheta$

$$\boldsymbol{S} = \frac{1}{\vartheta} \varrho_0 \phi_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \vartheta).$$

7. Physically realistic examples of model $(PF)_\theta$. Special cases

In literature it is common to use the absolute temperature as the independent thermal variable. For this reason in this chapter we shall focus our attention on the extended phase-field model $(PF)_\theta$. We present physically realistic examples of this model which depend on the specific choice of the extra vector field $\boldsymbol{h}^e$. These examples will be used in Part II to discuss relations of model $(PF)_\theta$ to well-known phase-field models with conserved and nonconserved order parameters. Moreover, for further reference we present separately the model $(PF)_\theta$ with suppressed elastic effects and with suppressed thermal effects.

7.1. Phase-field model $(PF)_\theta$ in anisotropic case. Taking into account Remark 6.5 let us give the formulation of model $(PF)_\theta$ admitting anisotropic situation, that is admitting that tensors of rank differing by an odd integer are allowed to be coupled. We note that the corresponding field equations have been already given by (6.2.24) with $\boldsymbol{h}^e = \boldsymbol{h}^e(\mathcal{Z}_\theta)$ an arbitrary vector field.

Here let us express the model explicitly.

The state space is specified by

$$\mathcal{Z}_\theta = \left\{ \boldsymbol{F}, \boldsymbol{D}\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta, \boldsymbol{D}\frac{1}{\theta}, \bar{\mu}, \boldsymbol{D}\bar{\mu}, \chi_{,t} \right\}, \tag{1.1}$$

where $\theta > 0$ and $\bar{\mu} = \mu/\theta$. The model is governed by two thermodynamic potentials, the free energy $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ which is strictly concave with respect to θ for all $\boldsymbol{F}, \chi, \boldsymbol{D}\chi$, and the dissipation potential $\mathcal{D} = \hat{\mathcal{D}}(\mathcal{X}; \boldsymbol{\omega})$ with

$$\begin{aligned} &\mathcal{X} := \left(\bar{\mu}, \boldsymbol{D}\bar{\mu}, \boldsymbol{D}\frac{1}{\theta}, \chi_{,t} \right), \\ &\boldsymbol{\omega} := (\boldsymbol{F}, \boldsymbol{D}\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta), \quad \{\mathcal{X}; \boldsymbol{\omega}\} = \mathcal{Z}_\theta, \end{aligned} \tag{1.2}$$

which is nonnegative, convex in $\mathcal{X}$ and such that $\mathcal{D}(\boldsymbol{0}; \boldsymbol{\omega}) = 0$. The set $\mathcal{X}$ is identified with thermodynamic forces and the set $\boldsymbol{\omega}$ with state variables.

The unknowns are the fields of displacement $\boldsymbol{u}$, the order parameter χ, the rescaled chemical potential $\bar{\mu} = \mu/\theta$ and the absolute temperature $\theta > 0$ satisfying the system of differential equations:

$$
\begin{aligned}
&\varrho_0 \ddot{\boldsymbol{u}} - \nabla \cdot \boldsymbol{S} = \varrho_0 \boldsymbol{b}, \\
&\varrho_0 \dot{\chi} + \nabla \cdot \boldsymbol{j}^d - \varrho_0 r^d = \varrho_0 \tau, \\
&\varrho_0 \bar{\mu} = \frac{\delta(\varrho_0 f/\theta)}{\delta \chi} + \boldsymbol{h}^e \cdot \nabla \frac{1}{\theta} + a^d, \\
&\varrho_0 \dot{e} + \nabla \cdot (\boldsymbol{q}^d - \dot{\chi} \boldsymbol{h}^e) - \boldsymbol{S} \cdot \dot{\boldsymbol{F}} = \varrho_0 g,
\end{aligned} \tag{1.3}
$$

where $e = \hat{e}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ and $\boldsymbol{S} = \hat{S}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ are determined by the relations

$$
\begin{aligned}
&e = f(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta) - \theta f_{,\theta}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta), \\
&\boldsymbol{S} = \varrho_0 f_{,\boldsymbol{F}}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta), \quad \text{satisfying} \quad \boldsymbol{S}\boldsymbol{F}^T = \boldsymbol{F}\boldsymbol{S}^T,
\end{aligned} \tag{1.4}
$$

and $r^d = \hat{r}^d(\mathcal{X}, \boldsymbol{\omega})$, $\boldsymbol{j}^d = \hat{\boldsymbol{j}}^d(\mathcal{X}, \boldsymbol{\omega})$, $\boldsymbol{q}^d = \hat{\boldsymbol{q}}^d(\mathcal{X}, \boldsymbol{\omega})$, $a^d = \hat{a}^d(\mathcal{X}, \boldsymbol{\omega})$ are subject to the residual dissipation inequality

$$
\varrho_0 \sigma := -\bar{\mu} \varrho_0 r^d - \boldsymbol{D}\bar{\mu} \cdot \boldsymbol{j}^d + \boldsymbol{D}\frac{1}{\theta} \cdot \boldsymbol{q}^d + \chi_{,t} a^d \geq 0 \tag{1.5}
$$

for all variables $\{\mathcal{X}; \boldsymbol{\omega}\} = \mathcal{Z}_\theta$.
The quantity σ is the specific entropy production. The superscript d indicates that the quantity is dissipative, i.e., contributes to the entropy production. By the Edelen's decomposition theorem the quantities r^d, $\boldsymbol{j}^d$, $\boldsymbol{q}^d$ and a^d are given by

$$
-\varrho_0 r^d = \mathcal{D}_{,\bar{\mu}}, \quad -\boldsymbol{j}^d = \mathcal{D}_{,\boldsymbol{D}\bar{\mu}}, \quad \boldsymbol{q}^d = \mathcal{D}_{,\boldsymbol{D}(1/\theta)}, \quad a^d = \mathcal{D}_{,\chi_{,t}}. \tag{1.6}
$$

We remind the simplified notation

$$
\mathcal{D}_{,\bar{\mu}} = \frac{\partial \mathcal{D}}{\partial \bar{\mu}}, \quad \mathcal{D}_{,\boldsymbol{D}\bar{\mu}} = \frac{\partial \mathcal{D}}{\partial \boldsymbol{D}\bar{\mu}}, \quad \text{and so forth.}
$$

The vector field $\boldsymbol{h}^e = \hat{\boldsymbol{h}}^e(\mathcal{X}; \boldsymbol{\omega})$ is not restricted by the entropy principle, thus can be selected arbitrarily in consistency with the frame invariance and other physical requirements.

The functions $\varrho_0 = \varrho_0(\boldsymbol{X})$, $\boldsymbol{b} = \boldsymbol{b}(\boldsymbol{X}, t)$, $\tau = \tau(\boldsymbol{X}, t)$ and $g = g(\boldsymbol{X}, t)$ are given data.

REMARK 7.1. The statements of Theorem 6.7 and Corollaries 6.8–6.11 remain valid for the phase-field model $(PF)_\theta$ (1.1)–(1.6). More precisely, in view of the decomposition

$$
\boldsymbol{q} = \boldsymbol{q}^d - \dot{\chi} \boldsymbol{h}^e, \tag{1.7}
$$

it follows that solutions of system (1.1)–(1.6) satisfy the entropy equation and inequality (compare (6.2.36))

$$
\varrho_0 \dot{\eta} + \nabla \cdot \boldsymbol{\Psi} = \varrho_0 \sigma - \bar{\mu} \varrho_0 \tau + \frac{\varrho_0 g}{\theta} \geq -\bar{\mu} \varrho_0 \tau + \frac{\varrho_0 g}{\theta} \tag{1.8}
$$

with the entropy flux admitting the splitting

$$
\begin{aligned}
\boldsymbol{\Psi} &= -\bar{\mu} \boldsymbol{j}^d + \frac{1}{\theta} \boldsymbol{q}^d + \dot{\chi} \frac{\varrho_0 f_{,\boldsymbol{D}\chi} - \boldsymbol{h}^e}{\theta} \\
&\equiv \boldsymbol{\Psi}^d + \dot{\chi} \boldsymbol{h}^\eta.
\end{aligned} \tag{1.9}
$$

Here

$$
\boldsymbol{\Psi}^d := -\bar{\mu} \boldsymbol{j}^d + \frac{1}{\theta} \boldsymbol{q}^d \tag{1.10}
$$

is the standard entropy flux (associated with dissipative fluxes), and

$$\dot{\chi}\boldsymbol{h}^\eta \quad \text{with} \quad \boldsymbol{h}^\eta := \frac{1}{\theta}(\varrho_0 f_{,\boldsymbol{D}\chi} - \boldsymbol{h}^e) \tag{1.11}$$

is the extra nonequilibrium entropy flux.

Let us note that according to the splitting (1.9), the extra nonequilibrium energy flux, $-\dot{\chi}\boldsymbol{h}^e$, and the extra nonequilibrium entropy flux, $\dot{\chi}\boldsymbol{h}^\eta$, are linked by the equality

$$\dot{\chi}(\boldsymbol{h}^e + \theta\boldsymbol{h}^\eta) = \dot{\chi}\varrho_0 f_{,\boldsymbol{D}\chi}, \tag{1.12}$$

that is

$$\boldsymbol{h}^e + \theta\boldsymbol{h}^\eta = \varrho_0 f_{,\boldsymbol{D}\chi}. \tag{1.13}$$

For further purposes let us recall the equivalent formulation of the entropy inequality (1.8) expressed in terms of the free energy (dissipation) inequality. It results by summing up energy equation $(1.3)_4$ and entropy equation (1.8) multiplied by $-\theta$.

In result it follows that solutions of system (1.1)–(1.6) satisfy the free energy equation and inequality

$$\begin{aligned} &\varrho_0\dot{f} - \varrho_0\eta\dot{\theta} + \nabla\cdot(\bar{\mu}\theta\boldsymbol{j}^d - \dot{\chi}\varrho_0 f_{,\boldsymbol{D}\chi}) \\ &\quad - \bar{\mu}\nabla\theta\cdot\boldsymbol{j}^d + \frac{1}{\theta}\nabla\theta\cdot\boldsymbol{q}^d + \dot{\chi}\nabla\theta\cdot\boldsymbol{h}^\eta - \varrho_0 f_{,\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} \\ &= -\theta\varrho_0\sigma + \theta\bar{\mu}\varrho_0\tau \le \theta\bar{\mu}\varrho_0\tau, \end{aligned} \tag{1.14}$$

where

$$f = e - \theta\eta, \quad \mu = \theta\bar{\mu},$$

$\boldsymbol{\Psi}$ is given by (1.9)–(1.11), and the dissipation scalar $\varrho_0\sigma$ is given by (1.5)

7.2. Equivalent forms of equations for the chemical potential and internal energy balance. For further discussion we collect here equivalent forms of equation $(1.3)_3$ and $(1.3)_4$.

LEMMA 7.2. *Let us consider system (1.3). Then*

(i) *the chemical potential equation* $(1.3)_3$ *admits the forms:*

$$\begin{aligned} \varrho_0\bar{\mu} &= \frac{\delta(\varrho_0 f/\theta)}{\delta\chi} + \boldsymbol{h}^e\cdot\nabla\frac{1}{\theta} + a^d \\ &= \frac{1}{\theta}\frac{\delta(\varrho_0 f)}{\delta\chi} + \frac{1}{\theta}\boldsymbol{h}^\eta\cdot\nabla\theta + a^d \\ &= \frac{1}{\theta}\frac{\delta(\varrho_0 e)}{\delta\chi} - \frac{\delta(\varrho_0\eta)}{\delta\chi} - (\varrho_0 e_{,\boldsymbol{D}\chi} - \boldsymbol{h}^e)\cdot\nabla\frac{1}{\theta} + a^d, \end{aligned} \tag{2.1}$$

or, equivalently, in terms of $\mu = \theta\bar{\mu}$,

$$\begin{aligned} \varrho_0\mu &= \frac{\delta(\varrho_0 f)}{\delta\chi} + \boldsymbol{h}^\eta\cdot\nabla\theta + \theta a^d \\ &= \frac{\delta(\varrho_0 e)}{\delta\chi} - \theta\frac{\delta(\varrho_0\eta)}{\delta\chi} + \frac{1}{\theta}(\varrho_0 e_{,\boldsymbol{D}\chi} - \boldsymbol{h}^e)\cdot\nabla\theta + \theta a^d. \end{aligned} \tag{2.2}$$

(ii) *the energy balance equation* $(1.3)_4$ *admits the forms:*

$$\begin{aligned}
&\varrho_0\dot{e} + \nabla\cdot(\boldsymbol{q}^d - \dot{\chi}\boldsymbol{h}^e) - \varrho_0 f_{,\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} = \varrho_0 g,\\
&\theta\varrho_0\dot{\eta} + \nabla\cdot(\boldsymbol{q}^d - \dot{\chi}\boldsymbol{h}^e) + \varrho_0 f_{,\chi}\dot{\chi} + \varrho_0 f_{,\boldsymbol{D}\chi}\cdot\nabla\dot{\chi} = \varrho_0 g,\\
&\varrho_0 c_{\boldsymbol{F}}\dot{\theta} + \nabla\cdot(\boldsymbol{q}^d - \dot{\chi}\boldsymbol{h}^e) + \varrho_0(f-\theta f_{,\theta})_{,\chi}\dot{\chi} + \varrho_0(f-\theta f_{,\theta})_{,\boldsymbol{D}\chi}\cdot\nabla\dot{\chi}\\
&\quad - \varrho_0\theta f_{,\theta\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} = \varrho_0 g,
\end{aligned}\tag{2.3}$$

where

$$c_{\boldsymbol{F}} = e_{,\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) = -\theta f_{,\theta\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)$$

is the specific heat at constant deformation.

Proof.

(i) The equalities in (2.1) follow directly from the definition of the first variation and the thermodynamic relations (see Lemma 3.1)

$$\begin{aligned}
f(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) &= e(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) - \theta\eta(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta),\\
\eta(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) &= -f_{,\theta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta).
\end{aligned}\tag{2.4}$$

In fact,

$$\begin{aligned}
\varrho_0\bar{\mu} &= \frac{\delta(\varrho_0 f/\theta)}{\delta\chi} + \boldsymbol{h}^e\cdot\nabla\frac{1}{\theta} + a^d = \frac{\varrho_0 f_{,\chi}}{\theta} - \nabla\cdot\left(\frac{\varrho_0 f_{,\boldsymbol{D}\chi}}{\theta}\right) + \boldsymbol{h}^e\cdot\nabla\frac{1}{\theta} + a^d\\
&= \frac{1}{\theta}[\varrho_o f_{,\chi} - \nabla\cdot(\varrho_0 f_{,\boldsymbol{D}\chi})] - (\varrho_0 f_{,\boldsymbol{D}\chi} - \boldsymbol{h}^e)\cdot\nabla\frac{1}{\theta} + a^d\\
&= \frac{1}{\theta}\frac{\delta(\varrho_0 f)}{\delta\chi} + \frac{1}{\theta}\boldsymbol{h}^\eta\cdot\nabla\theta + a^d,
\end{aligned}$$

which proves equality $(2.1)_2$. Further, using (2.4), we obtain

$$\begin{aligned}
\varrho_0\bar{\mu} &= \frac{\delta(\varrho_0 f/\theta)}{\delta\chi} + \boldsymbol{h}^e\cdot\nabla\frac{1}{\theta} + a^d\\
&= \frac{\varrho_0}{\theta}(e_{,\chi} - \theta\eta_{,\chi}) - \nabla\cdot\left[\frac{\varrho_0(e_{,\boldsymbol{D}\chi} - \theta\eta_{,\boldsymbol{D}\chi})}{\theta}\right] + \boldsymbol{h}^e\cdot\nabla\frac{1}{\theta} + a^d\\
&= \frac{1}{\theta}[\varrho_0 e_{,\chi} - \nabla\cdot(\varrho_0 e_{,\boldsymbol{D}\chi})] - [\varrho_0\eta_{,\chi} - \nabla\cdot(\varrho_0\eta_{,\boldsymbol{D}\chi})] - (\varrho_0 e_{,\boldsymbol{D}\chi} - \boldsymbol{h}^e)\cdot\nabla\frac{1}{\theta} + a^d\\
&= \frac{1}{\theta}\frac{\delta(\varrho_0 e)}{\delta\chi} - \frac{\delta(\varrho_0\eta)}{\delta\chi} - (\varrho_0 e_{,\boldsymbol{D}\chi} - \boldsymbol{h}^e)\cdot\nabla\frac{1}{\theta} + a^d,
\end{aligned}$$

which yields equality $(2.1)_3$.

(ii) The entropy form $(2.3)_2$ follows immediately from $(2.3)_1$ on account of the identity

$$\dot{e} = (f+\theta\eta) = \dot{f} + \dot{\theta}\eta + \theta\dot{\eta} = \theta\dot{\eta} + f_{,\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} + f_{,\chi}\dot{\chi} + f_{,\boldsymbol{D}\chi}\cdot\nabla\dot{\chi}.$$

The temperature form $(2.3)_3$ results from $(2.3)_1$ on account of the identity

$$\dot{e} = e_{,\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} + e_{,\chi}\dot{\chi} + e_{,\boldsymbol{D}\chi}\cdot\nabla\dot{\chi} + e_{,\theta}\dot{\theta},$$

which leads to

$$\varrho_0 e_{,\theta}\dot{\theta} + \nabla\cdot(\boldsymbol{q}^d - \dot{\chi}\boldsymbol{h}^e) + \varrho_0 e_{,\chi}\dot{\chi} + \varrho_0 e_{,\boldsymbol{D}\chi}\cdot\nabla\dot{\chi} - \varrho_0(f-e)_{,\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} = \varrho_0 g.$$

Then the use of thermodynamic relations (2.4) provides $(2.3)_3$. ■

7.3. Model $(PF)_\theta$ in case of infinitesimal deformations. In applications it is often of interest to consider models within the linearized elasticity theory appropriate to situations in which the displacement gradient $\nabla \boldsymbol{u}$ is small. The corresponding model can be deduced by repeating the considerations of Chapters 5 and 6 assuming from the outset that the deformation gradient is infinitesimal.

We follow the same procedure as used e.g. in Gurtin [83, Sect. 4.4], Fried-Gurtin [72, Sect 6]. Namely, in consistency with the frame invariance we redefine $\boldsymbol{F}$ to be the infinitesimal strain tensor

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}(\boldsymbol{u}) = \frac{1}{2}(\nabla \boldsymbol{u} + (\nabla \boldsymbol{u})^T), \tag{3.1}$$

and replace the angular momentum balance $(2.2.1)_3$ by the requirement that $\boldsymbol{S}$ is symmetric

$$\boldsymbol{S} = \boldsymbol{S}^T. \tag{3.2}$$

The arguments leading to the formulation of phase-field model $(PF)_\theta$ with extra flux $\boldsymbol{h}^e$ remain unchanged. In result we get the following statement appropriate to the situation of infinitesimal deformations.

The state space is given by

$$\mathcal{Z}_\theta^l := \left\{\boldsymbol{\varepsilon}, \boldsymbol{D}\boldsymbol{\varepsilon}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta, \boldsymbol{D}\frac{1}{\theta}, \bar{\mu}, \boldsymbol{D}\bar{\mu}, \chi_{,t}\right\}, \tag{3.3}$$

where $\theta > 0$ and $\bar{\mu} = \mu/\theta$.

There are two thermodynamic potentials, the free energy $f = \hat{f}(\boldsymbol{\varepsilon}, \chi, \boldsymbol{D}\chi, \theta)$ which is strictly concave with respect to θ, and the dissipation potential $\mathcal{D} = \hat{\mathcal{D}}(\mathcal{X}; \boldsymbol{\omega})$ with

$$\begin{aligned} &\mathcal{X} = \left(\bar{\mu}, \boldsymbol{D}\bar{\mu}, \boldsymbol{D}\frac{1}{\theta}, \chi_{,t}\right), \\ &\boldsymbol{\omega} = (\boldsymbol{\varepsilon}, \boldsymbol{D}\boldsymbol{\varepsilon}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta), \quad \{\mathcal{X}; \boldsymbol{\omega}\} = \mathcal{Z}_\theta, \end{aligned} \tag{3.4}$$

which is nonnegative, convex in $\mathcal{X}$ and such that $\mathcal{D}(\boldsymbol{0}, \boldsymbol{\omega}) = 0$.

The unknowns are the fields $\boldsymbol{u}$, χ, $\bar{\mu}$ and $\theta > 0$ satisfying the sytem of differential equations:

$$\begin{aligned} &\varrho_0 \ddot{\boldsymbol{u}} - \nabla \cdot \boldsymbol{S} = \varrho_0 \boldsymbol{b}, \\ &\varrho_0 \dot{\chi} + \nabla \cdot \boldsymbol{j}^d - \varrho_0 r^d = \varrho_0 r, \\ &\varrho_0 \bar{\mu} = \frac{\delta(\varrho_0 f/\theta)}{\delta\chi} + \boldsymbol{h}^e \cdot \nabla\frac{1}{\theta} + a^d, \\ &\varrho_0 \dot{e} + \nabla \cdot (\boldsymbol{q}^d - \dot{\chi}\boldsymbol{h}^e) - \boldsymbol{S} \cdot \dot{\boldsymbol{\varepsilon}} = \varrho_0 g, \end{aligned} \tag{3.5}$$

where

$$\begin{aligned} &e = \hat{e}(\boldsymbol{\varepsilon}, \chi, \boldsymbol{D}\chi, \theta), \quad \boldsymbol{S} = \hat{\boldsymbol{S}}(\boldsymbol{\varepsilon}, \chi, \boldsymbol{D}\chi, \theta), \quad r^d = \hat{r}^d(\mathcal{X}; \boldsymbol{\omega}), \\ &\boldsymbol{j}^d = \hat{\boldsymbol{j}}^d(\mathcal{X}; \boldsymbol{\omega}), \qquad \boldsymbol{q}^d = \hat{\boldsymbol{q}}^d(\mathcal{X}; \boldsymbol{\omega}), \qquad a^d = \hat{a}^d(\mathcal{X}; \boldsymbol{\omega}) \end{aligned}$$

are determined by the relations

$$\begin{aligned} &e = f - \theta f_{,\theta}, \\ &\boldsymbol{S} = \varrho_0 f_{,\boldsymbol{\varepsilon}}, \quad \text{satisfying} \quad \boldsymbol{S} = \boldsymbol{S}^T, \\ &-\varrho_0 r^d = \mathcal{D}_{,\bar{\mu}}, \quad -\boldsymbol{j}^d = \mathcal{D}_{,\boldsymbol{D}\bar{\mu}}, \quad \boldsymbol{q}^d = \mathcal{D}_{,\boldsymbol{D}(1/\theta)}, \quad a^d = \mathcal{D}_{,\chi_{,t}}, \end{aligned} \tag{3.6}$$

and $\boldsymbol{h}^e = \hat{\boldsymbol{h}}^e(\mathcal{X};\boldsymbol{\omega})$ is a vector field not restricted by the entropy principle.

One can see that in case of infinitesimal deformations the formulation (3.3)–(3.6) follows directly from the general one (1.1)–(1.3) after replacing deformation gradient $\boldsymbol{F}$ by the infinitesimal strain tensor $\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}(\boldsymbol{u})$.

7.4. Physically realistic examples of extra vector field and corresponding model equations. The phase-field model $(PF)_\theta$ (cf. (1.1)–(1.6)) involves an extra unspecified vector field $\boldsymbol{h} \equiv \boldsymbol{h}^e = \hat{\boldsymbol{h}}^e(\mathcal{X};\boldsymbol{\omega})$. The solutions of this model satisfy the entropy inequality (1.8) with the entropy flux involving the extra term

$$\boldsymbol{h}^\eta = \frac{1}{\theta}(\varrho_0 f_{,\boldsymbol{D}\chi} - \boldsymbol{h}^e).$$

We discuss here four physically realistic examples of the extra terms $\boldsymbol{h}^e$, $\boldsymbol{h}^\eta$, and present the corresponding field equations. The examples include the following:

$(PF)_\theta$ (i) extra energy and extra entropy terms

$$\boldsymbol{h}^e = \varrho_0 e_{,\boldsymbol{D}\chi} \quad \text{and} \quad \boldsymbol{h}^\eta = -\varrho_0 \eta_{,\boldsymbol{D}\chi};$$

$(PF)_\theta$ (ii) extra entropy term

$$\boldsymbol{h}^e = \boldsymbol{0} \quad \text{and} \quad \boldsymbol{h}^\eta = \frac{1}{\theta}\varrho_0 f_{,\boldsymbol{D}\chi},$$

$(PF)_\theta$ (iii) extra energy term

$$\boldsymbol{h}^e = \varrho_0 f_{,\boldsymbol{D}\chi} \quad \text{and} \quad \boldsymbol{h}^\eta = \boldsymbol{0};$$

$(PF)_\theta$ (iv) Combination of models (ii) and (iii)

$$\boldsymbol{h}^e = (1-\alpha)\varrho_0 f_{,\boldsymbol{D}\chi} \quad \text{and} \quad \boldsymbol{h}^\eta = \frac{1}{\theta}\alpha\varrho_0 f_{,\boldsymbol{D}\chi}$$

where $\alpha \in [0,1]$ is an arbitrary number. This yields a one-parameter family of thermodynamically consistent phase-field models. Model (ii) is achieved with $\alpha = 1$ and model (iii) with $\alpha = 0$.

Such extra terms appear in the phase-field models known in literature, see Part II.

$(PF)_\theta$ **(i) Model with extra energy and entropy terms**

In view of thermodynamic relations (2.4) the equality (cf. (1.13))

$$\boldsymbol{h}^e + \theta\boldsymbol{h}^\eta = \varrho_0 f_{,\boldsymbol{D}\chi}$$

suggests that

$$\begin{aligned}\boldsymbol{h}^e = \hat{\boldsymbol{h}}^e(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) &= \varrho_0 e_{,\boldsymbol{D}\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) \\ &= \varrho_0 f_{,\boldsymbol{D}\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) - \theta\varrho_0 f_{,\theta\boldsymbol{D}\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)\end{aligned} \tag{4.1}$$

and

$$\begin{aligned}\boldsymbol{h}^\eta = \hat{\boldsymbol{h}}^\eta(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) &= -\varrho_0 \eta_{,\boldsymbol{D}\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) \\ &= \varrho_0 f_{,\theta\boldsymbol{D}\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta),\end{aligned}$$

so that the corresponding energy and entropy fluxes are

$$\begin{aligned} \boldsymbol{q} &= \boldsymbol{q}^d - \dot{\chi}\varrho_0 e_{,\boldsymbol{D}\chi}, \\ \boldsymbol{\Psi} &= \hat{\boldsymbol{\Psi}}^d - \dot{\chi}\varrho_0\eta_{,\boldsymbol{D}\chi} \quad \text{with} \quad \boldsymbol{\Psi}^d = -\bar{\mu}\boldsymbol{j}^d + \frac{1}{\theta}\boldsymbol{q}^d. \end{aligned} \tag{4.2}$$

Recalling Lemma 7.2, one can see that in such a case the phase-field system (1.3) takes on the following form:

$$\begin{aligned} &\varrho_0\ddot{\boldsymbol{u}} - \nabla\cdot(\varrho_0 f_{,\boldsymbol{F}}) = \varrho_0\boldsymbol{b}, \\ &\varrho_0\dot{\chi} + \nabla\cdot\boldsymbol{j}^d - \varrho_0 r^d = \varrho_0\tau, \\ &\varrho_0\bar{\mu} = \frac{1}{\theta}\left[\frac{\delta(\varrho_0 e)}{\delta\chi} - \theta\frac{\delta(\varrho_0\eta)}{\delta\chi}\right] + a^d, \\ &\varrho_0\dot{e} + \nabla\cdot(\boldsymbol{q}^d - \dot{\chi}\varrho_0 e_{,\boldsymbol{D}\chi}) - \varrho_0 f_{,\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} = g, \end{aligned} \tag{4.3}$$

where $f = \hat{f}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)$ $e = \hat{e}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)$ and $\eta = \hat{\eta}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta)$ are linked by thermodynamic relations (2.4), and the quantities

$$r^d = \hat{r}^d(\mathcal{X};\boldsymbol{\omega}), \quad \boldsymbol{j}^d = \boldsymbol{j}^d(\mathcal{X};\boldsymbol{\omega}); \quad \boldsymbol{q}^d = \hat{\boldsymbol{q}}^d(\mathcal{X};\boldsymbol{\omega}), \quad a^d = \hat{a}^d(\mathcal{X};\boldsymbol{\omega})$$

are given by

$$-r^d = \mathcal{D}_{,\bar{\mu}}, \quad -\boldsymbol{j}^d = \mathcal{D}_{,\boldsymbol{D}\bar{\mu}}, \quad \boldsymbol{q}^d = \mathcal{D}_{,\boldsymbol{D}(1/\theta)}, \quad a^d = \mathcal{D}_{,\chi_{,t}}.$$

It is of interest to note that the corresponding temperature form of equation $(4.3)_4$ is

$$\varrho_0 c_{\boldsymbol{F}}\dot{\theta} + \nabla\cdot\boldsymbol{q}^d + \frac{\delta(\varrho_0 e)}{\delta\chi}\dot{\chi} + \theta\varrho_0\eta_{,\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} = g \tag{4.4}$$

with $c_{\boldsymbol{F}}$ the specific heat at constant deformation.

The solutions of system (4.3) satisfy the entropy inequality

$$\begin{aligned} &\varrho_0\dot{\eta} + \nabla\cdot(\boldsymbol{\Psi}^d - \dot{\chi}\varrho_0\eta_{,\boldsymbol{D}\chi}) = \varrho_0\sigma - \bar{\mu}\varrho_0\tau + \frac{\varrho_0 g}{\theta} \\ &\geq -\bar{\mu}\varrho_0\tau + \frac{\varrho_0 g}{\theta}, \end{aligned} \tag{4.5}$$

with the entropy production

$$\varrho_0\sigma = -\bar{\mu}\varrho_0 r^d - \boldsymbol{D}\bar{\mu}\cdot\boldsymbol{j}^d + \boldsymbol{D}\frac{1}{\theta}\cdot\boldsymbol{q}^d + \chi_{,t}a^d.$$

REMARK 7.3. We underline an important property of the rescaled chemical potential $\bar{\mu}$ given by $(4.3)_3$ and the corresponding chemical potential $\mu = \theta\bar{\mu}$. Namely, their main (nondissipative) parts

$$\varrho_0\bar{\mu} - a^d = \frac{1}{\theta}\left[\frac{\delta(\varrho_0 e)}{\delta\chi} - \theta\frac{\delta(\varrho_0\eta)}{\delta\chi}\right]$$

and

$$\varrho_0\mu - \theta a^d = \frac{\delta(\varrho_0 e)}{\delta\chi} - \theta\frac{\delta(\varrho_0\eta)}{\delta\chi}$$

are independent of temperature gradient $\nabla\theta$.

Indeed, on account of thermodynamic relations (2.4), the following identities hold true

$$\begin{aligned}
\frac{\delta(\varrho_0 e)}{\delta\chi} - \theta\frac{\delta(\varrho_0\eta)}{\delta\chi} &= \varrho_0 e_{,\chi} - \nabla\cdot(\varrho_0 e_{,D\chi}) - \theta\varrho_0\eta_{,\chi} + \theta\nabla\cdot(\varrho_0\eta_{,D\chi})\\
&= \varrho_0 f_{,\chi} - \nabla\cdot(\varrho_0 f_{,D\chi}) - \varrho_0\eta_{,D\chi}\cdot\nabla\theta\\
&= \varrho_0 f_{,\chi} - \nabla\cdot(\varrho_0 f_{,D\chi}) + \varrho_0 f_{,\theta D\chi}\cdot\nabla\theta\\
&= \varrho_0 f_{,\chi} - \varrho_0 f_{,\chi,_{iF}}\cdot \boldsymbol{F}_{,i} - \varrho_0 f_{,\chi,_{i\chi}}\chi_{,i} - \varrho_0 f_{,\chi,_{i}\chi,_{j}}\chi_{,ji},
\end{aligned}$$

which demonstrates that the expression in question is actually independent of $\nabla\theta$.

This property has not only a physical importance but is also favorable from the point of view of the mathematical analysis of the corresponding phase-field models.

Another remarkable property of the discussed example is the fact that extra energy flux, $\dot{\chi}\varrho_0 e_{,D\chi}$, comprises just the contribution from the internal energy, and the extra entropy flux, $-\dot{\chi}\varrho_0\eta_{,D\chi}$, the corresponding contribution from the entropy.

$(PF)_\theta$ (ii) **Model with extra entropy term**

In this case

$$\boldsymbol{h}^e = \boldsymbol{0} \quad \text{and} \quad \boldsymbol{h}^\eta = \hat{\boldsymbol{h}}^\eta(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) = \frac{1}{\theta}\varrho_0 f_{,D\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta), \tag{4.6}$$

so that the energy and entropy fluxes are

$$\begin{aligned}
&\boldsymbol{q} = \boldsymbol{q}^d,\\
&\Psi = \Psi^d + \frac{1}{\theta}\dot{\chi}\varrho_0 f_{,D\chi} \quad \text{with} \quad \Psi^d = -\bar{\mu}\boldsymbol{j}^d + \frac{1}{\theta}\boldsymbol{q}^d.
\end{aligned} \tag{4.7}$$

The energy flux is standard (dissipative) whereas the entropy flux is modified by the extra gradient term. In view of Lemma 7.2 the corresponding system reads

$$\begin{aligned}
&\varrho_0\ddot{\boldsymbol{u}} - \nabla\cdot(\varrho_0 f_{,\boldsymbol{F}}) = \varrho_0\boldsymbol{b},\\
&\varrho_0\dot{\chi} + \nabla\cdot\boldsymbol{j}^d - \varrho_0 r^d = \varrho_0\tau,\\
&\varrho_0\bar{\mu} = \frac{\delta(\varrho_0 f/\theta)}{\delta\chi} + a^d,\\
&\varrho_0\dot{e} + \nabla\cdot\boldsymbol{q}^d - \varrho_0 f_{,\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} = \varrho_0 g.
\end{aligned} \tag{4.8}$$

The temperature form of equation $(4.8)_4$ is

$$\begin{aligned}
&\varrho_0 c_{\boldsymbol{F}}\dot{\theta} + \nabla\cdot\boldsymbol{q}^d + \varrho_0(f-\theta f_{,\theta})_{,\chi}\dot{\chi} + \varrho_0(f-\theta f_{,\theta})_{,D\chi}\cdot\nabla\dot{\chi}\\
&\quad - \varrho_0\theta f_{,\theta\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} = \varrho_0 g.
\end{aligned} \tag{4.9}$$

The solutions of system (4.8) satisfy the entropy equation and inequality

$$\begin{aligned}
&\varrho_0\dot{\eta} + \nabla\cdot\left(\boldsymbol{\Psi}^d + \frac{1}{\theta}\dot{\chi}\varrho_0 f_{,D\chi}\right) = \varrho_0\sigma - \bar{\mu}\varrho_0\tau + \frac{\varrho_0 g}{\theta}\\
&\geq -\bar{\mu}\varrho_0\tau + \frac{\varrho_0 g}{\theta},
\end{aligned} \tag{4.10}$$

with the specific entropy production σ as in (4.5).

REMARK 7.4. It is of interest to notice that if the free energy f is of entropic type (see Section 3.6), that is its gradient-energetic contribution is zero,

$$e_{,D\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) = \boldsymbol{0},$$

then, according to thermodynamic relations (2.4),

$$f_{,D\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) = -\theta\eta_{,D\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) = \theta f_{,\theta D\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta). \tag{4.11}$$

Thus, in such a case

$$\boldsymbol{h}^e = \varrho_0 e_{,D\chi} = \boldsymbol{0} \quad \text{and} \quad \boldsymbol{h}^\eta = -\varrho_0\eta_{,D\chi} = \frac{1}{\theta}\varrho_0 f_{,D\chi}, \tag{4.12}$$

so that the version $(PF)_\theta$ (ii) coincides with $(PF)_\theta$ (i).
In particular, the rescaled chemical potential $\bar{\mu}$ defined by $(4.8)_3$ enjoys the property that its nondissipative part $\delta(\varrho_0 f/\theta)/\delta\chi$ is independent of temperature gradient $\nabla\theta$.
Basides, in such a case the temperature equation (4.9) simplifies to

$$\varrho_0 c_{\boldsymbol{F}}\dot{\theta} + \nabla\cdot\boldsymbol{q}^d + \varrho_0(f-\theta f_{,\theta})_{,\chi}\dot{\chi} - \varrho_0\theta f_{,\theta\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} = \varrho_0 g. \tag{4.13}$$

$(PF)_\theta$ (iii) **Model with extra energy term**

In this case

$$\boldsymbol{h}^e = \hat{\boldsymbol{h}}^e(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) = \varrho_0 f_{,D\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) \quad \text{and} \quad \boldsymbol{h}^\eta = \boldsymbol{0}, \tag{4.14}$$

so that the energy and entropy fluxes are

$$\begin{aligned} &\boldsymbol{q} = \boldsymbol{q}^d - \dot{\chi}\varrho_0 f_{,D\chi}, \\ &\boldsymbol{\Psi} = \boldsymbol{\Psi}^d \quad \text{with} \quad \boldsymbol{\Psi}^d = -\bar{\mu}\boldsymbol{j}^d + \frac{1}{\theta}\boldsymbol{q}^d. \end{aligned} \tag{4.15}$$

The energy flux contains the extra gradient term and the entropy flux is standard (dissipative). On account of Lemma 7.2 the corresponding system reads

$$\begin{aligned} &\varrho_0\ddot{\boldsymbol{u}} - \nabla\cdot(\varrho_0 f_{,\boldsymbol{F}}) = \varrho_0\boldsymbol{b}, \\ &\varrho_0\dot{\chi} + \nabla\cdot\boldsymbol{j}^d - \varrho_0 r^d = \varrho_0\tau, \\ &\varrho_0\bar{\mu} = \frac{1}{\theta}\frac{\delta(\varrho_0 f)}{\delta\chi} + a^d, \\ &\varrho_0\dot{e} + \nabla\cdot(\boldsymbol{q}^d - \dot{\chi}\varrho_0 f_{,D\chi}) - \varrho_0 f_{,\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} = \varrho_0 g. \end{aligned} \tag{4.16}$$

The temperature form of equation $(4.16)_4$ is

$$\begin{aligned} &\varrho_0 c_{\boldsymbol{F}}\dot{\theta} + \nabla\cdot(\boldsymbol{q}^d - \dot{\chi}\varrho_0 f_{,D\chi}) + \varrho_0(f-\theta f_{,\theta})_{,\chi}\dot{\chi} + \varrho_0(f-\theta f_{,\theta})_{,D\chi}\cdot\nabla\dot{\chi} \\ &\quad - \theta\varrho_0 f_{,\theta\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} = \varrho_0 g. \end{aligned} \tag{4.17}$$

The solutions of system (4.16) satisfy the entropy inequality

$$\varrho_0\dot{\eta} + \nabla\cdot\boldsymbol{\Psi}^d = \varrho_0\sigma - \bar{\mu}\varrho_0\tau + \frac{\varrho_0 g}{\theta} \geq -\bar{\mu}\varrho_0\tau + \frac{\varrho_0 g}{\theta} \tag{4.18}$$

with the standard entropy flux

$$\boldsymbol{\Psi}^d = -\bar{\mu}\boldsymbol{j}^d + \frac{1}{\theta}\boldsymbol{q}^d,$$

and the specific entropy production σ as in (4.5).

REMARK 7.5. If the free energy is of energetic type (see Section 3.6), that is its gradient-entropic contribution is zero,

$$\eta_{,D\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) = -f_{,\theta D\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) = \boldsymbol{0},$$

then by thermodynamic relations (2.4),

$$f_{,D\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) = e_{,D\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta). \tag{4.19}$$

Hence, in such a case

$$\boldsymbol{h}^e = \varrho_0 e_{,D\chi} = \varrho_0 f_{,D\chi} \quad \text{and} \quad \boldsymbol{h}^\eta = -\varrho_0 \eta_{,D\chi} = \boldsymbol{0}, \tag{4.20}$$

so that model $(PF)_\theta$ (iii) coincides with $(PF)_\theta$ (i).
Then, in particular, the chemical potential $(4.16)_3$ enjoys the property that its nondissipative part $\delta(\varrho_0 f)/\delta\chi$ is independent of temperature gradient $\nabla\theta$.

Moreover, it is of interest to notice that in such a case the temperature equation (4.17) admits the form

$$\varrho_0 c_{\boldsymbol{F}}\dot{\theta} + \nabla\cdot\boldsymbol{q}^d + \frac{\delta(\varrho_0 f)}{\delta\chi}\dot{\chi} - \theta\varrho_0 f_{,\theta\chi}\dot{\chi} - \theta\varrho_0 f_{,\theta\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} = \varrho_0 g. \tag{4.21}$$

$(PF)_\theta$ (iv) **Combination of models with extra entropy and energy terms**

In this case

$$\begin{aligned} \boldsymbol{h}^e &= \hat{\boldsymbol{h}}^e(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) = (1-\alpha)\varrho_0 f_{,D\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) \quad \text{and} \\ \boldsymbol{h}^\eta &= \hat{\boldsymbol{h}}^\eta(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) = \frac{1}{\theta}\alpha\varrho_0 f_{,D\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta), \quad \alpha\in[0,1], \end{aligned} \tag{4.22}$$

so that the energy and entropy fluxes are

$$\begin{aligned} \boldsymbol{q} &= \boldsymbol{q}^d - \dot{\chi}(1-\alpha)\varrho_0 f_{,D\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) \quad \text{and} \\ \boldsymbol{\Psi} &= \boldsymbol{\Psi}^d + \dot{\chi}\frac{1}{\theta}\alpha\varrho_0 f_{,D\chi}(\boldsymbol{F},\chi,\boldsymbol{D}\chi,\theta) \quad \text{with} \quad \boldsymbol{\Psi}^d = -\bar{\mu}\boldsymbol{j}^d + \frac{1}{\theta}\boldsymbol{q}^d. \end{aligned} \tag{4.23}$$

The corresponding system reads

$$\begin{aligned} &\varrho_0\ddot{\boldsymbol{u}} - \nabla\cdot(\varrho_0 f_{,\boldsymbol{F}}) = \varrho_0\boldsymbol{b}, \\ &\varrho_0\dot{\chi} + \nabla\cdot\boldsymbol{j}^d - \varrho_0 r^d = \varrho_0\tau, \\ &\varrho_0\bar{\mu} = \frac{\delta(\varrho_0 f/\theta)}{\delta\chi} + (1-\alpha)\varrho_0 f_{,D\chi}\cdot\nabla\frac{1}{\theta} + a^d \\ &\quad = \frac{1}{\theta}\frac{\delta(\varrho_0 f)}{\delta\chi} - \alpha\varrho_0 f_{,D\chi}\cdot\nabla\frac{1}{\theta} + a^d, \\ &\varrho_0\dot{e} + \nabla\cdot[\boldsymbol{q}^d - \dot{\chi}(1-\alpha)\varrho_0 f_{,D\chi}] - \varrho_0 f_{,\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} = \varrho_0 g. \end{aligned} \tag{4.24}$$

Model (4.8) with extra entropy term is achieved from (4.24) for $\alpha = 1$ whereas model (4.16) with extra energy term for $\alpha = 0$.

7.5. Conserved phase-field model $(PF)_\theta$ with extra vector field. In this section we specify the phase-field model $(PF)_\theta$ with extra terms (cf. (1.1)–(1.3)) in case of the conserved dynamics of the phase variable, i.e., $\boldsymbol{j}\neq\boldsymbol{0}$ and $r\equiv 0$. For a comparison with well-established phase-field systems known in literature we present two alternative formulations of the model which depend on the representation of the solution of the residual dissipation inequality.

7.5.1. Formulation. The state space is the same as in (1.1),

$$\mathcal{Z}_\theta = \left\{\boldsymbol{F},\boldsymbol{D}\boldsymbol{F},\chi,\boldsymbol{D}\chi,\boldsymbol{D}^2\chi,\theta,\boldsymbol{D}\frac{1}{\theta},\bar{\mu},\boldsymbol{D}\bar{\mu},\chi_{,t}\right\}, \quad \theta>0, \quad \bar{\mu}=\frac{\mu}{\theta},$$

splitted now into the set of thermodynamic forces

$$\mathcal{X} = \left(\boldsymbol{D}\bar{\mu}, \boldsymbol{D}\frac{1}{\theta}, \chi_{,t} \right),$$

and the set of state variables

$$\boldsymbol{\omega} = (\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta, \bar{\mu}), \quad \{\mathcal{X}; \boldsymbol{\omega}\} = \mathcal{Z}_\theta.$$

There are given two thermodynamic potentials, the free energy $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ which is strictly concave with respect to θ for all $\boldsymbol{F}, \chi, D\chi$, and the dissipation potential $\mathcal{D} = \hat{\mathcal{D}}(\mathcal{X}; \boldsymbol{\omega})$ which is nonnegative, convex in $\mathcal{X}$ and such that $\mathcal{D}(\boldsymbol{0}; \boldsymbol{\omega}) = 0$.

The unknowns are the fields $\boldsymbol{u}$, χ, $\bar{\mu} = \mu/\theta$ and $\theta > 0$, satisfying the system of differential equations (1.3) with $r^d \equiv 0$:

$$\begin{aligned}
&\varrho_0 \ddot{\boldsymbol{u}} - \nabla \cdot (\varrho_0 f_{,\boldsymbol{F}}) = \varrho_0 \boldsymbol{b}, \\
&\varrho_0 \dot{\chi} + \nabla \cdot \boldsymbol{j}^d = \varrho_0 \tau, \\
&\varrho_0 \bar{\mu} = \frac{\delta(\varrho_0 f/\theta)}{\delta \chi} + \boldsymbol{h}^e \cdot \nabla \frac{1}{\theta} + a^d, \\
&\varrho_0 \dot{e} + \nabla \cdot (\boldsymbol{q}^d - \dot{\chi} \boldsymbol{h}^e) - \varrho_0 f_{,\boldsymbol{F}} \cdot \dot{\boldsymbol{F}} = \varrho_0 g,
\end{aligned} \tag{5.1}$$

where

$$\begin{aligned}
&e = f - \theta f_{,\theta}, \\
&-\boldsymbol{j}^d = \mathcal{D}_{,\boldsymbol{D}\bar{\mu}}, \quad \boldsymbol{q}^d = \mathcal{D}_{,\boldsymbol{D}(1/\theta)}, \quad a^d = \mathcal{D}_{,\chi_{,t}},
\end{aligned} \tag{5.2}$$

and the extra vector field $\boldsymbol{h}^e$ is specified by one of the physically realistic examples discussed in Section 7.4.

We recall that solutions of system (5.1) satisfy the entropy inequality (cf. (1.8))

$$\varrho_0 \dot{\eta} + \nabla \cdot \boldsymbol{\Psi} = \varrho_0 \sigma - \bar{\mu} \varrho_0 \tau + \frac{\varrho_0 g}{\theta} \geq -\bar{\mu} \varrho_0 \tau + \frac{\varrho_0 g}{\theta} \tag{5.3}$$

with the entropy flux

$$\boldsymbol{\Psi} = \boldsymbol{\Psi}^d + \dot{\chi} \boldsymbol{h}^\eta,$$

where

$$\boldsymbol{\Psi}^d = -\bar{\mu} \boldsymbol{j}^d + \frac{1}{\theta} \boldsymbol{q}^d, \quad \boldsymbol{h}^e + \theta \boldsymbol{h}^\eta = \varrho_0 f_{,\boldsymbol{D}\chi},$$

and the entropy production given by

$$\varrho_0 \sigma = -\boldsymbol{D}\bar{\mu} \cdot \boldsymbol{j}^d + \boldsymbol{D}\frac{1}{\theta} \cdot \boldsymbol{q}^d + \chi_{,t} a^d \geq 0 \quad \text{(compare (1.5))}.$$

In some situations we shall use the equivalent formulation of the entropy inequality (5.3) in the form of the free energy (dissipation) inequality (compare (1.14)).

COROLLARY 7.6. *The solutions of system (5.1) satisfy the following free energy inequality which is an equivalent statement of (5.3):*

$$\begin{aligned}
&\varrho_0 \dot{f} + \varrho_0 \dot{\theta} \eta + \nabla \cdot (\bar{\mu} \theta \boldsymbol{j}^d - \dot{\chi} \varrho_0 f_{,\boldsymbol{D}\chi}) - \bar{\mu} \nabla \theta \cdot \boldsymbol{j}^d + \frac{1}{\theta} \nabla \theta \cdot \boldsymbol{q}^d \\
&\quad + \dot{\chi} \nabla \theta \cdot \boldsymbol{h}^\eta - \varrho_0 f_{,\boldsymbol{F}} \cdot \dot{\boldsymbol{F}} = -\theta \varrho_0 \sigma + \theta \bar{\mu} \varrho_0 \tau \leq \theta \bar{\mu} \varrho_0 \tau,
\end{aligned} \tag{5.4}$$

where dissipation scalar $\varrho_0 \sigma$ is as in (5.3).

Proof. (5.4) results by subtracting from the energy equation $(5.1)_4$ the entropy equation (5.3) multiplied by θ. ∎

7.5.2. Alternative representation. The representation $(5.2)_2$ of dissipative quantites $\boldsymbol{j}^d$, $\boldsymbol{q}^d$ and a^d is associated with the Edelen's decomposition theorem (see Lemma 4.1). For further comparison with models known in literature we present here an alternative representation which is based on Gurtin's result stated in Lemma 4.4. This representation is given by

$$\begin{aligned}
-\boldsymbol{j}^d &= \boldsymbol{L}_{jj}\boldsymbol{D}\bar{\mu} + \boldsymbol{L}_{jq}\boldsymbol{D}\frac{1}{\theta} + \boldsymbol{l}_{ja}\chi_{,t},\\
\boldsymbol{q}^d &= \boldsymbol{L}_{qj}\boldsymbol{D}\bar{\mu} + \boldsymbol{L}_{qq}\boldsymbol{D}\frac{1}{\theta} + \boldsymbol{l}_{qa}\chi_{,t},\\
a^d &= \boldsymbol{l}_{aj}\cdot\boldsymbol{D}\bar{\mu} + \boldsymbol{l}_{aq}\cdot\boldsymbol{D}\frac{1}{\theta} + l_{aa}\chi_{,t},
\end{aligned} \tag{5.5}$$

where the matrices $\boldsymbol{L}_{jj}$, $\boldsymbol{L}_{jq}$, $\boldsymbol{L}_{qj}$, $\boldsymbol{L}_{qq}$, the vectors $\boldsymbol{l}_{ja}$, $\boldsymbol{l}_{qa}$, $\boldsymbol{l}_{aj}$, $\boldsymbol{l}_{aq}$, and the scalar $\boldsymbol{l}_{aa}$ are constitutive moduli that may depend on the variables $\mathcal{Z}_\theta = \{\mathcal{X};\boldsymbol{\omega}\}$, and are consistent with the inequality

$$\begin{aligned}
&\begin{bmatrix} \boldsymbol{D}\bar{\mu} \\ \boldsymbol{D}\frac{1}{\theta} \\ \chi_{,t} \end{bmatrix} \cdot \begin{bmatrix} \boldsymbol{L}_{jj} & \boldsymbol{L}_{jq} & \boldsymbol{L}_{ja} \\ \boldsymbol{L}_{qj} & \boldsymbol{L}_{qq} & \boldsymbol{l}_{qa} \\ \boldsymbol{l}_{aj}^T & \boldsymbol{l}_{aq}^T & l_{aa} \end{bmatrix} \begin{bmatrix} \boldsymbol{D}\bar{\mu} \\ \boldsymbol{D}\frac{1}{\theta} \\ \chi_{,t} \end{bmatrix}\\
&\equiv \mathcal{X}\cdot\boldsymbol{B}(\mathcal{X};\boldsymbol{\omega})\mathcal{X} \geq 0 \quad \text{for all variables } \mathcal{Z}_\theta = \{\mathcal{X};\boldsymbol{\omega}\}.
\end{aligned} \tag{5.6}$$

REMARK 7.7. In the context of the Cahn-Hilliard equation matrix $\boldsymbol{L}_{jj}$ represents the mobility tensor, $\boldsymbol{L}_{qq}$ is the heat conductivity tensor, and scalar l_{aa} is the diffusional viscosity coefficient. The matrices $\boldsymbol{L}_{jq}$, $\boldsymbol{L}_{qj}$ account for the couplings between mass diffusion and heat conduction, and vectors $\boldsymbol{l}_{ja}$, $\boldsymbol{l}_{aj}$ and $\boldsymbol{l}_{qa}$, $\boldsymbol{l}_{aq}$ account for anisotropic cross-coupling effects.

According to Curie's principle (see, e.g., De Groot and Mazur [45, Chap. 6]) in isotropic systems tensors of rank differing by an odd integer cannot be coupled. Therefore in the isotropic case

$$\boldsymbol{l}_{ja} = \boldsymbol{l}_{aj} = \boldsymbol{l}_{qa} = \boldsymbol{l}_{aq} = \boldsymbol{0}.$$

With the use of (5.5) system (5.1) takes the form

$$\begin{aligned}
&\varrho_0\ddot{\boldsymbol{u}} - \nabla\cdot(\varrho_0 f_{,\boldsymbol{F}}) = \varrho_0\boldsymbol{b},\\
&\varrho_0\dot{\chi} - \nabla\cdot\left(\boldsymbol{L}_{jj}\nabla\bar{\mu} + \boldsymbol{L}_{jq}\nabla\frac{1}{\theta} + \boldsymbol{l}_{ja}\dot{\chi}\right) = \varrho_0\tau,\\
&\varrho_0\bar{\mu} = \frac{1}{\theta}[\varrho_0 f_{,\chi} - \nabla\cdot(\varrho_0 f_{,\boldsymbol{D}\chi})] + \boldsymbol{l}_{aj}\nabla\bar{\mu} + (\boldsymbol{l}_{aq} + \boldsymbol{h}^e - \varrho_0 f_{,\boldsymbol{D}\chi})\cdot\nabla\frac{1}{\theta} + l_{aa}\dot{\chi},\\
&\varrho_0\dot{e} + \nabla\cdot\left[\boldsymbol{L}_{qj}\nabla\bar{\mu} + \boldsymbol{L}_{qq}\nabla\frac{1}{\theta} + (\boldsymbol{l}_{qa} - \boldsymbol{h}^e)\dot{\chi}\right] - \varrho_0 f_{,\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} = \varrho_0 g.
\end{aligned} \tag{5.7}$$

In Part II the conserved phase-field model $(PF)_\theta$, expressed in the form (5.1) or (5.7), will be compared with several well-known phase-field models in two distinct situations of suppressed either elastic or thermal effects.

7.5.3. Conserved model $(PF)_\theta$ with suppressed elastic effects. Let us specify system (5.1) in the situation of suppressed elastic effects.

Assume $\boldsymbol{u} \equiv \boldsymbol{0}$, so that

$$\boldsymbol{x} = \boldsymbol{y}(\boldsymbol{X},t) = \boldsymbol{X}, \quad \boldsymbol{v} = \boldsymbol{0}, \quad \boldsymbol{F} = \boldsymbol{I}, \quad \varrho = \varrho_0/\det \boldsymbol{F} = \varrho_0,$$

and the referential and spatial operations become identical

$$\nabla f = \operatorname{grad} f, \quad \dot{f} = f_t.$$

Then, provided the equation of linear momentum balance $(5.1)_1$ is identically satisfied, system (5.1) refers to the spatial description of a two-phase, conserved system at rest. It reads as follows

$$\begin{aligned} &\varrho_0\chi_t + \nabla\cdot\boldsymbol{j}^d = \varrho_0\tau,\\ &\varrho_0\bar{\mu} = \frac{\delta(\varrho_0 f/\theta)}{\delta\chi} + \boldsymbol{h}^e\cdot\nabla\frac{1}{\theta} + a^d,\\ &\varrho_0 e_t + \nabla\cdot(\boldsymbol{q}^d - \chi_t\boldsymbol{h}^e) = \varrho_0 g, \end{aligned} \tag{5.8}$$

where all differential operations refer to the spatial description.

The state space is now

$$\mathcal{Z}_\theta|_{u=\mathbf{0}} = \left\{\chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta, \boldsymbol{D}\frac{1}{\theta}, \bar{\mu}, \boldsymbol{D}\bar{\mu}, \chi_{,t}\right\} \equiv \{\mathcal{X}|_{u=\mathbf{0}}; \boldsymbol{\omega}|_{u=\mathbf{0}}\},$$

splitted into the set of thermodynamic forces

$$\mathcal{X}|_{u=\mathbf{0}} = \left(\boldsymbol{D}\bar{\mu}, \boldsymbol{D}\frac{1}{\theta}, \chi_{,t}\right)$$

and the set of state variables

$$\boldsymbol{\omega}|_{u=\mathbf{0}} = (\chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta, \bar{\mu}).$$

The system (5.8) is governed by the free energy $f = \hat{f}(\chi, \boldsymbol{D}\chi, \theta)$ which is strictly concave with respect to θ for all $\chi, \boldsymbol{D}\chi$, and the dissipation potential $\mathcal{D} = \hat{\mathcal{D}}(\mathcal{X}_{u=\mathbf{0}}; \boldsymbol{\omega}|_{u=\mathbf{0}})$ which is nonnegative, convex in $\mathcal{X}|_{u=\mathbf{0}}$ and such that $\mathcal{D}(\mathbf{0}; \boldsymbol{\omega}|_{u=\mathbf{0}}) = 0$.

As in $(5.2)_1$, the internal energy is given by

$$e = \hat{e}(\chi, \boldsymbol{D}\chi, \theta) = f(\chi, \boldsymbol{D}\chi, \theta) - \theta f_{,\theta}(\chi, \boldsymbol{D}\chi, \theta),$$

the extra vector field $\boldsymbol{h}^e = \hat{\boldsymbol{h}}^e(\mathcal{Z}_\theta|_{u=\mathbf{0}})$ is selected according to one of the physically realistic examples $(PF)_\theta$ (i)–$(PF)_\theta$ (iv) given in Section 7.4.
Moreover the dissipative quantites $\boldsymbol{j}^d = \boldsymbol{j}^d(\mathcal{Z}_\theta|_{u=\mathbf{0}})$, $\boldsymbol{q}^d = \boldsymbol{q}^d(\mathcal{Z}_\theta|_{u=\mathbf{0}})$, $a^d = a^d(\mathcal{Z}_\theta|_{u=\mathbf{0}})$ are represented either in the form $(5.2)_2$ or (5.5).

7.5.4. Conserved model $(PF)_\theta$ with suppressed thermal effects. We specify now system (5.1) in the situation of suppressed thermal effects. Let us assume that temperature is constant, normalized to unity, $\theta \equiv 1$, and that energy equation $(5.1)_4$ is identically satisfied. Then system (5.1) reduces to

$$\begin{aligned} &\varrho_0\ddot{\boldsymbol{u}} - \nabla\cdot(\varrho_0 f_{,\boldsymbol{F}}) = \varrho_0\boldsymbol{b},\\ &\varrho_0\dot{\chi} + \nabla\cdot\boldsymbol{j}^d = \varrho_0\tau,\\ &\varrho_0\mu = \frac{\delta(\varrho_0 f)}{\delta\chi} + a^d, \end{aligned} \tag{5.9}$$

with the free energy $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi)$, the chemical potential $\mu = \bar{\mu} = \frac{\mu}{1}$, and the state space

$$\mathcal{Z}_\theta|_{\theta=1} = \{\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \mu, \boldsymbol{D}\mu, \chi_{,t}\} \equiv \{\mathcal{X}|_{\theta=1}; \boldsymbol{\omega}|_{\theta=1}\} \tag{5.10}$$

splitted into the set of thermodynamic forces

$$\mathcal{X}|_{\theta=1} = (\boldsymbol{D}\mu, \chi_{,t}) \tag{5.11}$$

and the set of state variables

$$\boldsymbol{\omega}|_{\theta=1} = (\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \mu). \tag{5.12}$$

The dissipation potential, with the properties as before, is given by

$$\mathcal{D} = \hat{\mathcal{D}}(\mathcal{X}|_{\theta=1}; \boldsymbol{\omega}|_{\theta=1}), \tag{5.13}$$

and the dissipative quantities $\boldsymbol{j}^d = \hat{\boldsymbol{j}}^d(\mathcal{Z}_\theta|_{\theta=1})$, $a^d = \hat{a}^d(\mathcal{Z}_\theta|_{\theta=1})$ admit representations either in the form $(5.2)_2$,

$$-\boldsymbol{j}^d = \mathcal{D}_{,\boldsymbol{D}\mu}, \quad a^d = \mathcal{D}_{,\chi_{,t}},$$

or in the form (5.5) which now reduces to

$$\begin{aligned} -\boldsymbol{j}^d &= \boldsymbol{L}_{jj}\boldsymbol{D}\mu + \boldsymbol{l}_{ja}\chi_{,t}, \\ a^d &= \boldsymbol{l}_{aj} \cdot \boldsymbol{D}\mu + l_{aa}\chi_{,t}. \end{aligned} \tag{5.14}$$

Here the moduli $\boldsymbol{L}_{jj}$, $\boldsymbol{l}_{ja}$, $\boldsymbol{l}_{aj}$, l_{aa} may depend on the variables $\mathcal{Z}_\theta|_{\theta=1}$, and are consistent with the inequality

$$\begin{bmatrix} \boldsymbol{D}\mu \\ \chi_{,t} \end{bmatrix} \cdot \begin{bmatrix} \boldsymbol{L}_{jj} & \boldsymbol{l}_{ja} \\ \boldsymbol{l}_{aj}^T & l_{aa} \end{bmatrix} \begin{bmatrix} \boldsymbol{D}\mu \\ \chi_{,t} \end{bmatrix} \equiv \mathcal{X} \cdot \boldsymbol{B}(\mathcal{X}; \boldsymbol{\omega})\mathcal{X}|_{\theta=1} \geq 0 \tag{5.15}$$

for all variables $\mathcal{Z}_\theta|_{\theta=1} = \{\mathcal{X}|_{\theta=1}; \boldsymbol{\omega}|_{\theta=1}\}$.
According to (5.4), the solutions of model (5.9) with suppressed thermal effects satisfy the free energy inequality

$$\begin{aligned} &\varrho_0\dot{f} + \nabla \cdot (\mu\boldsymbol{j}^d - \dot{\chi}\varrho_0 f_{,\boldsymbol{D}\chi}) - \varrho_0 f_{,\boldsymbol{F}} \cdot \dot{\boldsymbol{F}} \\ &= -\varrho_0\sigma + \mu\varrho_0\tau \leq \mu\varrho_0\tau, \end{aligned} \tag{5.16}$$

where

$$\varrho_0\sigma = -\boldsymbol{D}\mu \cdot \boldsymbol{j}^d + \chi_{,t}a^d \geq 0 \quad \text{for all} \quad \mathcal{Z}_\theta|_{\theta=1}.$$

7.6. Nonconserved phase-field model $(PF)_\theta$ with extra vector field. In this section we specify the phase-field model $(PF)_\theta$ with extra terms (cf. (1.1)–(1.6)) in the case of the nonconserved dynamics of the phase variable, i.e., $\boldsymbol{j} \equiv \boldsymbol{0}$ and $r \neq 0$.
As in Section 7.5, we present two alternative formulations of the model which depend on the representation of the solution to the residual dissipation inequality.

7.6.1. Formulation. The state space is now

$$\mathcal{Z}_\theta = \left\{\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta, \boldsymbol{D}\frac{1}{\theta}, \bar{\mu}, \chi_{,t}\right\}, \quad \theta > 0, \quad \bar{\mu} = \frac{\mu}{\theta},$$

splitted into the set of thermodynamic forces

$$\mathcal{X} = \left(\bar{\mu}, \boldsymbol{D}\frac{1}{\theta}, \chi_{,t}\right)$$

and the set of state variables

$$\boldsymbol{\omega} = (\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta), \quad \{\mathcal{X};\boldsymbol{\omega}\} = \mathcal{Z}_\theta.$$

There are given the free energy $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi, \theta)$ which is strictly concave with respect to θ for all $\boldsymbol{F}, \chi, \boldsymbol{D}\chi$, and the dissipation potential $\mathcal{D} = \hat{\mathcal{D}}(\mathcal{X};\boldsymbol{\omega})$ which is non-negative, convex in $\mathcal{X}$ and such that $\mathcal{D}(\boldsymbol{0};\boldsymbol{\omega}) = 0$.

The unknowns are the fields $\boldsymbol{u}$, χ, $\bar{\mu} = \mu/\theta$ and $\theta > 0$ satisfying system of differential equations (1.3) with $\boldsymbol{j} \equiv \boldsymbol{0}$:

$$\begin{aligned}
&\varrho_0\ddot{\boldsymbol{u}} - \nabla\cdot(\varrho_0 f_{,\boldsymbol{F}}) = \varrho_0\boldsymbol{b},\\
&\varrho_0\dot{\chi} - \varrho_0 r^d = \varrho_0\tau,\\
&\varrho_0\bar{\mu} = \frac{\delta(\varrho_0 f/\theta)}{\delta\chi} + \boldsymbol{h}^e\cdot\nabla\frac{1}{\theta} + a^d,\\
&\varrho_0\dot{e} + \nabla\cdot(\boldsymbol{q}^d - \dot{\chi}\boldsymbol{h}^e) - \varrho_0 f_{,\boldsymbol{F}}\cdot\dot{\boldsymbol{F}} = \varrho_0 g,
\end{aligned}\tag{6.1}$$

where

$$\begin{aligned}
&e = f - \theta f_{,\theta},\\
&-\varrho_0 r^d = \mathcal{D}_{,\bar{\mu}}, \quad \boldsymbol{q}^d = \mathcal{D}_{,\boldsymbol{D}(1/\theta)}, \quad a^d = \mathcal{D}_{,\chi_{,t}},
\end{aligned}\tag{6.2}$$

and the extra vector field $\boldsymbol{h}^e$ is specified according to one of the examples in Section 7.4.

We recall that solutions of system (6.1) satisfy the entropy inequality (cf. (1.8))

$$\varrho_0\dot{\eta} + \nabla\cdot\Psi = \varrho_0\sigma - \bar{\mu}\varrho_0\tau + \frac{\varrho_0 g}{\theta} \geq -\bar{\mu}\varrho_0\tau + \frac{\varrho_0 g}{\theta}\tag{6.3}$$

with the entropy flux

$$\Psi = \Psi^d + \dot{\chi}\boldsymbol{h}^\eta,$$

where

$$\Psi^d = \frac{1}{\theta}\boldsymbol{q}^d, \quad \boldsymbol{h}^e + \theta\boldsymbol{h}^\eta = \varrho_0 f_{,\boldsymbol{D}\chi},$$

and the entropy production given by

$$\varrho_0\sigma = -\bar{\mu}\varrho_0 r^d + \boldsymbol{D}\frac{1}{\theta}\cdot\boldsymbol{q}^d + \chi_{,t}a^d \geq 0 \quad \text{for all variables } \mathcal{Z}_\theta.$$

Alternative representation

As in the conserved case (see Section 7.5) we introduce here an alternative representation of the dissipative quantities r^d, $\boldsymbol{q}^d$ and a^d, which is based on Gurtin's Lemma 4.4.1. The representation is given by

$$\begin{aligned}
&-\varrho_0 r^d = l_{rr}\bar{\mu} + \boldsymbol{l}_{rq}\cdot\boldsymbol{D}\frac{1}{\theta} + l_{ra}\chi_{,t},\\
&\boldsymbol{q}^d = \boldsymbol{l}_{qr}\bar{\mu} + \boldsymbol{L}_{qq}\boldsymbol{D}\frac{1}{\theta} + \boldsymbol{l}_{qa}\chi_{,t},\\
&a^d = l_{ar}\bar{\mu} + \boldsymbol{l}_{aq}\cdot\boldsymbol{D}\frac{1}{\theta} + l_{aa}\chi_{,t},
\end{aligned}\tag{6.4}$$

where the matrix $\boldsymbol{L}_{qq}$, the vectors $\boldsymbol{l}_{rq}$, $\boldsymbol{l}_{qr}$, $\boldsymbol{l}_{qa}$, $\boldsymbol{l}_{aq}$ and the scalars l_{rr}, l_{ra}, l_{ar}, l_{aa} are constituvie moduli that may depend on variables $\mathcal{Z}_\theta = \{\mathcal{X};\boldsymbol{\omega}\}$, and are consistent with the inequality

$$\begin{bmatrix} \bar{\mu} \\ \boldsymbol{D}\frac{1}{\theta} \\ \chi_{,t} \end{bmatrix} \cdot \begin{bmatrix} l_{rr} & \boldsymbol{l}_{rq}^T & l_{ra} \\ \boldsymbol{l}_{qr} & \boldsymbol{L}_{qq} & \boldsymbol{l}_{qa} \\ l_{ar} & \boldsymbol{l}_{aq}^T & l_{aa} \end{bmatrix} \begin{bmatrix} \bar{\mu} \\ \boldsymbol{D}\frac{1}{\theta} \\ \chi_{,t} \end{bmatrix} \tag{6.5}$$
$$\equiv \mathcal{X} \cdot \boldsymbol{B}(\mathcal{X}; \boldsymbol{\omega})\mathcal{X} \geq 0 \;\; \text{for all variables} \;\; \mathcal{Z}_\theta = \{\mathcal{X}; \boldsymbol{\omega}\}.$$

The vectors $\boldsymbol{l}_{rq}$, $\boldsymbol{l}_{qr}$, $\boldsymbol{l}_{qa}$ and $\boldsymbol{l}_{aq}$ represent anisotropic cross-coupling effects. By the Curie's principle they must vanish in isotropic systems; then

$$\boldsymbol{l}_{rq} = \boldsymbol{l}_{qr} = \boldsymbol{l}_{qa} = \boldsymbol{l}_{aq} = \boldsymbol{0}.$$

For further purposes let us write down the explicit form of equations (6.1) accounting for the representation (6.4):

$$\begin{aligned} &\varrho_0 \ddot{\boldsymbol{u}} - \nabla \cdot (\varrho_0 f_{,\boldsymbol{F}}) = \varrho_0 \boldsymbol{b}, \\ &\varrho_0 \dot{\chi} + \left(l_{rr}\bar{\mu} + \boldsymbol{l}_{rq} \cdot \nabla \frac{1}{\theta} + l_{ra}\dot{\chi} \right) = \varrho_0 \tau, \\ &\varrho_0 \bar{\mu} = \frac{1}{\theta}[\varrho_0 f_{,\chi} - \nabla \cdot (\varrho_0 f_{,\boldsymbol{D}\chi})] + l_{ar}\bar{\mu} + (\boldsymbol{l}_{aq} + \boldsymbol{h}^e - \varrho_0 f_{,\boldsymbol{D}\chi}) \cdot \nabla \frac{1}{\theta} + l_{aa}\dot{\chi}, \\ &\varrho_0 \dot{e} + \nabla \cdot \left[\boldsymbol{l}_{qr}\bar{\mu} + \boldsymbol{L}_{qq}\nabla\frac{1}{\theta} + (\boldsymbol{l}_{qa} - \boldsymbol{h}^e)\dot{\chi} \right] - \varrho_0 f_{,\boldsymbol{F}} \cdot \dot{\boldsymbol{F}} = \varrho_0 g. \end{aligned} \tag{6.6}$$

In Part II the nonconserved model $(PF)_\theta$, expressed in the form (6.1) or (6.6), will be compared with well-known phase-field models in two situations of suppressed either elastic or thermal effects.

7.6.2. Nonconserved model $(PF)_\theta$ with suppressed elastic effects. Let us specify system (6.1) in the situation of suppressed elastic effects.

Assume $\boldsymbol{u} = \boldsymbol{0}$, so that

$$\boldsymbol{x} = \boldsymbol{y}(\boldsymbol{X}, t) = \boldsymbol{X}, \quad \boldsymbol{v} = \boldsymbol{0}, \qquad \boldsymbol{F} = \boldsymbol{I}, \quad \varrho = \varrho_0 / \det \boldsymbol{F} = \varrho_0,$$

and the referential and spatial operations are identical

$$\nabla f = \operatorname{grad} f, \quad \dot{f} = f_t.$$

Then, provded the equation of linear momentum balance $(6.1)_1$ is identically satisfied, system (6.1) refers to the spatial description of a two-phase, nonconserved system at rest. It reads

$$\begin{aligned} &\varrho_0 \chi_t - \varrho_0 r^d = \varrho_0 \tau, \\ &\varrho_0 \bar{\mu} = \frac{\delta(\varrho_0 f/\theta)}{\delta \chi} + \boldsymbol{h}^e \cdot \nabla \frac{1}{\theta} + a^d, \\ &\varrho_0 e_t + \nabla \cdot (\boldsymbol{q}^d - \chi_t \boldsymbol{h}^e) = \varrho_0 g, \end{aligned} \tag{6.7}$$

where all differential operations refer to the spatial description.

The state space in now

$$\mathcal{Z}_\theta|_{\boldsymbol{u}=\boldsymbol{0}} = \left\{ \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \boldsymbol{D}\frac{1}{\theta}, \bar{\mu}, \chi_{,t} \right\} \equiv \{\mathcal{X}|_{\boldsymbol{u}=\boldsymbol{0}}; \boldsymbol{\omega}|_{\boldsymbol{u}=\boldsymbol{0}}\},$$

splitted into the set of thermodynamic forces

$$\mathcal{X}|_{u=0} = \left(\bar{\mu}, \boldsymbol{D}\frac{‘1}{\theta}, \chi_{,t}\right),$$

and the set of state variables

$$\boldsymbol{\omega}|_{u=0} = (\chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \theta).$$

The system (6.7) is governed by the free energy $f = \hat{f}(\chi, \boldsymbol{D}\chi, \theta)$ which is strictly concave with respect to θ for all $\chi, \boldsymbol{D}\chi$, and the dissipation potential $\mathcal{D} = \hat{\mathcal{D}}(\mathcal{X}|_{u=0}, \boldsymbol{\omega}|_{u=0})$ which is nonnegative, convex in $\mathcal{X}|_{u=0}$ and such that $\mathcal{D}(\mathbf{0}; \boldsymbol{\omega}|_{u=0}) = 0$.

As in $(6.2)_1$, the internal energy is

$$e = \hat{e}(\chi, \boldsymbol{D}\chi, \theta) = f(\chi, \boldsymbol{D}\chi, \theta) - \theta f_{,\theta}(\chi, \boldsymbol{D}\chi, \theta),$$

the extra vector field $\boldsymbol{h}^e = \hat{\boldsymbol{h}}^e(\mathcal{Z}_\theta|_{u=0})$ is selected according to one of the examples in Section 7.4, and the dissipative quantities $r^d = \hat{r}^d(\mathcal{Z}_\theta|_{u=0})$, $\boldsymbol{q}^d = \hat{\boldsymbol{q}}^d(\mathcal{Z}_\theta|_{u=0})$, $a^d = \hat{a}^d(\mathcal{Z}_\theta|_{u=0})$ are represented either in the form $(6.2)_2$ or (6.4).

7.6.3. Nonconserved model $(PF)_\theta$ with suppressed thermal effects. We specify now system (6.1) in the situation of suppressed thermal effects. Let us assume that temperature is constant, normalized to unity, $\theta \equiv 1$, and that energy equation $(6.1)_4$ is identically satisfied. Then (6.1) reduces to

$$\begin{aligned} &\varrho_0 \ddot{\boldsymbol{u}} - \nabla \cdot (\varrho_0 f_{,\boldsymbol{F}}) = \varrho_0 \boldsymbol{b}, \\ &\varrho_0 \dot{\chi} - \varrho_0 r^d = \varrho_0 \tau, \\ &\varrho_0 \mu = \frac{\delta(\varrho_0 f)}{\delta \chi} + a^d \end{aligned} \tag{6.8}$$

with the free energy given by $f = \hat{f}(\boldsymbol{F}, \chi, \boldsymbol{D}\chi)$, the chemical potential $\mu = \bar{\mu} \equiv \frac{\mu}{1}$, the state space

$$\mathcal{Z}_\theta|_{\theta=1} = \{\boldsymbol{F}, \boldsymbol{DF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi, \mu, \chi_{,t}\} \equiv \{\mathcal{X}|_{\theta=1}; \boldsymbol{\omega}|_{\theta=1}\},$$

splitted into the set of thermodynamic forces

$$\mathcal{X}|_{\theta=1} = (\mu, \chi_{,t})$$

and the set of state variables

$$\boldsymbol{\omega}|_{\theta=1} = (\boldsymbol{FDF}, \chi, \boldsymbol{D}\chi, \boldsymbol{D}^2\chi).$$

The quantities $r^d = \hat{r}^d(\mathcal{Z}_\theta|_{\theta=1})$ and $a^d = \hat{a}^d(\mathcal{Z}_\theta|_{\theta=1})$ are subjest to the residual dissipation inequality

$$\varrho_0 \sigma := -\mu \varrho_0 r^d + \chi_{,t} a^d \geq 0 \quad \text{for all variables } \mathcal{Z}_\theta|_{\theta=1}. \tag{6.9}$$

The dissipation potential

$$\mathcal{D} = \hat{\mathcal{D}}(\mathcal{X}|_{\theta=1}; \boldsymbol{\omega}|_{\theta=1})$$

has the properties as before, i.e., is nonnegative, convex in $\mathcal{X}|_{\theta=1}$ and such that $\mathcal{D}(\mathbf{0}; \boldsymbol{\omega}|_{\theta=1}) = 0$.

The dissipative quantities $r^d = \hat{r}^d(\mathcal{Z}_\theta|_{\theta=1})$ and $a^d = \hat{a}^d(\mathcal{Z}_\theta|_{\theta=1})$ admit representations either in the form $(6.2)_2$, viz.

$$-\varrho_0 r^d = \mathcal{D}_{,\mu}, \quad a^d = \mathcal{D}_{,\chi_{,t}}, \tag{6.10}$$

or in the form (6.4) which in the present situation reduces to

$$\begin{aligned} -\varrho_0 r^d &= l_{rr}\mu + l_{ra}\chi_{,t}, \\ a^d &= l_{ar}\mu + l_{aa}\chi_{,t}. \end{aligned} \tag{6.11}$$

The scalar moduli l_{rr}, l_{ra}, l_{ar}, l_{aa} may depend on the variables $\mathcal{Z}_\theta|_{\theta=1}$ and are consistent with the inequality

$$\begin{bmatrix} \mu \\ \chi_{,t} \end{bmatrix} \cdot \begin{bmatrix} l_{rr} & l_{ra} \\ l_{ar} & l_{aa} \end{bmatrix} \begin{bmatrix} \mu \\ \chi_{,t} \end{bmatrix} \equiv \mathcal{X} \cdot \boldsymbol{B}(\mathcal{X};\boldsymbol{\omega})\mathcal{X}|_{\theta=1} \geq 0 \tag{6.12}$$

for all variables $\mathcal{Z}_\theta|_{\theta=1}$.

According to (1.14) the solutions of system (6.8) satisfy the free energy (dissipation) inequality

$$\begin{aligned} &\varrho_0 \dot{f} - \nabla \cdot (\dot{\chi}\varrho_0 f_{,\boldsymbol{D}\chi}) - \varrho_0 f_{,\boldsymbol{F}} \cdot \dot{\boldsymbol{F}} \\ &= -\varrho_0\sigma + \mu\varrho_0\tau \leq \mu\varrho_0\tau, \end{aligned} \tag{6.13}$$

with dissipation scalar $\varrho_0\sigma$ given by (6.9).

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