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

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## 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 particular 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 Roitburd [141], Umantsev [139], [140], [142], and Umantsev and Olson [143].

For overview 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 been 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, Schimperna, 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 transformation 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 Roitburd [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 potentials, 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 consists of three main steps.

In the first step we consider the system of balance laws with a set of constitutive variables relevant for the phase transition under consideration. Distinctive elements in this set are variables representing higher gradients of the order parameter and its time derivative. The presence of such variables is characteristic for theories involving free energies of Landau-Ginzburg type. 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  $\mathbf{y}(\mathbf{X}, t) = \mathbf{X} + \mathbf{u}(\mathbf{X}, t)$ , where  $\mathbf{u} = (u_i)$  is the displacement vector;  $\mathbf{F} = \nabla \mathbf{y} = \mathbf{I} + \nabla \mathbf{u}$ , subject to the condition  $\det \mathbf{F} > 0$ , is the deformation gradient.

We deal with the following quantities in the material representation:

$\varrho_0 = \varrho_0(\mathbf{X}) > 0$  – mass density given once and for all along with the body and the fixed reference configuration,

$\mathbf{S} = (S_{ij})$  – referential stress tensor,

$\mathbf{b} = (b_i)$  – specific body force,

$\chi$  – scalar order parameter (phase variable),

$\mathbf{j} = (j_i)$  – order parameter flux,

$r$  – specific rate of production of the phase variable,

$\tau$  – specific rate of supply of the phase variable from the exterior,

$\mu$  – chemical potential,

$\theta > 0$  – absolute temperature,

$\bar{\mu} = \mu/\theta$  – rescaled chemical potential,

$\mathbf{q} = (q_i)$  – referential heat flux vector,

$g$  – specific rate of supply of heat,

$e$  – specific internal energy,

$\eta$  – specific entropy,

$f = e - \theta\eta$  – free energy (Helmholtz) function,

$\phi = f/\theta$  – rescaled free energy,

$\sigma$  – specific entropy production,

$\Psi = (\Psi_i)$  – referential entropy flux,

$c_{\mathbf{F}}$  – specific heat at constant deformation.

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

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

$$\begin{aligned} \mathcal{X} &:= \left( \frac{\mu}{\theta}, \mathbf{D} \frac{\mu}{\theta}, \mathbf{D} \frac{1}{\theta}, \chi, t \right) && \text{— thermodynamic forces,} \\ \omega &:= (\mathbf{F}, \mathbf{D}\mathbf{F}, \chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \theta) && \text{— state variables,} \end{aligned}$$

which is nonnegative, convex in  $\mathcal{X}$  and such that  $\mathcal{D}(\mathbf{0}; \omega) = 0$ . Above  $\mathbf{D}\chi, \mathbf{D}^2\chi, \chi, t$ , etc. denote variables corresponding to  $\nabla\chi, \nabla^2\chi, \dot{\chi}$ , respectively. Here and in what follows all derivatives are material;  $\nabla$  and  $\nabla \cdot$  are the gradient and the divergence with respect to material point  $\mathbf{X}$ , 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  $\mathbf{u}, \chi, \bar{\mu} := \frac{\mu}{\theta}$  and  $\theta > 0$  satisfying the following system of differential equations in  $\Omega \subset \mathbb{R}^3$  and time  $t \in [0, T]$ ,  $T > 0$ :

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

subject to appropriate initial and boundary conditions. Here

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

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

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

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

The quantity  $\sigma$  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  $r^d, \mathbf{j}^d, \mathbf{q}^d, a^d$  are given by

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

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)<sub>2</sub> combines various types of dynamics of the order parameter:

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

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

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

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  $\mathbf{h}^e = \hat{\mathbf{h}}^e(\mathcal{X};\omega)$  which contributes to the nonstationary energy flux (superscript  $e$  indicates energy). The vector field  $\mathbf{h}^e$  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  $\mathbf{F}$ . In particular, the free energy should satisfy

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

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

Apart from this restriction the vector field  $\mathbf{h}^e$  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  $\mathbf{h}^e$  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

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

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

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

Above

$$\Psi^d := -\frac{\mu}{\theta} \mathbf{j}^d + \frac{1}{\theta} \mathbf{q}^d \quad (1.8)$$

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

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

is an extra nonequilibrium entropy flux.

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

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

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.,  $\mathbf{b} = \mathbf{0}$ ,  $\tau = 0$ ,  $g = 0$ , and if the boundary conditions on the domain boundary  $S$  imply that

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

where  $\mathbf{n}$  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

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

This provides the Lyapunov relation.

One can see that the distinguishing elements in system (1.1)–(1.3) are nonstandard energy and entropy fluxes,  $\mathbf{q}$  and  $\Psi$  which contain extra nonstationary terms. The relation (1.10) indicates that in phase-field models with the first-order gradient free energy (i.e.,  $f_{,D\chi} \neq \mathbf{0}$ ) 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  $\mathbf{h}^e$  and  $\mathbf{h}^\eta$ :

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

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

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

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

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

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

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  $\mathbf{h}^e$ , assuming standard forms of the free energy  $f = \hat{f}(\mathbf{F}, \chi, \mathbf{D}\chi, \theta)$  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 method 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  $f = \hat{f}(\mathbf{F}, \chi, \mathbf{D}\chi, \theta)$ , e.g., the Landau-Ginzburg free energy. Such relations – well known for classical systems with volumetric free energies – in case 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  $\theta$  and inverse temperature  $\vartheta = 1/\theta$  in place of entropy  $\eta$  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  $\mathbf{h}^e$  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 consistency 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  $\mathbf{h}^e$ . 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 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-known 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 comparison 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  $\mathbf{I}$  is defined by  $\mathbf{I}\mathbf{u} = \mathbf{u}$  for every vector  $\mathbf{u}$ ;  $\mathbf{S}^T$ ,  $\text{tr}\mathbf{S}$ ,  $\mathbf{S}^{-1}$  and  $\det \mathbf{S}$ , respectively, denote the transpose, trace, inverse, and determinant of a tensor  $\mathbf{S}$ .

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

In Cartesian components

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

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

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

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

The term field signifies a function of a material point  $\mathbf{X} \in \mathbb{R}^3$  and time  $t$ .

The superimposed dot, e.g.,  $\dot{f}$ , denotes the material time derivative of the field  $f$  (with respect to  $t$  holding  $\mathbf{X}$  fixed),  $\nabla$  and  $\nabla \cdot$  denote the material gradient and the divergence (with respect to  $\mathbf{X}$  holding  $t$  fixed).

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

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

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

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

This gives the following representation

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

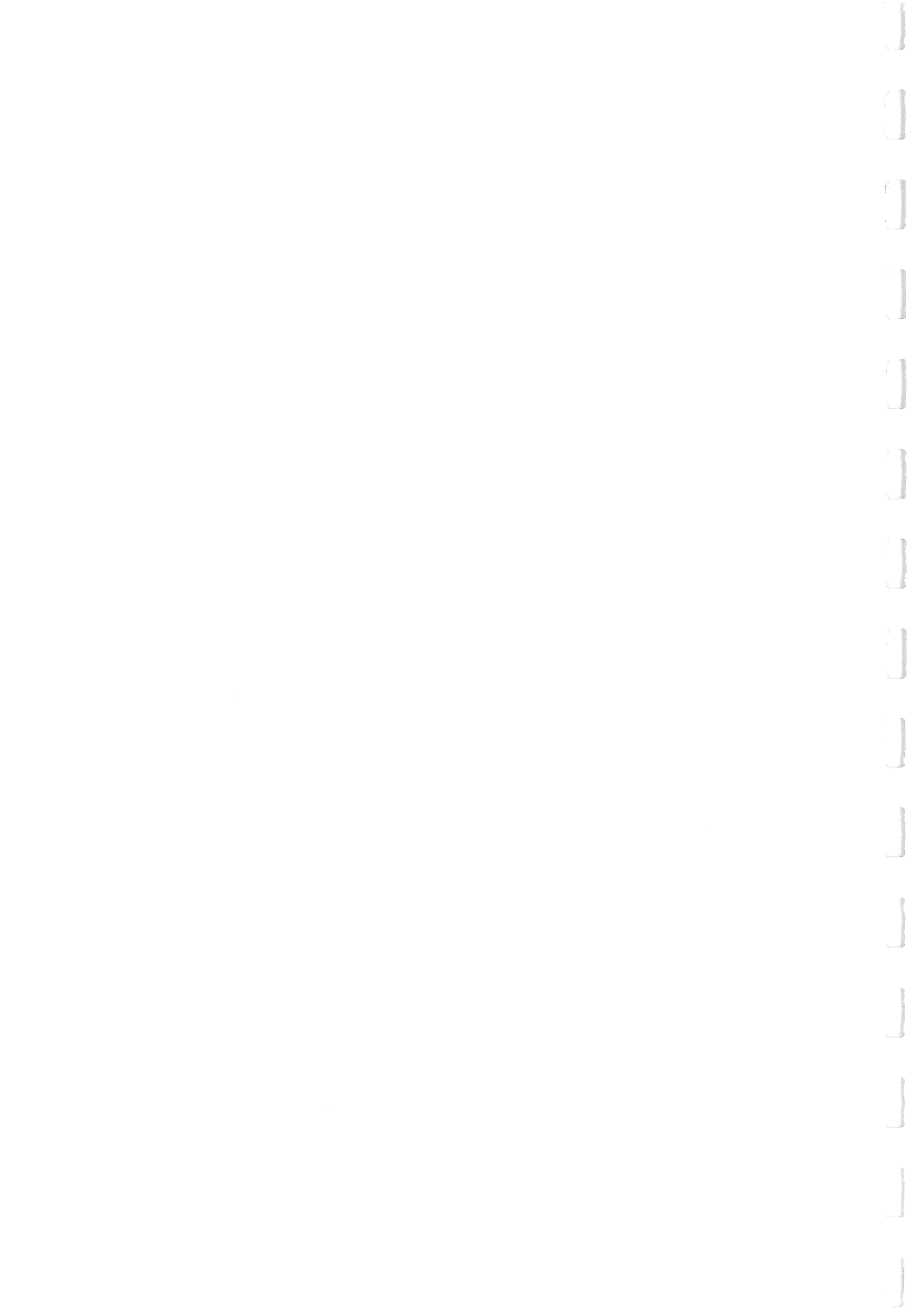
In situations that may cause confusion we shall distinguish between functions and their values. Functions are then denoted by "hats", e.g.,  $f = \hat{f}(\mathbf{F}, \chi, \mathbf{D}\chi, \theta)$ .

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 II

Applications



## 8. Examples of thermodynamic potentials

To set a stage for a comparison with phase-field models known in the literature which will be presented in the subsequent chapters, we collect here some typical examples of the free energy and the dissipation potentials.

**8.1. The Helmholtz free energy for phase-field models with an order parameter.** A general model of the Helmholtz free energy density describing phase transitions we deal with in this work has so-called *Landau-Ginzburg form*. More precisely, it is composed of two parts

$$f(\mathbf{F}, \chi, \mathbf{D}\chi, \theta) = f_V(\mathbf{F}, \chi, \theta) + f_G(\mathbf{F}, \chi, \mathbf{D}\chi, \theta), \quad (1.1)$$

where the first part  $f_V(\mathbf{F}, \chi, \theta) = f(\mathbf{F}, \chi, \mathbf{0}, \theta)$  represents the volumetric (homogenous) free energy whereas as the second one  $f_G(\mathbf{F}, \chi, \mathbf{D}\chi, \theta)$  is the gradient (inhomogeneous) free energy associated with diffused (not sharp) phase interfaces.

We assume that the classical Gibbs relations remain valid in the case of gradient type free energy (1.1) (see Section 3.2)

$$f = e - \theta\eta, \quad \eta = -f_{,\theta}. \quad (1.2)$$

The specific heat at constant deformation is given by (see Section 3.3)

$$c_{\mathbf{F}} = e_{,\theta} = \theta\eta_{,\theta} = -\theta f_{,\theta\theta}. \quad (1.3)$$

According to (1.2), the splitting (1.1) of  $f$  implies the analogous splittings of the internal energy  $e$  and the entropy  $\eta$  into the volumetric and gradient parts

$$e = e_V + e_G, \quad \eta = \eta_V + \eta_G, \quad (1.4)$$

satisfying

$$\begin{aligned} e_V &= f_V + \theta\eta_V, & \eta_V &= -f_{V,\theta}, \\ e_G &= f_G + \theta\eta_G, & \eta_G &= -f_{G,\theta}. \end{aligned} \quad (1.5)$$

Similarly, the specific heat  $c_{\mathbf{F}}$  splits into the volumetric and the gradient part

$$c_{\mathbf{F}} = c_V + c_G, \quad (1.6)$$

where

$$\begin{aligned} c_V &= e_{V,\theta} = \theta\eta_{V,\theta} = -\theta f_{V,\theta\theta}, \\ c_G &= e_{G,\theta} = \theta\eta_{G,\theta} = -\theta f_{G,\theta\theta}. \end{aligned} \quad (1.7)$$

**8.1.1. The gradient energy.** A typical example of the gradient energy considered in the present work is given in the following isotropic form

$$f_G(\chi, D\chi, \theta) = \frac{1}{2} \varkappa(\chi, \theta) |D\chi|^2, \quad (1.8)$$

where  $\varkappa(\chi, \theta)$  is a positive function, usually a small interfacial parameter. Consequently, in the case of gradient energy (1.8), we have

$$e_G = \frac{1}{2} \varkappa_e |D\chi|^2, \quad \eta_G = -\frac{1}{2} \varkappa_\eta |D\chi|^2, \quad (1.9)$$

where

$$\varkappa_e := \varkappa - \theta \varkappa_{,\theta}, \quad \varkappa_\eta := \varkappa_{,\theta}, \quad \varkappa_e + \theta \varkappa_\eta = \varkappa. \quad (1.10)$$

Correspondingly, we call  $\varkappa_e$  the *energetic* and  $\varkappa_\eta$  the *entropic interfacial parameter*.

According to (1.10) the coefficient  $\varkappa(\chi, \theta)$  is made up of the energetic and entropic contributions.

The energetic contribution  $\varkappa_e$  is due to interaction between different molecules in the mixture whereas the entropic one  $\varkappa_\eta$  is due to the connectivity of subunits of a molecule. In application to concrete systems one can distinguish special cases of the gradient term in the free energy:

(i) *of energetic type*  $\varkappa(\chi, \theta) = \varkappa_e(\chi) > 0$ . Then

$$\begin{aligned} e_{,D\chi} &= (f - \theta f_{,\theta})_{,D\chi} = f_{,D\chi} = \varkappa D\chi = \varkappa_e(\chi) D\chi \\ \Leftrightarrow \eta_{,D\chi} &= -f_{,\theta D\chi} = -\varkappa_{,\theta} D\chi = \mathbf{0}. \end{aligned} \quad (1.11)$$

(ii) *of entropic type*  $\varkappa(\chi, \theta) = \theta \varkappa_\eta(\chi) > 0$ . Then

$$\begin{aligned} e_{,D\chi} &= (f - \theta f_{,\theta})_{,D\chi} = (\varkappa - \theta \varkappa_\eta(\chi)) D\chi = \mathbf{0} \\ \Leftrightarrow \theta \eta_{,D\chi} &= -\theta f_{,\theta D\chi} = -\theta \varkappa_\eta(\chi) D\chi = -\varkappa D\chi = -f_{,D\chi}. \end{aligned} \quad (1.12)$$

(iii) the sum of energetic and entropic terms

$$\varkappa(\chi, \theta) = \varkappa_e(\chi) + \theta \varkappa_\eta(\chi) > 0. \quad (1.13)$$

We note that in case the coefficient  $\varkappa(\chi, \theta)$  in (1.8) depends linearly on  $\theta$  there is no gradient contribution to the specific heat coefficient, i.e.,  $c_G = -\theta f_{G,\theta\theta} = 0$ .

**REMARK 8.1.** For phase transition models with gradient terms in the entropy density we refer, e.g., to [129], [130], [66], [145], [146], [83], [65], [29].

For models with gradient term in the internal energy density we refer, e.g., [7], [8], [139], [141], [146], [83], [72], [104], [105], [12].

Models with gradient terms both in the energy and in the entropy have been considered, e.g., in [10], [37], [113]. It is worth pointing out that such case is physically justified for models describing phase separation in binary polymer mixtures (see Section 8.5).

**8.2. The volumetric energy.** The volumetric free energy is usually postulated in the separable form

$$f_V(\mathbf{F}, \chi, \theta) = f_*(\theta) + W(\mathbf{F}, \chi, \theta) + f_0(\chi, \theta), \quad (2.1)$$

with the subsequent terms representing the thermal energy, the elastic energy, and the chemical (mixture) energy.



According to (1.2), (1.3), the separable form of  $f_V$  implies the separable forms of the volumetric parts of  $e$ ,  $\eta$  and  $c_F$ :

$$\begin{aligned} e_V &= e_* + e_W + e_0, \\ \eta_V &= \eta_* + \eta_W + \eta_0, \\ c_V &= c_* + c_W + c_0, \end{aligned} \quad (2.2)$$

with the corresponding contributions corresponding to  $f_*$ ,  $W$  and  $f_0$ .

**8.2.1. Thermal energy.** The most commonly used example of  $f_*$  is associated with constant thermal specific heat  $c_* = \text{const} > 0$ . It is given by (see, e.g., [20, Chap. 4.4], [55])

$$f_*(\theta) = -c_*\theta \ln \frac{\theta}{\theta_1} + c_*\theta + \bar{c} \quad (2.3)$$

with positive constants  $c_*$ ,  $\theta_1$ , and some constant  $\bar{c}$  immaterial from the point of view of differential equations. According to (1.2), (1.3), the entropy, the internal energy and the specific heat corresponding to (2.3) are

$$\begin{aligned} \eta_*(\theta) &= -f_{*,\theta} = c_* \ln \frac{\theta}{\theta_1}, \\ e_*(\theta) &= f_* + \theta\eta_* = c_*\theta + \bar{c}, \\ c_* &= e_{*,\theta}. \end{aligned} \quad (2.4)$$

Referring to Fabrizio, Giorgi, and Morro [55], we complement the above example by comments concerning the thermal specific heat.

According to the Debye theory the thermal heat is a function of the ratio  $\theta/\theta_D$ , with  $\theta_D$  denoting the *Debye temperature*, namely

$$c_*(\theta) = \bar{c}D(\theta/\theta_D), \quad \bar{c} > 0,$$

where  $D(\cdot)$  is the *Debye function*. It is defined by

$$D(\xi) = \xi^3 \int_0^{1/\xi} \frac{x^3}{\exp x - 1} dx - \frac{1}{4\xi \left( \exp \frac{1}{\xi} - 1 \right)}.$$

The Debye temperature  $\theta_D$  is a characteristic property of a given material.

The assumption of a constant specific heat – known as *Dulong-Petit law* – is relevant for sufficiently high temperatures  $\theta \gg \theta_D$ .

As  $\theta$  is much smaller than  $\theta_D$ , one may use the approximation

$$c_*(\theta) = c_0\theta^3, \quad c_0 > 0, \quad (2.5)$$

which is known as *the Debye law*.

Correspondingly  $f_*$ ,  $\eta_*$  and  $e_*$  take then the form

$$f_*(\theta) = -\frac{1}{12}c_0\theta^4, \quad \eta_*(\theta) = \frac{1}{3}c_0\theta^3, \quad e_*(\theta) = \frac{1}{4}c_0\theta^4. \quad (2.6)$$

At very low temperatures, the electronic contribution to the specific heat is significant and results in a linear term, so that

$$c_*(\theta) = c_0\theta^3 + c_1\theta, \quad c_0, c_1 > 0. \quad (2.7)$$

When the linear term becomes predominant, that is when one may use the approximation

$$c_*(\theta) = c_1\theta, \quad c_1 > 0, \quad (2.8)$$

then

$$f_*(\theta) = -\frac{1}{2}c_1\theta^2, \quad \eta_*(\theta) = c_1\theta, \quad e_*(\theta) = \frac{1}{2}c_1\theta^2. \quad (2.9)$$

Let us note that the examples (2.6) and (2.9) relevant at low temperatures, are consistent with the third law of thermodynamics

$$\eta_*(\theta) \rightarrow 0 \quad \text{as} \quad \theta \rightarrow 0. \quad (2.10)$$

**8.2.2. Elastic energy.** An example of elastic energy  $W(\mathbf{F}, \chi, \theta)$  for phase separation in a binary  $a - b$  alloy in case of infinitesimal deformations is (see, e.g., [48], [16], [78], [79]):

$$W(\boldsymbol{\varepsilon}(\mathbf{u})\chi, \theta) = \frac{1}{2}(\boldsymbol{\varepsilon}(\mathbf{u}) - \bar{\boldsymbol{\varepsilon}}(\chi, \theta)) \cdot \mathbf{A}(\chi, \theta)(\boldsymbol{\varepsilon}(\mathbf{u}) - \bar{\boldsymbol{\varepsilon}}(\chi, \theta)), \quad (2.11)$$

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

Tensors  $\mathbf{A}(\chi, \theta)$  and  $\bar{\boldsymbol{\varepsilon}}(\chi, \theta)$  are defined by

$$\begin{aligned} \mathbf{A}(\chi, \theta) &= (1 - z(\chi, \theta))\mathbf{A}_a + z(\chi, \theta)\mathbf{A}_b, \\ \bar{\boldsymbol{\varepsilon}}(\chi, \theta) &= (\theta - \theta_R)[(1 - z(\chi, \theta))\boldsymbol{\alpha}_a + z(\chi, \theta)\boldsymbol{\alpha}_b], \end{aligned} \quad (2.12)$$

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

$$z(\chi, \theta) = \frac{\chi_a(\theta) - \chi}{\chi_a(\theta) - \chi_b(\theta)}. \quad (2.13)$$

It interpolates, between temperature-dependent equilibrium (binodal) concentrations  $\chi_a(\theta)$  and  $\chi_b(\theta)$  of the  $a - b$  phase diagram. The nonlinear dependence of the elastic energy  $W$  on  $\theta$  gives rise to the corresponding internal energy  $e_W(\boldsymbol{\varepsilon}(\mathbf{u}), \chi, \theta)$ , the entropy  $\eta_W(\boldsymbol{\varepsilon}(\mathbf{u}), \chi, \theta)$  and the specific heat  $c_W(\boldsymbol{\varepsilon}(\mathbf{u}), \chi, \theta)$  contributions.

**8.2.3. Chemical (mixture) energy.** We give now typical examples of the volumetric free energies for binary mixtures.

**8.2.3.1. The regular solution model** (see Cahn and Hilliard [34]). Let  $\chi$  denote the mole fraction of one of two components in a binary system, so that  $\chi$  is subject to the constraint  $0 < \chi < 1$ . According to the regular solution theory the free energy of a (uniform) mixture is given by

$$f_0(\chi, \theta) = k_B\theta[\chi \ln \chi + (1 - \chi) \ln(1 - \chi)] + \omega_e\chi(1 - \chi), \quad (2.14)$$

where  $k_B$  is the Boltzmann's constant, for simplicity assumed  $k_B = 1$ , and  $\omega_e$  is a positive parameter related to molecular interactions.

The term  $-k_B[\chi \ln \chi + (1 - \chi) \ln(1 - \chi)]$  corresponds to the configurational entropy per molecule and  $\omega_e\chi(1 - \chi)$  is the enthalpy of mixing of a two-component mixture.

Taking into account that

$$f_{0,\chi\chi} = \frac{\theta}{\chi(1-\chi)} - 2\omega_e,$$

we note that there is a critical value  $\omega_c := 2\theta$  such that for  $\omega_e < \omega_c$  the free energy  $f_0$  is convex, thus the mixture is entirely miscible, while for  $\omega_e > \omega_c$ ,  $f_0$  is concave, so that phase separation may occur. Equivalently, phase separation may occur if  $\theta < \theta_c := \omega_e/2$ .

We note that the entropy, internal energy and the specific heat associated with free energy (2.14) are given by

$$\eta_0 = -k_B[\chi \ln \chi + (1-\chi) \ln(1-\chi)], \quad e_0 = \omega_e \chi(1-\chi), \quad c_0 = 0. \quad (2.15)$$

**8.2.3.2. The Flory-Huggins model [69].** The model describes a binary mixture of polymer molecules of different types  $j$ , each consisting of  $N_j$  segments. Let  $\chi_j > 0$  be the volume fraction of segments of type  $j$ , so that  $\chi_1 + \chi_2 = 1$ . Let the order parameter be  $\chi := \chi_1$ , so that  $0 < \chi < 1$  and  $\chi_2 = 1 - \chi$ . According to the Flory theory, see [69, Chap. 12, 31, 64], the mixture part of the free energy of such a system has the form

$$f_0(\chi, \theta) = k_B \theta \left[ \frac{\chi}{N_1} \ln \chi + \frac{1-\chi}{N_2} \ln(1-\chi) \right] + \omega(\chi, \theta) \chi(1-\chi), \quad (2.16)$$

where for simplicity we assume the Boltzmann's constant  $k_B = 1$ . The negative of the term in the square parenthesis in (2.16) corresponds to configurational entropy per molecule, and the second term accounts for intersegmental interactions. The parameter  $\omega$  (traditionally denoted by  $\chi$ ), called the *Flory-Huggins interaction parameter*, is in general postulated in the form (see e.g., [43, Chap 3], [44], [13], [119])

$$\omega(\chi, \theta) = \omega_e + \theta \omega_\eta(\chi), \quad (2.17)$$

where the subindices  $e$  and  $\eta$  indicate the energetic and entropic contributions, respectively. The standard case is  $\omega_e = \text{const} > 0$  and  $\omega_\eta = \text{const} \geq 0$ . For other empirical formulas  $\omega_e$  and  $\omega_\eta(\chi)$  we refer e.g., to [119, Chap. 3], [13].

We note that setting  $N_1 = 1$  the free energy (2.16) describes polymer-solvent mixture with  $\chi = \chi_1$  being the volume fraction of the solvent.

It is worth noting that for  $\omega \equiv \omega_e = \text{const} > 0$ , the Flory-Huggins free energy (2.16) has the same qualitative features as the regular solution model in the Cahn-Hilliard theory. In particular, in the symmetric case  $N_1 = N_2 = N$ , there exists a critical value  $\omega_{\text{crit}} := 2\theta/N$  such that for  $\omega < \omega_{\text{crit}}$ ,  $f_0$  is strictly convex in  $\chi$  so that the mixture is entirely miscible. For  $\omega > \omega_{\text{crit}}$ ,  $f_0$  takes on the double-well form so that phase separation may occur.

Let us note that the entropy, the internal energy and the specific heat corresponding to model (2.16), (2.17) are given by

$$\begin{aligned} \eta_0 &= -k_B \left[ \frac{\chi}{N_1} \ln \chi + \frac{1-\chi}{N_2} \ln(1-\chi) \right] - \omega_\eta(\chi) \chi(1-\chi), \\ e_0 &= \omega_e \chi(1-\chi), \quad c_0 = 0. \end{aligned} \quad (2.18)$$

**8.2.3.3. The Landau and the Devonshire models.** Such models have the form of the polynomials

$$f_0(\chi, \theta) = f_*(\theta) + \sum_{j=1}^m a_j(\theta)\chi^j, \quad m \in \mathbf{N}, \quad (2.19)$$

with  $\chi \in (-\infty, +\infty)$ . They arise by expanding the free energy  $f$  in  $\chi$  at a value  $\chi_c$  for  $\theta$  near  $\theta_c$ , where  $(\chi_c, \theta_c)$  is a critical point, i.e., such a point where a bifurcation for the set of extrema of  $f_0$  (characterized by the condition  $\partial f_0/\partial \chi = 0$ ) arises.

The classical Landau model of a free energy describing second order phase transitions is given by (see Landau and Lifshitz [93, Chap 14])

$$f_0(\chi, \theta) = f_*(\theta) + \alpha_1(\theta - \theta_c)\chi^2 + \alpha_2\chi^4 \quad (2.20)$$

with positive constants  $\alpha_1, \alpha_2$  and a critical temperature  $\theta_c$ .

A characteristic feature of (2.20) as a model of a second order temperature driven phase transition at  $\theta = \theta_c$  is that the coefficient in front of  $\chi^2$  changes sign at  $\theta = \theta_c$ . For  $\theta > \theta_c$ ,  $f$  attains a unique minimum at  $\chi = 0$ , and for  $\theta < \theta_c$  there are two symmetric lateral minima which continuously approach zero as  $\theta \nearrow \theta_c$ .

The Devonshire free energy has been originally introduced in [46] for ferroelectric materials and applied for shape memory alloys by Falk [56], [57], [58], [59], [60], [61]. It has the form of a sixth order polynomial

$$f_0(\chi, \theta) = f_*(\theta) + \alpha_1(\theta - \theta_c)\chi^2 - \alpha_2\chi^4 + \alpha_3\chi^6 \quad (2.21)$$

with positive constants  $\alpha_1, \alpha_2, \alpha_3$ . The function  $f_0(\cdot, \theta)$  may have up to three minima: the central minimum at  $\chi = 0$ , representing the high temperature phase, and two symmetric lateral minima corresponding to the two variants of the low temperature phase.

In the case of (2.21) the set of extrema changes discontinuously in  $\theta$  which reflects a first order phase transition, for more details we refer to [57], and to the monograph by Brokate and Sprekels [20].

The free energy (2.21) with  $\alpha_2 = 0$  and  $\chi = c - \frac{1}{2}$ , where  $c$  denotes concentration of one of the two components, that is

$$f_0(c, \theta) = f_*(\theta) + \alpha_1(\theta - \theta_c)\left(c - \frac{1}{2}\right)^2 + \alpha_3\left(c - \frac{1}{2}\right)^6, \quad (2.22)$$

with  $\alpha_1, \alpha_3 > 0$ , has been used in [106], [107] as a phenomenological model for phase separation in some solid solutions.

For numerical simulation of the nonisothermal Cahn-Hilliard model with such volumetric free energy we refer to [7].

For completeness we note that the entropy, the internal energy and the specific heat associated with the Landau model (2.20) are

$$\begin{aligned} \eta_0 &= -f_{*,\theta} - \alpha_1\chi^2, \\ e_0 &= f_* - \theta f_{*,\theta} - \alpha_1\theta_c\chi^4 + \alpha_2\chi^4, \\ c_0 &= -\theta f_{*,\theta\theta}, \end{aligned} \quad (2.23)$$

whereas that associated with the Devonshire model (2.21) are

$$\begin{aligned}\eta_0 &= -f_{*,\theta} - \alpha_1\chi^2, \\ e_0 &= f_* - \theta f_{*,\theta} - \alpha_1\theta_c\chi^2 - \alpha_2\chi^4 + \alpha_3\chi^6, \quad c_0 = -\theta f_{*,\theta\theta}.\end{aligned}\tag{2.24}$$

In the next sections we present gradient type free energies associated with the well-known phase transition models.

**8.3. The Caginalp free energy (see, e.g., [23], [25]).** The Caginalp free energy density is expressed in terms of an order parameter  $\chi$  and the temperature  $u$  which is scaled so that  $u = 0$  is the planar melting temperature. In the context of solid-liquid phase transitions the value  $\chi = -1$  is assumed to represent the low temperature phase (solid) while  $\chi = 1$  the high temperature phase (liquid). In this sense  $\chi$  is rather a "disorder" parameter than an "order" parameter. The free energy is expressed in the following Landau-Ginzburg form

$$f(\chi, \mathbf{D}\chi, u) = \frac{1}{a}\psi(\chi) - 2u\chi + \frac{1}{2}\xi^2|\mathbf{D}\chi|^2,\tag{3.1}$$

where

$$\psi(\chi) = \frac{1}{8}(\chi^2 - 1)^2\tag{3.2}$$

is a prototype double-well potential which may be generalized to other forms with similar qualitative properties, i.e., symmetric double-well potential with minima at  $\pm 1$ . The parameter  $\xi$  represents a length scale and a measure of the microscopic bonding, and  $a$  is a measure of the depth of the double well  $(\chi^2 - 1)^2$ . In terms of macroscopic properties,  $\varepsilon := \xi a^{1/2}$  is the interface thickness and  $\sigma := \frac{2}{3}\xi a^{-\frac{1}{2}}$  is the interface tension, see [23], [25].

**8.4. The Penrose-Fife free energy [129], [130].** A general form of the Penrose-Fife free energy density is given by (c.f., [129, e.g. (3.2)])

$$f(\chi, \mathbf{D}\chi, \theta) = f_V(\chi, \theta) + \frac{1}{2}\varkappa\theta|\mathbf{D}\chi|^2\tag{4.1}$$

where  $f_V$  is the volumetric part

$$f_V(\chi, \theta) = f_*(\theta)\nu_*(\chi) + \theta f_1(\chi) + f_2(\chi)\tag{4.2}$$

with smooth functions  $f_*$ ,  $\nu_*$ ,  $f_1$ ,  $f_2$ , and  $\varkappa$  is a positive constant. A typical form of  $f_V(\cdot, T)$  is that of a double-well potential having exactly two distinct minima.

The corresponding expressions for the entropy, the internal energy and the specific heat are

$$\begin{aligned}\eta(\chi, \mathbf{D}\chi, \theta) &= -f_{*,\theta}\nu_*(\chi) - f_1(\chi) - \frac{1}{2}\varkappa|\mathbf{D}\chi|^2, \\ e(\chi, \mathbf{D}\chi, \theta) &= (f_* - \theta f_{*,\theta})\nu_*(\chi) + f_2(\chi), \\ c &= c_* = -\theta f_{*,\theta\theta}\nu_*(\chi).\end{aligned}\tag{4.3}$$

A typical example considered by Penrose and Fife is the mean-field theory of Ising ferromagnets. In this case the order parameter  $\chi$  represents the fraction of lattice sites at which spins are pointing "up". Hence, the physically meaningful values of  $\chi$  are confined

to the interval  $[0, 1]$ . The corresponding functions  $\nu_*$ ,  $f_*$ ,  $f_1$ ,  $f_2$  have then the form:

$$\begin{aligned}\nu_*(\chi) &= \text{const} \text{ (equal zero if lattice vibrations are ignored),} \\ f_*(\theta) &= -c_*\theta \ln \frac{\theta}{\theta_1} + c_*\theta + \bar{c}, \\ f_1(\chi) &= k_B[\chi \ln \chi + (1 - \chi) \ln(1 - \chi)], \\ f_2(\chi) &= -a\chi^2 + b\chi + c\end{aligned}\tag{4.4}$$

with physical positive constants  $c_*$ ,  $\theta_1$ ,  $k_B$ ,  $a$ , constants  $b$ ,  $c$  and  $\bar{c}$  of arbitrary sign;  $c_*$  stands for the thermal specific heat,  $k_B$  is the Boltzmann's constant, and  $f_1(\chi)$  is the negative of the so-called configurational entropy per site.

Another example considered in [129], [130] concerns liquid-solid phase transition. Let us assume that the order parameter  $\chi \in [-1, 1]$  and  $\chi = -1$  represents the low temperature phase (solid) while  $\chi = 1$  represents the high temperature phase (liquid).

In such case  $\bar{\chi} = (1 + \chi)/2$  with  $\bar{\chi} \in [0, 1]$  is the concentration of the liquid phase.

A relevant expression for the volumetric free energy is

$$\begin{aligned}f_V(\chi, \theta) &= f_*(\theta) + \left(1 - \frac{\theta}{\theta_c}\right)(-a\chi^2 + b\chi + c) + \frac{\theta}{4\theta_c}(\chi^2 - 1)^2, \\ &\equiv f_*(\theta)\nu_*(\chi) + \theta f_1(\chi) + f_2(\chi),\end{aligned}\tag{4.5}$$

where

$$\begin{aligned}f_*(\theta) &= -c_*\theta \ln \frac{\theta}{\theta_c} + c_*\theta, \quad \nu_*(\chi) \equiv 1, \\ f_1(\chi) &= -\frac{1}{\theta_c}(-a\chi^2 + b\chi + c) + \frac{1}{4\theta_c}(\chi^2 - 1)^2 \\ f_2(\chi) &= -a\chi^2 + b\chi + c,\end{aligned}\tag{4.6}$$

with  $\theta_c > 0$ ,  $a > 0$ ,  $b$ ,  $c$  some physical constants,  $\theta_c$  denoting a transition temperature.

The corresponding expressions for the volumetric parts of the entropy and the internal energy are

$$\begin{aligned}\eta_V(\chi, \theta) &= c_* \ln \frac{\theta}{\theta_c} + \frac{1}{\theta_c}(-a\chi^2 + b\chi + c) - \frac{1}{4\theta_c}(\chi^2 - 1)^2, \\ e_V(\chi, \theta) &= c_*\theta - a\chi^2 + b\chi + c.\end{aligned}\tag{4.7}$$

A characteristic feature of the free energy (4.5) is that when  $\theta = \theta_c$ ,  $f_V$  considered as a function of  $\chi$  has a double-well form with two equal minima at  $\chi = \pm 1$ . Consequently, it is possible for two phases to coexist in equilibrium at this temperature, one with  $\chi = -1$  and the other with  $\chi = 1$ . The quadratic polynomial in (4.5)

$$\psi(\chi) = \frac{1}{4}(\chi^2 - 1)^2\tag{4.8}$$

is a prototype double-well potential. The form (4.8) can be replaced by any other double-well function with two equal minima.

At temperatures  $\theta \neq \theta_c$ , the free energy  $f_V(\cdot, \theta)$  given by (4.5) can have either one local minimum or two. When it has two minima, then if  $b \neq 0$ , the two minima have different free energies and therefore cannot coexist in equilibrium. Thus  $\theta_c$  is the unique temperature of phase equilibrium. Such situation is typical for melting transitions (at fixed

pressure). On the other hand if  $b = 0$  the two minima are equal and so a two-phase equilibrium is possible over the entire range of temperatures for which  $f_V(\cdot, \theta)$  has two minima. Such situation appears, for example, in a ferromagnet in zero magnetic field (see [130]).

The latent heat  $L$  is the difference in internal energy between the two phases when they are in thermodynamic equilibrium with one another. It is therefore

$$L = e_V(1, \theta_c) - e_V(-1, \theta_c) = 2b, \quad (4.9)$$

according to the convention that the more disordered phase  $\chi = 1$  has the higher energy. Thus, if  $b \neq 0$  then there is latent heat at  $\theta_c$ , and if  $b = 0$  then there is no latent heat over a range of temperatures.

**8.5. The Flory-Huggins-de Gennes free energy.** The Flory-Huggins-de Gennes (FHdG) free energy describes phase separation in binary polymer mixtures. For a binary mixture of polymer molecules of type  $i = 1, 2$ , each consisting of  $N_i$  segments, respectively, the FHdG free energy of mixing per lattice site has the Landau-Ginzburg form, see de Gennes [43], [44]

$$f_{\text{FHdG}}(\chi, \nabla\chi, \theta) = f_0(\chi, \theta) + \frac{1}{2}\varkappa(\chi, \theta)|\nabla\chi|^2, \quad (5.1)$$

where  $\chi \in [0, 1]$  is the order parameter, i.e., the volume fraction  $\chi = \chi_1$  of component 1 under incompressibility condition,  $\chi_1 + \chi_2 = 1$ , and  $\theta > 0$  is the absolute temperature. The first term in (5.1) is the Flory-Huggins volumetric free energy given by (2.16). For simplicity we assume that the Boltzmann's constant  $k_B = 1$ .

The second term in (5.1) is the interfacial energy with the coefficient  $\varkappa$  made up of the energetic and the entropic contributions

$$\varkappa(\chi, \theta) = \varkappa_e + \theta\varkappa_\eta(\chi). \quad (5.2)$$

The energetic contribution  $\varkappa_e > 0$  is due to interaction between different molecules in the mixture whereas the entropic one  $\varkappa_\eta > 0$  is due to the connectivity of the segments within a polymer molecule. From different derivations, e.g., in [43], [44], it follows that

$$\begin{aligned} \varkappa_e &= \frac{1}{3}(R_{g_1}^2 + R_{g_2}^2)\omega_e, \\ \varkappa_\eta(\chi) &= \frac{1}{3}(R_{g_1}^2 + R_{g_2}^2)\omega_\eta + \frac{1}{3}\left(\frac{R_{g_1}^2}{N_1\chi} + \frac{R_{g_2}^2}{N_2(1-\chi)}\right), \end{aligned} \quad (5.3)$$

where  $R_{g_i}^2 = N_i\sigma_i^2/6$ . The formulas (5.3) involve two characteristic polymer quantities:  $R_{g_i}$  – the mean radius of gyration of  $i$ -th molecule, and  $\sigma_i$  – the size of segments in  $i$ -th molecule (lattice constant), which in three dimensional case are connected by the latter equation.

According to de Gennes [44, Note on page 4762] for most polymer-polymer mixtures,  $\varkappa_e$  is small in comparison with  $\varkappa_\eta$ , and therefore can be neglected. On the other hand, the other literature indicates that both  $\varkappa_e$  and  $\varkappa_\eta$  should be taken into account. For more detailed references we refer to [127].

Finally, let us note that in polymer mixtures – in contrast to small molecular ones – the gradient term introduces an infinite energy penalty near the pure phases  $\chi = 0$  and  $\chi = 1$ .

**8.6. Standard examples of isotropic dissipation potentials.** We present now some standard examples of the dissipation potential  $\mathcal{D}(\mathcal{X}; \omega)$  arising in phase-field models.

We recall that in case of conserved, phase-field model the sets of thermodynamic forces  $\mathcal{X}$  and state variables  $\omega$  are given by (see Subsection 7.5.1)

$$\mathcal{X} = \left( \mathbf{D} \frac{\mu}{\theta}, \mathbf{D} \frac{1}{\theta}, \chi, t \right), \quad \omega = \left( \mathbf{F}, \mathbf{D}\mathbf{F}, \chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \theta, \frac{\mu}{\theta} \right), \quad \bar{\mu} = \frac{\mu}{\theta}. \quad (6.1)$$

In case of nonconserved phase-field model (see Subsection 7.6.1)

$$\mathcal{X} = \left( \frac{\mu}{\theta}, \mathbf{D} \frac{1}{\theta}, \chi, t \right), \quad \omega = \left( \mathbf{F}, \mathbf{D}\mathbf{F}, \chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \theta \right), \quad \bar{\mu} = \frac{\mu}{\theta}. \quad (6.2)$$

For simplicity, let us assume the splitting

$$\mathcal{D}(\mathcal{X}; \omega) = \mathcal{D}_1 \left( \frac{\mu}{\theta}; \omega \right) + \mathcal{D}_2 \left( \mathbf{D} \frac{\mu}{\theta}; \omega \right) + \mathcal{D}_3 \left( \mathbf{D} \frac{1}{\theta}; \omega \right) + \mathcal{D}_4(\chi, t; \omega), \quad (6.3)$$

and restrict ourselves to the situation near thermodynamical equilibrium with potentials  $\mathcal{D}_k$ ,  $k = 1, 2, 3, 4$ , being of the second degree of homogeneity in the variables  $\bar{\mu} = \frac{\mu}{\theta}$ ,  $\mathbf{D}\bar{\mu} = \mathbf{D} \frac{\mu}{\theta}$ ,  $\mathbf{D} \frac{1}{\theta}$  and  $\chi, t$ , which represent the rescaled chemical potential, the gradient of the rescaled chemical potential, the gradient of the inverse temperature and time derivative of the order parameter, respectively.

The potential  $\mathcal{D}_1$  corresponds to a nonconserved order parameter dynamics whereas  $\mathcal{D}_2$  to a conserved one;  $\omega$  stands for the set of state variables.

The simplest examples are

$$\mathcal{D}_1 = \frac{1}{2} \alpha \left( \frac{\mu}{\theta} \right)^2, \quad \mathcal{D}_2 = \frac{1}{2} M \left| \mathbf{D} \frac{\mu}{\theta} \right|^2, \quad (6.4)$$

where  $\alpha$  and  $M$  are positive coefficients,  $\alpha$  represents a relaxation coefficient and  $M$  diffusional mobility. Actually, according to (7.6.2)<sub>2</sub>, the potential  $\mathcal{D}_1$  yields the following production term

$$\varrho_0 r^d = -\mathcal{D}_{1, \bar{\mu}} = -\mathcal{D}_{1, (\mu/\theta)} = -\alpha \frac{\mu}{\theta}. \quad (6.5)$$

Consequently, equation (7.6.1)<sub>2</sub> (with  $\tau = 0$ ) provides the well-known relaxation law for the nonconserved order parameter

$$\dot{\chi} = -\alpha \frac{\mu}{\theta}, \quad \alpha > 0. \quad (6.6)$$

According to (7.5.2)<sub>2</sub> the potential  $\mathcal{D}_2$  yields the known law for the mass flux

$$\mathbf{j}^d = -\mathcal{D}_{2, \mathbf{D}\bar{\mu}} = -\mathcal{D}_{2, \mathbf{D}(\mu/\theta)} = -M \mathbf{D} \frac{\mu}{\theta}, \quad M > 0, \quad (6.7)$$

and the corresponding diffusion equation (cf. (7.5.1)<sub>2</sub> with  $\tau = 0$ )

$$\varrho_0 \dot{\chi} - \nabla \cdot \left( M \nabla \frac{\mu}{\theta} \right) = 0. \quad (6.8)$$

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

$$\mathcal{D}_3 = \frac{1}{2} k \left| \mathbf{D} \log \theta \right|^2 = \frac{1}{2} k \theta^2 \left| \mathbf{D} \frac{1}{\theta} \right|^2, \quad (6.9)$$



where  $k > 0$  is the heat conductivity coefficient. Then, according to (7.5.2)<sub>3</sub>

$$\mathbf{q}^d = \mathcal{D}_{3, D(1/\theta)} = k\theta^2 \mathbf{D} \frac{1}{\theta} = -k \mathbf{D} \theta, \quad k > 0. \quad (6.10)$$

Finally, the potential  $\mathcal{D}_4$  corresponds to viscous diffusive effects. The simplest example is

$$\mathcal{D}_4 = \frac{1}{2} \beta \chi_{,t}^2, \quad (6.11)$$

where  $\beta > 0$  is a viscosity coefficient. By (7.5.2)<sub>4</sub> such potential yields the following law

$$\mathbf{a}^d = \mathcal{D}_{4, \chi, t} = \beta \chi_{,t}, \quad \beta > 0. \quad (6.12)$$

Finally we remark that the presented examples of dissipation potentials can be straightforward extended to anisotropic situations with nonconstant tensor-valued coefficients.

## 9. Well-known phase-field models with conserved order parameter. Relation to model $(PF)_\theta$

### 9.1. The Penrose-Fife model.

**9.1.1. General model equations.** The Penrose-Fife models [129] with conserved and nonconserved order parameters have been derived by means of variational arguments. Elastic effects have been suppressed. The derivation is based on the internal energy  $e$  as an independent thermal variable and the entropy density

$$\tilde{\eta}(\chi, \mathbf{D}\chi, e) = \tilde{\eta}_V(\chi, e) - \frac{1}{2}\varkappa|\mathbf{D}\chi|^2 \quad (1.1)$$

as the corresponding thermodynamic potential.

The coefficient  $\varkappa$  in (1.1) is assumed to be a positive constant (see assumption on  $\varkappa_1$  in [129, eq. (2.12)]).

This assumption together with the additional requirement that the internal energy density  $e$  is independent of the order parameter gradient  $\mathbf{D}\chi$  (see [129, eq. (2.10)]) plays a significant role in the Penrose-Fife variational arguments.

In case of conserved order parameter the Penrose-Fife model has the form of the following system (see [129, eq. (2.17), (2.19), (2.10), (2.11)]):

$$\begin{aligned} \chi_t + \nabla \cdot \left( m \nabla \frac{\delta \tilde{\eta}}{\delta \chi} \right) &= 0, \\ e_t + \nabla \cdot \left( k \nabla \frac{\delta \tilde{\eta}}{\delta e} \right) &= 0, \end{aligned} \quad (1.2)$$

where  $m, k$  are positive coefficients that may depend on  $\chi$  and on  $e$ , and  $\delta \tilde{\eta} / \delta \chi, \delta \tilde{\eta} / \delta e$  are the variational derivatives of  $\tilde{\eta}$  with respect to  $\chi$  and  $e$ , respectively. By (1.1), they are given by

$$\begin{aligned} \frac{\delta \tilde{\eta}}{\delta \chi} &= \tilde{\eta}_{,\chi} - \nabla \cdot \tilde{\eta}_{,\mathbf{D}\chi} = \tilde{\eta}_{V,\chi}(\chi, e) + \varkappa \Delta \chi, \\ \frac{\delta \tilde{\eta}}{\delta e} &= \tilde{\eta}_{V,e}(\chi, e). \end{aligned} \quad (1.3)$$

The underlying postulate in the Penrose-Fife derivation is that the free energy density  $f$  and the entropy density  $\tilde{\eta}$  are both concave in absolute temperature  $\theta$  and internal energy  $e$ , respectively, and that they obey the Legendre transform relations generalized to the situation of the additional dependence of the free energy and entropy densities on the order parameter gradient. On account of the transform relations, equations (1.3) are

expressed in the form (see, [129, eg. (2.13), (2.14) and (2.12)]):

$$\begin{aligned}\frac{\delta\tilde{\eta}}{\delta\chi} &= \frac{1}{\theta}(-f_{V,\chi}(\chi, \theta) + \varkappa\theta\Delta\chi), \\ \frac{\delta\tilde{\eta}}{\delta e} &= \frac{1}{\theta},\end{aligned}\tag{1.4}$$

where

$$f(\chi, \mathbf{D}\chi, \theta) = f_V(\chi, \theta) + \frac{1}{2}\varkappa\theta|\mathbf{D}\chi|^2, \quad \varkappa = \text{const} > 0,\tag{1.5}$$

is the corresponding free energy density. Consequently, the Penrose-Fife model (1.1), (1.2) expressed in terms of absolute temperature  $\theta$  becomes

$$\begin{aligned}\chi_t + \nabla \cdot \left[ m \nabla \left( \frac{1}{\theta} (-f_{V,\chi} + \varkappa\theta\Delta\chi) \right) \right] &= 0, \\ e_t + \nabla \cdot \left( k \nabla \frac{1}{\theta} \right) &= 0,\end{aligned}\tag{1.6}$$

where the internal energy  $e$  is related to the free energy  $f$  by the thermodynamic relation (see [129, eq. (2.8)])

$$e = \frac{\partial(f/\theta)}{\partial(1/\theta)}.\tag{1.7}$$

The equation (1.7) is equivalent to (see Lemma 3.1)

$$e = f - \theta f_{,\theta}.\tag{1.8}$$

Hence, for the free energy (1.5) we have

$$e = e_V(\chi, \theta) = f_V(\chi, \theta) - f_{V,\theta}(\chi, \theta).\tag{1.9}$$

A remarkable property of the Penrose-Fife model is that its underlying free energy density (1.5) has gradient term being a linear function of temperature  $\theta$ .

In terminology used in the present work this means it is of the entropic type, and consequently yields the internal energy  $e$  independent of  $\mathbf{D}\chi$ .

**9.1.2. Model equations for separable free energy.** In the development of their theory Penrose-Fife [129] have considered system (1.6) in case of the some special thermodynamic functions. More precisely, let us recall the Penrose-Fife free energy density [129, eq. (8.4.1)–(8.4.2)]

$$f(\chi, \mathbf{D}\chi, \theta) = f_V(\chi, \theta) + \frac{1}{2}\varkappa\theta|\mathbf{D}\chi|^2\tag{1.10}$$

with

$$f_V(\chi, \theta) = f_*(\theta)\nu_*(\chi) + \theta f_1(\chi) + f_2(\chi),$$

where  $f_*$ ,  $f_1$ ,  $f_2$ ,  $\nu_*$  are smooth functions of their arguments, and  $f_*$  is strictly concave. Then, by the thermodynamic relations (see Lemma 3.1), the corresponding internal

energy and entropy densities are

$$\begin{aligned} e(\chi, \mathbf{D}\chi, \theta) &= (f_*(\theta) - \theta f'_*(\theta))\nu_*(\chi) + f_2(\chi) \equiv e_V(\chi, \theta), \\ \eta(\chi, \mathbf{D}\chi, \theta) &= -(f'_*(\theta)\nu_*(\chi) + f_1(\chi)) - \frac{1}{2}\varkappa|\mathbf{D}\chi|^2 \\ &\equiv \eta_V(\chi, \theta) - \frac{1}{2}\varkappa|\mathbf{D}\chi|^2. \end{aligned} \quad (1.11)$$

Thus, in the Penrose-Fife model the internal energy density is purely volumetric (independent of order parameter gradient  $\mathbf{D}\chi$ ) and the entropy density contains the whole gradient term  $-\varkappa|\mathbf{D}\chi|^2/2$ .

On account of (1.10), (1.11), the Penrose-Fife model (1.6) specializes to the form (cf., [129, eq. (3.8) and conserved version of eq. (3.6)]):

$$\begin{aligned} \chi_t + \nabla \cdot \left[ m \nabla \left( -\frac{f_*(\theta)}{\theta} \nu'_*(\chi) - f'_1(\chi) - \frac{f'_2(\chi)}{\theta} + \varkappa \Delta \chi \right) \right] &= 0, \\ c_\nu(\chi, \theta) \theta_t + [(f_*(\theta) - \theta f'_*(\theta))\nu'_*(\chi) + f'_2(\chi)] \chi_t + \nabla \cdot \left( k \nabla \frac{1}{\theta} \right) &= 0, \end{aligned} \quad (1.12)$$

where

$$c_\nu(\chi, \theta) = -\theta f''_*(\theta) \nu_*(\chi)$$

is the specific heat at constant volume.

**9.1.3. Relation to conserved phase-field model  $(PF)_\theta$ .** Let us note that introducing the quantity

$$\bar{\mu} := \frac{\mu}{\theta} = \frac{\delta(f/\theta)}{\delta\chi} = \frac{f_{,\chi}}{\theta} - \nabla \cdot \left( \frac{f_{,\mathbf{D}\chi}}{\theta} \right), \quad (1.13)$$

which for free energy  $f$  given by (1.5) equals to

$$\bar{\mu} = \frac{f_{V,\chi}}{\theta} - \varkappa \Delta \chi,$$

the general Penrose-Fife model (1.6) can be expressed in the form

$$\begin{aligned} \chi_t - \nabla \cdot (m \nabla \bar{\mu}) &= 0, \\ \bar{\mu} &= \frac{\delta(f/\theta)}{\delta\chi}, \\ e_t + \nabla \cdot \left( k \nabla \frac{1}{\theta} \right) &= 0, \end{aligned} \quad (1.14)$$

where  $e = e_V(\chi, \theta)$  is related to  $f$  by (1.9).

Consequently, one can see that Penrose-Fife model (1.6) has the structure of the conserved phase-field system  $(PF)_\theta$  with suppressed elastic effects (see (7.5.8)) in the following special case:

$$\begin{aligned} f &= \hat{f}(\chi, \mathbf{D}\chi, \theta) \quad \text{given by (1.5),} \\ e &= e_V(\chi, \theta) \quad \text{given by (1.9)} \\ \varrho_0 &\equiv 1, \quad \tau = 0, \quad g = 0, \quad \mathbf{h}^e = \mathbf{0}, \\ -\mathbf{j}^d &= m \mathbf{D}\bar{\mu}, \quad \mathbf{q}^d = k \mathbf{D} \frac{1}{\theta}, \quad a^d = 0, \end{aligned} \quad (1.15)$$

with positive coefficients  $m = m(\chi, \theta)$ ,  $k = k(\chi, \theta)$ .

The corresponding dissipation potential is

$$\mathcal{D} = \frac{1}{2}m|D\bar{\mu}|^2 + \frac{1}{2}k\left|D\frac{1}{\theta}\right|^2, \quad (1.16)$$

thus refers to a situation near the thermodynamic equilibrium.

According to the classification in Section 7.4, the conserved Penrose-Fife model (1.6) can be regarded as the intersection of examples  $(PF)_\theta$  (i) and  $(PF)_\theta$  (ii) presented there. More precisely, it represents the model with no extra energy term but with the extra entropy term

$$\mathbf{h}^e = e_{,D\chi} = \mathbf{0} \quad \text{and} \quad \mathbf{h}^\eta = -\eta_{,D\chi} = \frac{1}{\theta}f_{,D\chi} = \kappa D\chi. \quad (1.17)$$

By (7.4.5), the solutions of the Penrose-Fife model (1.6) (and its equivalent version (1.14)) satisfy the entropy inequality

$$\eta_t + \nabla \cdot \Psi = \sigma \geq 0 \quad (1.18)$$

with the modified entropy flux

$$\Psi = \Psi^d - \chi_t \eta_{,D\chi} = \Psi^d + \chi_t \frac{1}{\theta} f_{,D\chi}, \quad (1.19)$$

where

$$\Psi^d = -\bar{\mu} \mathbf{j}^d + \frac{1}{\theta} \mathbf{q}^d = m\bar{\mu} D\bar{\mu} + k \frac{1}{\theta} D\frac{1}{\theta},$$

and the entropy production density

$$\sigma = -D\bar{\mu} \cdot \mathbf{j}^d + D\frac{1}{\theta} \cdot \mathbf{q}^d = m|D\bar{\mu}|^2 + k\left|D\frac{1}{\theta}\right|^2. \quad (1.20)$$

**9.1.4. Application of the duality relations.** To see more connections with the Penrose-Fife theory, and at the same time to underline the role of the duality relations presented in Section 3.5, we shall describe here in more detail the transform relations between the original energy form (1.2) and the temperature form (1.6) of the Penrose-Fife model.

By virtue of Lemma 3.3, for a given entropy density  $\tilde{\eta} = \hat{\eta}(\chi, D\chi, \bar{e})$  which is a concave function of internal energy  $\bar{e}$  (in consistency with the convention in Chapter 3 we write  $\bar{e} = e$ ), the following identities hold true

$$\begin{aligned} \hat{\eta}(\chi, D\chi, \bar{e}) + \hat{\phi}(\chi, D\chi, \vartheta) &= \vartheta \bar{e}, \\ \hat{\eta}_{,\bar{e}}(\chi, D\chi, \bar{e}) &= \vartheta, \end{aligned} \quad (1.21)$$

where

$$\vartheta = \frac{1}{\theta} \quad \text{and} \quad \phi = \hat{\phi}(\chi, D\chi, \vartheta) = \vartheta \hat{f}\left(\chi, D\chi, \frac{1}{\vartheta}\right)$$

are the inverse temperature and the rescaled free energy which is concave in  $\vartheta$  (equivalently,  $f$  is concave in  $\theta$ ).

Moreover, by Lemma 3.8, we have

$$\begin{aligned}
 -\hat{\eta}_{,\chi}(\chi, \mathbf{D}\chi, \bar{e}) &= \hat{\phi}_{,\chi}(\chi, \mathbf{D}\chi, \vartheta), \\
 -\hat{\eta}_{,\mathbf{D}\chi}(\chi, \mathbf{D}\chi, \bar{e}) &= \hat{\phi}_{,\mathbf{D}\chi}(\chi, \mathbf{D}\chi, \vartheta), \\
 -\frac{\delta\hat{\eta}}{\delta\chi}(\chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \bar{e}, \mathbf{D}\bar{e}) &= \frac{\delta\hat{\phi}}{\delta\chi}(\chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \vartheta, \mathbf{D}\vartheta),
 \end{aligned} \tag{1.22}$$

where  $\bar{e}$ ,  $\mathbf{D}\bar{e}$  and  $\vartheta$ ,  $\mathbf{D}\vartheta$  are related by the formulas

$$\begin{aligned}
 \bar{e} &= \hat{e}(\chi, \mathbf{D}\chi, \vartheta), \\
 \bar{e}_{,i} &= \hat{e}_{,\chi}(\chi, \mathbf{D}\chi, \vartheta)\chi_{,i} + \hat{e}_{,\mathbf{D}\chi}(\chi, \mathbf{D}\chi, \vartheta) \cdot \mathbf{D}\chi_{,i} \\
 &\quad + \hat{e}_{,\vartheta}(\chi, \mathbf{D}\chi, \vartheta)\vartheta_{,i}.
 \end{aligned} \tag{1.23}$$

For the Penrose-Fife free energy density (1.5) the corresponding rescaled free energy density is

$$\begin{aligned}
 \hat{\phi}(\chi, \mathbf{D}\chi, \vartheta) &= \vartheta \hat{f}\left(\chi, \mathbf{D}\chi, \frac{1}{\vartheta}\right) \\
 &= \vartheta f_V\left(\chi, \frac{1}{\vartheta}\right) + \frac{1}{2}\varkappa|\mathbf{D}\chi|^2.
 \end{aligned} \tag{1.24}$$

Then, by thermodynamic Gibbs relation (3.2.3)<sub>2</sub>, the internal energy  $\bar{e}$ , expressed as a function of inverse temperature  $\vartheta$ , is given by

$$\begin{aligned}
 \hat{e}(\chi, \mathbf{D}\chi, \vartheta) &= \hat{\phi}_{,\vartheta}(\chi, \mathbf{D}\chi, \vartheta) \\
 &= f_V\left(\chi, \frac{1}{\vartheta}\right) - \frac{1}{\vartheta}f_{V,(1/\vartheta)}\left(\chi, \frac{1}{\vartheta}\right),
 \end{aligned} \tag{1.25}$$

or equivalently, in terms of absolute temperature  $\theta = 1/\vartheta$ ,

$$\begin{aligned}
 \hat{e}(\chi, \mathbf{D}\chi, \theta) &\equiv \hat{e}\left(\chi, \mathbf{D}\chi, \frac{1}{\theta}\right) \\
 &= f_V(\chi, \theta) - \theta f_{V,\theta}(\chi, \theta) = e_V(\chi, \theta).
 \end{aligned}$$

Besides, by thermodynamic relation (3.2.3)<sub>1</sub>, the entropy density expressed as a function of  $\vartheta$  is

$$\begin{aligned}
 \hat{\eta}(\chi, \mathbf{D}\chi, \vartheta) &= -\hat{\phi}_{,\chi}(\chi, \mathbf{D}\chi, \vartheta) + \vartheta\hat{e}_{,\chi}(\chi, \mathbf{D}\chi, \vartheta) \\
 &= -f_{V,(1/\vartheta)}\left(\chi, \frac{1}{\vartheta}\right) - \frac{1}{2}\varkappa|\mathbf{D}\chi|^2,
 \end{aligned} \tag{1.26}$$

or equivalently in terms of  $\theta$ ,

$$\begin{aligned}
 \hat{\eta}(\chi, \mathbf{D}\chi, \theta) &\equiv \hat{\eta}\left(\chi, \mathbf{D}\chi, \frac{1}{\theta}\right) \\
 &= -f_{V,\theta}(\chi, \theta) - \frac{1}{2}\varkappa|\mathbf{D}\chi|^2 \\
 &\equiv \eta_V(\chi, \theta) - \frac{1}{2}\varkappa|\mathbf{D}\chi|^2.
 \end{aligned}$$

This confirms the Penrose-Fife expressions (1.11) with purely volumetric internal energy  $e$  and gradient type entropy  $\eta$ . Let us note that in such a case, according to formulas

(1.23), the transformation between internal energy  $\bar{e}$  and the inverse temperature  $\vartheta$  does not involve  $D\chi$ , and the transformation between  $D\bar{e}$  and  $D\vartheta$  does not involve  $D^2\chi$ .

By (1.1) (with  $e = \bar{e}$ ) and (1.21)<sub>2</sub> we have

$$\frac{\delta\bar{\eta}}{\delta\bar{e}} = \bar{\eta}_{,e} = \vartheta. \quad (1.27)$$

Thus, in view of relations (1.22)<sub>3</sub> and (1.27), one can see that the Penrose-Fife model in energy form (1.2) (with  $e = \bar{e}$ ) transforms into the following temperature form

$$\begin{aligned} \chi_t - \nabla \cdot \left( m \nabla \frac{\delta\phi}{\delta\chi} \right) &= 0, \\ \bar{e}_t + \nabla \cdot (k \nabla \vartheta) &= 0, \end{aligned} \quad (1.28)$$

where  $\bar{e} = \hat{e}(\chi, D\chi, \vartheta)$  is related to  $\phi = \hat{\phi}(\chi, D\chi, \vartheta)$  via the relation  $\bar{e} = \phi_{,\vartheta}$ . Clearly, for  $\phi$  given by (1.24), system (1.28) yields exactly the temperature form (1.6) of the Penrose-Fife model.

## 9.2. Phase-field model with the rescaled free energy.

**9.2.1. Model equation.** A conserved phase-field model based on the rescaled free energy  $\phi = \hat{\phi}(\chi, D\chi, 1/\theta) = f(\chi, D\chi, \theta)/\theta$  has been introduced and studied in a line of papers by H. W. Alt and the author [5], [6], [7], [8].

The basis of the model is the Landau-Ginzburg theory of phase transitions and the nonequilibrium thermodynamics. The arguments of the derivation are different than those used by Penrose and Fife [129]. The main difference is that the internal energy density  $e$  is not required to be independent of the order parameter gradient  $D\chi$ . Except this assumption, the resulting system has the same structure as the Penrose-Fife model.

The key idea behind the construction of the model with the rescaled free energy consists in a generalization of the classical Cahn-Hilliard definition (see [34]) of the chemical potential associated with the gradient type free energy density  $f = \hat{f}(\chi, D\chi)$  at constant temperature

$$\mu := \frac{\delta f}{\delta\chi} = f_{,\chi} - \nabla \cdot f_{,D\chi} \quad (2.1)$$

to the nonisothermal situation. The generalization involves a rescaled chemical potential  $\bar{\mu}$  defined by

$$\bar{\mu} := \frac{\mu}{\theta} = \frac{\delta(f/\theta)}{\delta\chi} = \frac{f_{,\chi}}{\theta} - \nabla \cdot \left( \frac{f_{,D\chi}}{\theta} \right). \quad (2.2)$$

The equation (2.2) has been rigorously justified in [10]. It is also recovered in Chapter 6 of the present work. The corresponding model has the form

$$\begin{aligned} \chi_t - \nabla \cdot \left( l_{11} \nabla \bar{\mu} + l_{12} \nabla \frac{1}{\theta} \right) &= 0, \\ \bar{\mu} &= \frac{\delta(f/\theta)}{\delta\chi}, \\ e_t + \nabla \cdot \left( l_{21} \nabla \bar{\mu} + l_{22} \nabla \frac{1}{\theta} \right) &= g, \end{aligned} \quad (2.3)$$

where the internal energy  $e = \hat{e}(\chi, \mathbf{D}\chi, \theta)$  is related to the free energy  $f = \hat{f}(\chi, \mathbf{D}\chi, \theta)$  by the relation  $e = f - \theta f_{,\theta}$ , and the coefficients  $l_{ik} = \hat{l}_{ik}(\chi, \bar{\mu}, \theta)$ ,  $i, k = 1, 2$ , are assumed to satisfy the conditions

$$l_{11} > 0, \quad l_{22} > 0, \quad l_{11}l_{22} - l_{12}l_{21} > 0. \quad (2.4)$$

We underline that on the contrary to the Penrose-Fife model, in (2.3) the internal energy  $e = \hat{e}(\chi, \mathbf{D}\chi, \theta)$  may depend on  $\mathbf{D}\chi$ . This is a significant extension.

**9.2.2. Relation to the conserved phase-field model  $(PF)_\theta$ .** One can see that model (2.3) with the rescaled free energy has the structure of the conserved phase-field system  $(PF)_\theta$  (ii) with suppressed elastic effects (see (7.5.7)) in the following special case:

$$\begin{aligned} f &= \hat{f}(\chi, \mathbf{D}\chi, \theta), \quad e = \hat{e}(\chi, \mathbf{D}\chi, \theta) = f - \theta f_{,\theta}, \\ \varrho_0 &\equiv 1, \quad \tau = 0, \\ \mathbf{h}^e &= \mathbf{0} \quad \text{and} \quad \mathbf{h}^\eta = \frac{1}{\theta} f_{,\mathbf{D}\chi}, \\ -\mathbf{j}^d &= l_{11} \mathbf{D}\bar{\mu} + l_{12} \mathbf{D}\frac{1}{\theta}, \\ \mathbf{q}^d &= l_{21} \mathbf{D}\bar{\mu} + l_{22} \mathbf{D}\frac{1}{\theta}, \\ a^d &= 0, \end{aligned} \quad (2.5)$$

with coefficients  $l_{ik} = l_{ik}(\chi, \bar{\mu}, \theta)$ ,  $i, k = 1, 2$ , satisfying (2.4). We note that with such linear form of  $\mathbf{j}^d$  and  $\mathbf{q}^d$  in  $\mathbf{D}\bar{\mu}$  and  $\mathbf{D}\frac{1}{\theta}$  model (2.3) is restricted to the situation near the thermodynamic equilibrium.

Moreover, recalling (1.17), let us note that like in the Penrose-Fife model the extra energy term  $\mathbf{h}^e = \mathbf{0}$ , but since  $e_{,\mathbf{D}\chi} \neq \mathbf{0}$ , the extra entropy term  $\mathbf{h}^\eta = \frac{1}{\theta} f_{,\mathbf{D}\chi} \neq -\eta_{,\mathbf{D}\chi}$ .

On account of (7.4.10), the solutions of model (2.3) satisfy the entropy inequality

$$\eta_t + \nabla \cdot \Psi = \sigma \geq 0 \quad (2.6)$$

with the modified entropy flux

$$\Psi = \Psi^d + \chi_t \frac{1}{\theta} f_{,\mathbf{D}\chi}, \quad (2.7)$$

where

$$\Psi^d = -\bar{\mu} \mathbf{j}^d + \frac{1}{\theta} \mathbf{q}^d.$$

Due to assumption (2.4) the entropy production density  $\sigma$  satisfies

$$\begin{aligned} \sigma &= -\mathbf{D}\bar{\mu} \cdot \mathbf{j}^d + \mathbf{D}\frac{1}{\theta} \cdot \mathbf{q}^d \\ &= \begin{bmatrix} \mathbf{D}\bar{\mu} \\ \mathbf{D}\frac{1}{\theta} \end{bmatrix} \cdot \begin{bmatrix} l_{11} & l_{12} \\ l_{21} & l_{22} \end{bmatrix} \begin{bmatrix} \mathbf{D}\bar{\mu} \\ \mathbf{D}\frac{1}{\theta} \end{bmatrix} \geq 0. \end{aligned} \quad (2.8)$$

### 9.2.3. Remarks.

REMARK 9.1. The issue of the existence of solutions to model (2.3) as well as numerical results have been addressed in [7], [8]. Differently than in the Penrose-Fife free energy



(1.5) it has been assumed there that the free energy is given by

$$f(\chi, \mathbf{D}\chi, \theta) = f_V(\chi, \theta) + \frac{1}{2}\varkappa|\mathbf{D}\chi|^2, \quad \varkappa = \text{const} > 0, \quad (2.9)$$

that is it is the sum of the volumetric part and the gradient part of the energetic type (independent of  $\theta$ ).

Then the corresponding internal energy and entropy densities are

$$\begin{aligned} e(\chi, \mathbf{D}\chi, \theta) &= e_V(\chi, \theta) + \frac{1}{2}\varkappa|\mathbf{D}\chi|^2, \\ \eta(\chi, \mathbf{D}\chi, \theta) &= \eta_V(\chi, \theta) \end{aligned} \quad (2.10)$$

with

$$e_V = f_V - \theta f_{V,\theta}, \quad \eta_V = -f_{V,\theta}.$$

Thus, in this case – on the contrary to (1.5) and (1.10) – the entropy density is purely volumetric and the internal energy density contains the whole gradient term  $\varkappa|\mathbf{D}\chi|^2/2$ . For (2.9) system (2.3) turns into the form

$$\begin{aligned} \chi_t - \nabla \cdot \left( l_{11} \nabla \frac{\mu}{\theta} + l_{12} \nabla \frac{1}{\theta} \right) &= 0, \\ \frac{\mu}{\theta} &= \frac{f_{V,\chi}(\chi, \theta)}{\theta} - \nabla \cdot \left( \frac{\varkappa}{\theta} \nabla \chi \right), \\ \left( e_V(\chi, \theta) + \frac{1}{2}\varkappa|\nabla \chi|^2 \right)_{,t} + \nabla \cdot \left( l_{21} \nabla \frac{\mu}{\theta} + l_{22} \nabla \frac{1}{\theta} \right) &= g. \end{aligned} \quad (2.11)$$

This system, complemented by initial and boundary conditions, has been studied in [8]. The analysis there indicates that essential difficulties come from the presence of the gradient term  $\varkappa|\nabla \chi|^2/2$  in energy equation (2.11)<sub>3</sub> and the singularity of the coefficient  $\varkappa/\theta$  in equation (2.11)<sub>2</sub>.

Let us also note that for system (2.11) the extra energy and entropy terms are equal to

$$\mathbf{h}^e = \mathbf{0}, \quad \mathbf{h}^\eta = \frac{1}{\theta} f_{,\mathbf{D}\chi} = \frac{1}{\theta} \varkappa \mathbf{D}\chi. \quad (2.12)$$

**REMARK 9.2.** Model (2.3) with the rescaled free energy has been generalized by A. Morro [109] by accounting for additional mass balance equation with nonzero mass production, free energy density  $f = \hat{f}(\varrho, \chi, \mathbf{D}\chi, \theta)$ , and the macroscopic motion of the body in the spatial description.

**9.3. The Caginalp model.** The Caginalp phase-field model, originally derived for solidification problems with nonconserved order parameter [23], has been also extended to problems with a conserved order parameter [24], [26]. The corresponding model is expressed in terms of an order parameter  $\chi$  and the temperature  $u$  which is scaled so that  $u = 0$  is the planar melting temperature. The value  $\chi = -1$  is assumed to represent the low temperature phase (solid) and  $\chi = 1$  the high temperature phase (liquid). The underlying Landau-Ginzburg free energy density is given by (8.3.1)–(8.3.2). The model

equations have the form (see [26])

$$\begin{aligned} \tau\chi_t + \xi^2\Delta \left[ \xi^2\Delta\chi - \left( \frac{1}{a}\psi'(\chi) - 2u \right) \right] &= 0, \\ cu_t + \frac{L}{2}\chi_t - k\Delta u &= 0, \end{aligned} \quad (3.1)$$

where the parameter  $\xi$  represents a length scale and a measure of the microscopic bonding,  $\tau = \alpha\xi^2$  is a relaxation time with  $\alpha$  denoting the microscopic relaxations scaling. The nonmonotone function  $\psi'(\chi) = (\chi^3 - \chi)/2$  is the derivative of the prototype double-well potential  $\psi(\chi) = (\chi^2 - 1)^2/8$ . This potential can be generalized to other forms with similar qualitative properties, i.e., symmetric, double-well potential with minima at  $\pm 1$ . The parameter  $a$  is a measure of the depth of the double well  $\psi(\chi)/a$ . The positive parameters  $c$ ,  $k$  and  $L$  represent respectively the specific heat, the thermal conductivity and the latent heat of phase transition.

The equation (3.1)<sub>1</sub> is derived from the free energy (8.3.1) according to the dynamical equation

$$\tau\chi_t = \xi^2\Delta \frac{\delta f}{\delta\chi}, \quad (3.2)$$

which in a common terminology due to Hohenberg and Halperin [87] is referred to as Model B.

Equation (3.1)<sub>2</sub> represents the energy balance relevant near the phase transition temperature  $\theta_c$ .

**9.3.1. Links to the Penrose-Fife model.** System (3.1) can be viewed as a linearized version of the Penrose-Fife model (1.12) corresponding to the free energy density (compare (8.4.1)–(8.4.2))

$$f(\chi, \mathbf{D}\chi, \theta) = f_*(\theta) + \theta f_1(\chi) + f_2(\chi) + \frac{1}{2}\varkappa\theta|\mathbf{D}\chi|^2, \quad \varkappa = \text{const} > 0, \quad (3.3)$$

with

$$\begin{aligned} f_*(\theta) &= -c_*\theta \ln \frac{\theta}{\theta_c} + c_*\theta, & \nu_*(\chi) &= 1, \quad c_* = \text{const} > 0, \\ f_1(\chi) &= -\frac{L}{2\theta_c}\chi + \frac{L}{4a\theta_c}\psi(\chi), & f_2(\chi) &= \frac{L}{2}\chi. \end{aligned} \quad (3.4)$$

The internal energy, the entropy and the specific heat corresponding to (3.3), (3.4) are

$$\begin{aligned} e(\chi, \theta) &= c_*\theta + \frac{L}{2}\chi, \\ \eta(\chi, \mathbf{D}\chi, \theta) &= c_* \ln \frac{\theta}{\theta_c} + \frac{L}{2\theta_c}\chi - \frac{L}{4a\theta_c}\psi(\chi) - \frac{1}{2}\varkappa|\mathbf{D}\chi|^2, \\ c(\chi, \theta) &= c_*. \end{aligned} \quad (3.5)$$

Inserting formulas (3.4) into (1.12) and letting  $m = \text{const}$ ,  $k = \bar{k}\theta^2$ , where  $\bar{k}$  is a positive constant, one gets

$$\begin{aligned} \chi_t + m\Delta \left[ \varkappa\Delta\chi - \frac{L}{4a\theta_c}\psi'(\chi) - \frac{L}{2}\left( \frac{1}{\theta} - \frac{1}{\theta_c} \right) \right] &= 0, \\ c\theta_t + \frac{L}{2}\chi_t - \bar{k}\Delta\theta &= 0, \end{aligned} \quad (3.6)$$

where  $\psi'(\chi) = (\chi^3 - \chi)/2$  and  $c = c_* = \text{const} > 0$ .

Let

$$u := \frac{\theta - \theta_c}{\theta_c} \quad (3.7)$$

denote a small deviation from the critical temperature  $\theta_c$ . After linearization of equation (3.6)<sub>1</sub> around  $\theta_c$  by replacing the term

$$\frac{L}{2} \left( \frac{1}{\theta} - \frac{1}{\theta_c} \right) \quad \text{with} \quad -\frac{L}{2\theta_c} u,$$

system (3.6) takes on the Caginalp's form

$$\begin{aligned} \alpha \xi^2 \chi_t + \xi^2 \Delta^2 \chi - \Delta \left[ \frac{1}{a} \psi'(\chi) - 2u \right] &= 0, \\ cu_t + \frac{L}{2} \chi_t - \bar{k} \Delta u &= 0, \end{aligned} \quad (3.8)$$

where the coefficients

$$\xi^2 := \frac{4\theta_c \varkappa}{L} \quad \text{and} \quad \alpha = \frac{1}{m\varkappa}$$

are related to the length scale and the relaxation scaling, respectively.

#### 9.4. The Falk's model based on entropy as independent thermal variable.

F. Falk in [62] has set up a class of phase-field models for fluid mixtures in the frame of irreversible thermodynamics. The models generalize the Cahn-Hilliard theory to the multicomponent mixtures in the presence of heat conduction and macroscopic motion. The models are based on the entropy as an independent thermal variable and the internal energy as a thermodynamic potential. They are characterized by the presence of the extra entropy flux.

The Falk model, confined to the situation of a two-component system at rest, turns out to have the structure of the model with the rescaled free energy (2.3) (in the case  $l_{12} = l_{21} = 0$ ,  $\varrho_0 = 1$ , and nonzero external supplies  $\tau \neq 0$ ,  $g \neq 0$ )

$$\begin{aligned} \chi_t + \nabla \cdot \mathbf{j}^d &= \tau, \\ \bar{\mu} &:= \frac{\mu}{\theta} = \frac{f, \chi}{\theta} - \nabla \cdot \left( \frac{f, \mathbf{D}\chi}{\theta} \right), \\ e_t + \nabla \cdot \mathbf{q}^d &= g \end{aligned} \quad (4.1)$$

with the mass and energy fluxes  $\mathbf{j}^d$ ,  $\mathbf{q}^d$  satisfying the dissipation inequality

$$-\nabla \bar{\mu} \cdot \mathbf{j}^d + \nabla \cdot \frac{1}{\theta} \cdot \mathbf{q}^d \geq 0. \quad (4.2)$$

For more explicit comparison with Falk's model, let us formulate system (4.1) in terms of the entropy  $\eta$  as the independent thermal variable and the internal energy  $\tilde{e} = \tilde{e}(\chi, \mathbf{D}\chi, \eta)$ , expressed as a function of the entropy, as a thermodynamic potential.

To this purpose we apply the thermodynamic relations (see (3.5.6)<sub>2</sub>, (3.8.1)<sub>2,3,4</sub>)

$$\begin{aligned}\theta &= \tilde{e}_{,\eta}, \\ f_{,x} &= \tilde{e}_{,x}, \quad f_{,Dx} = \tilde{e}_{,Dx}, \quad \frac{\delta f}{\delta \chi} = \frac{\delta \tilde{e}}{\delta \chi}, \\ e_t &= \tilde{e}_t,\end{aligned}\tag{4.3}$$

which allow to transform system (4.1) into the form

$$\begin{aligned}\chi_t + \nabla \cdot \mathbf{j}^d &= \tau, \\ \bar{\mu} &= \frac{\tilde{e}_{,x}}{\tilde{e}_{,\eta}} - \nabla \cdot \left( \frac{\tilde{e}_{,Dx}}{\tilde{e}_{,\eta}} \right), \\ \tilde{e}_t + \nabla \cdot \mathbf{q}^d &= g\end{aligned}\tag{4.4}$$

with  $\mathbf{j}^d$ ,  $\mathbf{q}^d$  satisfying (4.2).

We indicate show now that system (4.4) satisfies the entropy equation and inequality the same as derived in [62]. To this purpose let us multiply equation (4.4)<sub>1</sub> by  $-\bar{\mu}$ , equation (4.4)<sub>2</sub> by  $\chi_t$ , and equation (4.4)<sub>3</sub> by  $1/\tilde{e}_{,\eta}$ , and then summ up the resulting expressions to get the following equality

$$\begin{aligned}-\bar{\mu}\tau + \frac{1}{\tilde{e}_{,\eta}}g &= -\bar{\mu}\nabla \cdot \mathbf{j}^d - \frac{\tilde{e}_{,x}}{\tilde{e}_{,\eta}}\chi_t + \chi_t \nabla \cdot \left( \frac{\tilde{e}_{,Dx}}{\tilde{e}_{,\eta}} \right) \\ &+ (\tilde{e}_{,x}\chi_t + \tilde{e}_{,Dx} \cdot \nabla \chi_t + \tilde{e}_{,\eta}\eta_t) \frac{1}{\tilde{e}_{,\eta}} + \frac{1}{\tilde{e}_{,\eta}}\nabla \cdot \mathbf{q}^d \\ &= \eta_t + \nabla \cdot \left( -\bar{\mu}\mathbf{j}^d + \frac{1}{\tilde{e}_{,\eta}}\mathbf{q}^d + \chi_t \frac{\tilde{e}_{,Dx}}{\tilde{e}_{,\eta}} \right) \\ &+ \nabla \bar{\mu} \cdot \mathbf{j}^d - \nabla \cdot \frac{1}{\tilde{e}_{,\eta}} \cdot \mathbf{q}^d.\end{aligned}\tag{4.5}$$

This provides the entropy inequality

$$\begin{aligned}\eta_t + \nabla \cdot \Psi &= -\nabla \bar{\mu} \cdot \mathbf{j}^d + \nabla \cdot \frac{1}{\tilde{e}_{,\eta}} \cdot \mathbf{q}^d - \bar{\mu}\tau + \frac{1}{\tilde{e}_{,\eta}}g \\ &\geq -\bar{\mu}\tau + \frac{1}{\tilde{e}_{,\eta}}g,\end{aligned}\tag{4.6}$$

with the entropy flux

$$\Psi = -\bar{\mu}\mathbf{j}^d + \frac{1}{\tilde{e}_{,\eta}}\mathbf{q}^d + \chi_t \frac{\tilde{e}_{,Dx}}{\tilde{e}_{,\eta}}.\tag{4.7}$$

Using the identities (4.3), the fact that  $\bar{\mu} = \frac{\mu}{\theta}$ , and the equality

$$\chi_t = -\nabla \cdot \mathbf{j}^d,\tag{4.8}$$

which is valid in the case  $\tau = 0$ , the flux  $\Psi$  can be expressed as

$$\Psi = -\frac{\mu}{\theta}\mathbf{j}^d + \frac{1}{\theta}\mathbf{q}^d - (\nabla \cdot \mathbf{j}^d) \frac{f_{,Dx}}{\theta}.\tag{4.9}$$

Equation (4.6) with the flux  $\Psi$  in the form (4.9) is identical to that derived by Falk (see [62, eq. (2.25)] for a body at rest,  $\mathbf{v} = \mathbf{0}$ ).

We remark that according to Falk's notion, in the case of gradient-type internal energy  $\tilde{e} = \hat{e}(\chi, \mathbf{D}\chi, \eta)$ , the quantity  $\tilde{e}_{,\chi}$  is called the *chemical potential* whereas  $\tilde{e}_{,\mathbf{D}\chi}$  the *hyperpotential*.

**9.5. The nonisothermal phase separation models based on a microforce balance.** Applying the Fried and Gurtin concept of a microforce balance (see [72], [73], [74], [75], [83]), A. Miranville and G. Schimperna [104] have derived a class of nonisothermal Cahn-Hilliard models with the modified energy equation and the standard entropy equation. The authors generalize the energy equation by accounting for the rate of working due to a microstress, like in the Fried-Gurtin theory [72]. The Miranville-Schimperna model has the structure of the conserved phase-field system  $(PF)_\theta$  with suppressed elastic effects and  $\varrho_0 = 1$  in the case including extra energy term  $\mathbf{h}^e = f_{,\mathbf{D}\chi}$  and no extra entropy term  $\mathbf{h}^\eta = \mathbf{0}$  (see (7.5.7) with  $f = f(\chi, \mathbf{D}\chi, \theta)$ ,  $\varrho_0 = 1$ ,  $\mathbf{h}^e = f_{,\mathbf{D}\chi}$  and  $\mathbf{j}^d, \mathbf{q}^d, a^d$  given by (7.5.5)):

$$\begin{aligned} \chi_t - \nabla \cdot \left( \mathbf{L}_{jj} \nabla \frac{\mu}{\theta} + \mathbf{L}_{jq} \nabla \frac{1}{\theta} + l_{ja} \chi_t \right) &= \tau, \\ \frac{\mu}{\theta} &= \frac{1}{\theta} (f_{,\chi} - \nabla \cdot f_{,\mathbf{D}\chi}) + l_{aj} \cdot \nabla \frac{\mu}{\theta} + l_{aq} \cdot \nabla \frac{1}{\theta} + l_{aa} \chi_t, \\ e_t + \nabla \cdot \left( \mathbf{L}_{qj} \nabla \frac{\mu}{\theta} + \mathbf{L}_{qq} \nabla \frac{1}{\theta} + l_{qa} \chi_t - \chi_t f_{,\mathbf{D}\chi} \right) &= g, \end{aligned} \quad (5.1)$$

where the matrices  $\mathbf{L}_{jj}$ ,  $\mathbf{L}_{jq}$ ,  $\mathbf{L}_{qj}$ ,  $\mathbf{L}_{qq}$ , the vectors  $l_{ja}$ ,  $l_{aj}$ ,  $l_{aq}$ ,  $l_{qa}$  and the scalar  $l_{aa}$  satisfy the inequality (7.5.6).

According to (7.4.18) the scheme (5.1) is consistent with the entropy equation and inequality

$$\begin{aligned} \eta_t + \nabla \cdot \Psi &= -\nabla \frac{\mu}{\theta} \cdot \mathbf{j}^d + \nabla \frac{1}{\theta} \cdot \mathbf{q}^d + \chi_t a^d - \frac{\mu}{\theta} \tau + \frac{1}{\theta} g \\ &\geq -\frac{\mu}{\theta} \tau + \frac{1}{\theta} g, \end{aligned} \quad (5.2)$$

where the entropy flux has the standard form

$$\Psi = -\frac{\mu}{\theta} \mathbf{j}^d + \frac{1}{\theta} \mathbf{q}^d. \quad (5.3)$$

System (5.1) is the same as the Miranville-Schimperna model with kinetic effects (see [104, eq. (3.8)–(3.10)]).

Assuming that the viscous (kinetic) effects in representation (7.5.5) of  $\mathbf{j}^d$ ,  $\mathbf{q}^d$ ,  $a^d$  are neglected, i.e.,

$$\begin{aligned} -\mathbf{j}^d &= \mathbf{L}_{jj} \mathbf{D} \frac{\mu}{\theta} + \mathbf{L}_{jq} \mathbf{D} \frac{1}{\theta}, \\ \mathbf{q}^d &= \mathbf{L}_{qj} \mathbf{D} \frac{\mu}{\theta} + \mathbf{L}_{qq} \mathbf{D} \frac{1}{\theta}, \\ a^d &= 0, \end{aligned} \quad (5.4)$$

system (5.1) reduces to

$$\begin{aligned}\chi_t - \nabla \cdot \left( \mathbf{L}_{jj} \nabla \frac{\mu}{\theta} + \mathbf{L}_{jq} \nabla \frac{1}{\theta} \right) &= \tau, \\ \mu &= f_{,\chi} - \nabla \cdot f_{,D\chi}, \\ e_t + \nabla \cdot \left( \mathbf{L}_{qj} \nabla \frac{\mu}{\theta} + \mathbf{L}_{qq} \nabla \frac{1}{\theta} - \chi_t f_{,D\chi} \right) &= g.\end{aligned}\tag{5.5}$$

System (5.5) is the same as the Miranville-Schimperna model with kinetic effects not taken into account (see [104, eq. (2.23)–(2.26)]).

**9.6. The Cahn-Hilliard-de Gennes and generalized Penrose-Fife models for polymer phase separation.** The models of this group have been discussed in detail in [127]. They are governed by the Flory-Huggins-de Gennes (FHdG) free energy density presented in Section 8.5. In case of constant temperature the classical Cahn-Hilliard model can be directly generalized to degenerate singular Cahn-Hilliard-de Gennes model describing isothermal phase separation in a binary polymer mixture.

Since the gradient term in the FHdG free energy is made up of energetic and entropic contributions the corresponding thermodynamically consistent model for nonisothermal phase separation in polymer mixtures, set up in [127], has the structure of model  $(PF)_\theta$  with suppressed elastic effects and  $\varrho_0 = 1$  in the case including extra energy and extra entropy terms

$$\mathbf{h}^e = e_{,D\chi}, \quad \mathbf{h}^\eta = \eta_{,D\chi}, \quad \mathbf{h}^e + \theta \mathbf{h}^\eta = f_{,D\chi}.\tag{6.1}$$

The model reads as follows (see [127, eq. (2.3), (2.17)])

$$\begin{aligned}\chi_t - \nabla \cdot \left( \mathbf{L}_{jj} \nabla \frac{\mu}{\theta} + \mathbf{L}_{jq} \nabla \frac{1}{\theta} + l_{ja} \chi_t \right) &= 0, \\ \frac{\mu}{\theta} &= \frac{f_{,\chi}}{\theta} - \nabla \cdot \left( \frac{f_{,D\chi}}{\theta} \right) + e_{,D\chi} \cdot \nabla \frac{1}{\theta} + l_{aj} \cdot \nabla \frac{\mu}{\theta} + l_{aq} \cdot \nabla \frac{1}{\theta} + l_{aa} \chi_t, \\ e_t + \nabla \cdot \left( \mathbf{L}_{qj} \nabla \frac{\mu}{\theta} + \mathbf{L}_{qq} \nabla \frac{1}{\theta} + l_{qa} \chi_t - \chi_t e_{,D\chi} \right) &= g,\end{aligned}\tag{6.2}$$

where the matrices  $\mathbf{L}_{jj}$ ,  $\mathbf{L}_{jq}$ ,  $\mathbf{L}_{qj}$ ,  $\mathbf{L}_{qq}$ , the vectors  $l_{ja}$ ,  $l_{aj}$ ,  $l_{aq}$ ,  $l_{qa}$  and the scalar  $l_{aa}$  satisfy the inequality (7.5.6). We remind that in this model the free energy  $f$  is given by the FHdG form

$$f_{\text{FHdG}}(\chi, D\chi, \theta) = f_0(\chi, \theta) + \frac{1}{2}(\varkappa_e + \theta \varkappa_\eta(\chi)) |D\chi|^2,\tag{6.3}$$

where  $f_0$  is the Flory-Huggins mixture free energy given by (8.2.16),  $\varkappa_e$  a positive constant and the coefficient  $\varkappa_\eta(\chi)$ , which is singular in  $\chi$ , is given by (8.5.3).

Here it is of interest to note that in polymer mixtures – in contrast to small molecular ones – the gradient term in (6.3) introduces an infinite energy penalty near the pure phases.

On account of (7.4.5) the solutions of (6.2) satisfy the entropy inequality

$$\eta_t + \nabla \cdot (\Psi^d - \chi_t \eta_{,D\chi}) = -\nabla \frac{\mu}{\theta} \cdot \mathbf{j}^d + \nabla \frac{1}{\theta} \cdot \mathbf{q}^d + \chi_t a^d + \frac{g}{\theta} \geq \frac{g}{\theta}$$

with the entropy flux involving extra term  $-\chi_t \eta_{,D\chi}$ .

**9.7. Isothermal Cahn-Hilliard system coupled with elasticity.** In this section we compare the conserved scheme  $(PF)_\theta$  with suppressed thermal effects presented in Subsection 7.5.4, with the analogous models introduced in a line of papers by E. Fried and M. E. Gurtin [72], [73], [75], [83]. They have developed a thermodynamical theory of phase transitions based on a microforce balance in addition to the basic balance laws and a mechanical version of the second law. Parallel to that theory, M. Frémond [70], [71] have proposed a theory based on microscopic motions as a tool of modelling various phase transitions, specifically shape memory and damage problems. Despite of different ideas Frémond's approach bears some resemblance to the Fried-Gurtin theory.

**9.7.1. Model equations.** Let us recall the conserved model (7.5.8) with suppressed thermal effects,  $\theta \equiv 1$ ,  $\varrho_0 \equiv 1$ , and with the quantities  $\mathbf{j}^d$  and  $a^d$  given by (see (7.5.14))

$$\begin{aligned} -\mathbf{j}^d &= \mathbf{L}_{jj} \mathbf{D}\mu + l_{ja} \chi_{,t}, \\ a^d &= l_{aj} \cdot \mathbf{D}\mu + l_{aa} \chi_{,t}. \end{aligned} \quad (7.1)$$

Here the moduli, the matrix  $\mathbf{L}_{jj}$ , the vectors  $l_{ja}$ ,  $l_{aj}$  and the scalar  $l_{aa}$ , may depend on the variables

$$\mathcal{Z} = \mathcal{Z}_\theta|_{\theta=1} = \{\mathbf{F}, \mathbf{D}\mathbf{F}, \chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \mu, \mathbf{D}\mu, \chi_{,t}\}, \quad (7.2)$$

and are consistent with the inequality (see (7.5.15))

$$\begin{bmatrix} \mathbf{D}\mu \\ \chi_{,t} \end{bmatrix} \cdot \begin{bmatrix} \mathbf{L}_{jj} & l_{ja} \\ l_{ja}^T & l_{aa} \end{bmatrix} \begin{bmatrix} \mathbf{D}\mu \\ \chi_{,t} \end{bmatrix} \geq 0 \quad \text{for all variables } \mathcal{Z}. \quad (7.3)$$

The corresponding system of equations is (see (7.5.9) with  $\varrho_0 = 1$  and (7.1)):

$$\begin{aligned} \ddot{\mathbf{u}} - \nabla \cdot f_{,\mathbf{F}}(\mathbf{F}, \chi, \nabla\chi) &= \mathbf{b}, \\ \dot{\chi} - \nabla \cdot (\mathbf{L}_{jj} \nabla\mu + l_{ja} \dot{\chi}) &= \tau, \\ \mu &= f_{,\chi}(\mathbf{F}, \chi, \nabla\chi) - \nabla \cdot f_{,\mathbf{D}\chi}(\mathbf{F}, \chi, \nabla\chi) + l_{aj} \cdot \nabla\mu + l_{aa} \dot{\chi}. \end{aligned} \quad (7.4)$$

System (7.4) is supplemented by the inequality (7.3) and the frame invariance restrictions discussed in Subsection 6.1.2.

On account of (7.5.16), the solutions of (7.4) satisfy the free energy inequality

$$\dot{f} - \mathbf{S} \cdot \dot{\mathbf{F}} + \nabla \cdot (\mu \mathbf{j}^d - \dot{\chi} f_{,\mathbf{D}\chi}) = -\sigma + \mu\tau \leq \mu\tau, \quad (7.5)$$

where the stress  $\mathbf{S} = f_{,\mathbf{F}}$ .

For later comparison with Gurtin's theory we note that multiplying equation (7.4)<sub>2</sub> by  $\mu$  and subtracting the result from inequality (7.5), the latter becomes

$$\dot{f} - \mathbf{S} \cdot \dot{\mathbf{F}} - (\nabla \cdot f_{,\mathbf{D}\chi} + \mu) \dot{\chi} - f_{,\mathbf{D}\chi} \cdot \nabla \dot{\chi} + \mathbf{j}^d \cdot \nabla \mu = -\sigma \leq 0. \quad (7.6)$$

Moreover, recalling Section 7.3, let us formulate system (7.4) under assumption of infinitesimal deformations

$$\begin{aligned} \ddot{\mathbf{u}} - \nabla \cdot f_{,\varepsilon}(\varepsilon(\mathbf{u}), \chi, \nabla\chi) &= \mathbf{b}, \\ \dot{\chi} - \nabla \cdot (\mathbf{L}_{jj} \nabla\mu + l_{ja} \dot{\chi}) &= \tau, \\ \mu &= f_{,\chi}(\varepsilon(\mathbf{u}), \chi, \nabla\chi) - \nabla \cdot f_{,\mathbf{D}\chi}(\varepsilon(\mathbf{u}), \chi, \nabla\chi) + l_{aj} \cdot \nabla\mu + l_{aa} \dot{\chi}, \end{aligned} \quad (7.7)$$

where  $f = \hat{f}(\varepsilon(\mathbf{u}), \chi, \mathbf{D}\chi)$  and the quantities  $\mathbf{L}_{jj}$ ,  $l_{ja}$ ,  $l_{aj}$ ,  $l_{aa}$ , possibly depending on

$$\mathcal{Z}^i = \{\varepsilon, \mathbf{D}\varepsilon, \chi, \mathbf{D}\chi, \mathbf{D}^2\chi, \mu, \mathbf{D}\mu, \chi_{,t}\},$$

are consistent with the inequality (7.3) for all variables  $\mathcal{Z}^l$ .

We shall indicate that systems (7.4) and (7.7) coincide with that derived by the Fried-Gurtin theory. In particular, our differential equation for the chemical potential (negative of the multiplier associated with the balance law for the order parameter) turns out to be identical with the Fried-Gurtin microforce balance.

**9.7.2. Links to the Gurtin model.** To see in detail the connections between the presented multipliers-based approach and the microforce balance approach to the Cahn-Hilliard model with elasticity, we recall here the main postulates of Gurtin's theory [83]. We use our notation with the following correspondences to the notation of [83]:

$\chi \Leftrightarrow \varrho$  order parameter,  $\mathbf{j} \Leftrightarrow \mathbf{h}$  mass flux,  
 $\tau \Leftrightarrow m$  external mass supply,  
 $l_{ja} \Leftrightarrow \mathbf{a}$ ,  $l_{aj} \Leftrightarrow \mathbf{b}$  corss-coupling terms,  
 $\mathbf{L}_{jj} \Leftrightarrow \mathbf{A}$  mobility tensor,  $\mathbf{A} \Leftrightarrow \mathbf{C}$  elasticity tensor,  
 $f \Leftrightarrow \psi$  free energy.

The other notation is the same. Moreover, in [83] the following additional fields are considered as primitive quantities:

$\boldsymbol{\xi}$  – microstress (vector),  
 $\pi$  – internal microforce (scalar),  
 $\gamma$  – external microfoce (scalar).

The postulates in [83] are the following:

(G1) The unknowns are the fields  $\mathbf{u}$ ,  $\chi$  and  $\mu$ .

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

$$-\nabla \cdot \mathbf{S} = \mathbf{b}, \quad (7.8)$$

the angular momentum balance

$$\mathbf{S}\mathbf{F}^T = \mathbf{F}\mathbf{S}^T, \quad (7.9)$$

the mass balance

$$\dot{\chi} + \nabla \cdot \mathbf{j} = \tau, \quad (7.10)$$

and the microforce balance

$$\nabla \cdot \boldsymbol{\xi} + \pi + \gamma = 0. \quad (7.11)$$

Here and in what follows all derivatives are material (Lagrangian).

(G3) The second law is assumed in the form of the dissipation inequality (see [83, eq. (4.6)])

$$\dot{f} + \nabla \cdot (-\mathbf{S}^T \dot{\mathbf{u}} + \mu \mathbf{j} - \dot{\chi} \boldsymbol{\xi}) \leq \dot{\mathbf{u}} \cdot \mathbf{b} + \mu \tau + \dot{\chi} \gamma, \quad (7.12)$$

which in view of (7.8)–(7.11) is equivalent to (see [83, eq. (4.7)])

$$\dot{f} - \mathbf{S} \cdot \dot{\mathbf{F}} + (\pi - \mu) \dot{\chi} - \boldsymbol{\xi} \cdot \nabla \dot{\chi} + \mathbf{j} \cdot \nabla \mu \leq 0. \quad (7.13)$$

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

$$\mathcal{Z}_0 := \{\mathbf{F}, \chi, \mathbf{D}\chi, \mu, \mathbf{D}\mu\}$$



and constitutive equations are (see [83, eq. (4.8)])

$$f = \hat{f}(\mathcal{Z}_0), \quad \mathbf{S} = \hat{\mathbf{S}}(\mathcal{Z}_0), \quad \mathbf{j} = \hat{\mathbf{j}}(\mathcal{Z}_0), \quad \boldsymbol{\xi} = \hat{\boldsymbol{\xi}}(\mathcal{Z}_0), \quad \pi = \hat{\pi}(\mathcal{Z}_0). \quad (7.14)$$

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

$$\begin{aligned} f &\rightarrow f, \quad \mathbf{S} \rightarrow \mathbf{Q}\mathbf{S}, \quad \mathbf{j} \rightarrow \mathbf{j}, \quad \boldsymbol{\xi} \rightarrow \boldsymbol{\xi}, \quad \pi \rightarrow \pi, \\ (\mathbf{F}, \chi, \mathbf{D}\chi, \mu, \mathbf{d}\mu) &\rightarrow (\mathbf{Q}\mathbf{F}, \chi, \mathbf{D}\chi, \mu, \mathbf{D}\mu) \end{aligned}$$

for all orthogonal tensors  $\mathbf{Q}$ . This leads to the restrictions

$$\begin{aligned} \hat{f}(\mathcal{Z}_0) &= \hat{f}(\bar{\mathcal{Z}}_0), \quad \hat{\mathbf{S}}(\mathcal{Z}_0) = \mathbf{F}\hat{\mathbf{S}}(\bar{\mathcal{Z}}_0), \quad \hat{\mathbf{j}}(\mathcal{Z}_0) = \hat{\mathbf{j}}(\bar{\mathcal{Z}}_0), \\ \hat{\boldsymbol{\xi}}(\mathcal{Z}_0) &= \hat{\boldsymbol{\xi}}(\bar{\mathcal{Z}}_0), \quad \hat{\pi}(\mathcal{Z}_0) = \hat{\pi}(\bar{\mathcal{Z}}_0) \end{aligned} \quad (7.15)$$

with

$$\bar{\mathcal{Z}}_0 := \{\mathbf{C}, \chi, \mathbf{D}\chi, \mu, \mathbf{D}\mu\}, \quad \mathbf{C} = \mathbf{F}^T \mathbf{F}.$$

We add that restricted relations (7.15) are not used in the general development of the theory in [83] which is simpler in terms of the deformation gradient  $\mathbf{F}$  (see also Remark 2.3). We outline the main results proved in [83]:

- The compatibility of constitutive equations (7.14) with dissipation inequality (7.13) implies the following restrictions

$$\begin{aligned} f &= \hat{f}(\mathbf{F}, \chi, \mathbf{D}\chi), \quad \mathbf{S} = \hat{\mathbf{S}}(\mathbf{F}, \chi, \mathbf{D}\chi) = f_{,\mathbf{F}}(\mathbf{F}, \chi, \mathbf{D}\chi), \\ \boldsymbol{\xi} &= \hat{\boldsymbol{\xi}}(\mathbf{F}, \chi, \mathbf{D}\chi) = f_{,\mathbf{D}\chi}(\mathbf{F}, \chi, \mathbf{D}\chi), \end{aligned} \quad (7.16)$$

$$\begin{aligned} \pi &= \hat{\pi}(\mathbf{F}, \chi, \mathbf{D}\chi, \mu) = \mu - f_{,\chi}(\mathbf{F}, \chi, \mathbf{D}\chi), \\ \mathbf{j} &= -\mathbf{L}_{jj} \mathbf{D}\mu \end{aligned} \quad (7.17)$$

with tensor  $\mathbf{L}_{jj} = \hat{\mathbf{L}}_{jj}(\mathcal{Z}_0)$  consistent with the inequality

$$\mathbf{D}\mu \cdot \mathbf{L}_{jj} \mathbf{D}\mu \geq 0 \quad \text{for all variables } \mathcal{Z}_0.$$

- Balance laws (7.8)–(7.11) together with relations (7.16), (7.17) yield the system (see [83, eq. (4.15)])

$$\begin{aligned} -\nabla \cdot f_{,\mathbf{F}}(\mathbf{F}, \chi, \nabla\chi) &= \mathbf{b}, \\ \dot{\chi} - \nabla \cdot (\mathbf{L}_{jj} \nabla\mu) &= \tau, \\ \mu - f_{,\chi}(\mathbf{F}, \chi, \nabla\chi) + \nabla \cdot f_{,\mathbf{D}\chi}(\mathbf{F}, \chi, \nabla\chi) + \gamma &= 0. \end{aligned} \quad (7.18)$$

We note that this system is identical with (7.4) provided  $\ddot{\mathbf{u}} = \mathbf{0}$ ,  $\mathbf{l}_{aj} = \mathbf{l}_{ja} = \mathbf{0}$ ,  $l_{aa} = \gamma = 0$ , and the set  $\mathcal{Z}$  replaced by  $\mathcal{Z}_0$ .

- The considerations in [83, Sec. 3.4, 4.1] allow to deduce that the inclusion of the kinetics in the constitutive variables, that is replacement of the set  $\mathcal{Z}_0$  in (G4) by

$$\mathcal{Z}_1 := \{\mathbf{F}, \chi, \mathbf{D}\chi, \mu, \mathbf{D}\mu, \chi, t\}, \quad (7.19)$$

leads to relations (7.16), and

$$\begin{aligned} \pi &= \mu - f_{,\chi}(\mathbf{F}, \chi, \mathbf{D}\chi) + \pi_{\text{dis}}, \\ \mathbf{j} &= -(\mathbf{L}_{jj} \mathbf{D}\mu + \mathbf{l}_{ja} \chi, t), \\ \pi_{\text{dis}} &= -(\mathbf{l}_{aj} \cdot \mathbf{D}\mu + l_{aa} \chi, t), \end{aligned} \quad (7.20)$$

where  $\pi_{\text{dis}}$  represents the dissipative part of the internal microforce, and the quantities  $\mathbf{L}_{jj} = \hat{\mathbf{L}}_{jj}(\mathcal{Z}_1)$ ,  $l_{ja} = \hat{l}_{ja}(\mathcal{Z}_1)$ ,  $l_{aj} = \hat{l}_{aj}(\mathcal{Z}_1)$ ,  $l_{aa} = \hat{l}_{aa}(\mathcal{Z}_1)$  are consistent with the inequality (7.3) for all variables  $\mathcal{Z}_1$ . Then balance laws (7.8)–(7.11) together with relations (7.16), (7.20) yield the system which is identical with our system (7.4) if  $\dot{\mathbf{u}} = \mathbf{0}$ ,  $\gamma = 0$  and the set  $\mathcal{Z}_1$  in place of  $\mathcal{Z}$ .

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

- The generalized Cahn-Hilliard models with elasticity obtained by two approaches have the same structure. The only difference is the set of state variables which is  $\mathcal{Z}$  given by (7.2) in our model and  $\mathcal{Z}_1$  given by (7.19) in the Gurtin model.
- The term  $f_{,D\chi}(\mathbf{F}, \chi, \nabla\chi)$  in differential equation (7.4)<sub>3</sub> for the chemical potential corresponds to the microstress while the term  $\mu - f_{,\chi}(\mathbf{F}, \chi, \nabla\chi)$  to the internal microforce.
- The quantity  $-a^d = -(l_{aj} \cdot \mathbf{D}\mu + l_{aa}\chi_{,t})$  in our model corresponds to the dissipative part of the internal microforce in Gurtin's model.
- The free energy inequality (7.6) coincides with the microforce balance (7.11) (with  $\gamma = 0$ ) and the dissipation inequality (7.13) postulated in [83].
- Our postulate of treating the multiplier (equal to the negative of the chemical potential) as an independent variable corresponds to Gurtin's postulate of an additional balance law for the microforce. The differential equations for the chemical potential and the microforce balance are identical.
- Under assumption of infinitesimal deformations and  $\dot{\mathbf{u}} = \mathbf{0}$ , our system (7.7) coincides with that given in [83, Sec. 4.4]. In such a case the relevant form of the free energy is (see Subsection 8.2.2)

$$f(\boldsymbol{\varepsilon}(\mathbf{u}), \chi, \mathbf{D}\chi) = W(\boldsymbol{\varepsilon}(\mathbf{u}), \chi) + \psi(\chi) + \frac{1}{2}\varkappa|\mathbf{D}\chi|^2, \quad \varkappa > 0, \quad (7.21)$$

where

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

is the elastic energy,  $\mathbf{A}(\chi) = (A_{ijkl}(\chi))$  is the fourth order elasticity tensor,  $\bar{\boldsymbol{\varepsilon}}(\chi) = (\bar{\boldsymbol{\varepsilon}}_{ij}(\chi))$  is the symmetric eigenstrain tensor, and  $\psi(\chi)$  is a double-well potential whose wells define the phases, with the standard form

$$\psi(\chi) = \frac{1}{2}\chi^2(1 - \chi)^2.$$

## 10. Well-known phase-field models with nonconserved order parameter. Relation to model $(PF)_\theta$

### 10.1. The Penrose-Fife model.

**10.1.1. General model equations.** The Penrose-Fife model with nonconserved order parameter has been derived by similar variational arguments as that with the conserved order parameter. The derivation is based on the internal energy  $e$  as an independent thermal variable and the entropy density (9.1.1) as the corresponding thermodynamic potential. It is important that the coefficient  $\varkappa$  in (9.1.1) is assumed to be a positive constant. The model has the form of the following system (see [129, eq. (2.15), (2.19), (2.10), (2.11)]):

$$\begin{aligned} \chi_t &= l \frac{\delta \tilde{\eta}}{\delta \chi}, \\ e_t + \nabla \cdot \left( k \nabla \frac{\delta \tilde{\eta}}{\delta e} \right) &= 0 \end{aligned} \tag{1.1}$$

with positive coefficients  $l, k$  which may depend on  $\chi$  and on  $e$ . In (1.1),  $\delta \tilde{\eta} / \delta \chi$  and  $\delta \tilde{\eta} / \delta e$  are the variational derivatives of  $\tilde{\eta}$  with respect to  $\chi$  and  $e$ , respectively. For entropy potential (9.1.1) they are

$$\begin{aligned} \frac{\delta \tilde{\eta}}{\delta \chi} &= \tilde{\eta}_{V,\chi}(\chi, e) + \varkappa \Delta \chi, \\ \frac{\delta \tilde{\eta}}{\delta e} &= \tilde{\eta}_{V,e}(\chi, e). \end{aligned} \tag{1.2}$$

As in the conserved case, with the use of the transform relations, equations (1.2) are expressed in the form

$$\begin{aligned} \frac{\delta \tilde{\eta}}{\delta \chi} &= \frac{1}{\theta} (-f_{V,\chi}(\chi, \theta) + \varkappa \theta \Delta \chi), \\ \frac{\delta \tilde{\eta}}{\delta e} &= \frac{1}{\theta}, \end{aligned} \tag{1.3}$$

where

$$f(\chi, \mathbf{D}\chi, \theta) = f_V(\chi, \theta) + \frac{1}{2} \varkappa \theta |\mathbf{D}\chi|^2, \quad \varkappa = \text{const} > 0, \tag{1.4}$$

is the corresponding free energy density.

We point out again that this free energy is of the entropic type (with gradient term being a linear function of  $\theta$ ), and consequently yields the internal energy

$$e = \frac{\partial(f/\theta)}{\partial(1/\theta)} = f_V(\chi, \theta) - \theta f_{V,\theta}(\chi, \theta) =: e_V(\chi, \theta) \tag{1.5}$$

independent of  $\mathbf{D}\chi$ . In result, the Penrose-Fife model (1.1) expressed in terms of  $\theta$  takes the form

$$\begin{aligned}\chi_t &= l \frac{1}{\theta} (-f_{V,\chi} + \varkappa \theta \Delta \chi), \\ e_t + \nabla \cdot \left( k \nabla \frac{1}{\theta} \right) &= 0.\end{aligned}\tag{1.6}$$

**10.1.2. Relation to nonconserved phase-field model  $(PF)_\theta$ .** Let us now introduce the quantity (rescaled chemical potential)

$$\bar{\mu} := \frac{\mu}{\theta} = \frac{\delta(f/\theta)}{\delta\chi} = \frac{f_{,\chi}}{\theta} - \nabla \cdot \left( \frac{f_{,\mathbf{D}\chi}}{\theta} \right),\tag{1.7}$$

which for free energy  $f$  given by (1.4) equals to

$$\bar{\mu} = \frac{f_{V,\chi}}{\theta} - \varkappa \Delta \chi.\tag{1.8}$$

Then the nonconserved Penrose-Fife model (1.6) can be expressed as

$$\begin{aligned}\chi_t + l \bar{\mu} &= 0, \\ \bar{\mu} &= \frac{\delta(f/\theta)}{\delta\chi}, \\ e_t + \nabla \cdot \left( k \nabla \frac{1}{\theta} \right) &= 0,\end{aligned}\tag{1.9}$$

where  $e = e_V(\chi, \theta)$  is related to  $f$  by (1.5). Thus, we see that the Penrose-Fife model (1.6) has the structure of the nonconserved phase-field system  $(PF)_\theta$  with suppressed elastic effects (see (7.6.7)) in the following special case:

$$\begin{aligned}f &= \hat{f}(\chi, \mathbf{D}\chi, \theta) \text{ given by (1.4),} \\ e &= e_V(\chi, \theta) \text{ given by (1.5),} \\ e_0 &\equiv 1, \quad \tau = 0, \quad g = 0, \quad \mathbf{h}^e = \mathbf{0}, \\ -r^d &= l \bar{\mu}, \quad \mathbf{q}^d = k \mathbf{D} \frac{1}{\theta}, \quad a^d = 0,\end{aligned}\tag{1.10}$$

with positive coefficients  $l = l(\chi, \theta)$ ,  $k = k(\chi, \theta)$ . The corresponding dissipation potential is quadratic in  $(\bar{\mu}, \mathbf{D} \frac{1}{\theta})$

$$\mathcal{D} = \frac{1}{2} l |\bar{\mu}|^2 + \frac{1}{2} k \left| \mathbf{D} \frac{1}{\theta} \right|^2,\tag{1.11}$$

thus refers to a situation near the thermodynamic equilibrium. In conclusion, according to the classification in Section 7.4, the nonconserved Penrose-Fife model (1.6) can be regarded as the intersection of examples  $(PF)_\theta$  (i) and  $(PF)_\theta$  (ii) given there. More precisely, it represents the model with no extra energy term but with the extra entropy term

$$\mathbf{h}^e = e_{,\mathbf{D}\chi} = \mathbf{0} \quad \text{and} \quad \mathbf{h}^\eta = -\eta_{,\mathbf{D}\chi} = \frac{1}{\theta} f_{,\mathbf{D}\chi} = \varkappa \mathbf{D}\chi.\tag{1.12}$$

Recalling (7.4.5), we see that solutions of model (1.6) (and its equivalent version (1.9)) satisfy the entropy inequality

$$\eta_t + \nabla \cdot \Psi = \sigma \geq 0\tag{1.13}$$

with the modified entropy flux

$$\Psi = \Psi^d - \chi_t \eta_{,D\chi} = \Psi^d + \chi_t \frac{1}{\theta} f_{,D\chi}, \tag{1.14}$$

where

$$\Psi^d = \frac{1}{\theta} \mathbf{q}^d = k \frac{1}{\theta} \mathbf{D} \frac{1}{\theta}.$$

The entropy production density is

$$\sigma = -\bar{\mu} r^d + \mathbf{D} \frac{1}{\theta} \cdot \mathbf{q}^d = l \bar{\mu}^2 + k \left| \mathbf{D} \frac{1}{\theta} \right|^2 \geq 0. \tag{1.15}$$

**10.1.3. The Penrose-Fife model for liquid-solid phase transitions. Links to the Caginalp's model.** For liquid-solid phase transitions Penrose and Fife [129], [130] have proposed the free energy of the form (1.4) with  $f_V(\chi, \theta)$  given by (8.4.5)–(8.4.6). For such free energy system (1.6) becomes (see [130, eq. (6), (7)]):

$$\begin{aligned} \chi_t - l \varkappa \Delta \chi + l \left[ \left( \frac{1}{\theta} - \frac{1}{\theta_c} \right) (-2a\chi + b) + \frac{1}{\theta_c} \psi'(\chi) \right] &= 0, \\ c_\nu \theta_t + (-2a\chi + b) \chi_t + \nabla \cdot \left( k \nabla \frac{1}{\theta} \right) &= 0, \end{aligned} \tag{1.16}$$

where

$$c_\nu = c_*, \quad \psi'(\chi) = \chi^3 - \chi.$$

For a comparison with the standard phase-field model is it of interest to recall here the main conclusions from the Penrose-Fife study [130] of the effect of various choices of the parameters  $a$  and  $b$  in model (1.16).

Case I.  $a = 0, b = 0$ .

There is no coupling between the order parameter and temperature fields. The order parameter obeys the Allen-Cahn equation and the temperature obeys the heat equation.

Case II.  $a \neq 0, b = 0$

There is no latent heat (see (8.4.9)), so the model describes a second order phase transition.

Case III.  $a = 0, b > 0$

In this case defining the quantity

$$u = \frac{\theta - \theta_c}{\theta_c}, \tag{1.17}$$

linearizing equation (1.16) around  $\theta_c$  by replacing  $\frac{1}{\theta} - \frac{1}{\theta_c}$  with  $-\frac{u}{\theta_c}$ , and moreover assuming

$$k = \bar{k} \theta^2 \tag{1.18}$$

with  $\bar{k} = \text{const} > 0$ , system (1.16) with  $a = 0$  becomes

$$\begin{aligned} \alpha \chi_t - \Delta \chi + \frac{1}{\xi^2} (\psi'(\chi) - bu) &= 0, \\ c_\nu u_t + b \chi_t - \bar{k} \Delta u &= 0, \end{aligned} \tag{1.19}$$

where

$$\alpha = \frac{1}{l \varkappa}, \quad \xi^2 = \varkappa \theta_c.$$

System represents the standard phase-field model for nonconserved order parameter, known as *Caginalp's model*. The quantity  $L = 2b$  is the latent heat of phase transition (see (8.4.9)).

Case IV.  $a \neq 0, b > 0$

A linearization of equation (1.16)<sub>1</sub> around  $\theta_c$  and assumption (1.18) lead to the system

$$\begin{aligned} \alpha\chi_t - \Delta\chi + \frac{1}{\varepsilon^2}[\psi'(\chi) + u(2a\chi - b)] &= 0, \\ c_\nu u_t - (2a\chi - b)\chi_t - \bar{k}\Delta\chi &= 0. \end{aligned} \quad (1.20)$$

This system extends the standard phase-field model by an extra term involving  $2a\chi$  in each equation. A detailed analysis of the motion of phase boundaries in all four of these cases is given in Fife and Penrose [66].

It should be underlined that the Caginalp model (1.19) was established prior to the original Penrose-Fife model. As a matter of fact it was just the lack of a proper thermodynamic setting of model (1.19) 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], Alt and the author [5], [6], [7], [9], [10], Wang et al. [145].

Let us mention that thermodynamically consistent phase transition models with modified entropy flux have been proposed by Wang et al. [145], Fabrizio-Giorgi-Morro [53]. The models in [53] admit variable mass density and thereby are applicable also to phase transitions at constant pressure. The authors [53] specify thermodynamic functions and resulting differential equations for solid-fluid transition at constant pressure.

**10.2. The Fried-Gurtin phase-field model based on microforce balance.** In this section we compare the nonconserved phase-field scheme  $(PF)_\theta$  with suppressed elastic effects, presented in Subsection 7.6.2, with the analogous model introduced by Fried and Gurtin [72] on a basis of a microforce balance.

**10.2.1. Model equations.** Let us consider system (7.6.7) with the extra energy term  $h^e = f_{,D\chi}$ , and  $\varrho_0 \equiv 1$ :

$$\begin{aligned} \chi_t - r^d &= \tau, \\ \frac{\mu}{\theta} &= \frac{f_{,\chi}}{\theta} - \nabla \cdot \left( \frac{f_{,D\chi}}{\theta} \right) + f_{,D\chi} \cdot \nabla \frac{1}{\theta} + a^d, \\ e_t + \nabla \cdot (\mathbf{q}^d - \chi_t f_{,D\chi}) &= g, \end{aligned} \quad (2.1)$$

where  $e = f - \theta f_{,\theta}$ ,  $f = \hat{f}(\chi, \mathbf{D}\chi, \theta)$ , and  $r^d, \mathbf{q}^d, a^d$  admit representation (7.6.4).

For a comparison with the Fried-Gurtin model we introduce the following simplifying assumption:

$$l_{rq} = l_{qr} = \mathbf{0}, \quad l_{ra} = l_{ar} = 0, \quad (2.2)$$

and

$$l_{rr} > 0, \quad \begin{bmatrix} \mathbf{D}\frac{1}{\theta} \\ \chi_{,t} \end{bmatrix} \cdot \begin{bmatrix} \mathbf{L}_{qq} & l_{qa} \\ \mathbf{l}_{\alpha q}^T & l_{aa} \end{bmatrix} \begin{bmatrix} \mathbf{D}\frac{1}{\theta} \\ \chi_{,t} \end{bmatrix} \geq 0, \quad (2.3)$$

where  $l_{rr}$ ,  $\mathbf{L}_{qq}$ ,  $l_{qa}$ ,  $l_{aq}$ ,  $l_{aa}$  are constitutive moduli possibly dependent on the variables  $\chi$ ,  $\mathbf{D}\chi$ ,  $\mathbf{D}^2\chi$ ,  $\theta$ ,  $\mathbf{D}\frac{1}{\theta}$ ,  $\chi_t$ . Then

$$\begin{aligned} -r^d &= l_{rr} \frac{\mu}{\theta}, \\ \mathbf{q}^d &= \mathbf{L}_{qq} \mathbf{D} \frac{1}{\theta} + l_{qa} \chi_t, \\ a^d &= l_{aq} \cdot \mathbf{D} \frac{1}{\theta} + l_{aa} \chi_t, \end{aligned} \quad (2.4)$$

so that system (2.1) becomes

$$\begin{aligned} \chi_t + l_{rr} \frac{\mu}{\theta} &= \tau, \\ \frac{\mu}{\theta} &= \frac{1}{\theta} (f_{,\chi} - \nabla \cdot f_{,\mathbf{D}\chi}) + l_{aq} \cdot \nabla \frac{1}{\theta} + l_{aa} \chi_t, \\ e_t + \nabla \cdot \left[ \mathbf{L}_{qq} \nabla \frac{1}{\theta} + (l_{qa} - f_{,\mathbf{D}\chi}) \chi_t \right] &= g. \end{aligned} \quad (2.5)$$

Upon eliminating  $\frac{\mu}{\theta}$  and writing the energy equation (2.5)<sub>3</sub> in temperature form (see (7.2.3)), we get

$$\begin{aligned} \chi_t + l_{rr} \left[ \frac{1}{\theta} (f_{,\chi} - \nabla \cdot f_{,\mathbf{D}\chi}) + l_{aq} \cdot \nabla \frac{1}{\theta} + l_{aa} \chi_t \right] &= \tau, \\ c_\nu \theta_t + (f - \theta f_{,\theta})_{,\chi} \chi_t + (f - \theta f_{,\theta})_{,\mathbf{D}\chi} \cdot \nabla \chi_t \\ + \nabla \cdot \left[ \mathbf{L}_{qq} \nabla \frac{1}{\theta} + (l_{qa} - f_{,\mathbf{D}\chi}) \chi_t \right] &= g, \end{aligned} \quad (2.6)$$

where

$$c_\nu = -\theta f_{,\theta\theta}(\chi, \mathbf{D}\chi, \theta)$$

is the specific heat at constant volume.

Further, with the help of the notation

$$\begin{aligned} \beta &= \theta \left( \frac{1}{l_{rr}} + l_{aa} \right) > 0, \quad \mathbf{k} = -\frac{1}{\theta} l_{aq}, \quad \bar{\tau} = \tau \frac{\theta}{l_{rr}}, \\ \mathbf{K} &= \frac{\mathbf{L}_{qq}}{\theta^2}, \quad \mathbf{b} = -l_{qa}, \end{aligned} \quad (2.7)$$

system (2.6) may be expressed in the form

$$\begin{aligned} \beta \chi_t + f_{,\chi} - \nabla \cdot f_{,\mathbf{D}\chi} + \mathbf{k} \cdot \nabla \theta &= \bar{\tau}, \\ c_\nu \theta_t - \nabla \cdot [\mathbf{K} \nabla \theta + \mathbf{b} \chi_t] - \theta f_{,\theta\chi} \chi_t - \theta f_{,\theta\mathbf{D}\chi} \cdot \nabla \chi_t \\ + (f_{,\chi} - \nabla \cdot f_{,\mathbf{D}\chi}) \chi_t &= g. \end{aligned} \quad (2.8)$$

We shall indicate that system (2.8) coincides with that derived by Fried and Gurtin on the basis of a microforce balance (see [72, eq. (3.19)]). Before doing this let us point out a special case of system (2.8) with omitted cross-coupling terms  $\mathbf{k} = \mathbf{b} = \mathbf{0}$  (i.e.,  $l_{aq} = l_{qa} = \mathbf{0}$ ) and  $\bar{\tau} = g = 0$ .

Then, after replacing in (2.8)<sub>2</sub> the term  $f_{,\chi} - \nabla \cdot f_{,\mathbf{D}\chi}$  by its value given by (2.8)<sub>1</sub>, we get

$$\begin{aligned} \beta \chi_t &= -(f_{,\chi} - \nabla \cdot f_{,\mathbf{D}\chi}), \\ c_\nu \theta_t - \nabla \cdot (\mathbf{K} \nabla \theta) &= \theta f_{,\theta\chi} \chi_t + \theta f_{,\theta\mathbf{D}\chi} \cdot \nabla \chi_t + \beta \chi_t^2. \end{aligned} \quad (2.9)$$

Here we remark that this system, introduced by Fried and Gurtin (see [72, eq. (3.21)]), has the same structure as models due to Miranville and Schimperna, as well as due to Frémond (see Sections 10.2.3 and 10.3).

**10.2.2. Links to the Fried-Gurtin model.** For a more detailed comparison with the Fried-Gurtin model we outline first the main results of their theory based on a microforce balance. We use our notation with the following correspondences to the notation of [72]:

$$\begin{aligned} \chi &\leftrightarrow \varphi \text{ order parameter,} & f &\leftrightarrow \psi \text{ free energy,} \\ e &\leftrightarrow \varepsilon \text{ internal energy,} & \theta &\leftrightarrow \vartheta \text{ absolute temperature,} \\ \mathbf{q}^d &\leftrightarrow q \text{ heat flux (dissipative),} \\ g &\leftrightarrow r \text{ external heat supply.} \end{aligned}$$

The other notation is the same. Moreover, in [72] the following additional fields are considered as primitive quantities:

$$\begin{aligned} \boldsymbol{\xi} &- \text{microstress (vector),} \\ \pi &- \text{internal microforce (scalar),} \\ \gamma &- \text{external microforce.} \end{aligned}$$

The postulates in [72] are:

(FG1) The unknowns are the fields  $\chi$  and  $\theta$ .

(FG2) The underlying laws are: the microforce balance (i.e., a balance for interactions at a microscopic level)

$$\nabla \cdot \boldsymbol{\xi} + \pi + \gamma = 0, \quad (2.10)$$

and the energy balance

$$e_t + \nabla \cdot (\mathbf{q}^d - \chi_t \boldsymbol{\xi}) = g + \chi_t \gamma. \quad (2.11)$$

(FG3) The second law is assumed in the local form of the Clausius-Duhem inequality

$$\eta_t + \nabla \cdot \frac{\mathbf{q}^d}{\theta} \geq \frac{g}{\theta}. \quad (2.12)$$

It is seen that the entropy flux has the classical form while the energy flux is modified by an additional working term  $-\chi_t \boldsymbol{\xi}$ . On account of (2.10) and the thermodynamic relation  $f = e - \theta \eta$ , the equivalent forms of (2.11) and (2.12) are (see [72, eq. (3.6), (3.7)]):

$$e_t + \nabla \cdot \mathbf{q}^d - \boldsymbol{\xi} \cdot \nabla \chi_t + \pi \chi_t = g, \quad (2.13)$$

and

$$f_t + \eta \theta_t - \boldsymbol{\xi} \cdot \nabla \chi_t + \pi \chi_t + \frac{\mathbf{q}^d \cdot \nabla \theta}{\theta} \leq 0. \quad (2.14)$$

(FG4) The set of constitutive variables is

$$\mathcal{Z} = \{\chi, \mathbf{D}\chi, \theta, \mathbf{D}\theta, \chi_t, \theta_t\},$$

and the constitutive equations are (see [72, eq. (3.8)])

$$\hat{f} = \hat{f}(\mathcal{Z}), \quad \hat{\eta} = \hat{\eta}(\mathcal{Z}), \quad \hat{\mathbf{q}}^d = \hat{\mathbf{q}}^d(\mathcal{Z}), \quad \hat{\boldsymbol{\xi}} = \hat{\boldsymbol{\xi}}(\mathcal{Z}), \quad \hat{\pi} = \hat{\pi}(\mathcal{Z}). \quad (2.15)$$

The main results proved in [72] are as follows:



- The compatibility of constitutive equations (2.15) with dissipation inequality (2.14) implies the relations

$$\begin{aligned} f &= \hat{f}(\chi, \mathbf{D}\chi, \theta), \quad \eta = -f_{,\theta}(\chi, \mathbf{D}\chi, \theta), \\ \boldsymbol{\xi} &= f_{,\mathbf{D}\chi}(\chi, \mathbf{D}\chi, \theta), \end{aligned} \quad (2.16)$$

and the inequality (see [72, eq. (3.11)])

$$\frac{\mathbf{q}^d(\mathcal{Z}) \cdot \mathbf{D}\theta}{\theta} + [f_{,\chi}(\chi, \mathbf{D}\chi, \theta) + \pi(\mathcal{Z})]_{\chi,t} \leq 0 \quad (2.17)$$

for all variables  $\mathcal{Z}$ .

- The inequality (2.17) yields representations (see [72, eq. (3.12), (3.13)])

$$\begin{aligned} \mathbf{q}^d &= -\mathbf{K}\mathbf{D}\theta - \mathbf{b}\chi_{,t}, \\ \pi &= -f_{,\chi} - \mathbf{k} \cdot \mathbf{D}\theta - \beta\chi_{,t}, \end{aligned} \quad (2.18)$$

in which the matrix  $\mathbf{K}$ , the vectors  $\mathbf{b}$ ,  $\mathbf{k}$  and the scalar  $\beta$ , that may depend on the variables  $\mathcal{Z}$ , satisfy

$$\begin{bmatrix} \mathbf{D}\theta \\ \chi_{,t} \end{bmatrix} \cdot \begin{bmatrix} \mathbf{K}/\theta & \mathbf{b}/\theta \\ \mathbf{k}^T & \beta \end{bmatrix} \begin{bmatrix} \mathbf{D}\theta \\ \chi_{,t} \end{bmatrix} \geq 0 \quad (2.19)$$

for all variables  $\mathcal{Z}$ .

The functions

$$\begin{aligned} \pi_{eq}(\chi, \mathbf{D}\chi, \theta) &= -f_{,\chi}(\chi, \mathbf{D}\chi, \theta), \\ \pi_{noneq}(\mathcal{Z}) &= -\mathbf{k}(\mathcal{Z}) \cdot \mathbf{D}\theta - \beta(\mathcal{Z})\chi_{,t} \end{aligned} \quad (2.20)$$

represent the equilibrium and the nonequilibrium parts of the internal microforce

$$\pi = \pi_{eq} + \pi_{noneq}.$$

- Balance laws (2.10) and (2.11) together with relations (2.16), (2.18) yield the system (see [72, eq. (3.19)]):

$$\begin{aligned} \beta\chi_{,t} &= -f_{,\chi} + \nabla \cdot f_{,\mathbf{D}\chi} - \mathbf{k} \cdot \nabla\theta + \gamma, \\ c_\nu\theta_t - \nabla \cdot [\mathbf{K}\nabla\theta + \mathbf{b}\chi_{,t}] - \theta f_{,\theta\chi}\chi_{,t} - \theta f_{,\theta\mathbf{D}\chi} \cdot \nabla\chi_t \\ &+ (f_{,\chi} - \nabla \cdot f_{,\mathbf{D}\chi} - \gamma)\chi_t = g, \end{aligned} \quad (2.21)$$

where  $c_\nu = -\theta f_{,\theta\theta}$  is the specific heat at constant volume, and  $\mathbf{K}$ ,  $\mathbf{k}$ ,  $\mathbf{b}$ ,  $\beta$  satisfy the inequality (2.19).

A comparison of systems (2.8) and (2.21) indicates that Fried-Gurtin model based on a microforce balance has the same structure as our nonconserved phase-field model  $(PF)_\theta$  with suppressed elastic effects in the case of the standard entropy flux and the energy flux modified by the extra term  $-\chi_{,t}f_{,\mathbf{D}\chi}$ . In the Fried-Gurtin theory the term  $f_{,\mathbf{D}\chi}(\chi, \mathbf{D}\chi, \theta)$  represents the *microstress* while the term  $f_{,\chi}(\chi, \mathbf{D}\chi, \theta)$  corresponds to the *equilibrium part of the internal microforce*.

### 10.2.3. The Miranville-Schimperna models based on a microforce balance.

Continuing the Fried-Gurtin program of modelling phase transitions on a basis of a microforce balance Miranville and Schimperna [104], [105] have developed and studied mathematically nonisothermal Cahn-Hilliard and Allen-Cahn models. In this section we focus on their results concerning the Allen-Cahn model and on the links to our model

$(PF)_\theta$ . In particular, the system (4.7)–(4.8) in [104] coincides with the system (2.5) rewritten, upon eliminating  $\mu/\theta$  in the form

$$\begin{aligned} \tilde{\beta}\chi_t + l_{aq} \cdot \nabla \frac{1}{\theta} + \frac{1}{\theta} f_{,\chi} - \frac{1}{\theta} \nabla \cdot f_{,D\chi} &= 0, \\ e_t + \nabla \cdot \left( l_{qq} \nabla \frac{1}{\theta} + l_{qa} \chi_t - f_{,D\chi} \chi_t \right) &= 0, \end{aligned} \quad (2.22)$$

where

$$\tilde{\beta} = \frac{1}{l_{rr}} + l_{aa},$$

the constitutive moduli the matrix  $l_{qq}$ , the vectors  $l_{aq}$ ,  $l_{qa}$  and the scalars  $l_{rr} > 0$ ,  $l_{aa}$  may depend on the variables  $\{\chi, D\chi, D^2\chi, \theta, D\frac{1}{\theta}, \chi_t\}$  and satisfy the definiteness condition (2.3). This condition is equivalent to the dissipation inequality (4.4) in [104].

By suitable choice of the parameters  $\tilde{\beta}$ ,  $l_{qq}$ ,  $l_{aq}$ ,  $l_{qa}$  and specifying the form of the free energy one can obtain from (2.22) various forms of PDE's specialized to particular phase transitions.

In [105] system (2.22) has been studied from the point of view of the existence and uniqueness of solutions in the following special case:

$$\begin{aligned} l_{aq} = l_{qa} = \mathbf{0}, \\ l_{qq} = \theta^2 \mathbf{I}, \quad \tilde{\beta} = \frac{\beta}{\theta}, \quad \beta = \text{const} > 0, \end{aligned} \quad (2.23)$$

and the free energy density with gradient term of energetic type

$$f(\chi, D\chi, \theta) = -c_0\theta^2 + c(\theta - \theta_c)\chi^2 + \psi(\chi) + \frac{\varkappa}{2}|D\chi|^2, \quad (2.24)$$

where  $c_0$ ,  $c$ ,  $\theta_c$ ,  $\varkappa$  are positive constants and  $\psi(\chi)$  is a double-well potential.

Let us note that in this case the corresponding expressions for the internal energy and entropy are

$$\begin{aligned} e(\chi, D\chi, \theta) &= c_0\theta^2 - c\theta_c\chi^2 + \psi(\chi) + \frac{\varkappa}{2}|D\chi|^2, \\ \eta(\chi, D\chi, \theta) &= 2c_0\theta - c\chi^2. \end{aligned} \quad (2.25)$$

The corresponding specific heat is a linear function of temperature

$$c_\nu = e_{,\theta} = 2c_0\theta, \quad (2.26)$$

on the contrary to the standard example with the thermal energy  $f_*(\theta) = -c_*\theta \ln \theta$  which yields constant thermal specific heat  $c_\nu = c_* > 0$ .

The assumption (2.26) is motivated by mathematical reasons ensuring the existence of global in time solutions. In the case (2.23), (2.24) system (2.22) reduces to

$$\begin{aligned} \beta\chi_t - \varkappa\Delta\chi + \psi'(\chi) &= -2c(\theta - \theta_c)\chi, \\ c_0(\theta^2)_t - \Delta\theta + \psi'(\chi)\chi_t - 2c\theta_c\chi_t - \varkappa\Delta\chi\chi_t &= 0. \end{aligned} \quad (2.27)$$

After replacing the term  $-\varkappa\Delta\chi$  which appears as the last one on the left-hand side of (2.27)<sub>2</sub> by its value given in (2.27)<sub>1</sub>, system (2.27) becomes

$$\begin{aligned} \beta\chi_t - \varkappa\Delta\chi + \psi'(\chi) &= -2c(\theta - \theta_c)\chi, \\ c_0(\theta^2)_t - \Delta\theta &= 2c\theta_c\chi_t + \beta\chi_t^2. \end{aligned} \quad (2.28)$$

This system, defined on  $\Omega \times (0, T)$ , has been analysed in [105] with the initial conditions

$$\chi|_{t=0} = \chi_0, \quad \theta|_{t=0} = \theta_0 \quad \text{in } \Omega,$$

and boundary conditions

$$\mathbf{n} \cdot \nabla \chi = 0, \quad \mathbf{n} \cdot \nabla \theta - n_0(\theta - \theta_\Gamma) = 0 \quad \text{on } S \times (0, T),$$

where  $\chi_0, \theta_0$  are given data and  $n_0 > 0, \theta_\Gamma > 0$  are given constants.

System (2.28) with more general form of the term  $c_0(\theta^2)_t$  has been recently analysed in [76].

Let us remark that for the free energy of the form

$$f(\chi, \mathbf{D}\chi, \theta) = -c_*\theta \log \theta + c(\theta - \theta_c)\chi + \psi(\chi) + \frac{\varkappa}{2}|\mathbf{D}\chi|^2, \quad (2.29)$$

with positive constants  $c_*, c, \theta_c, \varkappa$ , and  $\psi$  being a double-well potential, system (2.22) with  $\mathbf{l}_{aq} = \mathbf{l}_{qa} = \mathbf{0}$  leads to (compare (2.9))

$$\begin{aligned} \beta\chi_t - \varkappa\Delta\chi + \psi'(\chi) &= -c(\theta - \theta_c), \\ c_*\theta_t + \nabla \cdot (\mathbf{L}_{qq}\nabla\theta) &= c\theta\chi_t + \beta\chi_t^2, \end{aligned} \quad (2.30)$$

where  $\beta = \tilde{\beta}\theta$ . System (2.30) with

$$\mathbf{L}_{qq} = k\theta^2\mathbf{I}, \quad k = \text{const} > 0, \quad \text{i.e., with } \mathbf{q}^d = -k\nabla\theta, \quad (2.31)$$

has the form of some models proposed by M. Frémond for irreversible phase transitions, studied mathematically e.g., in [41], [99].

REMARK 10.1. Nonconserved phase-field model with the extra energy flux has been recently introduced by Benzoni-Gavage et al. [12] in the context of solid-liquid phase transitions. It has been analyzed there from the point of view of local well-posedness and characterization of sharp interface limits by formal asymptotic analysis.

**10.3. Frémond's models based on microscopic motions.** In this section we shall show that our nonconserved phase-field system  $(PF)_\theta$  with suppressed elastic effects (see (7.6.7)), with extra energy term  $\mathbf{h}^e = f_{,\mathbf{D}\chi}$  is consistent with a smooth version of phase transition models proposed by M. Frémond in the frame of his theory based on microscopic motions, see [70], also [17]. It is important to mention that Frémond's approach bears strong resemblance to the Fried-Gurtin theory based on a microforce balance. Both are essentially two-scales approaches founded on balance laws on macro- and micro-scales.

The Frémond's approach is more general, however, in the sense of admitting nonsmooth thermodynamic functions. Thus, it may be applied to a very wide class of phase transitions, including irreversible phase changes (like solidification of glu) and problems with internal constraints.

**10.3.1. Comparison with Frémond's model.** Within our framework we can compare only with a smooth version of Frémond's models. Let us consider nonconserved system  $(PF)_\theta$  with suppressed elastic effects (see (7.6.7) with  $f = \hat{f}(\chi, \mathbf{D}\chi, \theta)$ ,  $\varrho_0 \equiv 1$ ) with the extra energy term  $\mathbf{h}^e = f_{,\mathbf{D}\chi}$ , and the constitutive relations for  $-r^d, \mathbf{q}^d, a^d$  with

neglected all off-diagonal elements, i.e.,

$$l_{rq} = l_{qr} = l_{qa} = l_{aq} = 0, \quad l_{ra} = l_{ar} = l_{aa} = 0,$$

and

$$l_{rr} = \hat{l}_{rr}(\chi, \theta) > 0, \quad L_{qq} = \bar{k}I, \quad \bar{k} = \bar{k}(\chi, \theta) > 0.$$

Then, by (7.6.4),

$$-r^d = l_{rr} \frac{\mu}{\theta}, \quad \mathbf{q}^d = \bar{k} \mathbf{D} \frac{1}{\theta}, \quad a^d = 0, \quad (3.2)$$

so that the corresponding dissipation potential is

$$\mathcal{D} = \frac{1}{2} l_{rr} \left( \frac{\mu}{\theta} \right)^2 + \frac{1}{2} \bar{k} \left| \mathbf{D} \frac{1}{\theta} \right|^2. \quad (3.3)$$

In view of (3.1), (3.2), system (7.6.7) (with  $\tau = g = 0$ ) reduces to

$$\begin{aligned} \chi_t + l_{rr} \frac{\mu}{\theta} &= 0, \\ \frac{\mu}{\theta} &= \frac{f_{,\chi}}{\theta} - \frac{1}{\theta} \nabla \cdot f_{,D\chi}, \\ e_t + \nabla \cdot \left( \bar{k} \nabla \frac{1}{\theta} - f_{,D\chi} \chi_t \right) &= 0. \end{aligned} \quad (3.4)$$

Hence, upon eliminating  $\frac{\mu}{\theta}$ , we have

$$\begin{aligned} \tilde{\beta} \chi_t + \frac{1}{\theta} f_{,\chi} - \frac{1}{\theta} \nabla \cdot f_{,D\chi} &= 0, \\ e_t + \nabla \cdot \left( \bar{k} \nabla \frac{1}{\theta} - f_{,D\chi} \chi_t \right) &= 0, \end{aligned} \quad (3.5)$$

where  $\tilde{\beta} = 1/l_{rr} > 0$ . The equivalent form of (3.5) expressed in terms of temperature is (compare (2.6))

$$\begin{aligned} \beta \chi_t &= -(f_{,\chi} - \nabla \cdot f_{,D\chi}), \\ c_\nu \theta_t + \nabla \cdot \left( \bar{k} \nabla \frac{1}{\theta} \right) &= \theta f_{,\theta\chi} \chi_t + \theta f_{,\theta D\chi} \cdot \nabla \chi_t - (f_{,\chi} - \nabla \cdot f_{,D\chi}) \chi_t, \end{aligned} \quad (3.6)$$

where

$$\beta = \tilde{\beta} \theta = \theta / l_{rr} > 0, \quad c_\nu = -\theta f_{,\theta\theta}(\chi, \mathbf{D}\chi, \theta).$$

Replacing the term  $(f_{,\chi} - \nabla \cdot f_{,D\chi})$  in (3.6)<sub>2</sub> by its value given by (3.6)<sub>1</sub> we arrive at the system with the same structure as (2.9), i.e.,

$$\begin{aligned} \beta \chi_t &= -(f_{,\chi} - \nabla \cdot f_{,D\chi}), \\ c_\nu \theta_t + \nabla \cdot \left( \bar{k} \nabla \frac{1}{\theta} \right) &= \theta f_{,\theta\chi} \chi_t + \theta f_{,\theta D\chi} \cdot \nabla \chi_t + \beta \chi_t^2. \end{aligned} \quad (3.7)$$

Following Frémond's theory, let us assume the free energy in the form, see e.g. Bonfanti, Frémond, and Luterotti [18, e.g. (1.3)]

$$f(\chi, \mathbf{D}\chi, \theta) = -c_* \theta \ln \theta - \frac{L}{\theta_c} (\theta - \theta_c) \chi + \psi(\chi) + \frac{\varkappa}{2} |\mathbf{D}\chi|^2, \quad (3.8)$$

where  $\psi(\chi) = \frac{1}{4}(\chi^2 - 1)^2$  is the standard double-well potential, and  $c_*$ ,  $L$ ,  $\theta_c$ ,  $\varkappa$  are positive constants representing the thermal specific heat at constant volume the latent heat,

the critical temperature and the interfacial parameter, respectively. The corresponding expressions for the internal energy and the entropy are

$$\begin{aligned} e &= f - \theta f_{,\theta} = c_*\theta + L\chi + \psi(\chi) + \frac{\varkappa}{2}|\mathbf{D}\chi|^2, \\ \eta &= -f_{,\theta} = c_*(\ln\theta + 1) + \frac{L}{\theta_c}\chi. \end{aligned} \quad (3.9)$$

In addition to (3.8) let us assume that

$$\beta = \text{const} > 0, \quad \bar{k} = k\theta^2 \quad \text{with } k = \text{const} > 0. \quad (3.10)$$

Then system (3.7) becomes

$$\begin{aligned} \beta\chi_t - \varkappa\Delta\chi &= \frac{L}{\theta_c}(\theta - \theta_c) - \psi'(\chi), \\ c_\nu\theta_t - k\Delta\theta + \frac{L}{\theta_c}\theta\chi_t &= \beta\chi_t^2, \end{aligned} \quad (3.11)$$

where

$$\psi'(\chi) = \chi^3 - \chi \quad \text{and} \quad c_\nu = c_* = \text{const} > 0.$$

This system represents a simple version of Frémond's model restricted to the situation of no internal constraints, i.e., a smooth free energy, and a reversible phase transition, i.e., no constraint on the sign of  $\chi_t$ .

**REMARK 10.2.** It is of interest to point out the difference between the Frémond free energy (3.8) and that by Penrose and Fife (see (8.4.1), (8.4.5), (8.4.6)). In the Frémond's free energy the terms characteristic for phase transitions, i.e., the double-well potential  $\psi(\chi)$  and the gradient term  $\frac{\varkappa}{2}|\mathbf{D}\chi|^2$  are of energetic type (independent of temperature), thus contributing only to the internal energy. This is on the contrary to the Penrose-Fife free energy where the last mentioned terms are of entropic type, i.e., they are linear functions of temperature, thus contribute only to the entropy.

**10.3.2. Nonsmooth version of Frémond's model.** In case of the internal constraint  $\chi \in [0, 1]$  the Frémond model postulates the free energy of the form (see e.g., [41, eq. (1.5)])

$$f(\chi, \mathbf{D}\chi, \theta) = -c_*\theta \ln\theta - \frac{L}{\theta_c}(\theta - \theta_c)\chi + I_{[0,1]}(\chi) + \frac{\varkappa}{2}|\mathbf{D}\chi|^2, \quad (3.12)$$

where positive constants  $c_*$ ,  $L$ ,  $\theta_c$ ,  $\varkappa$  stand for the thermal specific heat, the latent heat, the transition temperature, and the interfacial parameter, respectively. The function  $I_{[0,1]}(\chi)$ , accounting for the constraint  $\chi \in [0, 1]$  is the indicator function of the convex set  $[0, 1] \subset \mathbb{R}$ , defined by

$$I_{[0,1]}(\chi) = \begin{cases} 0 & \text{if } \chi \in [0, 1] \\ +\infty & \text{if } \chi \notin [0, 1]. \end{cases} \quad (3.13)$$

Let us note that the indicator function  $I_{[0,1]}(\chi)$  in the nonsmooth free energy (3.12) replaces the double-well potential  $\psi(\chi)$  in the smooth energy (3.8).

Consequently, substituting (formally)  $\psi'(\chi)$  in equation (3.11)<sub>1</sub> by the subgradient of the

indicator function

$$\partial I_{[0,1]}(\chi) = \begin{cases} (-\infty, 0] & \text{if } \chi = 0, \\ 0 & \text{if } 0 < \chi < 1 \\ [0, +\infty) & \text{if } \chi = 1, \end{cases} \quad (3.14)$$

system (3.11) becomes

$$\begin{aligned} \beta\chi_t - \varkappa\Delta\chi + \zeta &= \frac{L}{\theta_c}(\theta - \theta_c), \\ c_\nu\theta_t - k\Delta\theta + \frac{L}{\theta_c}\theta\chi_t &= \beta\chi_t^2, \end{aligned} \quad (3.15)$$

where

$$\zeta \in \partial I_{[0,1]}(\chi).$$

System (3.15) is an example of a nonsmooth Frémond-type model accounting for the internal constraints.

Various nonsmooth Frémond's models relevant for irreversible phase transitions have been analysed mathematically by many authors, e.g., [17], [41], [18], [99], [95] [132].

**10.3.3. Basic principles of Frémond's theory.** For a more detailed comparison we recall briefly the derivation of system (3.11) within Frémond's theory (see [17]).

The underlying hypotheses of Frémond's theory are the principle of virtual power and the postulate that the microscopic movements give rise to macroscopic effects.

From the virtual power principle it follows that the microscopic differential equation of motion (in case of neglected microscopic accelerations) is

$$\nabla \cdot \mathbf{H} - B + A = 0, \quad (3.16)$$

where  $\mathbf{H}$  is a microscopic energy flux vector,  $B$  is an interior microscopic force, and  $A$  represents an external source of microscopic work.

The energy balance equation is modified by terms taking into account the power of the microscopic movements due to the interior forces  $B$  and  $\mathbf{H}$ :

$$e_t + \nabla \cdot \mathbf{q} = B\chi_t + \mathbf{H} \cdot \nabla\chi_t. \quad (3.17)$$

The constitutive laws for  $e$ ,  $\mathbf{q}$ ,  $B$  and  $\mathbf{H}$  are governed by the free energy  $f$  and the pseudo-potential of dissipation  $\Phi$ .

The free energy  $f$  is given by

$$f(\chi, \mathbf{D}\chi, \theta) = -c_*\theta \ln \theta - \frac{L}{\theta_c}(\theta - \theta_c)\chi + \frac{1}{4}(\chi^2 - 1)^2 + \frac{\varkappa}{2}|\mathbf{D}\chi|^2, \quad (3.18)$$

and the pseudo-potential of dissipation  $\Phi$  by

$$\Phi(\theta, \mathbf{D}\theta, \chi, \chi_t) = \frac{\beta}{2}\chi_t^2 + \frac{k}{2\theta}|\mathbf{D}\theta|^2, \quad (3.19)$$

where  $\beta > 0$  is a coefficient related to the evolution of the interface and  $k > 0$  is the heat conductivity coefficient.

The constitutive laws for  $B$ ,  $\mathbf{H}$  and  $\mathbf{q}$  are given by

$$B = f_{,\chi} + \Phi_{,\chi_t}, \quad \mathbf{H} = f_{,\mathbf{D}\chi}, \quad \mathbf{q} = -\theta\Phi_{,\mathbf{D}\theta}. \quad (3.20)$$

The internal energy  $e$  is related to the free energy  $f$  by the Gibbs relation

$$e = f + \theta\eta = f - \theta f_{,\theta}. \quad (3.21)$$

For  $f$  and  $\Phi$  given by (3.18), (3.19) this yields

$$\begin{aligned} B &= -\frac{L}{\theta_c}(\theta - \theta_c) + \chi^3 - \chi + \beta\chi_{,t}, \\ \mathbf{H} &= \varkappa\mathbf{D}\chi, \quad \mathbf{q} = -k\mathbf{D}\theta, \\ e &= c_*\theta + L\chi + \frac{1}{4}(\chi^2 - 1)^2 + \frac{\varkappa}{2}|\mathbf{D}\chi|^2. \end{aligned} \quad (3.22)$$

Equations (3.16) (with  $A = 0$ ), (3.17) together with constitutive laws (3.22) yield system (3.11).

We add that in [18] more general classes of models accounting for microscopic accelerations were considered. In such a case equation (3.16) is replaced by

$$\varrho\chi_{tt} - \nabla \cdot \mathbf{H} + B - A = 0 \quad (3.23)$$

where  $\varrho$  is the mass density.

REMARK 10.3. The Frémond microscopic balance (3.16) with constitutive laws (3.20) yields the equation identical to that resulting from the Fried-Gurtin microforce balance (2.10) with constitutive laws (2.16)<sub>2</sub> and (2.18)<sub>2</sub> with  $\mathbf{k} = \mathbf{0}$  (compare equations (3.11) and (2.21)).

We add also that in view of the equality

$$\frac{\mu}{\theta} = -\frac{1}{l_{rr}}\chi_t, \quad (3.24)$$

which follows from equation (2.5)<sub>1</sub> with  $\tau = 0$ , our dissipation potential (3.3) can be expressed as

$$\mathcal{D} = \frac{1}{2l_{rr}}\chi_{,t}^2 + \frac{\bar{k}}{2\theta^4}|\mathbf{D}\theta|^2. \quad (3.25)$$

Thus for an appropriate choice of the coefficients  $l_{rr}$  and  $\bar{k}$  it becomes identical with Frémond's pseudo-potential of dissipation (3.19).

REMARK 10.4. A recent direction in the study of phase-field models is related to taking into account nonlocal interaction phenomena whose physical relevance was already described in the pioneering papers by van der Waals [144], and Cahn and Hilliard [34]. However, only recently both isothermal and nonisothermal models containing nonlocal terms have been analysed in a systematic way, see, e.g., Krejčí, Rocca and Sprekels [92] and the references there.

**10.4. The Umantsev model.** On a basis of physical and thermodynamical considerations, A. Umantsev and co-authors [141], [139], [143], [140], [142] have worked out a thermodynamic relations for dynamics of phase transition in a nonlocal medium described by a nonconserved order parameter and temperature.

The model is based on the Lqandau-Ginzburg free energy density (we use our notation)

$$f = \hat{f}(\chi, \mathbf{D}\chi, \theta) = f_V(\chi, \theta) + \frac{1}{2}\varkappa|\mathbf{D}\chi|^2, \quad \varkappa = \text{const} > 0, \quad (4.1)$$

with volumetric energy  $f_V$  and gradient term of energetic type (i.e., independent of temperature). The corresponding internal energy and entropy densities are

$$\begin{aligned} e &= f - \theta f_{,\theta} = e_V(\chi, \theta) + \frac{1}{2} \kappa |\mathbf{D}\chi|^2, & e_V &= f_V - \theta f_{V,\theta}, \\ \eta &= -f_{,\theta} = -f_{V,\theta}(\chi, \theta). \end{aligned} \quad (4.2)$$

The resulting system has the following form (see [143, eq. (3.1), 3.2])

$$\begin{aligned} \beta \chi_t &= -(f_{,\chi} - \kappa \Delta \chi), \\ c_\nu \theta_t - \nabla \cdot (k \nabla \theta) + (e_{V,\chi} - \kappa \Delta \chi) \chi_t &= 0, \end{aligned} \quad (4.3)$$

where  $1/\beta > 0$  is the coefficient determining the characteristic time of relaxation,  $k > 0$  is the heat conductivity coefficient, and  $c_\nu = -\theta f_{,\theta\theta}$  is the specific heat.

Since

$$e_{V,\chi} = f_{,\chi} - \theta f_{,\theta\chi},$$

equation (4.3)<sub>2</sub> can be written as

$$c_\nu \theta_t - \nabla \cdot (k \nabla \theta) = \theta f_{,\theta\chi} \chi_t - (f_{,\chi} - \kappa \Delta \chi) \chi_t. \quad (4.4)$$

After replacing the term  $(f_{,\chi} - \kappa \Delta \chi)$  in (4.4) by its value given by (4.3)<sub>1</sub> we arrive at the system

$$\begin{aligned} \beta \chi_t &= -(f_{,\chi} - \kappa \Delta \chi), \\ c_\nu \theta_t - \nabla \cdot (k \nabla \theta) &= \theta f_{,\theta\chi} \chi_t + \beta \chi_t^2. \end{aligned} \quad (4.5)$$

this system has the same structure as (2.9) and (3.7) simplified by the condition  $f_{,\theta D\chi} = \mathbf{0}$  (due to the fact that free energy (4.1) is of energetic type).

We remark that in the above mentioned papers by Umantsev et al. not only the study of dynamics of phase transition kinetics is performed but also numerical analysis including all stages of phase transformations in materials, nucleation, growth and coarsening.



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