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V. A. Cimmelli · F. Oliveri · A. R. Pace

A nonlocal phase-field model of Ginzburg–Landau–Korteweg fluids

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Abstract A thermodynamic model of Korteweg fluids undergoing phase transition and/or phase separation is developed within the framework of weakly nonlocal thermodynamics. Compatibility with second law of thermodynamics is investigated by applying a generalized Liu procedure recently introduced in the literature. Possible forms of the free energy and of the stress tensor, which generalize some earlier ones proposed by several authors in the last decades, are carried out. Owing to the new procedure applied for exploiting the entropy principle, the thermodynamic potentials are allowed to depend on the whole set of variables spanning the state space, including the gradients of the unknown fields, without postulating neither the presence of an energy or entropy extra-flux, nor an additional balance law for microforce.

Keywords Extended Liu procedure · Weakly nonlocal thermodynamics · Continua with scalar internal variable · Phase field · Ginzburg–Landau equation

1 Introduction

Models of phase segregation and phase diffusion have received increasing attention in the last three decades [1–8], due to their growing importance in modern technology. In general, these models involve an order parameter $\varphi \in [0, 1]$, such that if $\varphi = 0$ or $\varphi = 1$, only one phase occurs, while if $\varphi \in (0, 1)$, two coexisting phases are allowed. For this reason, φ is often referred to as *phase field*. The main advantage of this approach is that φ is given by a smooth function with respect to the space and time variables, avoiding so the modeling of jump discontinuities that arise in the sharp interface approach [9]. There are two celebrated evolution equations for φ : the Ginzburg–Landau (GL) equation [10] (also named Allen–Chan equation [11]) and the Cahn–Hilliard (CH) equation [12]. Both are parabolic but of different order. In this paper, we are content to the GL equation, which, in its simplest formulation, may be written as

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$$\dot{\varphi} = \mu\varphi_{,ii} - \beta f'(\varphi), \quad (1)$$

where β and μ are positive constants, $\dot{\varphi}$ denotes the material time derivative of φ , $\varphi_{,i}$ ($i = 1, 2, 3$) denotes the partial derivative of φ with respect to the coordinate x_i (the Einstein convention of sum over repeated indices is used), and a prime denotes the derivative with respect to the argument. Function f is a double-well potential, accounting for the two-phase constitution of the system, and coincides with the local part of the free energy

$$\psi(\varphi) = f(\varphi) + \frac{1}{2}\mu\varphi_{,i}^2. \quad (2)$$

Later on, the constitutive equation (2) has been extended to two-phase Ginzburg–Landau fluids as follows [2–7]:

$$\psi(\rho, \theta, \varphi, \varphi_{,i}) = \psi_0(\rho, \theta, \varphi) + \frac{1}{2}\mu(\rho, \theta, \varphi)\varphi_{,i}^2. \quad (3)$$

Equation (3) leads to the constitutive equation for the Cauchy stress [2,3,6,7]

$$T_{ij} = -p(\rho, \theta, \varphi)\delta_{ij} + 2\mu(\rho, \theta, \varphi)\frac{\partial\psi}{\partial\varphi_{,i}}\frac{\partial\psi}{\partial\varphi_{,j}}, \quad (4)$$

where $p = \rho^2 \frac{\partial\psi}{\partial\rho}$ is the pressure, and μ a material function that generalizes the constant in Eq. (1).

It is worth observing that both the equations above contain the gradient of the phase field only, but not the gradient of mass density and temperature, and this is the consequence of a certain privileged physical assumption and/or mathematical procedure, which regards only the phase field and not the other variables too.

Ginzburg–Landau equation (1) was so named by Gurtin [1], because of its capability to model the ordering of the atoms within unit cells on a lattice in superconductivity [10]. Moreover, Gurtin first embodied Eq. (1) within the general framework of continuum thermodynamics [1]. His derivation relies on the belief that the fundamental physical laws, which involve energy, should account for the expenditure of power associated with the microscopic kinematical process. Therefore, the balance of the microforce driving the ordering of the atoms is postulated, [1,2,8]. The constitutive equations are weakly nonlocal in space and time, since they are allowed to depend on φ , $\text{grad } \varphi$, and $\dot{\varphi}$. Systematic derivations of Eq. (1) from a different point of view have been obtained by Fabrizio, Giorgi and Morro [3], and by Morro [6,7]. These authors regard the phase field as a scalar internal variable, ruled by an evolution equation that is determined by second law of thermodynamics. The constitutive equations are weakly nonlocal in space, while a generalized local form of the entropy inequality, allowing for an entropy extra-flux, is postulated. We consider the above derivations illuminating. However, both rely on new physical postulates, the first one being based on the existence of a microforce, which drives the ordering of the atoms, and the second one based on the existence of an entropy extra-flux, first introduced by Müller in exploiting the entropy principle in continuum physics [13], which influences the evolution of φ . From the point of view of the basic physical laws, one theory excludes the other one, so that their capability of obtaining the GL equation does not constitute, “per se,” a proof of the existence of the microforce or of the entropy extra-flux. GL equation may also be obtained by a more general evolution relation for thermoelastic materials with additional scalar-valued degrees of freedom [14].

In recent papers [15–20], we approached the problem of the thermodynamic compatibility of gradient continuum theories from a purely mathematical point of view. We proved that if all the equations ruling the evolution of the independent thermodynamic variables are substituted into the entropy inequality, no additional physical hypothesis is necessary, and the thermodynamic compatibility may be achieved whatever the form of the entropy inequality is. Within this framework, we have studied in-depth the thermodynamics of Korteweg fluids with scalar [17,18] and vectorial [20] internal variable.

This method has meaningful similarities with that applied in [21–24] for deriving the classical Ginzburg–Landau equation and its generalizations. In fact, also in this case, the phase field is regarded as an internal variable and the entropy inequality is exploited through a generalization of the classical Liu procedure. However, the following important differences are worth mentioning:

- only the first-order gradient of the evolution equation for the internal variable is considered as additional constraint for the entropy inequality, although the state space contains the gradient of the internal variable up to the order three [21];
- the Ginzburg–Landau equation is obtained by applying the force–current decomposition [25] of the reduced entropy inequality [21];

- in [23] the Nyíri form of the entropy current [26] is postulated, while in [21,22] the Nyíri form is assumed for a part of the entropy current, in order to obtain further generalizations beyond the classical form of Ginzburg–Landau equation.

Our aim here is to apply the mathematical procedure illustrated above in order to derive explicit constitutive equations for the free energy, the stress, and the heat flux, in the presence of the coexisting phases of Korteweg-type fluids, in which the capillary forces manifest themselves at a macroscopic level, for instance by determining the form of the interface between the phases [27]. Thus, the model can be validated by classical experiments, such as the static and dynamic methods to measure the surface tension (see [27], Ch. 1, for a detailed description).

The role of capillary forces in the equilibrium between phases has been well understood since 1805 by Young [28], who was interested in determining the nature of the surface between different liquids (see also [29] for an extensive survey on the development of capillarity theory). Later on, in 1893, van der Waals [30] studied the interface between a liquid and its vapor, and represented it by a thin intermediate region in which the properties of the material deviate appreciably from those of the materials on either side [29,30]. However, the idea that capillarity effects in fluids can be modeled through the presence of density gradients in the stress tensor is due to the Dutch physicist Korteweg, who in 1901 proposed the following constitutive equation for the elastic part of the Cauchy stress

$$T_{ij} = (-p + \alpha \rho_{,kk} + \beta \rho_{,k}^2) \delta_{ij} + \gamma \rho_{,i} \rho_{,j} + \delta \rho_{,ij}, \quad (5)$$

where p is the pressure of the fluid, while α , β , γ , and δ are suitable material functions of ρ and the temperature θ , [31].

In modern terminology, Eq. (5) represents a special example of constitutive equation of differential material of grade 3, since the constitutive equations are permitted to depend on the derivatives of the local displacement of order less than or equal to 3 [32–34]. The thermodynamics of Korteweg fluids of grade 3 has been studied extensively in [19]. Second-grade Korteweg fluids, instead, are characterized by constitutive equations depending on the derivatives of the local displacement of order less than or equal to 2 [16–18]. Heida and Málek [35] studied these materials from a different perspective with respect to [16–18], which will be specified below. Models for phase transitions of Korteweg fluids of grade 2 have been developed by Heida et al. [29], and by Lowengrub and Truskinowski [36].

The latter authors proposed a new procedure for modeling the interface in a binary mixture, supposed to be not very sharp and of comparable size to its radius of curvature. The constitutive equations depend nonlocally on a scalar variable related to the concentration of the constituents. As a result, they essentially derive an equation that couples the Euler (or Navier–Stokes) equation with the Cahn–Hilliard equation. In building up their model, Lowengrub and Truskinowski take into account also computational and mathematical issues concerning the properties that the resulting system of governing equations should have.

A different analysis is made by Heida et al. [29], who developed their model in the framework of a more general procedure for deriving the restrictions imposed by second law of thermodynamics on the constitutive equations. To this end, they appeal to the requirement that among all admissible constitutive relations, the appropriate ones maximize the rate of entropy production [37]. The procedure requires to prescribe the constitutive equations for only two scalars: the entropy and the entropy production. Then, the thermodynamic restrictions are obtained by regarding the rate of entropy production as a bilinear product of thermodynamic forces and conjugated thermodynamic fluxes [25]. The same method has been applied in [35] to study the thermodynamics of second-grade Korteweg fluids in the absence of phase transition.

The approach that we present here, on one side, follows the same philosophy of the one by Heida et al. [29], since we try to develop our model within a very general framework, which can be applied to any class of materials, without any hypothesis “ad hoc.” On the other side, it differs from that of these authors, because it is based on a mathematical procedure only and does not require any specific physical assumption. On the contrary, to apply their method, Heida, Málek and Rajagopal need to assume a suitable constitutive equation for the rate of entropy production and also to postulate that the appropriate constitutive equations maximize such a rate. As the same authors say, “this assumption is not a principle or a law with a status such as the balance of energy or the second law of thermodynamics. However, it seems to lead to sensible models within the context of a diverse class of material response such as viscoelasticity, classical plasticity, twinning, phase transformations, and chemically reacting mixtures.” Although we share this point of view, we prefer to build up our model on the basis of universal physical principles only, such as second law of thermodynamics. On the other hand, we also agree with Heida, Málek and Rajagopal when they claim that “if the current mathematics is incapable of

129 dealing with the model, then one would perforce have to invent the mathematics necessary to deal with the
 130 problem on hand.” According to this philosophy, in the present paper, we apply the method of exploitation of
 131 the entropy inequality developed in [15, 18], together with the theory of second-grade Korteweg fluids with
 132 a scalar internal variable [20], in order to generalize the constitutive equations (3) and (4) modeling phase
 133 transitions of Korteweg fluids with first-order gradients in the state space. Thus, after deriving the GL equation,
 134 we investigate the thermodynamic restrictions ensuring its compatibility with second law of thermodynamics.
 135 From them, we infer suitable constitutive equations for entropy, free energy, Cauchy stress, and heat flux, which
 136 are compatible with GL equation. Finally, we consider some earlier GL models, developed within different
 137 frameworks, and prove that all of them may be recovered as particular cases of the present one. In our opinion,
 138 this is enough to prove the generality of the present approach, which does not require any special physical
 139 assumption but is based only on a new mathematical procedure.

140 2 Two-phase Ginzburg–Landau–Korteweg fluid

141 Let us consider the material class with state space

$$142 \quad Z = \{\rho, \rho_{,k}, \epsilon, \epsilon_{,k}, \varphi, \varphi_{,k}\}, \quad (6)$$

143 with ρ as the mass density, ϵ as the internal energy per unit mass, and φ as the internal variable. We suppose
 144 that the evolution of these systems is governed by the following local balances of mass, linear momentum,
 145 energy, and internal variable [2, 6, 20]

$$146 \quad \rho_{,t} + \rho_{,j}v_j + \rho v_{j,j} = 0, \quad (7)$$

$$147 \quad \rho v_{i,t} + \rho v_{i,j}v_j - T_{ij,j} = 0, \quad (8)$$

$$148 \quad \rho \epsilon_{,t} + \rho \epsilon_{,j}v_j - T_{ij}v_{i,j} + q_{j,j} = 0, \quad (9)$$

$$149 \quad \rho \varphi_{,t} + \rho \varphi_{,j}v_j + \Phi_{j,j} = r, \quad (10)$$

150 where v_i , T_{ij} , q_j , and Φ_j are the components of velocity, Cauchy stress, heat flux, and flux of internal variable,
 151 respectively. Moreover, r means the production of internal variable, while the symbol $f_{,t}$ denotes the partial
 152 derivative of f with respect to time. For the sake of simplicity, we have assumed that body forces and heat
 153 sources vanish.

154 Second law of thermodynamics, which determines the direction of the real-world thermodynamic processes,
 155 locally reads [39–42]

$$156 \quad \rho s_{,t} + \rho s_{,j}v_j + \left(\frac{q_j}{\theta}\right)_{,j} \geq 0, \quad (11)$$

157 where s is the entropy per unit mass and θ the temperature. It is worth observing that we assumed the entropy
 158 flux in the classical form (\mathbf{q}/θ) [39, 42]. Our model will be developed in the framework of weakly nonlocal
 159 irreversible thermodynamics [40–42], so that a particular material will be characterized by suitable constitutive
 160 equations for \mathbf{T} , \mathbf{q} , Φ , r , and s , which are allowed to depend on the gradients of the unknown fields too.

161 We notice that an order parameter is not necessarily extensive, so that, in several cases, the balance law for
 162 the order parameter should be substituted by the evolution equation

$$163 \quad \rho \varphi_{,t} + \rho \varphi_{,j}v_j = f(Z), \quad (12)$$

164 with f a regular function defined on the state space. Nonetheless, often the balance form is necessary as, for
 165 instance, when the phase transition is described by letting the body occur in N phases but regarding these
 166 phases as a single body to which additional scalar variables, the phase fields $\varphi^1 \dots \varphi^N$, are ascribed [4–7].
 167 In such a case, the fields $\varphi^1 \dots \varphi^N$ are identified with the concentrations $c^1 = \rho_1/\rho, \dots, c^N = \rho_N/\rho$, of the
 168 different phases, each of which is governed by the balance equation

$$169 \quad \rho c_{,t}^\alpha + \rho c_{,j}^\alpha v_j + J_{j,j}^\alpha = r^\alpha, \quad \alpha = 1 \dots N, \quad (13)$$

170 where J_j^α are the components of the diffusion flux of the α -th phase, and r^α is the mass supply of the α -th
 171 phase due to the phase transition.

172 On the other hand, once constitutive equations have been assigned for the flux and for the production of
 173 internal variable, Eq. (10) takes the form (12) whenever the flux is divergence-free or vanishes. Thus, the
 174 balance form encompasses the evolutionary one.

We investigate the compatibility of the approach above with second law of thermodynamics by applying the generalized Liu procedure [43], developed in a series of papers by Cimmelli et al. [15, 16, 18]. It consists in subtracting to Eq. (11) a linear combination of Eq. (7) and Eqs. (9)–(10), and of their gradient extensions, governing the evolution of $\text{grad } \rho$, $\text{grad } \epsilon$, and $\text{grad } \varphi$, respectively. The coefficients entering this linear combination for including the constraints imposed by the balance equations of mass, internal energy, and internal variable are $\lambda^{(m)}$, $\lambda^{(e)}$, and $\lambda^{(iv)}$, respectively. Beside them, we introduce in the entropy inequality the coefficients $\Lambda_i^{(m)}$, $\Lambda_i^{(e)}$, and $\Lambda_i^{(iv)}$, which account for the constraints imposed by the first-order gradients of the balance equations of mass, internal energy, and internal variable, respectively. All of them play the role of Lagrange multipliers [43].

In this way, some lengthy calculations yield the following thermodynamic restrictions as necessary and sufficient conditions to fulfill the entropy inequality (11) along arbitrary thermodynamic processes

$$\lambda^{(m)} = \rho \frac{\partial s}{\partial \rho}, \quad (14)$$

$$\Lambda_i^{(m)} = \rho \frac{\partial s}{\partial \rho_{,i}}, \quad (15)$$

$$\lambda^{(e)} = \frac{\partial s}{\partial \epsilon} - \frac{\rho_{,j}}{\rho} \Lambda_j^{(e)}, \quad (16)$$

$$\Lambda_i^{(e)} = \frac{\partial s}{\partial \epsilon_{,i}}, \quad (17)$$

$$\lambda^{(iv)} = \frac{\partial s}{\partial \varphi} - \frac{\rho_{,j}}{\rho} \Lambda_j^{(iv)}, \quad (18)$$

$$\Lambda_i^{(iv)} = \frac{\partial s}{\partial \varphi_{,i}}, \quad (19)$$

$$\left\langle \Lambda_j^{(e)} \frac{\partial q_k}{\partial \rho_{,m}} + \Lambda_j^{(iv)} \frac{\partial \Phi_k}{\partial \rho_{,m}} \right\rangle = 0, \quad (20)$$

$$\left\langle \Lambda_j^{(e)} \frac{\partial q_k}{\partial \epsilon_{,m}} + \Lambda_j^{(iv)} \frac{\partial \Phi_k}{\partial \epsilon_{,m}} \right\rangle = 0, \quad (21)$$

$$\left\langle \Lambda_j^{(e)} \frac{\partial q_k}{\partial \varphi_{,m}} + \Lambda_j^{(iv)} \frac{\partial \Phi_k}{\partial \varphi_{,m}} \right\rangle = 0, \quad (22)$$

$$h(\rho, \rho_{,i}, \rho_{,ik}, \epsilon, \epsilon_{,i}, \epsilon_{,ik}, \varphi, \varphi_{,i}, \varphi_{,ik}) \geq 0. \quad (23)$$

In the equations above, the symbol $\langle F_{abc\dots} \rangle$ denotes the symmetric part of the tensor function F with respect to all its indices.

The reduced entropy inequality (23), which is too long to be reported here in detail, takes a nonclassical form, since it depends not only on the elements of the state space but on the higher derivatives $\rho_{,ij}$, $\epsilon_{,ij}$, and $\varphi_{,ij}$ too. It can be easily verified that (23) involves the higher derivatives through both quadratic and linear terms. By denoting with X_α the generic element of the set of the independent higher derivatives, a direct inspection shows that it may be rewritten in the form

$$A_{\alpha\beta} X_\alpha X_\beta + B_\alpha X_\alpha + C \geq 0, \quad (24)$$

where the functions $A_{\alpha\beta}$, B_α , and C depend only on the state functions. Note that the mathematical structure of the left-hand side of Eq. (24) implies that the matrix $A_{\alpha\beta}$ is symmetric. The first term in the left-hand side of (24) can be nonnegative for arbitrary values of the X_α if and only if the matrix with entries $A_{\alpha\beta}$ is positive semidefinite. The linear term in X_α , instead, must vanish, since the coefficients B_α are independent of the X_α , otherwise the quantity $B_\alpha X_\alpha$ could take arbitrary negative values, thus violating the inequality (24). Thus, by the arbitrariness of X_α , it follows the additional restriction $B_\alpha = 0$, which yields the following further

210 relationships between the constitutive quantities \mathbf{T} , \mathbf{q} , Φ , r , and s .

$$\begin{aligned}
211 \quad & \left\langle \frac{\partial^2 s}{\partial \rho, k \partial \epsilon} q_i + \frac{\partial s}{\partial \epsilon} \frac{\partial q_i}{\partial \rho, k} - \lambda^{(e)} \frac{\partial q_i}{\partial \rho, k} - \lambda^{(iv)} \frac{\partial \Phi_i}{\partial \rho, k} + \Lambda_i^{(e)} \frac{\partial T_{lj}}{\partial \rho, k} v_{l,j} \right. \\
212 \quad & \left. - \Lambda_i^{(e)} \left(\frac{\partial q_k}{\partial \rho} + \frac{\partial^2 q_j}{\partial \rho, k \partial \rho} \rho, j + \frac{\partial^2 q_j}{\partial \rho, k \partial \epsilon} \epsilon, j + \frac{\partial^2 q_j}{\partial \rho, k \partial \varphi} \varphi, j \right) \right. \\
213 \quad & \left. - \Lambda_j^{(e)} \left(\frac{\partial^2 q_i}{\partial \rho \partial \rho, k} \rho, j + \frac{\partial^2 q_i}{\partial \epsilon \partial \rho, k} \epsilon, j + \frac{\partial^2 q_i}{\partial \varphi \partial \rho, k} \varphi, j \right) \right. \\
214 \quad & \left. - \Lambda_i^{(iv)} \left(\frac{\partial \Phi_k}{\partial \rho} + \frac{\partial^2 \Phi_j}{\partial \rho, k \partial \rho} \rho, j + \frac{\partial^2 \Phi_j}{\partial \rho, k \partial \epsilon} \epsilon, j + \frac{\partial^2 \Phi_j}{\partial \rho, k \partial \varphi} \varphi, j - \frac{\partial r}{\partial \rho, k} \right) \right. \\
215 \quad & \left. - \Lambda_j^{(iv)} \left(\frac{\partial^2 \Phi_i}{\partial \rho \partial \rho, k} \rho, j + \frac{\partial^2 \Phi_i}{\partial \epsilon \partial \rho, k} \epsilon, j + \frac{\partial^2 \Phi_i}{\partial \varphi \partial \rho, k} \varphi, j \right) \right\rangle = 0, \tag{25}
\end{aligned}$$

$$\begin{aligned}
216 \quad & \left\langle \frac{\partial^2 s}{\partial \epsilon, k \partial \epsilon} q_i + \frac{\partial s}{\partial \epsilon} \frac{\partial q_i}{\partial \epsilon, k} - \lambda^{(e)} \frac{\partial q_i}{\partial \epsilon, k} - \lambda^{(iv)} \frac{\partial \Phi_i}{\partial \epsilon, k} - \rho (\Lambda_i^{(e)} v_k - \Lambda_k^{(e)} v_i) + \Lambda_i^{(e)} \frac{\partial T_{lj}}{\partial \epsilon, k} v_{l,j} \right. \\
217 \quad & \left. - \Lambda_i^{(e)} \left(\frac{\partial q_k}{\partial \epsilon} + \frac{\partial^2 q_j}{\partial \epsilon, k \partial \rho} \rho, j + \frac{\partial^2 q_j}{\partial \epsilon, k \partial \epsilon} \epsilon, j + \frac{\partial^2 q_j}{\partial \epsilon, k \partial \varphi} \varphi, j \right) \right. \\
218 \quad & \left. + \Lambda_j^{(e)} \left(\frac{\partial^2 q_i}{\partial \rho \partial \epsilon, k} \rho, j + \frac{\partial^2 q_i}{\partial \epsilon \partial \epsilon, k} \epsilon, j + \frac{\partial^2 q_i}{\partial \varphi \partial \epsilon, k} \varphi, j \right) \right. \\
219 \quad & \left. - \Lambda_i^{(iv)} \left(\frac{\partial \Phi_k}{\partial \epsilon} + \frac{\partial^2 \Phi_j}{\partial \epsilon, k \partial \rho} \rho, j + \frac{\partial^2 \Phi_j}{\partial \epsilon, k \partial \epsilon} \epsilon, j + \frac{\partial^2 \Phi_j}{\partial \epsilon, k \partial \varphi} \varphi, j - \frac{\partial r}{\partial \epsilon, k} \right) \right. \\
220 \quad & \left. - \Lambda_j^{(iv)} \left(\frac{\partial^2 \Phi_i}{\partial \rho \partial \epsilon, k} \rho, j + \frac{\partial^2 \Phi_i}{\partial \epsilon \partial \epsilon, k} \epsilon, j + \frac{\partial^2 \Phi_i}{\partial \varphi \partial \epsilon, k} \varphi, j \right) \right\rangle = 0, \tag{26}
\end{aligned}$$

$$\begin{aligned}
221 \quad & \left\langle \frac{\partial^2 s}{\partial \varphi, k \partial \epsilon} q_i + \frac{\partial s}{\partial \epsilon} \frac{\partial q_i}{\partial \varphi, k} - \lambda^{(e)} \frac{\partial q_i}{\partial \varphi, k} - \lambda^{(iv)} \frac{\partial \Phi_i}{\partial \varphi, k} - \rho (\Lambda_i^{(iv)} v_k - \Lambda_k^{(iv)} v_i) \right. \\
222 \quad & \left. - \Lambda_i^{(e)} \left(\frac{\partial q_k}{\partial \varphi} + \frac{\partial^2 q_j}{\partial \varphi, k \partial \rho} \rho, j + \frac{\partial^2 q_j}{\partial \varphi, k \partial \epsilon} \epsilon, j + \frac{\partial^2 q_j}{\partial \varphi, k \partial \varphi} \varphi, j \right) \right. \\
223 \quad & \left. + \Lambda_i^{(e)} \frac{\partial T_{lj}}{\partial \varphi, k} v_{l,j} + \Lambda_j^{(e)} \left(\frac{\partial^2 q_i}{\partial \rho \partial \varphi, k} \rho, j + \frac{\partial^2 q_i}{\partial \epsilon \partial \varphi, k} \epsilon, j + \frac{\partial^2 q_i}{\partial \varphi \partial \varphi, k} \varphi, j - \frac{\partial r}{\partial \varphi, k} \right) \right. \\
224 \quad & \left. - \Lambda_i^{(iv)} \left(\frac{\partial \Phi_k}{\partial \varphi} + \frac{\partial^2 \Phi_j}{\partial \varphi, k \partial \rho} \rho, j + \frac{\partial^2 \Phi_j}{\partial \varphi, k \partial \epsilon} \epsilon, j + \frac{\partial^2 \Phi_j}{\partial \varphi, k \partial \varphi} \varphi, j \right) \right\rangle = 0. \tag{27}
\end{aligned}$$

225 Finally, recalling that the higher derivatives do not depend on the state space, while C is defined on the
 226 state space, we conclude that the residual inequality $C \geq 0$ holds.

227 3 Ginzburg–Landau–Korteweg free energy

228 In order to derive meaningful consequences of the thermodynamic restrictions above, let us observe that Eq.
 229 (1) may be easily obtained by choosing

$$230 \quad \Phi_i = -\rho \mu \varphi, i, \quad r = -\mu \rho, i \varphi, i - \rho \beta f'(\varphi). \tag{28}$$

231 More difficult is to prove the thermodynamic compatibility of the constitutive equations (2) and (28), since
 232 the entropy principle, in its classical formulation, denies the dependence of the thermodynamic potentials on the
 233 gradients of the basic fields [39, 42]. To achieve that task, we first substitute Eqs. (28) into the thermodynamic
 234 restrictions (20)–(22), getting so

$$\left\langle \frac{\partial s}{\partial \epsilon_{,j}} \frac{\partial q_k}{\partial \rho_{,n}} \right\rangle = 0, \quad (29)$$

$$\left\langle \frac{\partial s}{\partial \epsilon_{,j}} \frac{\partial q_k}{\partial \epsilon_{,n}} \right\rangle = 0, \quad (30)$$

$$\left\langle \frac{\partial s}{\partial \epsilon_{,j}} \frac{\partial q_k}{\partial \varphi_{,n}} - \frac{\partial s}{\partial \varphi_{,j}} \rho \mu \delta_{kn} \right\rangle = 0. \quad (31)$$

Then, since Eqs. (29)–(31) do not prevent the specific entropy to depend on the gradient of ρ , ϵ , and φ , we are allowed to postulate a constitutive equation for it which is simple, includes the gradients of the aforementioned quantities, is in accordance with the theory of representation of isotropic scalar functions depending on scalars and vectors [44], and fulfills the principle of maximum entropy at the equilibrium [45]. The most general second-order polynomial isotropic scalar function having the aforementioned properties is

$$s = s_0 + \tilde{s}_1 \rho_{,i}^2 + 2\tilde{s}_2 \rho_{,i} \epsilon_{,i} + 2\tilde{s}_3 \rho_{,i} \varphi_{,i} + \tilde{s}_4 \epsilon_{,i}^2 + 2\tilde{s}_5 \epsilon_{,i} \varphi_{,i} + \tilde{s}_6 \varphi_{,i}^2, \quad (32)$$

where s_0 and \tilde{s}_i ($i = 1, \dots, 6$) depend on ρ , ϵ , and φ . Nevertheless, in view of the subsequent analysis, and in order to produce a case where conditions (20)–(22) can be easily integrated, we choose the coefficients \tilde{s}_i ($i = 1, \dots, 6$) as follows:

$$\tilde{s}_1 = s_1, \quad \tilde{s}_2 = \kappa s_2, \quad \tilde{s}_3 = s_2, \quad \tilde{s}_4 = \kappa^2 s_3, \quad \tilde{s}_5 = \kappa s_3, \quad \tilde{s}_6 = s_3, \quad (33)$$

where s_1, s_2, s_3 , and κ depend on ρ, ϵ , and φ .

Remark 1 The entropy, as a state function of a thermodynamic system, is well defined only for quasi-static thermodynamic processes, in which the system undergoes very slow transformations and passes through equilibrium states only. The local equilibrium principle, which states that outside the equilibrium the thermodynamic systems may be described, locally in space and time, by the same state functions of the equilibrium, allows to extend the definition of entropy to nonequilibrium situations, as a chart of local mappings [46–48]. Then, the constitutive equation (32) should be understood as an extension of the constitutive equation, which holds at the equilibrium, to nonequilibrium situations [46–48]. For thermodynamic processes passing through equilibrium states only, in which all the unknown fields are constant in space and time, the right-hand side of Eq. (32) reduces to s_0 . Thus, we call s_0 the *equilibrium entropy*. It is worth observing that in our approach, φ is regarded as an internal variable, so that at the equilibrium it reduces to a function of the standard thermodynamic variables [49], namely $\varphi_{eq} = F(\rho, \epsilon)$. As a consequence, $\nabla \varphi_{eq} = \frac{\partial F}{\partial \rho} \cdot \nabla \rho|_{eq} + \frac{\partial F}{\partial \epsilon} \cdot \nabla \epsilon|_{eq} = \mathbf{0}$, since both the gradients of ρ and ϵ vanish at the equilibrium. A fortiori the previous conclusion is true if φ is interpreted as an additional degree of freedom, since these quantities are zero at the equilibrium [49].

For the sake of completeness, let us consider the case in which the phase field is not ruled by Eq. (10), but represents an order parameter ϱ for a system in which the following microforce balance equation

$$\xi_{i,i} + \pi + \gamma = 0, \quad (34)$$

holds [1]. In Eq. (34), ξ_i are the components of the microstress, and the scalar body forces π and γ represent internal and external forces distributed over the volume of the body, respectively. As observed in [1], γ has a dynamical nature, so that at the equilibrium the previous equation reduces to $\xi_{i,i} + \pi = 0$, with given constitutive representations for the microstress $\boldsymbol{\xi}$ and for the internal microforce π in terms of ϱ and $\nabla \varrho$. In such a case, at the equilibrium, the gradient of ϱ cannot vanish, otherwise the internal microforce would result not balanced. However, if π_{eq} is constant in space, then $\nabla \varrho|_{eq}$ is constant as well, and Eq. (32) gives as the equilibrium entropy the family of functions $s_{eq} = s_0 + c_0$, where c_0 is a constant.

The principle of maximum entropy at the equilibrium requires that the entropy of a thermodynamic system gets its maximum in correspondence with an equilibrium state. As a consequence, in nonequilibrium situations, we must have

$$\int_c \rho s dc \leq \int_c \rho s_0 dc, \quad (35)$$

for an arbitrary material particle c . Such a constraint is satisfied if the nonlocal part of the right-hand side of Eq. (32) results to be a negative semidefinite quadratic form. This is true if the relations

$$s_1 < 0, \quad s_3 < \frac{s_2^2}{s_1}, \quad (36)$$

hold true. By substituting Eq. (32) in Eqs. (14)–(19), we get the Lagrange multiplier $\lambda^{(m)}$ by simple derivation of s with respect to ρ , and the further Lagrange multipliers

$$\Lambda_i^{(m)} = \rho(2s_1\rho_{,i} + 2\kappa s_2\epsilon_{,i} + 2s_2\varphi_{,i}), \quad (37)$$

$$\lambda^{(e)} = \frac{\partial s}{\partial \epsilon} - \frac{1}{\rho}(2\kappa s_2\rho_{,j}^2 + 2\kappa^2 s_3\epsilon_{,j}\rho_{,j} + 2\kappa s_3\rho_{,j}\varphi_{,j}), \quad (38)$$

$$\Lambda_i^{(e)} = 2\kappa s_2\rho_{,i} + 2\kappa^2 s_3\epsilon_{,i} + 2\kappa s_3\varphi_{,i}, \quad (39)$$

$$\lambda^{(iv)} = \frac{\partial s}{\partial \varphi} - \frac{1}{\rho}(2s_2\rho_{,j}^2 + 2\kappa s_3\epsilon_{,j}\rho_{,j} + 2s_3\rho_{,j}\varphi_{,j}), \quad (40)$$

$$\Lambda_i^{(iv)} = 2s_2\rho_{,i} + 2\kappa s_3\epsilon_{,i} + 2s_3\varphi_{,i}. \quad (41)$$

Moreover, a possible constitutive equation for the heat flux allowing to satisfy the restrictions (29)–(31) is

$$q_i = q_{0i} + \frac{\rho\mu}{\kappa}\varphi_{,i}, \quad (42)$$

where the functions q_{0i} depend on ρ , ϵ , and φ . Equation (42) means that the heat flow through the fluid is driven by the inhomogeneity of the phase field. It is worth observing that it does not represent the most general situation but only a particular solution of Eqs. (29)–(31). More general situations, in which the heat flux depends on the gradient of ρ and ϵ too, are possible. On the other hand, a constitutive equation for the Cauchy stress depending on ρ , ϵ , φ , and their gradients must be in accordance with the theory of representation of isotropic tensor functions depending on scalars and vectors [44], and must encompass the Korteweg constitutive equation modeling the Cauchy stress of fluids moving in capillary channels, which, in the case of first-order nonlocality, reads [33]

$$T_{ij} = (-p + \alpha\rho_{,k}^2)\delta_{ij} + \delta\rho_{,i}\rho_{,j}, \quad (43)$$

where the pressure p and the material functions α and δ depend on ρ and θ . Then, we generalize Eq. (43) as follows

$$T_{ij} = (\tau_0 + \tau_1\rho_{,k}^2 + \tau_2\epsilon_{,k}^2 + \tau_3\varphi_{,k}^2)\delta_{ij} + \tau_4\rho_{,i}\rho_{,j} + \tau_5\epsilon_{,i}\epsilon_{,j} + \tau_6\varphi_{,i}\varphi_{,j} + 2\tau_7\langle\rho_{,i}\epsilon_{,j}\rangle + 2\tau_8\langle\rho_{,i}\varphi_{,j}\rangle + 2\tau_9\langle\epsilon_{,i}\varphi_{,j}\rangle, \quad (44)$$

wherein the functions τ_i ($i = 0, 1, \dots, 9$) depend on ρ , ϵ , and φ .

That way, the thermodynamic model depends on the 18 material parameters s_i , $i = 0, \dots, 3$, κ , τ_i , $i = 0, \dots, 9$, and q_{0i} , which can be determined in order to satisfy the 18 thermodynamic restrictions (25)–(27).

The considerations above lead to the conclusion that the constitutive equations (28), (32), (42), and (44), which characterize the Ginzburg–Landau–Korteweg fluid under consideration, are fully compatible with second law of thermodynamics.

From now on, we will limit ourselves to consider situations close to the equilibrium, in which the absolute temperature θ is well defined by the “coldness” $\frac{1}{\theta} = \frac{\partial s_0}{\partial \epsilon}$. Under the hypothesis of invertibility of that function, ϵ can be expressed as function of ρ , θ and φ , and s as function of ρ , θ , φ , and their gradients, namely

$$s = \hat{s}_0 + \hat{s}_1\rho_{,i}^2 + 2\hat{s}_2\rho_{,i}\theta_{,i} + \hat{s}^3\theta_{,i}^2 + 2\hat{s}_4\rho_{,i}\varphi_{,i} + 2\hat{s}_5\theta_{,i}\varphi_{,i} + \hat{s}_6\varphi_{,i}^2, \quad (45)$$

311 where the functions \hat{s}_i ($i = 0, \dots, 6$) depend now on ρ , θ , and φ , and are given by

$$\begin{aligned}
\hat{s}_0 &= s_0(\rho, \epsilon(\rho, \theta, \varphi), \varphi), \\
\hat{s}_1 &= s_1 + 2\kappa s_2 \frac{\partial \epsilon}{\partial \rho} + \kappa^2 s_3 \left(\frac{\partial \epsilon}{\partial \rho} \right)^2, \\
\hat{s}_2 &= 2\kappa s_2 \frac{\partial \epsilon}{\partial \theta} + 2\kappa^2 s_3 \frac{\partial \epsilon}{\partial \theta} \frac{\partial \epsilon}{\partial \rho}, \\
\hat{s}_3 &= \kappa^2 s_3 \left(\frac{\partial \epsilon}{\partial \theta} \right)^2, \\
\hat{s}_4 &= 2\kappa s_2 \frac{\partial \epsilon}{\partial \varphi} + 2\kappa^2 s_3 \frac{\partial \epsilon}{\partial \rho} \frac{\partial \epsilon}{\partial \varphi} + 2s_2 + 2\kappa s_3 \frac{\partial \epsilon}{\partial \rho}, \\
\hat{s}_5 &= 2\kappa^2 s_3 \frac{\partial \epsilon}{\partial \theta} \frac{\partial \epsilon}{\partial \varphi} + 2\kappa s_3 \frac{\partial \epsilon}{\partial \theta}, \\
\hat{s}_6 &= \kappa^2 s_3 \left(\frac{\partial \epsilon}{\partial \varphi} \right)^2 + 2\kappa s_3 \frac{\partial \epsilon}{\partial \varphi}.
\end{aligned} \tag{46}$$

313 Moreover, the constitutive equation (44) can be written as

$$\begin{aligned}
T_{ij} &= (\hat{\tau}_0 + \hat{\tau}_1 \rho_{,k}^2 + \hat{\tau}_2 \theta_{,k}^2 + \hat{\tau}_3 \varphi_{,k}^2) \delta_{ij} + \hat{\tau}_4 \rho_{,i} \rho_{,j} + \hat{\tau}_5 \theta_{,i} \theta_{,j} + \hat{\tau}_6 \varphi_{,i} \varphi_{,j} \\
&\quad + 2\hat{\tau}_7 \langle \rho_{,i} \theta_{,j} \rangle + 2\hat{\tau}_8 \langle \rho_{,i} \varphi_{,j} \rangle + 2\hat{\tau}_9 \langle \theta_{,i} \varphi_{,j} \rangle,
\end{aligned} \tag{47}$$

316 wherein the functions $\hat{\tau}_i$ ($i = 0, 1, \dots, 9$) depend on ρ , θ , and φ .

317 Then, let us define the Helmholtz free energy ψ by the Legendre transformation

$$\begin{aligned}
\psi &= \epsilon - \theta s \\
&= \psi_0 - \theta (\hat{s}_1 \rho_{,i}^2 + 2\hat{s}_2 \rho_{,i} \theta_{,i} + \hat{s}_3 \theta_{,i}^2 + 2\hat{s}_4 \rho_{,i} \varphi_{,i} + 2\hat{s}_5 \theta_{,i} \varphi_{,i} + \hat{s}_6 \varphi_{,i}^2),
\end{aligned} \tag{48}$$

320 where

$$\psi_0(\rho, \theta, \varphi) = \epsilon(\rho, \theta, \varphi) - \theta \hat{s}_0(\rho, \theta, \varphi). \tag{49}$$

322 By taking into account Eq. (48), if the constraints

$$\begin{aligned}
\hat{\tau}_4 &= 4\theta^2 \tau \hat{s}_4^2, & \hat{\tau}_5 &= 4\theta^2 \tau \hat{s}_5^2, & \hat{\tau}_6 &= 4\theta^2 \tau \hat{s}_6^2, \\
\hat{\tau}_7 &= 4\theta^2 \tau \hat{s}_4 \hat{s}_5, & \hat{\tau}_8 &= 4\theta^2 \tau \hat{s}_4 \hat{s}_6, & \hat{\tau}_9 &= 4\theta^2 \tau \hat{s}_5 \hat{s}_6,
\end{aligned} \tag{50}$$

324 where τ is a function of ρ , θ , and φ , are satisfied, Eq. (47) may be rewritten as follows

$$T_{ij} = (\hat{\tau}_0 + \hat{\tau}_1 \rho_{,k}^2 + \hat{\tau}_2 \theta_{,k}^2 + \hat{\tau}_3 \varphi_{,k}^2) \delta_{ij} + \tau \frac{\partial \psi}{\partial \varphi_{,i}} \frac{\partial \psi}{\partial \varphi_{,j}}, \tag{51}$$

326 thus extending to Korteweg fluids the constitutive equation (4) for the Cauchy stress, which holds for two-phase
327 Ginzburg–Landau fluids [1–8].

328 4 Discussion

329 From the results in the previous sections, it emerges clearly the importance of the constitutive equation of the
330 free energy in GL models. In fact, beside determining the GL equation, the free energy influences the Cauchy
331 stress too, allowing for nonlocal terms into its constitutive equations. Moreover, the form of the free energy is
332 also important in proving existence and uniqueness of initial and boundary value problems [50]. Therefore, it
333 is worth investigating how much general Eq. (48) is. Below, we show that Eq. (48) encompasses several GL
334 free energies proposed in the literature in the past decades. First, we observe that if

$$\psi_0(\rho, \theta, \varphi) = f(\varphi), \quad \mu = -2\theta \hat{s}_6, \tag{52}$$

where $f(\varphi)$ is the double-well function whose derivatives enter the GL equation, then the constitutive equation (48) for the free energy reduces to Eq. (2) either for isothermal and homogeneous phases, or for vanishing coefficients \hat{s}_i ($i = 1, \dots, 5$). That way, the earlier model by Gurtin [1,8] is recovered, so that our approach is capable of reproducing the results obtained by postulating the microforce balance.

Fabrizio, Giorgi, and Morro [3] obtained a generalization of Eq. (2) of the form

$$\psi(\rho, \theta, \varphi, \varphi_i) = \phi_1(\rho, \theta, \varphi) + \phi_2(\rho, \theta) + \frac{1}{2}\mu(\rho, \theta)\varphi_i^2, \quad (53)$$

which is still included in Eq. (48) if

$$\begin{aligned} \psi_0(\rho, \theta, \varphi) &= \phi_1(\rho, \theta, \varphi) + \phi_2(\rho, \theta), \\ \mu &= -2\theta\hat{s}_6. \end{aligned} \quad (54)$$

Thus, although we did not postulate any entropy extra-flux, our model encompasses some earlier models in which such a quantity plays a fundamental role.

Equation (48) also includes a proposal by Penrose and Fife [51], which involves the entropy potential instead of the Ginzburg–Landau free energy. Along with what is expected from the second law of thermodynamics, the authors prove that the value of the entropy functional cannot decrease along solution paths [51]. In a further paper [52], they make a suitable choice of the free energy functional and establish a systematic connection with the standard phase-field model. That way, they obtain a local free energy, which takes the form

$$\psi_0(\theta, \varphi) = \frac{\theta}{4\theta_0}(\varphi^2 - 1)^2 + \left(1 - \frac{\theta}{\theta_0}\right)(-a\varphi^2 + b\varphi + c) - \frac{\theta}{\theta_0} \ln\left(\frac{\theta}{\theta_0}\right), \quad (55)$$

wherein θ_0 is the transition temperature and a, b, c are constants.

Indeed, by taking

$$\begin{aligned} \epsilon(\theta, \varphi) &= \epsilon_1(\theta) + \theta\epsilon_2(\varphi) + \epsilon_3(\varphi), \\ \hat{s}_0(\theta, \varphi) &= \hat{s}_{01}(\theta) + \hat{s}_{02}(\varphi), \end{aligned} \quad (56)$$

along with the conditions

$$\begin{aligned} \epsilon_1(\theta) - \theta\hat{s}_{01}(\theta) &= -\frac{\theta}{\theta_0} \ln\frac{\theta}{\theta_0}, \\ \epsilon_2(\varphi) - \hat{s}_{02}(\varphi) &= \frac{1}{\theta_0} \left[\frac{(\varphi^2 - 1)^2}{4} - (-a\varphi^2 + b\varphi + c) \right], \\ \epsilon_2(\varphi) &= -a\varphi^2 + b\varphi + c, \\ \hat{s}_i &= 0, \quad i = 1, \dots, 6, \\ \frac{d\epsilon_1}{d\theta} + \epsilon_2(\varphi) &> 0, \quad \forall \theta, \varphi, \end{aligned} \quad (57)$$

the constitutive equation (55) is recovered. We notice that last condition in (57) guarantees the positivity of specific heat in arbitrary thermodynamic processes.

In most of the examples mentioned above, the free energy is nonlocal with respect to the phase field only, while in our case it depends on the gradients of all the thermodynamic variables, thus allowing for the description of the capillary phases. This is a consequence of the general procedure applied, which allows to treat the phase field as the other thermodynamic variables. The generality of the method is also confirmed by its capability to reproduce different models, obtained in different frameworks and by applying different mathematical techniques. To achieve that task, we needed suitable constitutive equations for the flux and for the production of internal variable, namely Eqs. (28), which have been postulated according to the theorems of representation of isotropic scalar and vector functions [44], and in such a way to recover the Ginzburg–Landau equation. We also needed a suitable constitutive equation for the specific entropy. Thus, starting from Eq. (32), i.e., the most general second-order polynomial isotropic scalar function, depending on scalars and vectors [44], which satisfies the principle of maximum entropy at the equilibrium [45], we made the additional assumptions (33), which are crucial to integrate the system of thermodynamic restrictions. Of course, more general hypotheses are possible, at the price of an increasing difficulty in getting information from the thermodynamic restrictions.

377 To our knowledge, the model presented here was never proposed in the literature earlier.

378 As final remark, we would like to stress that the problem of the form of the fundamental physical laws
379 when dealing with nonstandard phenomena, such as the phase transition, deserves consideration. Our belief is
380 that it should be considered from the experimental point of view, by direct measurements of the expenditure
381 of power and of the entropy production for different classes of materials. Since that task has not yet been
382 achieved, any assumption in this field contains a certain degree of arbitrariness. Analogously, we believe that
383 the words microforce and microstress could be, in a certain sense, misleading since one could suppose that
384 they are microscopic quantities for which the laws of microscopic physics (quantum mechanics, statistical
385 mechanics) should be applied. Indeed, these are macroscopic quantities whose local balances may be derived
386 by the classical procedures of continuum mechanics. Hence, it should be possible to measure them. However, to
387 our knowledge, such a kind of measurements does not exist. Thus, in order to avoid any kind of arbitrariness, we
388 approached the problem from a purely mathematical point of view, by including the gradients of the balance
389 equations into the entropy inequality. Although the method can be cumbersome, here we showed that it is
390 possible to find particular solutions of the set of thermodynamic restrictions leading to meaningful models.

391 From the physical point of view, the model presented here is useful in the analysis of the coexisting phases
392 of Korteweg-type fluids and in the modeling of the capillary forces occurring in the phase transition. It is based
393 on the universal physical principles only, such as second law of thermodynamics, and can be validated by
394 classical experiments, such as the static and dynamic methods to measure the surface tension [27].

395 From the mathematical point of view, the model is based on very general mathematical tools, which
396 are also suitable to study phase transitions in higher-grade nonlocal materials as, for instance, third-grade
397 Korteweg fluids. These phenomena, which have been not yet analyzed in-depth, will be the subject of our
398 future researches.

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