



Thermodynamically consistent phase field approach to phase transformations with interface stresses

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Abstract

Thermodynamically consistent phase field theory for multivariant martensitic transformations is developed with the main focus on introducing correct interface stresses (tension). The nontrivial point is that the interface tension (physical phenomenon) is introduced with the help of some geometric nonlinearities, even when strains are infinitesimal. Total stress at the diffuse interface consists of elastic and dissipative parts which are determined by the solution of the coupled system of phase field and viscoelasticity equations and the introduced interface stresses. An explicit expression for the free energy is derived that results in the desired expression for the interface stresses consistent with the sharp interface for the propagating nonequilibrium interface. Analytical expressions for nonequilibrium interface energy, width, entropy excess, as well as distribution of the interface tension are derived and parametrically studied. Interface stress tensor distribution is also obtained and analyzed for a critical martensitic nucleus. The possibility of extending the developed approach to other phenomena and more general models is discussed.

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1. Introduction

The phase field approach is widely used for the simulation of various first-order phase transformations, including martensitic phase transformations [1–11] and melting [12,13]. For martensitic phase transformations, the deformation of the crystal lattice of the high-temperature phase, austenite (A), into the low-temperature phase, martensite (M), is described in the small strain approximation by the transformation strain tensor ε_r . Due to the symmetry of the crystal lattices of A and M, there is a finite number n of crystallographically equivalent martensitic variants [14,15]. In the phase field approach, each of the martensitic variants is described by an order parameter η_i , $i = 1, 2, \dots, n$, and the evolution of each of variant is

governed by the Ginzburg–Landau equations. Hence, the evolution of a multiconnected martensitic microstructure can be simulated by the solution of the Ginzburg–Landau equations, coupled to elasticity equations, without explicit tracking of the interfaces. Instead of sharp interfaces, the solution exhibits a finite-width (diffuse) interface, within which order parameters smoothly vary between the values in contacting phases. Recent advances in phase field theory and simulation include incorporation of advanced mechanics [3,4,10], large-strain [16] and dynamic [17] formulations, introducing an athermal threshold for diffuse interface motion [8,18], microscale formulation [6], and the description of surface-induced phenomena for martensitic transformations [19–21] and melting [22,23]. It is known [24] that each material surface or interface is subjected to a biaxial tension with a magnitude equal to the surface energy γ (Fig. 1). This surface tension causes a jump in normal stresses across an interface equal to $2\gamma/r$, where r is the

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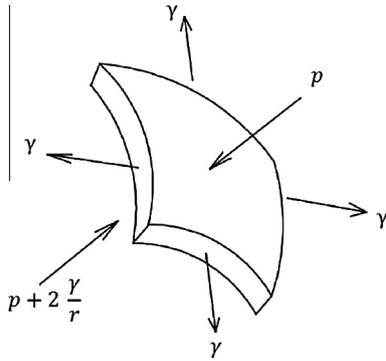


Fig. 1. Each material surface is subjected to a biaxial tension with a magnitude equal to the surface energy γ .

mean interface radius. Strictly speaking, this is true for external or internal surfaces (interfaces) that do not support elastic stresses, e.g. for liquid–liquid and liquid–gas interfaces. Interfaces in solids and solid–liquid interfaces generate additional surface stresses due to their elastic deformations. The elastic interface stresses may be both tensile or compressive. There is significant research literature devoted to the formulation of constitutive equations for elastic interfaces (e.g. [25–28] and review articles [29,30]). However, the main problem is that the material parameters for interfaces are unknown. In addition, a question arises whether complex, strongly heterogeneous fields across an interface of properties, strains and stresses can be formalized through simple constitutive equations.

Here, we will develop a model for the coherent elastic interfaces within the phase field approach. We will limit ourselves to isotropic interface energy and tension. The main point is that the elastic contribution to the surface stresses comes directly from the solution of the Ginzburg–Landau and elasticity equations for a phase transformation problem. In solutions to such problems, in particular, problems presented in Refs. [19–23], elastic stresses localized at the diffuse interface are present and take into account the variation of elastic properties across an interface, finite interface width and heterogeneity of stresses across an interface and along an interface. This is a much more detailed model for elastic interface stresses than any sharp interface model. What is missing in this model is the structural contribution to the interface stresses shown in Fig. 1. Since the thickness of martensitic variants is of the order of 1 nm and they possess sharp tips, surface tension should play a significant role in the nucleation and evolution of martensitic nanostructure. However, the correct expression for surface tension in the phase field approach to martensitic transformation is lacking. Even for liquid–liquid and liquid–solid diffuse interfaces, for which expressions for surface tension have been known [12,13,31], these stresses are not completely consistent with the sharp-interface limit shown in Fig. 1 because interface tension is not localized at the interface [13] or contains an additional hydrostatic pressure (see Section 9). Our equations in Refs. [19,20,22] resolve this problem but offer

correct results only for a stationary interface at phase equilibrium temperature $\theta = \theta_e$. Inconsistency with the sharp-interface approach means that the theory contains internal contradictions.

In this paper, a strict thermodynamic derivation of the phase field equations that include interface tension (stresses) is developed. We introduce proper terms in the energy potential, resulting in an expression for surface tension for single-variant phase transformations that is thermodynamically consistent and consistent with the sharp-interface limit shown in Fig. 1 for an arbitrary temperature and non-equilibrium interface. Then, we generalize results for multi-variant martensitic transformations. Such a theory includes a much more detailed and advanced model for a coherent interface than existing sharp-interface models [29,30]. This approach also advances models for solid–liquid, liquid–liquid and liquid–gas diffuse interfaces, making them consistent with the sharp interface approach for nonequilibrium conditions. The current paper provides consistent thermodynamic justification for our previous works on introducing interface stresses [19,20,22,32] and strictly generalizes them for an arbitrary nonequilibrium interface, critical nuclei and other microstructures.

We designate contractions of tensors $A = \{A_{ij}\}$ and $B = \{B_{ji}\}$ over one and two indices as $A \cdot B = \{A_{ij} B_{jk}\}$ and $A:B = A_{ij} B_{ji}$, respectively. The subscripts s and a designate the symmetric and the skew-symmetric part of a second-rank tensor; subscripts e , t and θ mean elastic, transformational and thermal strains; I is the unit tensor; δ_{ij} is the Kronecker delta; ∇ and $\bar{\nabla}$ are the gradient operators in the deformed and undeformed state, respectively (when this distinction is important); and \otimes designates a dyadic product and $:=$ is equal by definition.

In the sharp-interface approximation, the singular part of the stress tensor corresponding to the biaxial surface tension in Fig. 1 is:

$$\sigma_{st} = \gamma(I - n \otimes n)\delta(\Sigma), \quad (1)$$

where n is the unit normal to the interface and $\delta(\Sigma)$ is the Dirac delta function at the interface Σ . Indeed, since $I = n \otimes n + k \otimes k + m \otimes m$, where k and m are mutually orthogonal unit vectors that are orthogonal to n (i.e. they are tangent to the interface), then: $\sigma_{st} = \gamma(k \otimes k + m \otimes m)\delta(\Sigma)$, i.e. σ_{st} represents equal biaxial tension. Since by definition of the Dirac delta function, $\int_{-\infty}^{\infty} \delta(\Sigma) d\zeta = 1$, where ζ is the coordinate along the n , then the magnitude of the force per unit interface length, tangent to the interface, acting at any chosen interface edges is: $\int_{-\infty}^{\infty} \gamma \delta(\Sigma) d\zeta = \gamma$. We would like to introduce a counterpart of the Eq. (1) in the phase field approach that would follow from the chosen energy function and a thermodynamic procedure.

The paper is organized as follows. In Section 2 thermodynamics laws are applied to the model with free energy depending on order parameters and their gradients. The general structure of the constitutive equations is derived in Section 3. The expression for the free energy that results

in the desired structure for the interface stress tensor is specified in Section 4 for a single order parameter. The nontrivial points are that even for negligible small strains we have (i) to use a finite strain formulation, (ii) to consider the gradient of the order parameters with respect to a deformed configuration; and (iii) to introduce the ratio of mass densities in the undeformed and deformed states ρ_0/ρ in some terms. Thus, surface tension (physical phenomenon) is introduced just by taking into account some geometric nonlinearities. In Section 5 an analytical solution to the Ginzburg–Landau equation for the nonequilibrium propagating interface is presented and its temperature-dependent energy is determined. The final choice of the free energy function that satisfies the desired conditions for the surface stresses at arbitrary temperature is presented in Section 6. An explicit expression for energy, width, entropy excess and the distribution of the interface stresses at the moving interface is derived and analyzed in Section 7. The distribution of the interface stresses for the martensitic critical nucleus is given in Section 8. In this case, mean pressure is present in addition to biaxial tension. Comparison with previous approaches is reported in Section 9. Section 10 contains explicit expressions for the Ginzburg–Landau equation and the expression for entropy. A complete system of equations is summarized in Section 11. Possible generalization of the expression for interface stresses for multiple martensitic variants is presented in Section 12. Section 13 contains concluding remarks.

2. Laws of thermodynamics

While keeping deformations small for simplicity, we will take into account some geometric nonlinearity necessary for obtaining the desired interface tension stresses. Consider an arbitrary volume V of multiphase material with a boundary S . This volume can be cut from any actual body, thus S is not an external surface and surface energy will not be included in the thermodynamics laws. The first law of thermodynamics can be presented in the form of the global (i.e. for the entire body) energy balance equation:

$$\int_S (\mathbf{p} \cdot \mathbf{v} - \mathbf{h} \cdot \mathbf{n}) dS + \int_S \mathbf{Q}_i^j \dot{\eta}_i \cdot \mathbf{n} dS + \int_V \rho (\mathbf{f} \cdot \mathbf{v} + r) dV = \frac{d}{dt} \int_V \rho (U + 0.5 \mathbf{v} \cdot \mathbf{v}) dV. \quad (2)$$

Here η_i are the order parameters that vary from 0 for austenite to 1 for the i th martensitic variant M_i ; $\mathbf{v} = \dot{\mathbf{u}}$ is the velocity, \mathbf{h} is the heat flux, \mathbf{n} is the unit outer normal to S (or to any surface or diffuse interface under study), t is the time, U is the specific (per unit mass) internal energy, ρ is the mass density, \mathbf{f} is the body force and r is the specific volumetric heat supply rate (e.g. due to electric heating), both per unit mass. As will be seen below, we must include extra generalized surface forces \mathbf{Q}_i^j conjugate to η_i in order to balance terms due to the dependence of the thermody-

amic potential on $\nabla \eta_i$. Otherwise, Eq. (2) is not applicable for an arbitrary volume.

The second law of thermodynamics will be accepted in the form of the global entropy balance equation combined with the Clausius–Duhem inequality for the whole volume V :

$$S_i := \frac{d}{dt} \int_V \rho s dV - \int_V \rho \frac{r}{\theta} dV + \int_S \frac{\mathbf{h}}{\theta} \cdot \mathbf{n} dS \geq 0, \quad (3)$$

where s is the specific entropy, S_i is the total entropy production rate, and $\theta \geq 0$ is the temperature. The entropy supply r/θ and flux \mathbf{h}/θ are completely defined by the heat supply and flux, and temperature and do not require additional constitutive equations. Transforming surface integrals into integrals over the volume with the help of the Gauss theorem, utilizing conservation of mass ($\frac{d}{dt} dm = \frac{d}{dt} (\rho dV) = 0$), after some transformations we obtain:

$$\int_V (\boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \rho \dot{U} - \nabla \cdot \mathbf{h} + \rho r + \nabla \cdot (\mathbf{Q}_i^j \dot{\eta}_i)) dV + \int_V (\nabla \cdot \boldsymbol{\sigma} + \rho \mathbf{f} - \rho \dot{\mathbf{v}}) \cdot \mathbf{v} dV = 0. \quad (4)$$

$$S_i := \int_V \left(\rho \dot{s} - \rho \frac{r}{\theta} + \nabla \cdot \frac{\mathbf{h}}{\theta} \right) dV \geq 0. \quad (5)$$

For an observer that moves with the constant velocity \mathbf{a} with respect to a fixed frame of reference, velocity \mathbf{v} in Eq. (4) should be substituted with $\mathbf{v} - \mathbf{a}$. Since \mathbf{a} is an arbitrary vector and the energy balance should be independent of an observer, the term in parenthesis in the second integral in Eq. (4) is identically zero: $\nabla \cdot \boldsymbol{\sigma} + \rho \mathbf{f} = \rho \dot{\mathbf{v}}$. Thus, adding generalized forces \mathbf{Q}_i^j does not affect the local momentum balance equation. Since equality (4) and inequality (5) are valid for an arbitrary volume, then they have to be valid for each material point:

$$\boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \rho \dot{U} - \nabla \cdot \mathbf{h} + \rho r + \nabla \cdot (\mathbf{Q}_i^j \dot{\eta}_i) = 0; \quad (6)$$

$$\rho \tilde{S}_i := \rho \dot{s} - \rho \frac{r}{\theta} + \nabla \cdot \frac{\mathbf{h}}{\theta} = \rho \dot{s} - \rho \frac{r}{\theta} + \frac{1}{\theta} \nabla \cdot \mathbf{h} - \frac{\nabla \theta}{\theta^2} \cdot \mathbf{h} \geq 0, \quad (7)$$

where \tilde{S}_i is the local entropy production rate. Introducing the local dissipation rate,

$$\rho \mathcal{D} := \rho \theta \tilde{S}_i = \rho \theta \dot{s} - \rho r + \nabla \cdot \mathbf{h} - \frac{1}{\theta} \mathbf{h} \cdot \nabla \theta \geq 0 \quad (8)$$

and resolving Eq. (6) for the expression $\nabla \cdot \mathbf{h} - \rho r$ and substituting it in Eq. (8), one obtains the following dissipation inequality:

$$\rho \mathcal{D} := \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \rho \dot{U} + \rho \theta \dot{s} + \nabla \cdot (\mathbf{Q}_i^j \dot{\eta}_i) - \frac{\nabla \theta}{\theta} \cdot \mathbf{h} \geq 0. \quad (9)$$

We assume that the heat conduction and other thermomechanical processes are mutually independent. Then the inequality (9) transforms to the Fourier inequality $-\frac{\nabla \theta}{\theta} \cdot \mathbf{h} \geq 0$ and results in the disappearance of the last term from Eq. (9) (while keeping the same designation \mathcal{D}). By introducing the specific Helmholtz free energy per unit mass $\psi = U - \theta s$, we obtain the final expression for the dissipation inequality, which we will use:

$$\rho \mathcal{D} = \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \rho \dot{\psi} - \rho s \dot{\theta} + \nabla \cdot (\mathbf{Q}_i^j \dot{\eta}_i) \geq 0. \quad (10)$$

3. Constitutive equations

We accept an additive decomposition of the strain tensor $\boldsymbol{\varepsilon}$

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_e + \boldsymbol{\varepsilon}_t(\eta_i) + \boldsymbol{\varepsilon}_\theta(\theta, \eta_i) \quad (11)$$

into elastic $\boldsymbol{\varepsilon}_e$, transformational $\boldsymbol{\varepsilon}_t$ and thermal $\boldsymbol{\varepsilon}_\theta$ parts. Let $\psi = \psi(\boldsymbol{\varepsilon}_e, \eta_i, \theta, \nabla\eta_i)$. The order parameter $\eta_i = 0$ for austenite and 1 for the i th martensitic variant. The derivation will be more compact if we will change the argument of ψ from $\boldsymbol{\varepsilon}_e$ to $\boldsymbol{\varepsilon}$:

$$\begin{aligned} \psi &= \psi(\boldsymbol{\varepsilon}_e, \eta_i, \theta, \nabla\eta_i) \\ &= \psi(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_t(\eta_i) - \boldsymbol{\varepsilon}_\theta(\theta, \eta_i), \eta_i, \theta, \nabla\eta_i) \\ &= \bar{\psi}(\boldsymbol{\varepsilon}, \eta_i, \theta, \nabla\eta_i). \end{aligned} \quad (12)$$

More importantly, the gradient energy depends on the gradient of the order parameters with respect to deformed state, $\nabla\eta_i$. In this case, time and space derivatives are not permutable and one has to use the known equation:

$$\dot{\nabla}\eta_i = \nabla\dot{\eta}_i - \nabla\eta_i \cdot \nabla\mathbf{v}, \quad (13)$$

see, for example, [33], where $\nabla\mathbf{v} = \dot{\boldsymbol{\varepsilon}} + \boldsymbol{\omega}$ is the velocity gradient and $\boldsymbol{\omega}$ is the spin with respect to the deformed state. As we will see, the convective term in Eq. (13) will make a proper contribution to the surface tension. Let us evaluate the term:

$$\begin{aligned} \nabla \cdot (\mathbf{Q}_i^n \dot{\eta}_i) &= (\nabla \cdot \mathbf{Q}_i^n) \dot{\eta}_i + \mathbf{Q}_i^n \cdot \nabla\dot{\eta}_i \\ &= (\nabla \cdot \mathbf{Q}_i^n) \dot{\eta}_i + \mathbf{Q}_i^n \cdot \dot{\nabla}\eta_i + \mathbf{Q}_i^n \otimes \nabla\eta_i : \nabla\mathbf{v}, \end{aligned} \quad (14)$$

where Eq. (13) was utilized. Substituting $\dot{\psi}$ into Eq. (9), and taking into account Eq. (14), we obtain:

$$\begin{aligned} \rho\mathcal{D} &= \left(\boldsymbol{\sigma} - \rho \frac{\partial \bar{\psi}}{\partial \boldsymbol{\varepsilon}} + (\mathbf{Q}_i^n \otimes \nabla\eta_i)_s \right) : \dot{\boldsymbol{\varepsilon}} + (\mathbf{Q}_i^n \otimes \nabla\eta_i)_a : \\ &\quad \boldsymbol{\omega} - \left(\rho s + \rho \frac{\partial \bar{\psi}}{\partial \theta} \right) \dot{\theta} - \left(\rho \frac{\partial \bar{\psi}}{\partial \eta_i} - \nabla \cdot \mathbf{Q}_i^n \right) \dot{\eta}_i \\ &\quad + \left(\mathbf{Q}_i^n - \rho \frac{\partial \bar{\psi}}{\partial \nabla\eta_i} \right) \cdot \dot{\nabla}\eta_i \geq 0. \end{aligned} \quad (15)$$

The assumption that the dissipation rate is independent of $\dot{\theta}$ leads to a constitutive equation for the entropy:

$$s = - \frac{\partial \bar{\psi}}{\partial \theta}. \quad (16)$$

Assuming that the dissipation rate is independent of $\dot{\nabla}\eta_i$, we obtain equations:

$$\mathbf{Q}_i^n = \rho \frac{\partial \bar{\psi}}{\partial \nabla\eta_i}, \quad (17)$$

which define the introduced generalized thermodynamic forces.

Remark 1. If the thermodynamic forces \mathbf{Q}_i^n were not introduced at the surface S in Eq. (2), it would be equivalent to imposing the boundary condition at S :

$$\mathbf{n} \cdot \frac{\partial \psi}{\partial \nabla\eta_i} = 0 \quad \text{or} \quad \eta_i(t) = \text{const}. \quad (18)$$

Since conditions Eq. (18) cannot be satisfied for an arbitrary surface, the global energy balance cannot be localized for an arbitrary material point without additional assumptions. That is why we introduced the thermodynamic forces \mathbf{Q}_i^n at the surface S from the very beginning, which simplified localization of the thermodynamic laws. Also, in this case the boundary conditions Eq. (18) could be accepted in a more general form: $\mathbf{n} \cdot \frac{\partial \psi}{\partial \nabla\eta_i} = H_i$ with some prescribed H_i . Indeed, considering S as an actual external surface of the body, adding the rate of the surface energy $\gamma_s(\eta_i)$ to the surface integral in Eq. (2), and localizing Eq. (2) for the surface S , one obtains:

$$\left(\mathbf{n} \cdot \mathbf{Q}_i^n + \frac{\partial \gamma_s(\eta_i)}{\partial \eta_i} \right) \dot{\eta}_i = 0. \quad (19)$$

Taking into account definition of \mathbf{Q}_i^n and arbitrariness of $\dot{\eta}_i$, we arrive at the following boundary conditions:

$$\rho \mathbf{n} \cdot \frac{\partial \psi}{\partial \nabla\eta_i} = - \frac{\partial \gamma_s(\eta_i)}{\partial \eta_i}. \quad (20)$$

It was justified in Refs. [19,22] for the single order parameter that: $\gamma_s(\eta) = \gamma_{sA} + (\gamma_{sM} - \gamma_{sA})(a_s \eta^2 + (4 - 2a_s)\eta^3 + (a_s - 3)\eta^4)$, where γ_{sA} and γ_{sM} are the surface energy of A and M and a_s is a parameter. Thus, when surface energy changes during the phase transformation, more general boundary conditions than Eq. (18) have to be applied. This leads to surface-induced pre-transformations and barrierless nucleation [19,20,22,23,34,35]. An expression for $\gamma(\eta_i)$ for the multiple order parameters is given in Refs. [19,20]. For equal surface energy of the phases, Eq. (20) reduces to Eq. (18).

We will limit ourselves to isotropic interface energy and tension. Consequently, $\bar{\psi}$ is an isotropic function of $\boldsymbol{\zeta}_i = \nabla\eta_i$, i.e. it may depend on invariants $a_{jk} = \boldsymbol{\zeta}_j \cdot \boldsymbol{\zeta}_k = a_{kj}$ for all k and j , $\bar{\psi} = \bar{\psi}(a_{jk})$. Let us show that:

$$\left(\frac{\partial \bar{\psi}}{\partial \nabla\eta_i} \otimes \nabla\eta_i \right)_a = 0, \quad (21)$$

because $\bar{\psi}$ is an isotropic function of $\boldsymbol{\zeta}_i = \nabla\eta_i$. Indeed, the second-rank tensor:

$$\begin{aligned} \frac{\partial \bar{\psi}}{\partial \boldsymbol{\zeta}_i} \otimes \boldsymbol{\zeta}_i &= \frac{\partial \bar{\psi}}{\partial a_{jk}} \frac{\partial a_{jk}}{\partial \boldsymbol{\zeta}_i} \otimes \boldsymbol{\zeta}_i \\ &= \frac{\partial \bar{\psi}}{\partial a_{jk}} (\boldsymbol{\zeta}_k \delta_{ji} \otimes \boldsymbol{\zeta}_i + \boldsymbol{\zeta}_j \delta_{ik} \otimes \boldsymbol{\zeta}_i) \\ &= \frac{\partial \bar{\psi}}{\partial a_{jk}} (\boldsymbol{\zeta}_k \otimes \boldsymbol{\zeta}_j + \boldsymbol{\zeta}_j \otimes \boldsymbol{\zeta}_k) \end{aligned} \quad (22)$$

is symmetric because a_{jk} is symmetric.

The term in Eq. (15) conjugate to $\dot{\boldsymbol{\varepsilon}}$ represent the generalized dissipative stresses $\boldsymbol{\sigma}_d$; the terms conjugate to $\dot{\eta}_i$ are the corresponding dissipative forces X_i . Then Eq. (15) simplifies to:

$$\rho \mathcal{D} = \boldsymbol{\sigma}_d : \dot{\boldsymbol{\varepsilon}} + X_i \dot{\eta}_i \geq 0. \quad (23)$$

This leads to constitutive equations for the stress tensor and an evolution equation for η_i :

$$\begin{aligned} \boldsymbol{\sigma} &= \rho \frac{\partial \bar{\psi}}{\partial \boldsymbol{\varepsilon}} - \rho \left(\nabla \eta_i \otimes \frac{\partial \bar{\psi}}{\partial \nabla \eta_i} \right)_s + \boldsymbol{\sigma}_d; \\ X_i &= -\rho \frac{\partial \bar{\psi}}{\partial \eta_i} + \nabla \cdot \left(\rho \frac{\partial \bar{\psi}}{\partial \nabla \eta_i} \right), \end{aligned} \quad (24)$$

provided that constitutive equations for $\boldsymbol{\sigma}_d$ and X_i are given. Next, we assume that the generalized rates, i.e. the deformation rate and $\dot{\eta}_i$, are thermodynamically independent. Then two stricter inequalities are valid:

$$\boldsymbol{\sigma}_d : \dot{\boldsymbol{\varepsilon}} \geq 0; \quad X_i \dot{\eta}_i \geq 0. \quad (25)$$

To satisfy these inequalities, one has to assume that $\boldsymbol{\sigma}_d = \boldsymbol{\sigma}_d(\dot{\boldsymbol{\varepsilon}})$ and $X_i = X_i(\dot{\eta}_j)$, otherwise the inequalities can be easily violated.

4. Specification of the Helmholtz energy for a single order parameter

First, let us present the expression for the Helmholtz free energy for 2–3–4 potential Eq. (12) in terms of η from Ref. [3], which neglects the interface tension:

$$\begin{aligned} \bar{\psi}_0(\boldsymbol{\varepsilon}, \eta, \theta, \nabla \eta) &= \psi^e(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_t(\eta) - \boldsymbol{\varepsilon}_\theta(\theta, \eta), \eta, \theta) + f(\theta, \eta) \\ &+ \psi^\nabla; \end{aligned} \quad (26)$$

$$\begin{aligned} f(\theta, \eta) &= \Delta G^\theta(\theta) \eta^3 (4 - 3\eta) + A(\theta) \eta^2 (1 - \eta)^2; \\ \psi^\nabla &= \frac{\beta}{2\rho_0} |\nabla \eta|^2. \end{aligned} \quad (27)$$

Here, ψ^e is the elastic energy and ψ^∇ is the simplest gradient energy; the terms $\Delta G^\theta(\theta) \eta^3 (4 - 3\eta)$ and $A(\theta) \eta^2 (1 - \eta)^2$ are parts of the thermal (chemical) energy $f(\theta, \eta)$ related to the thermal driving force for phase transformation and the double-well barrier, respectively, ΔG^θ is the difference between the thermal parts of the Gibbs energies of M and A; A and β are the double-well energy and gradient energy coefficients. To introduce interface tension, we accept the free energy in the following form:

$$\begin{aligned} \bar{\psi}(\boldsymbol{\varepsilon}, \eta, \theta, \nabla \eta) &= \psi^e(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_t(\eta) - \boldsymbol{\varepsilon}_\theta(\theta, \eta), \eta, \theta) + \frac{\rho_0}{\rho} \check{\psi}^\theta \\ &+ \tilde{\psi}^\theta + \frac{\rho_0}{\rho} \psi^\nabla; \end{aligned} \quad (28)$$

$$\tilde{\psi}^\theta + \check{\psi}^\theta = f(\theta, \eta); \quad \frac{\rho_0}{\rho} = 1 + \varepsilon_0;$$

$$\psi^\nabla = \frac{\beta}{2\rho_0} |\nabla \eta|^2, \quad (29)$$

where the proper division of $f(\theta, \eta)$ into two functions, $\tilde{\psi}^\theta$ and $\check{\psi}^\theta$, is to be determined and ε_0 is the volumetric strain. Note that for such ψ^∇ , one has $\mathcal{Q}^\nabla = (\rho/\rho_0)\beta \nabla \eta$. When $\rho_0/\rho = 1$ and the difference between gradients in the deformed and undeformed configurations is neglected, Eqs. (28) and (29) coincide with our previous equations in Refs.

[3,4] (i.e. Eqs. (26) and (27)), in which surface tension was neglected. Note that the material constants and functions in terms without ρ_0/ρ are defined per unit mass or (since $\rho_0 = \text{constant}$) per unit undeformed volume. The terms with ρ_0/ρ are multiplied by $dm\rho_0/\rho = \rho_0 dV$; then the material constants and functions (β and A) are defined per unit deformed volume dV . The reason why the two terms, $\check{\psi}^\theta$ and ψ^∇ , are multiplied by ρ_0/ρ will become clear after we evaluate the expression for stresses according to Eq. (24). While usually in the small strain approximation it is assumed $\rho_0/\rho \simeq 1$, since ρ_0/ρ is a linear function of volumetric strain ε_0 , keeping ρ_0/ρ results in additional contribution to stress even at infinitesimal strains. Indeed, since

$$\rho_0/\rho = 1 + \varepsilon_0 = 1 + \mathbf{I} : \boldsymbol{\varepsilon}, \quad \text{then} \quad d(\rho_0/\rho)/d\boldsymbol{\varepsilon} = \mathbf{I}. \quad (30)$$

$$\text{Also,} \quad \frac{\partial \bar{\psi}}{\partial \boldsymbol{\varepsilon}} = \frac{\partial \bar{\psi}}{\partial \boldsymbol{\varepsilon}_e} : \frac{\partial \boldsymbol{\varepsilon}_e}{\partial \boldsymbol{\varepsilon}} = \frac{\partial \bar{\psi}}{\partial \boldsymbol{\varepsilon}_e}. \quad (31)$$

Then it follows from Eqs. (24), (28) and (29):

$$\begin{aligned} \boldsymbol{\sigma} &= \rho_0 \frac{\partial \bar{\psi}}{\partial \boldsymbol{\varepsilon}} - \rho \frac{\partial \bar{\psi}}{\partial \nabla \eta} \otimes \nabla \eta + \boldsymbol{\sigma}_d \\ &= \rho_0 \frac{\partial \psi^e}{\partial \boldsymbol{\varepsilon}_e} + \rho_0 (\check{\psi}^\theta + \psi^\nabla) \mathbf{I} - \beta \nabla \eta \otimes \nabla \eta + \boldsymbol{\sigma}_d. \end{aligned} \quad (32)$$

In the first term, we used the simplification $\rho \simeq \rho_0$. Let us introduce $\mathbf{n} = \nabla \eta / |\nabla \eta|$, which for the solution representing diffuse interface defines the unit normal to the diffuse interface. Substituting Eq. (29) for ψ^∇ in Eq. (32), we further specify:

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_e + \boldsymbol{\sigma}_{st} + \boldsymbol{\sigma}_d; \quad \boldsymbol{\sigma}_e = \rho_0 \frac{\partial \psi^e}{\partial \boldsymbol{\varepsilon}_e}; \quad (33)$$

$$\begin{aligned} \boldsymbol{\sigma}_{st} &= \left(\rho_0 \check{\psi}^\theta + \frac{\beta}{2} |\nabla \eta|^2 \right) \mathbf{I} - \beta \nabla \eta \otimes \nabla \eta = \beta |\nabla \eta|^2 (\mathbf{I} - \mathbf{n} \otimes \mathbf{n}) \\ &+ \left(\rho_0 \check{\psi}^\theta - \frac{\beta}{2} |\nabla \eta|^2 \right) \mathbf{I}, \end{aligned} \quad (34)$$

Thus, we obtained decomposition of the stress tensor into an elastic part, $\boldsymbol{\sigma}_e$ (which looks exactly the same as without surface tension), dissipative part and a surface tension contribution, which should be localized at the diffuse interface and equal to zero in the bulk, i.e. for $\eta = 0$ and $\eta = 1$. This implies the requirement that the function $\check{\psi}^\theta$ should be localized at the diffuse interface. To obtain the desired biaxial surface tension, the last term must be identically zero for the solution representing a propagating interface. This condition will be used in Section 6 to define function $\check{\psi}^\theta$.

5. Solution to the Ginzburg–Landau equation for a propagating interface

To make a further simplification, let us evaluate the nonlocal term in X (Eq. (24)):

$$\nabla \cdot \left(\rho \frac{\partial \bar{\psi}}{\partial \nabla \eta} \right) = \beta \nabla \cdot \nabla \eta = \beta \nabla^2 \eta. \quad (35)$$

Then the simplest Ginzburg–Landau equation reads:

$$\dot{\eta} = LX = L \left(-\rho \frac{\partial \bar{\psi}}{\partial \eta} + \beta \nabla \cdot \nabla \eta \right). \quad (36)$$

Note that $d(\rho_0/\rho)/d\eta = 0$ because differentiation is performed at constant strain. This is one more advantage of using $\bar{\psi}$ as a function of the total strain, rather than elastic strain.

For the neglected strains and stresses (and, consequently, $\rho_0 = \rho$), propagation of the nonequilibrium plane interface moving in an infinite space along axes x is described by a closed-form solution to Eq. (36) [18]:

$$\eta_{in} = (1 + e^{-\zeta})^{-1}; \quad \zeta = k(x - ct). \quad (37)$$

Here, $c = 6L\rho_0\Delta G^\theta(\theta)/k$ is the interface velocity, and parameter

$$k = \sqrt{2\rho_0(A(\theta) - 3\Delta G^\theta(\theta))/\beta}; \quad \delta = 10/k \quad (38)$$

defines the interface width, δ . Note that different definitions of the interface width lead to a factor different from 10 [10,18,22]. Existence of k imposes a constraint on the temperature at which a solution exists $A(\theta) > 3\Delta G^\theta(\theta)$. One of the properties of solution Eq. (37), which will be used below, is:

$$d\eta_{in}/d\zeta = \eta_{in}(1 - \eta_{in}). \quad (39)$$

Using it and the definition of k in Eq. (38), we obtain an important relationship for the points of a propagating interface:

$$\begin{aligned} \psi^\nabla &= \frac{\beta}{2\rho_0} |\nabla \eta_{in}|^2 = \frac{\beta k^2}{2\rho_0} \left(\frac{d\eta_{in}}{d\zeta} \right)^2 \\ &= (A(\theta) - 3\Delta G^\theta(\theta)) \eta_{in}^2 (1 - \eta_{in})^2. \end{aligned} \quad (40)$$

According to the definition of the interface energy under the nonequilibrium condition (e.g. [22]), this energy is equal to the excess energy with respect to austenite in the austenitic region $x \leq x_i$ and with respect to martensite in the martensitic region $x > x_i$ (See Fig. 2):

$$\gamma := \int_{-\infty}^{x_i} \rho_0(\psi - \psi_A) dx + \int_{x_i}^{\infty} \rho_0(\psi - \psi_M) dx, \quad (41)$$

where x_i is the interface position, at which we assume $\eta = 0.5$. We have: $\psi_A = 0$, $\psi_M = \Delta G(\theta)$, and it follows from the condition $\eta = 0.5$ in Eq. (37) that $\zeta_i = 0$. Let us first evaluate the gradient energy contribution to γ , using Eq. (38) for k and Eq. (97) in Appendix A:

$$\begin{aligned} \Psi^\nabla &:= \int_{-\infty}^{\infty} \rho_0 \psi^\nabla dx = \frac{k\beta}{2} \int_{-\infty}^{\infty} \left(\frac{d\eta_{in}}{d\zeta} \right)^2 d\zeta = \frac{k\beta}{12} \\ &= \frac{\sqrt{2\beta\rho_0(A(\theta) - 3\Delta G^\theta(\theta))}}{12}. \end{aligned} \quad (42)$$

The total interface energy according to Eqs. (96), (97) and (38) for k is:

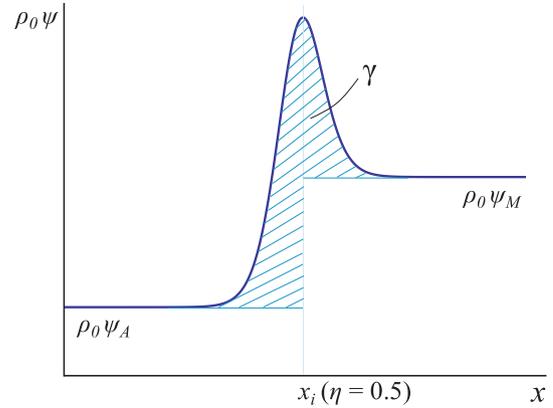


Fig. 2. Schematic for definition of the energy γ for nonequilibrium interface.

$$\begin{aligned} \gamma &= \frac{\rho_0(A(\theta) - 3\Delta G^\theta(\theta))}{6k} + \Psi^\nabla \\ &= \frac{\sqrt{2\beta\rho_0(A(\theta) - 3\Delta G^\theta(\theta))}}{12} + \Psi^\nabla = 2\Psi^\nabla \\ &= \frac{\sqrt{2\beta\rho_0(A(\theta) - 3\Delta G^\theta(\theta))}}{6} = \frac{k\beta}{6}. \end{aligned} \quad (43)$$

Thus, an important result is that for the nonequilibrium interface the total energy is twice the gradient energy. For the equilibrium interface, substituting $\Delta G^\theta = 0$ in Eqs. (40) and (43), we obtain:

$$\begin{aligned} \psi^\nabla &= \frac{\beta}{2\rho_0} |\nabla \eta_{in}|^2 = A(\theta_e) \eta_{in}^2 (1 - \eta_{in})^2; \\ \bar{\psi}_0 &= 2\psi^\nabla = 2A(\theta_e) \eta_{in}^2 (1 - \eta_{in})^2. \\ \gamma_e &= 2\Psi^\nabla = \frac{\sqrt{2\beta\rho_0 A(\theta_e)}}{6}; \quad \Psi^\nabla = \frac{\sqrt{2\beta\rho_0 A(\theta_e)}}{12}, \end{aligned} \quad (44)$$

which are the known relationships (e.g. [10]).

6. Final expression for free energy

To obtain the biaxial interface tension in Eq. (34) for the propagating interface, one has to define for the general case (i.e. for arbitrary distribution of η):

$$\check{\psi}^\theta := (A(\theta) - 3\Delta G^\theta(\theta)) \eta^2 (1 - \eta)^2. \quad (45)$$

Then, according to Eq. (40), for the nonequilibrium interface $\check{\psi}^\theta = \psi^\nabla = \frac{\beta}{2\rho_0} |\nabla \eta_{in}|^2$. It is clear that for the propagating interface Eq. (37), the function $\check{\psi}^\theta$ is localized at the diffuse interface, as required. Substituting Eq. (45) in the general expression for the interface tension (34), we obtain for the propagating interface:

$$\begin{aligned} \sigma_{st} &= \beta |\nabla \eta|^2 (\mathbf{I} - \mathbf{n} \otimes \mathbf{n}) = 2\rho_0 \check{\psi}^\theta (\mathbf{I} - \mathbf{n} \otimes \mathbf{n}) \\ &= \sigma_{st} (\mathbf{I} - \mathbf{n} \otimes \mathbf{n}), \end{aligned} \quad (46)$$

where σ_{st} is the magnitude of the biaxial interface stresses. Since $\psi^\nabla > 0$, interface stress $\sigma_{st} > 0$, i.e. it is always tensile.

Then for the solution Eq. (37) for the propagating interface, the magnitude of the force per unit interface length is equal to:

$$\int_{-\infty}^{\infty} \beta |\nabla \eta_m|^2 dx = 2 \int_{-\infty}^{\infty} \rho_0 \check{\psi} dx = 2\Psi^\nabla = \gamma, \quad (47)$$

i.e. to the nonequilibrium interface energy γ . In the derivation of Eq. 47, Eqs. 42 and 43 were utilized. Consequently, Eq. (34) for interface stresses for a nonequilibrium propagating interface transforms to the desired Eq. (1) for the sharp-interface limit. In addition,

$$\tilde{\psi}^\theta = f(\theta, \eta) - \check{\psi}^\theta = \Delta G^\theta(\theta) \eta^2 (3 - 2\eta). \quad (48)$$

7. Energy, width, entropy excess and stresses for a nonequilibrium interface

Energy and entropy excess. It is usually assumed [3]:

$$A = A_0(\theta - \theta_c), A_0 > 0; \quad \Delta G^\theta(\theta) = -\Delta s_0(\theta - \theta_e), \Delta s_0 < 0, \quad (49)$$

where θ_c is the critical temperature at which stress-free A loses its thermodynamic stability and Δs_0 is the difference in entropy between martensite and austenite at $\theta = \theta_e$. Then introducing dimensionless temperature, $\bar{\theta}$, parameter ϖ , their combination, \mathcal{Y} , and parameter \tilde{A} by the following equations:

$$\bar{\theta} := \frac{\theta - \theta_e}{\theta_e - \theta_c}; \quad \varpi := -\frac{3\Delta s_0}{A_0} > 0.5; \quad \mathcal{Y} := \bar{\theta}(1 - \varpi) + 1 \geq 0; \quad \tilde{A} := 2\rho_0 A_0(\theta_e - \theta_c), \quad (50)$$

the interface energy can be presented in the form:

$$\begin{aligned} \gamma &= \frac{\sqrt{2\beta(\theta)\rho_0 A_0 [(\theta - \theta_e)(1 - \varpi) + (\theta_e - \theta_c)]}}{6} \\ &= \frac{\sqrt{2\beta(\theta)\rho_0 A_0(\theta_e - \theta_c)}}{6} \sqrt{\bar{\theta}(1 - \varpi) + 1} \\ &= \frac{\sqrt{\beta(\theta)\tilde{A}}}{6} \sqrt{\mathcal{Y}}. \end{aligned} \quad (51)$$

The limitation $\varpi > 0.5$ comes from the following consideration. Since $\Delta s_0 < 0$, one has $\varpi > 0$. The critical temperature for the loss of stability of stress-free martensite, $\bar{\theta}_c$, was determined in Ref. [3] as:

$$\bar{\theta}_c := \theta_c + \frac{6\Delta s_0(\theta_e - \theta_c)}{6\Delta s_0 + A_0} = \theta_c - \frac{2\varpi(\theta_e - \theta_c)}{1 - 2\varpi}. \quad (52)$$

Then the obvious inequalities $\bar{\theta}_c > \theta_e > \theta_c$ imply $\varpi > 0.5$. A solution for a propagating interface exists and γ is a real number when $\bar{\theta}(1 - \varpi) + 1 > 0$, i.e.

$$\bar{\theta} \geq \frac{1}{\varpi - 1} \text{ for } \varpi < 1; \quad \bar{\theta} \leq \frac{1}{\varpi - 1} \text{ for } \varpi > 1, \quad (53)$$

with no limitations for $\varpi = 1$.

Excess of an interface entropy is calculated below for $\beta = const$:

$$s_i = -\frac{\partial \gamma}{\partial \theta} = \frac{\sqrt{2\beta\rho_0 A_0}}{12\sqrt{\theta_e - \theta_c}} \frac{\varpi - 1}{\sqrt{\bar{\theta}(1 - \varpi) + 1}}. \quad (54)$$

The dimensionless interface energy and excess entropy are defined as:

$$\bar{\gamma} := 6\gamma/\sqrt{\beta(\theta)\tilde{A}} = \sqrt{\bar{\theta}(1 - \varpi) + 1} = \sqrt{\mathcal{Y}}. \quad (55)$$

$$\bar{s}_i := \frac{12s_i\sqrt{\theta_e - \theta_c}}{\sqrt{2\beta\rho_0 A_0}} = \frac{\varpi - 1}{\sqrt{\bar{\theta}(1 - \varpi) + 1}}. \quad (56)$$

One of the additional assumptions that allow one to determine $\bar{\theta}_c$ was [3] $\theta_c = 0.5(\theta_e + \bar{\theta}_c)$. In this case one has $\varpi = 1$ [3] and the temperature dependence of the interface energy is determined solely by $\beta(\theta)$. If β is temperature independent, the interface energy is temperature independent as well and entropy excess is zero. In Fig. 3a, the dependence of $\bar{\gamma}$ vs. $\bar{\theta}$ is presented for various values of ϖ ; in Fig. 3b, the relationship between $\bar{\gamma}$ and ϖ is shown for various values of $\bar{\theta}$. Similar plots for the excess entropy are presented in Fig. 4. For $\theta = \theta_e$ (i.e. for $\bar{\theta} = 0$), one has $\bar{\gamma} = 1$ for any ϖ and the entropy excess $\bar{s}_i = \varpi - 1$. Thus, $\bar{\gamma}$ represents an interface energy normalized by its value at thermodynamic equilibrium temperature. If one changes the sign of $1 - \varpi$, the same value of $\bar{\gamma}$ can be obtained by changing the sign of $\bar{\theta}$, i.e. the $\bar{\gamma}$ curves for the same magnitude but different signs of $1 - \varpi$ are just reflected with respect to the vertical axis for $1.5 \geq \varpi \geq 0.5$. Deviation of $\bar{\gamma}$ from 1 increases with the magnitude of $\bar{\theta}$ and $1 - \varpi$. Since for small product $\bar{\theta}(1 - \varpi)$ the Taylor expansion leads to $\bar{\gamma} \simeq 1 + 0.5\bar{\theta}(1 - \varpi)$, the magnitude of deviation of $\bar{\gamma}$ from 1 is a linear function of $\bar{\theta}$ and $1 - \varpi$. The minimum value of $\bar{\gamma}$ is zero for $\bar{\theta}(1 - \varpi) + 1 = 0$. In this case, the entropy excess is ∞ for $\varpi > 1$ and is $-\infty$ for $\varpi < 1$. Since formally is not limited, the growth of $\bar{\gamma}$ is not limited as well. For $\varpi < 1$ (or $\varpi > 1$), the interface energy growth (reduces) with increasing temperature and excess entropy is negative (positive). It is important that the solution for a moving interface exists even for $\theta < \theta_c$ (i.e. $\bar{\theta} < -1$) and for $\theta > \bar{\theta}_c$ (i.e. for $\bar{\theta} > 1/(2\varpi - 1)$), i.e. outside the temperature range, for which both phases have local minima, provided that ≥ 0 . However, homogeneous nucleation may compete with the interface propagation, as was obtained numerically in Refs. [22,23].

Interface width. Parameter k can be determined by Eq. (38) or (43):

$$\begin{aligned} k &= \sqrt{\frac{2\rho_0 A_0 [(\theta - \theta_e)(1 - \varpi) + (\theta_e - \theta_c)]}{\beta(\theta)}} \\ &= \sqrt{\frac{\tilde{A}[\bar{\theta}(1 - \varpi) + 1]}{\beta(\theta)}} = \frac{6\gamma}{\beta}. \end{aligned} \quad (57)$$

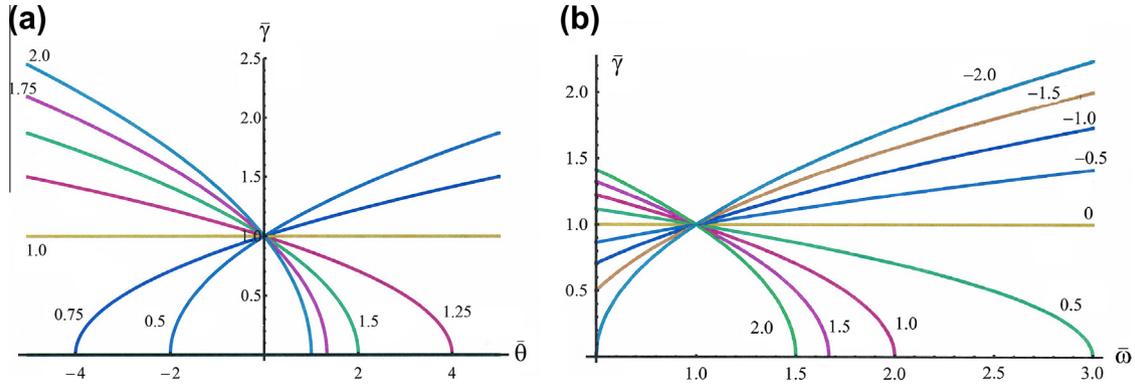


Fig. 3. The dimensionless nonequilibrium interface energy $\bar{\gamma}$ vs.: (a) dimensionless temperature $\bar{\theta}$ for various values of ϖ shown near curves; and (b) dimensionless values of ϖ for various dimensionless temperatures $\bar{\theta}$ shown near curves.

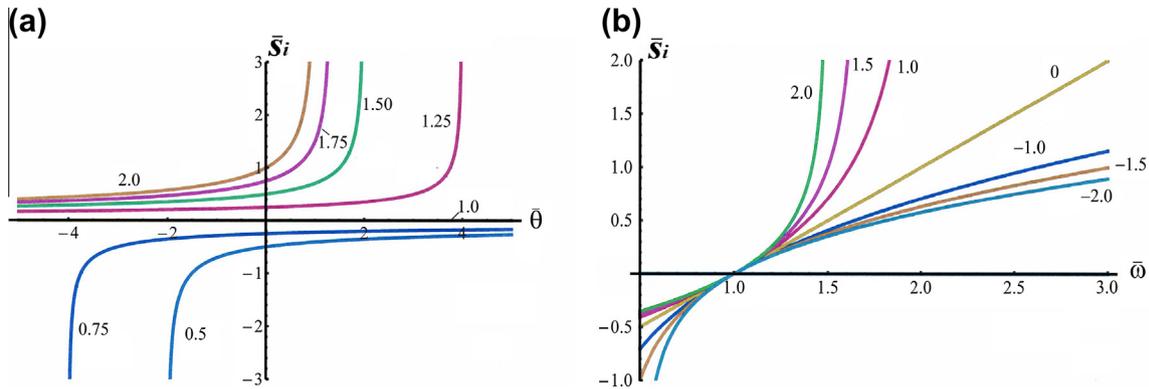


Fig. 4. The dimensionless nonequilibrium excess of the interface entropy \bar{s}_i vs.: (a) dimensionless temperature $\bar{\theta}$ for various values of ϖ shown near curves; and (b) dimensionless values of ϖ for various dimensionless temperatures $\bar{\theta}$ shown near curves.

Then the diffuse interface width at arbitrary and equilibrium temperature are:

$$\delta := \frac{10}{k} = 10 \sqrt{\frac{\beta(\theta)}{\tilde{A}[\theta(1-\varpi)+1]}} = \frac{5\beta}{3\gamma};$$

$$\delta(\theta_e) = 10 \sqrt{\frac{\beta(\theta_e)}{\tilde{A}}}. \tag{58}$$

The dimensionless width $\tilde{\delta}$ of the diffuse interface is defined as:

$$\tilde{\delta} := \frac{\delta(\theta)}{\delta(\theta_e)} = \frac{k(\theta_e)}{k(\theta)} = \sqrt{\frac{\beta(\theta)}{\beta(\theta_e)[\theta(1-\varpi)+1]}}$$

$$= \sqrt{\frac{\beta(\theta)}{\beta(\theta_e)\tilde{\Upsilon}}}. \tag{59}$$

It is simpler to analyze an alternative dimensionless width $\bar{\delta}$ of the diffuse interface:

$$\bar{\delta} := \tilde{\delta} \sqrt{\beta(\theta_e)/\beta(\theta)} = \sqrt{\tilde{\Upsilon}} = 1/\bar{\gamma}. \tag{60}$$

In Fig. 5a, the function $\bar{\delta}$ vs. $\bar{\theta}$ is presented for various values of ϖ ; in Fig. 5b, the dependence between $\bar{\delta}$ and ϖ is plotted for various values of $\bar{\theta}$. It is clear from Eq. (60) that

the singular case of zero interface energy corresponds to infinite interface width and the case of infinite $\bar{\gamma}$ $\bar{\delta} = 0$. However, their product is finite: $\gamma\delta = 5\beta/3$ and $\bar{\gamma}\bar{\delta} = 1$.

Interface tension. The magnitude of the biaxial interface stresses is:

$$\sigma_{st} = 2\rho_0\check{\psi}^\theta$$

$$= 2\rho_0A_0[(\theta - \theta_e)(1 - \varpi) + (\theta_e - \theta_c)]\eta_{in}^2(1 - \eta_{in})^2$$

$$= \tilde{A}\tilde{\Upsilon}\eta_{in}^2(1 - \eta_{in})^2; \tag{61}$$

Since the interface profile is the same for any t , we can consider without loss of generality $t = 0$. It is convenient to transform

$$e^{-\zeta} = e^{-kx} = e^{-\frac{10x}{\delta}} = e^{-\frac{10x\delta_e}{\delta}} = e^{-10y/\bar{\delta}}; \quad y := \frac{x}{\delta_e}, \tag{62}$$

where the dimensionless coordinate y is introduced in which the interface width $\simeq 1$ at $\theta = \theta_e$. Then the distribution of the dimensionless magnitude of the surface stresses is:

$$\sigma_{st} = \tilde{A}\tilde{\Upsilon} \frac{e^{-20y/\bar{\delta}}}{(1 + e^{-10y/\bar{\delta}})^4} = \frac{\tilde{A}\beta(\theta)}{\beta(\theta_e)\bar{\delta}^2} \frac{e^{-20y/\bar{\delta}}}{(1 + e^{-10y/\bar{\delta}})^4}, \tag{63}$$

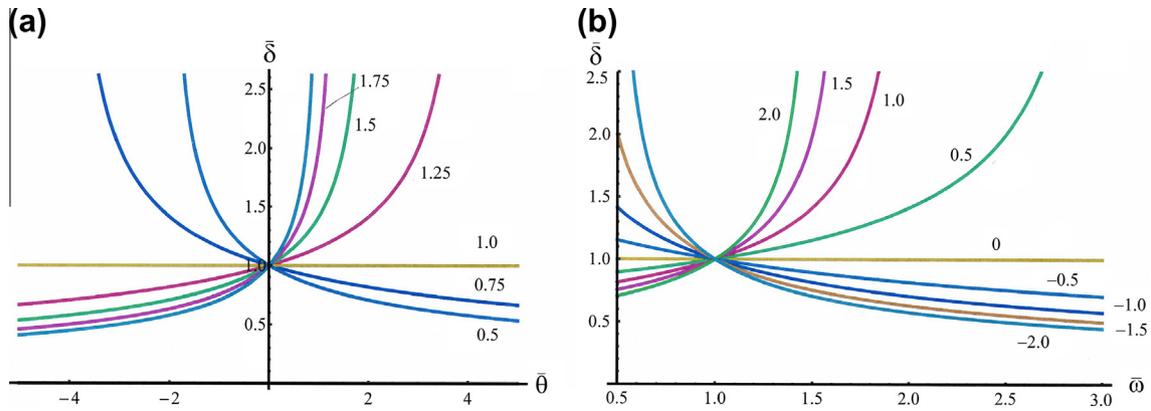


Fig. 5. The dimensionless interface width $\tilde{\delta}$ vs.: (a) dimensionless temperature $\bar{\theta}$ for various values of ϖ shown near curves; and (b) dimensionless values of \bar{w} for various dimensionless temperatures $\bar{\theta}$ shown near curves.

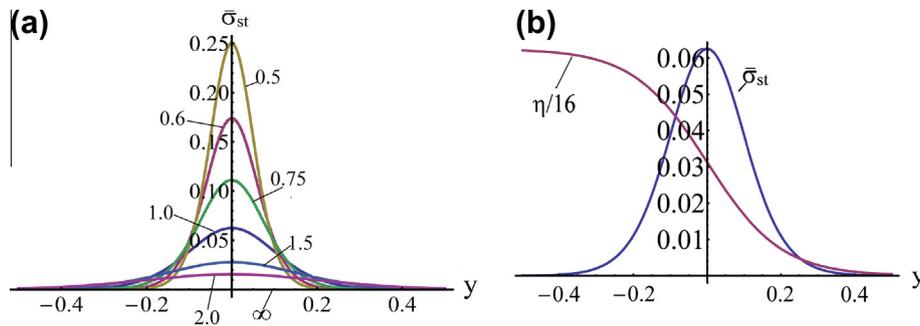


Fig. 6. (a) Distribution of the dimensionless biaxial surface tension $\bar{\sigma}_{st}(y)$ for the nonequilibrium interface for several dimensionless interface widths $\tilde{\delta}$ shown near curves. (b) Superposed plots of the interface profile $\eta(y)/16$ and dimensionless interface tension $\bar{\sigma}_{st}(y)$ for the dimensionless interface $\tilde{\delta} = 1$.

where Eqs. (37) and (59) have been used. Then one can introduce dimensionless magnitude of the surface stresses that can be presented solely in terms of the dimensionless width $\tilde{\delta}$:

$$\bar{\sigma}_{st} := \frac{\sigma_{st}\beta(\theta_e)}{A\beta(\theta)} = \frac{1}{\tilde{\delta}^2} \frac{e^{-20y/\tilde{\delta}}}{(1 + e^{-10y/\tilde{\delta}})^4}. \quad (64)$$

The maximum dimensionless surface stresses is $1/16\tilde{\delta}^2$ at $y=0$. A plot of $\bar{\sigma}_{st}(y)$ for several dimensionless interface widths $\tilde{\delta}$ is presented in Fig. 6a. In Fig. 6b, plots of the interface profile $\eta(y)/16$ and $\bar{\sigma}_{st}(y)$ for $\tilde{\delta} = 1$ are superposed to show how stresses are distributed with respect to the interface. For any $\tilde{\delta}$, the relative configuration of $\eta(y)/(16\tilde{\delta}^2)$ and $\bar{\sigma}_{st}(y)$ looks like in Fig. 6b. Using Eq. (59), interface stress can be expressed in terms of $\beta(\theta)$ and ϖ .

Note that for a finite sample with stress-free boundary condition, since the total traction is zero, the corresponding component of the elastic stresses is equal to the negative component of the surface stresses [19,20].

8. Interface stresses for critical martensitic nucleus

Let us consider a critical M nucleus within an A matrix, which exists for $\theta \leq \theta_e$. Using Eq. (101) in the Appendix, we obtain for each point:

$$\begin{aligned} \psi^\nabla &= f(\theta, \eta_c), \quad \psi(\theta, \eta_c) = \psi^\nabla + f(\theta, \eta_c) = 2\psi^\nabla \\ &= 2f(\theta, \eta_c). \end{aligned} \quad (65)$$

Substituting Eq. (65) into general expression for the tension Eq. (34), one derives:

$$\sigma_{st} = \rho_0\psi(\theta, \eta_c)(\mathbf{I} - \mathbf{n} \otimes \mathbf{n}) - \rho_0\tilde{\psi}^\theta(\theta, \eta_c)\mathbf{I}. \quad (66)$$

Consequently, for a critical M nucleus, the magnitude of the tensile biaxial interface tension is equal at each point to the local total free energy per unit volume $\rho_0\psi(\theta, \eta)$, i.e. it is positive (tensile). Thus, the total interface force is also equal to the total free energy of a critical nucleus. In addition, the tensile mean stress (negative pressure) $-\rho_0\tilde{\psi}^\theta > 0$ is applied to each point of a nucleus. The solution to Eq. (65) is [10]:

$$\begin{aligned} \eta_c &= 6 \left[6 - P + \sqrt{P^2 - 3P \cosh\left(20\sqrt{\bar{\theta} + 1} \frac{x}{l}\right)} \right]^{-1}; \\ P &:= \frac{4\varpi\bar{\theta}}{\bar{\theta} + 1}; \quad l := 40\sqrt{\frac{\beta}{A}}, \end{aligned} \quad (67)$$

where l is a typical temperature-independent width of the critical nucleus. Note that the actual width of the critical nucleus strongly depends on temperature and diverges at equilibrium temperature (e.g. [10]). Profiles of the critical nucleus $\eta_c(x/l)$ and the plots of the dimensionless magnitude of the biaxial surface stress $\tilde{\sigma}_{st}(x/l) := \frac{\psi(\theta, \eta_c)}{A_0(\theta_e - \theta_c)}$ and dimensionless

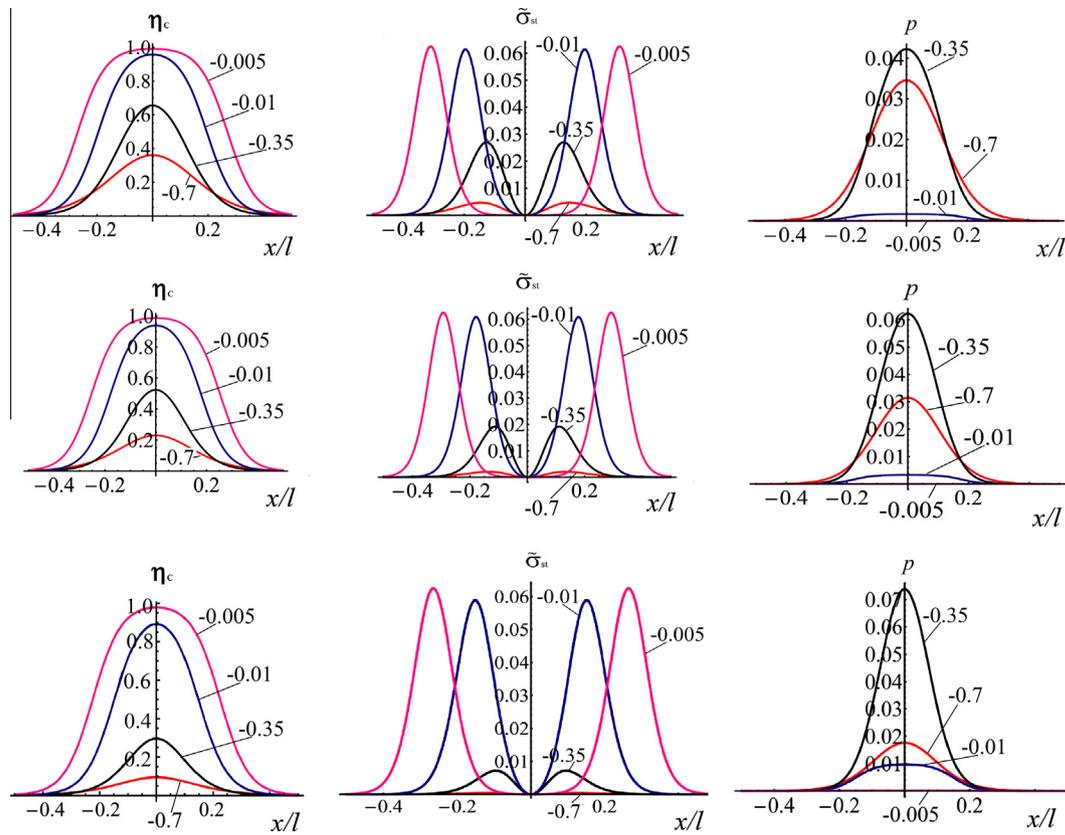


Fig. 7. Profile of the critical martensitic nucleus $\eta_c(x/l)$, and distribution of the dimensionless biaxial surface tension $\bar{\sigma}_{st}$ and dimensionless mean stress p for four temperatures shown near curves: 1st row for $\varpi = 0.5$, 2nd row for $\varpi = 1$ and 3rd row for $\varpi = 3$.

mean stress $p(x/l) := -\frac{\tilde{\psi}^\theta(\theta, \eta_c)}{A_0(\theta_e - \theta_c)}$ are shown in Fig. 7 for three values of ϖ and four temperatures. One can see that the surface tension is concentrated at the incomplete interfaces and is negligible at the center of a nucleus. The area below the $\bar{\sigma}_{st}(x/l)$ curve represents the total force and, consequently, the energy of the critical nucleus normalized by $A_0(\theta_e - \theta_c)$. At the same time, the mean stress is concentrated in the central region of the nucleus. The effect of temperature on the profile of the critical nucleus and interface stresses is much stronger than the effect of ϖ . Thus, an increase in ϖ slightly reduces the maximum value of η in the nucleus, reduces the magnitude of the interface tension for large overcooling (i.e. relatively large $|\bar{\theta}|$) and practically does not change it close to the equilibrium temperature. The magnitude of the mean stress is a nonmonotonous function of both ϖ and $\bar{\theta}$. For small overcooling $\bar{\theta} = -0.005$, the distribution $\eta_c(x/l)$ is very close to two equilibrium A – M interfaces at $\bar{\theta} = 0$ with almost complete A between them. The width of A and its completeness (closeness of maximum value of η_c to unity) increases with increasing ϖ . Such a profile implies that the mean stress is negligible, similar to a complete A – M interface and homogeneous A.

9. Comparison with known approaches

While we are not familiar with similar works on a solid–solid diffuse interface (except our recent papers [19–23],

which will be discussed below), there is a significant amount of work on surface tension in the phase field approach in the fluid dynamics literature. Thus, for an interface between two liquids [31] and between a solid and liquid, when the solid is described as a highly viscous liquid [12], it is natural to consider the gradient in the current deformed configuration, because this is the only privileged state for the liquid. Then the term $\frac{\partial \tilde{\psi}}{\partial \nabla \eta_i} \otimes \nabla \eta_i$ for stresses appears automatically. However, if this is the only term for interface stress, then it contains an extra spherical part in comparison with the sharp-interface equation (as it was in Ref. [31]). In Ref. [12], the gradient energy per unit deformed volume is considered, which is equivalent to multiplication by ρ_0/ρ and results in an additional term $\tilde{\psi}^\nabla \mathbf{I}$; but the term $\rho_0 \tilde{\psi} \mathbf{I}$ is missing in Ref. [12]. In Ref. [13], a very general treatment of the diffuse interface tension (including the case with anisotropic interface energy and tension) is considered. While elastic energy was not included, all other contributions were considered per unit current volume, which is equivalent to our Eq. (28) with $\tilde{\psi}^\theta$ also multiplied by ρ_0/ρ . For such a model, an additional term $\rho_0 \tilde{\psi}^\theta \mathbf{I}$ contributes to stress. For thermodynamic equilibrium, $\tilde{\psi}^\theta = 0$ and correspondence with the sharp interface model is proved. However, for deviation from the equilibrium, this stress is not localized at the diffuse interface but also produces a contribution $\tilde{\psi}^\theta(1) = \Delta G^\theta(\theta) \mathbf{I}$ in the phase with $\eta = 1$, which is contradictory. That is why we divided the total thermal energy into two parts and multiplied only that part by ρ_0/ρ , which

is localized at the diffuse interface and results in biaxial tension for a nonequilibrium interface.

In Refs. [19–23], a gradient with respect to the deformed configuration and multipliers ρ_0/ρ is introduced, and the goal of reproducing the interface tension at the equilibrium interface was achieved for the simplified model obeying Eq. (49) with $\varpi = 1$ by choosing:

$$\begin{aligned} \check{\psi}^\theta &= A_0(\theta_e - \theta_c)\eta^2(1 - \eta)^2; \\ \tilde{\psi}^\theta &= \frac{1}{3}A_0(\theta - \theta_e)\eta^2(3 - 2\eta), \end{aligned} \quad (68)$$

i.e. the double-well barrier is calculated at the phase equilibrium temperature θ_e , which makes surface tension independent of temperature (if β is temperature independent), or the temperature dependence of the interface tension is determined solely by $\beta(\theta)$. This expression differs from our current result for ψ^θ in Eq. (45) and, consequently, for the interface tension in Eq. (34) for the nonequilibrium temperature. However, for the particular case $\varpi = 1$ our current results coincide with Eq. (68) for an arbitrary temperature; they also coincide for $\theta = \theta_e$ and an arbitrary ϖ . That is why all the simulation results in Refs. [19–23] for a single order parameter are correct, because they were based on $\varpi = 1$.

10. Explicit equations for the order parameter and entropy

Let us obtain a more detailed form of the Ginzburg–Landau Eq. (36). Thus, $\frac{\partial \check{\psi}}{\partial \theta} = \frac{\partial \psi^e}{\partial \theta} + \frac{\rho_0}{\rho} \frac{\partial \check{\psi}^\theta}{\partial \theta} + \frac{\partial \tilde{\psi}^\theta}{\partial \theta}$. Next,

$$\begin{aligned} \rho \frac{\partial \psi^e}{\partial \eta} \Big|_{\varepsilon} &= \rho \frac{\partial \psi^e}{\partial \varepsilon_e} : \frac{\partial (\varepsilon - \varepsilon_t(\eta) - \varepsilon_\theta(\theta, \eta))}{\partial \eta} \Big|_{\varepsilon} + \rho \frac{\partial \psi^e}{\partial \eta} \Big|_{\varepsilon_e} \\ &= -\frac{\rho}{\rho_0} \sigma_e : \frac{\partial \varepsilon_t}{\partial \eta} - \frac{\rho}{\rho_0} \sigma_e : \frac{\partial \varepsilon_\theta}{\partial \eta} + \rho \frac{\partial \psi^e}{\partial \eta} \Big|_{\varepsilon_e}. \end{aligned} \quad (69)$$

We took into account Eq. (33) for elastic stresses σ_e . The last term is related to variable elastic properties of the phases. Substituting all terms in the Ginzburg–Landau Eq. (36), one obtains:

$$\begin{aligned} \dot{\eta} &= LX \\ &= L \left(\frac{\rho}{\rho_0} \sigma_e : \frac{\partial \varepsilon_t}{\partial \eta} + \frac{\rho}{\rho_0} \sigma_e : \frac{\partial \varepsilon_\theta}{\partial \eta} - \rho \frac{\partial \psi^e}{\partial \eta} \Big|_{\varepsilon_e} - \rho_0 \frac{\partial \check{\psi}^\theta}{\partial \eta} - \rho \frac{\partial \tilde{\psi}^\theta}{\partial \eta} + \beta \nabla^2 \eta \right). \end{aligned} \quad (70)$$

When one neglects the interface tension, dissipative stresses and any terms related to the finite strain, Eq. (70) reduces to:

$$\dot{\eta} = L \left(\sigma : \frac{\partial \varepsilon_t}{\partial \eta} + \sigma : \frac{\partial \varepsilon_\theta}{\partial \eta} - \rho_0 \frac{\partial \psi^e}{\partial \eta} \Big|_{\varepsilon_e} - \rho_0 \frac{\partial \check{\psi}^\theta}{\partial \eta} - \rho_0 \frac{\partial \tilde{\psi}^\theta}{\partial \eta} + \beta \nabla^2 \eta \right). \quad (71)$$

Thus, to take into account surface tension in the Ginzburg–Landau equation:

- (a) σ is substituted with $\frac{\rho}{\rho_0} \sigma_e$, which means that the surface tension does not explicitly contribute to the Ginzburg–Landau equation; rather, it affects the driving force by changing the stress distribution.

- (b) the term $\frac{\partial \check{\psi}^\theta}{\partial \eta}$ is multiplied by $\rho_0/\rho \simeq 1$;
- (c) gradient operator is calculated in the deformed configuration.

Remark 2. The reason that we keep in Eq. (70) the term $\frac{\rho}{\rho_0}$ and distinguish between ρ and ρ_0 , as well as between gradients in the deformed and undeformed configurations, which is usually neglected in the small-strain approximation, is the following. We found in numerical simulations that the sum of the local contributions to the driving force have a similar magnitude but the opposite sign to the terms with the Laplacian. Thus, a small difference in any of the terms can lead to a significant change in the total driving force. The same is valid for multivariant phase transformations.

Let us elaborate Eq. (16) for the entropy. Thus, $\frac{\partial \check{\psi}}{\partial \theta} = \frac{\partial \psi^e}{\partial \theta} + \frac{\rho_0}{\rho} \frac{\partial \check{\psi}^\theta}{\partial \theta} + \frac{\partial \tilde{\psi}^\theta}{\partial \theta} + \frac{\rho_0}{\rho} \frac{\partial \psi^{\nabla}}{\partial \theta}$. Next,

$$\begin{aligned} \rho \frac{\partial \psi^e}{\partial \theta} \Big|_{\varepsilon} &= \rho \frac{\partial \psi^e}{\partial \varepsilon_e} : \frac{\partial (\varepsilon - \varepsilon_t(\eta) - \varepsilon_\theta(\theta, \eta))}{\partial \theta} \Big|_{\varepsilon} + \rho \frac{\partial \psi^e}{\partial \theta} \Big|_{\varepsilon_e} \\ &= -\frac{\rho}{\rho_0} \sigma_e : \frac{\partial \varepsilon_\theta}{\partial \theta} + \rho \frac{\partial \psi^e}{\partial \theta} \Big|_{\varepsilon_e}. \end{aligned} \quad (72)$$

We took into account Eq. (33) for elastic stresses, σ_e . The last term is related to the temperature-dependent elastic properties of the phases. Substituting these results in Eq. (16), for the entropy we obtain:

$$\rho s = \frac{\rho}{\rho_0} \sigma_e : \frac{\partial \varepsilon_\theta}{\partial \theta} - \rho \frac{\partial \psi^e}{\partial \theta} \Big|_{\varepsilon_e} - \rho_0 \frac{\partial \check{\psi}^\theta}{\partial \theta} - \rho \frac{\partial \tilde{\psi}^\theta}{\partial \theta} - \frac{\partial \beta}{\partial \theta} \frac{1}{2} |\nabla \eta|^2. \quad (73)$$

Thus, if parameter β is temperature dependent, the entropy depends on the gradient of the order parameter. Differences between the expression for entropy for the case without and with surface tension are similar to those for the Ginzburg–Landau equation.

11. Complete system of equations

Below we collect the final complete system of equations for a single order parameter.

1. Kinematics

1.1. Decomposition of the strain tensor ε ; volumetric strain ε_0

$$\begin{aligned} \varepsilon &= (\overset{\circ}{\nabla} \mathbf{u})_s; \quad \varepsilon = \varepsilon_e + \varepsilon_t(\eta) + \varepsilon_\theta(\theta, \eta); \\ \frac{\rho_0}{\rho} &= 1 + \varepsilon_0; \quad \varepsilon_0 = \varepsilon : \mathbf{I}. \end{aligned} \quad (74)$$

1.2. Transformation ε_t and thermal ε_θ strains

$$\begin{aligned} \varepsilon_t &= \bar{\varepsilon}_t \varphi(a, \eta); \quad \varepsilon_\theta = \varepsilon_{\theta A} + (\varepsilon_{\theta M} - \varepsilon_{\theta A}) \varphi(a_\theta, \eta); \\ \varphi(a, \eta) &= a\eta^2(1 - \eta)^2 + (4\eta^3 - 3\eta^4). \end{aligned} \quad (75)$$

2. Helmholtz free energy per unit mass and its contributions

$$\bar{\psi}(\boldsymbol{\varepsilon}, \eta, \theta, \nabla \eta) = \psi^e(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_t(\eta) - \boldsymbol{\varepsilon}_\theta(\theta, \eta), \eta, \theta) + \frac{\rho_0}{\rho} \check{\psi}^\theta + \tilde{\psi}^\theta + \frac{\rho_0}{\rho} \psi^\nabla; \quad (76)$$

$$\check{\psi}^\theta = (A(\theta) - 3\Delta G^\theta(\theta))\eta^2(1-\eta)^2; \quad \tilde{\psi}^\theta = \Delta G^\theta(\theta)\eta^2(3-2\eta);$$

$$\psi^e = \frac{1}{2\rho_0} \boldsymbol{\varepsilon}_e : \mathbf{E}(\eta) : \boldsymbol{\varepsilon}_e; \quad \mathbf{E}(\eta) = \mathbf{E}_A + (\mathbf{E}_M - \mathbf{E}_A)\varphi(a_E, \eta); \quad \psi^\nabla = \frac{\beta}{2\rho_0} |\nabla \eta|^2. \quad (77)$$

3. Stress tensor

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_e + \boldsymbol{\sigma}_{st} + \boldsymbol{\sigma}_d; \quad (78)$$

$$\boldsymbol{\sigma}_e = \rho_0 \frac{\partial \psi^e}{\partial \boldsymbol{\varepsilon}_e} = \mathbf{E}(\eta) : \boldsymbol{\varepsilon}_e;$$

$$\boldsymbol{\sigma}_{st} = (\rho_0 \check{\psi}^\theta + \frac{\beta}{2} |\nabla \eta|^2) \mathbf{I} - \beta \nabla \eta \otimes \nabla \eta; \quad \boldsymbol{\sigma}_d = \mathbf{B} : \dot{\boldsymbol{\varepsilon}}. \quad (79)$$

4. Ginzburg–Landau equation

$$\dot{\eta} = LX$$

$$= L \left(\frac{\rho}{\rho_0} \boldsymbol{\sigma}_e : \frac{\partial \boldsymbol{\varepsilon}_t}{\partial \eta} + \frac{\rho}{\rho_0} \boldsymbol{\sigma}_e : \frac{\partial \boldsymbol{\varepsilon}_\theta}{\partial \eta} - \rho \frac{\partial \psi^e}{\partial \eta} \Big|_{\boldsymbol{\varepsilon}_e} - \rho_0 \frac{\partial \check{\psi}^\theta}{\partial \eta} - \rho \frac{\partial \tilde{\psi}^\theta}{\partial \eta} + \beta \nabla^2 \eta \right). \quad (80)$$

5. Momentum balance equation

$$\nabla \cdot \boldsymbol{\sigma} + \rho \mathbf{f} = \rho \dot{\mathbf{v}}. \quad (81)$$

6. Boundary conditions for the order parameter

$$\mathbf{n} \cdot \frac{\partial \psi}{\partial \nabla \eta} = H. \quad (82)$$

While the above equations are derived for an arbitrary nonlinear elasticity rule and relationship for dissipative stresses $\boldsymbol{\sigma}_d$, we specified them for linear anisotropic constitutive Eq. (79) with \mathbf{E} and \mathbf{B} for fourth-rank elastic moduli and viscosity tensors. Expressions for $\boldsymbol{\varepsilon}_t(\eta)$, $\boldsymbol{\varepsilon}_\theta(\theta, \eta)$ and $\mathbf{E}(\eta)$ are derived in Ref. [3], where a , a_θ and a_E are the material parameters and subscripts A and M designate austenite and martensite.

12. Generalization for multivariant transformations

We will use the following expression for the isotropic gradient energy [19,20]:

$$\rho_0 \psi^\nabla = \frac{\beta}{2} \left(\sum_{i=1}^n |\nabla \eta_i|^2 + b \sum_{i=1}^n \sum_{j=1, i \neq j}^n \nabla \eta_i \cdot \nabla \eta_j \right). \quad (83)$$

While in most numerical simulations $b = 0$ is used, i.e. ψ^∇ depends on the single material parameter β only, it is clear that it is impossible to vary the energy and the width of the

martensitic variant M_i – martensitic variant M_j interface independent of the energy and width of the austenite A – martensitic variant M_i interface. Substituting Eq. (83) in Eq. (25), we obtain an expression for stress tensor:

$$\boldsymbol{\sigma} = \rho_0 \frac{\partial \bar{\psi}}{\partial \boldsymbol{\varepsilon}} - \beta \sum_{i=1}^n \left(\nabla \eta_i \otimes \nabla \eta_i + b \nabla \eta_i \otimes \sum_{j=1, i \neq j}^n \nabla \eta_j \right) + \boldsymbol{\sigma}_d. \quad (84)$$

Substitution of Eq. (83) in Eq. (24) for the driving force for change in η_i , and then in the simplest Ginzburg–Landau equation $\dot{\eta}_j = L_{ij} X_i$, leads to:

$$\dot{\eta}_j = L_{ij} \left(-\rho \frac{\partial \bar{\psi}}{\partial \eta_i} + \beta (\nabla^2 \eta_i + b \sum_{k=1, k \neq i}^n \nabla^2 \eta_k) \right) L_{ij} = L_{ji}$$

$$j = 1, \dots, n. \quad (85)$$

Thus, the kinetic equations for the order parameters for $b \neq 0$ are coupled through Laplacians in addition to traditional coupling through the local energy terms and transformation strain. The expression for the Helmholtz free energy for the fifth-degree potential Eq. (12) will be accepted in the same form as in Eq. (28):

$$\bar{\psi}(\boldsymbol{\varepsilon}, \eta_i, \theta, \nabla \eta_i) = \psi^e(\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_t(\eta_i) - \boldsymbol{\varepsilon}_\theta(\theta, \eta_i), \eta_i, \theta)$$

$$+ \frac{\rho_0}{\rho} \check{\psi}^\theta + \tilde{\psi}^\theta + \frac{\rho_0}{\rho} \psi^\nabla. \quad (86)$$

To define $\check{\psi}^\theta$ and $\tilde{\psi}^\theta$, we first repeat the equation for the thermal energy derived in Ref. [4]:

$$\check{\psi}^\theta + \tilde{\psi}^\theta = \sum_{k=1}^n \left(A(\theta) \eta_k^2 (1 - \eta_k)^2 + \Delta G^\theta(\theta) \eta_k^3 (4 - 3\eta_k) \right)$$

$$+ \sum_{i=1}^{n-1} \sum_{j=i+1}^n \bar{F}_{ij}(\theta, \eta_i, \eta_j)$$

$$\bar{F}_{ij} = \eta_i \eta_j (1 - \eta_i - \eta_j) [B((\eta_i - \eta_j)^2 - \eta_i - \eta_j) + D \eta_i \eta_j]$$

$$+ (\bar{A} - A(\theta)) \eta_i^2 \eta_j^2 (\eta_i + \eta_j), \quad (87)$$

where B , D and \bar{A} are material parameters. Since in bulk, one of the order parameters is equal to one and all the others are zero, $\bar{F}_{ij} = 0$, i.e. $\bar{F}_{ij} = 0$ at the $A - M_j$ diffuse interfaces, \bar{F}_{ij} localizes at the $M_i - M_j$ diffuse interfaces, and can be included in the interface tension.

Substituting Eqs. 30, 31 and 86 in Eq. (84), we obtain for the stress tensor and its elastic and interface tension components:

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_e + \boldsymbol{\sigma}_{st} + \boldsymbol{\sigma}_d; \quad \boldsymbol{\sigma}_e = \rho_0 \frac{\partial \psi^e}{\partial \boldsymbol{\varepsilon}_e}. \quad (88)$$

$$\boldsymbol{\sigma}_{st} = \rho_0 (\psi^\nabla + \check{\psi}^\theta) \mathbf{I} - \beta \sum_{i=1}^n \left(\nabla \eta_i \otimes \nabla \eta_i + b \nabla \eta_i \otimes \sum_{j=1, i \neq j}^n \nabla \eta_j \right). \quad (89)$$

At the $M_i - M_j$ diffuse interface, all $\eta_k = 0$ for $k \neq i$ and $k \neq j$. Also: $\mathbf{n}_i = \frac{\nabla \eta_i}{|\nabla \eta_i|} = -\mathbf{n}_j = -\frac{\nabla \eta_j}{|\nabla \eta_j|}$. Consequently, at the $M_i - M_j$ diffuse interface one has:

$$\begin{aligned} \rho_0 \psi^\nabla &= \frac{\beta}{2} (|\nabla \eta_i|^2 + |\nabla \eta_j|^2 + 2b \nabla \eta_i \cdot \nabla \eta_j) \\ &= \frac{\beta}{2} (|\nabla \eta_i|^2 + |\nabla \eta_j|^2 - 2b |\nabla \eta_i| |\nabla \eta_j|). \end{aligned} \quad (90)$$

$$\begin{aligned} \sigma_{st} &= \rho_0 (\psi^\nabla + \check{\psi}_\theta) \mathbf{I} - \beta (\nabla \eta_i \otimes \nabla \eta_i + \nabla \eta_j \otimes \nabla \eta_j) \\ &\quad + 2b \nabla \eta_i \otimes \nabla \eta_j \\ &= \rho_0 (\psi^\nabla + \check{\psi}_\theta) \mathbf{I} - \mathbf{n}_i \otimes \mathbf{n}_i \beta (|\nabla \eta_i|^2 + |\nabla \eta_j|^2) \\ &\quad - 2b |\nabla \eta_i| |\nabla \eta_j| \\ &= \rho_0 (\psi^\nabla + \check{\psi}_\theta) \mathbf{I} - 2\rho_0 \psi^\nabla \mathbf{n}_i \otimes \mathbf{n}_i \\ &= 2\rho_0 \psi^\nabla (\mathbf{I} - \mathbf{n}_i \otimes \mathbf{n}_i) + \rho_0 (\check{\psi}_\theta - \psi^\nabla) \mathbf{I} \end{aligned} \quad (91)$$

Thus, the structure of the expression for surface tension for the $M_i - M_j$ diffuse interface is identical to that for the A - M interface in Eq. (34). It is not a problem to split the thermal energy into two parts to reproduce a proper expression for the interface tension for the austenite–martensite interfaces, because in this case just one order parameter is not zero and thermal energy reduces to the same form, as for a single order parameter. The main problem is that the martensite–martensite interface is described by simultaneous variation of two order parameters, and there is no analytical solution for the stationary or propagating interfaces and the expression for the interface energy and its relationship to the gradient energy. That is why we cannot find an analytical expression for $\check{\psi}_\theta$ from the condition $\check{\psi}_\theta := \psi^\nabla$ at the martensite–martensite interface that ensures biaxial tension in Eq. (91). In addition, we cannot prove that the magnitude of the surface tension is equal to the martensite–martensite interface energy. Thus, the only conditions that we will satisfy are obtaining the same expression for the interface tension for the austenite–martensite interface and that interface tension should be localized at the interfaces. One of the suggestions is:

$$\begin{aligned} \check{\psi}^\theta &= \sum_{k=1}^n (A(\theta) - 3\Delta G^\theta(\theta)) \eta_i^2 (1 - \eta_i)^2 \\ &\quad + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \bar{F}_{ij}(\theta, \eta_i, \eta_j); \\ \tilde{\psi}^\theta &= \sum_{k=1}^n \Delta G^\theta(\theta) \eta_i^2 (3 - 2\eta_i). \end{aligned} \quad (92)$$

In this case, all terms that localize at the diffuse interfaces are included in $\check{\psi}^\theta$, which is similar to the choice in Eq. (29). The term ψ^θ depends on the thermal driving force for the austenite–martensite transformation, since there is no thermal driving force for the $M_i - M_j$ transformation. However, formally, the terms \bar{F}_{ij} can be split between $\check{\psi}^\theta$ and $\tilde{\psi}^\theta$ in many ways, if some rationale could be found.

In the only works [19,20] where surface tension for multivariant transformation was considered under the assumptions in Eq. (49) and $\varpi = 1$, the following was accepted:

$$\begin{aligned} \check{\psi}^\theta &= \sum_{k=1}^n A_0 (\theta_e - \theta_c) \eta_i^2 (1 - \eta_i)^2 \\ &\quad + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \bar{F}_{ij}(\theta_e, \eta_i, \eta_j); \end{aligned} \quad (93)$$

$$\begin{aligned} \tilde{\psi}^\theta &= \sum_{k=1}^n \frac{1}{3} A_0 (\theta - \theta_e) \eta_i^2 (3 - 2\eta_i) \\ &\quad + \sum_{i=1}^{n-1} \sum_{j=i+1}^n (\bar{F}_{ij}(\theta, \eta_i, \eta_j) - \bar{F}_{ij}(\theta_e, \eta_i, \eta_j)). \end{aligned}$$

For such a choice, the temperature-independent part of all terms, which localize at the interfaces is included in $\check{\psi}^\theta$, and all temperature-dependent terms contribute to $\tilde{\psi}^\theta$. These expressions for $\theta \neq \theta_e$ do not reduce to the correct Eqs. (45) and (48) for the A - M_j interface. However, all calculations in Refs. [19,20] for $\theta = \theta_e$ are correct.

Similar to the consideration in Section 10, we obtain: $\frac{\partial \check{\psi}^\theta}{\partial \eta_i} = \frac{\partial \psi^e}{\partial \eta_i} + \frac{\rho_0}{\rho} \frac{\partial \check{\psi}^\theta}{\partial \eta_i} + \frac{\partial \psi^\theta}{\partial \eta_i}$. Then,

$$\begin{aligned} \rho \frac{\partial \psi^e}{\partial \eta_i} \Big|_{\varepsilon} &= \rho \frac{\partial \psi^e}{\partial \varepsilon_e} : \frac{\partial (\varepsilon - \varepsilon_t(\eta_i) - \varepsilon_\theta(\theta, \eta_i))}{\partial \eta_i} \Big|_{\varepsilon} + \rho \frac{\partial \psi^e}{\partial \eta_i} \Big|_{\varepsilon_e} \\ &= -\frac{\rho}{\rho_0} \sigma_e : \frac{\partial \varepsilon_t}{\partial \eta_i} - \frac{\rho}{\rho_0} \sigma_e : \frac{\partial \varepsilon_\theta}{\partial \eta_i} + \rho \frac{\partial \psi^e}{\partial \eta_i} \Big|_{\varepsilon_e}. \end{aligned} \quad (94)$$

After substitution of all contributions in the Ginzburg–Landau Eq. (85), one obtains:

$$\begin{aligned} \dot{\eta}_j &= L_{ji} \left(\frac{\rho}{\rho_0} \sigma_e : \frac{\partial \varepsilon_t}{\partial \eta_i} + \frac{\rho}{\rho_0} \sigma_e : \frac{\partial \varepsilon_\theta}{\partial \eta_i} - \rho \frac{\partial \psi^e}{\partial \eta_i} \Big|_{\varepsilon_e} \right. \\ &\quad \left. - \rho_0 \frac{\partial \check{\psi}^\theta}{\partial \eta_i} - \rho \frac{\partial \tilde{\psi}^\theta}{\partial \eta_i} + \beta \left(\nabla^2 \eta_i + b \sum_{k=1, k \neq i}^n \nabla^2 \eta_k \right) \right). \end{aligned} \quad (95)$$

Similar to the single-variant case, interface tension tensor σ_{st} and dissipative stresses do not appear in the expression for the driving force X_i , which depends only on elastic stresses σ_e . However, surface tension indirectly contributes to X_i by affecting stress distribution. Eq. (73) for entropy does not change. Note that the explicit expressions for $\varepsilon_t(-\eta_i)$ and $\varepsilon_\theta(\theta, \eta_i)$ are presented in Refs. [4,10]. All material parameters for the multivariant cubic–tetragonal phase transformations in NiAl alloys are presented in Refs. [4,10].

13. Concluding remarks

In this paper, a general continuum thermodynamic derivation of the main equations of the phase field approach to multivariant martensitic phase transformations is developed. The main focus was on the consistent introduction of the interface stress tensor that transforms to biaxial tension with a magnitude equal to the interface energy for the non-equilibrium propagating interface. It was justified that the gradient of the order parameters in the gradient energy should be evaluated in the deformed state and the gradient energy and the function $\check{\psi}$ determined by Eq. (45) should be multiplied $\rho_0/\rho = 1 + \varepsilon_0$. In such a way, we introduced

in Eq. (34) the interface tension (stress) tensor, σ_{st} , which is located at the diffuse interface ($\eta \neq 0$ and $\eta \neq 1$). For the case of a propagating plane interface, the expression for surface stresses reduces to biaxial tension with the force per unit area equal to the surface energy γ , providing the desired correspondence with a sharp-interface approach. This was achieved by utilizing an analytical solution for the nonequilibrium propagating austenite–martensite interface and determining its energy γ . The nontrivial point in the derivation is that in order to introduce the interface stresses, one has to include some geometrically nonlinear terms even if deformations are infinitesimally small. Thus, a physical phenomenon such as interface tension is introduced with the help of geometrical nonlinearity. It was also found that the interface stresses do not contribute explicitly to the Ginzburg–Landau equations. However, they change elastic stresses, which significantly affect the Ginzburg–Landau equations.

Explicit analytical expressions for energy, width, entropy excess and the distribution of the interface stresses at the nonequilibrium propagating austenite–martensite interface are derived and analyzed in detail. The distribution of the interface stress tensor for the martensitic critical nucleus is also given. In this case, an additional mean stress is acting at each point, which does not have counterparts for the sharp-interface approach. For multiple martensitic variants, we cannot unambiguously derive an expression for the interface stresses, because the martensite–martensite interface is described by two order parameters and an analytical solution for it is lacking. We did our best to suggest a consistent generalization for this case.

The developed thermodynamic approach and expression for the interface stresses are directly applicable to other temperature- and stress-induced transformations, including reconstructive phase transformations, melting/freezing [12,13,20,22,23,37], liquid–liquid transformation [31], amorphization/crystallization, evaporation, sublimation, etc.

In future work, the following generalizations can be performed. Anisotropic interface energy is usually achieved by assuming $\beta = \beta(\mathbf{n})$ [13,38]. In this case, Eq. (21) is not valid and surface tension results in a nonsymmetric stress tensor and torques the rotating interface towards a lower-energy configuration. However, any stable (i.e. non-rotating) propagating interface corresponding to a specific \mathbf{n} is described by the same analytic solution Eq. (37) with corresponding $\beta = \beta(\mathbf{n})$. Thus, the same approach is applicable, which will lead to the same expressions for ψ^θ and ψ^θ in Eq. (45).

The same approach can be applied to different thermodynamic potentials (e.g. six-degree potential, potential in hyperspherical order parameters [10,18] and two-parabola potential [34]), for which analytical solutions for a propagating interface are available. In addition, analytical solutions are available: (a) for a critical austenitic nucleus on martensite in an infinite sample [10]; for static austenite–martensite and martensite–martensite interfaces, as well as a critical nuclei in a finite sample, including nanostruc-

tures in a sample thinner than the interface width [39]; and (b) for surface-induced pre-transformed nanostructures in semi-infinite [34] and finite [35] samples. For these cases, one can also determine an analytical distribution of the components of the interface stress tensor even for cases when a complete interface is not formed. More precise expressions for the interface stresses can be introduced in numerical studies of multivariant martensitic phase transformations, twinning and melting [19,20,22,23], including surface-induced phenomena and instabilities [40]. Derived equations for the surface stresses and the Ginzburg–Landau equation can be implemented in commercial codes, e.g. COSMOL [41], which will increase the adequacy of the models in comparison with the current simplified equations. The phase field model for an external surface [21] may benefit from the more precise expression for surface tension for single and multiple martensitic variants as well. In all the above cases, the effect of a new expression for surface stresses on the elastic stresses and phase transformations is of principal importance. The combination of structural interface stresses and elastic interface stresses, which are directly determined as a result of the solution of the Ginzburg–Landau and elasticity equations, completes an advanced model for a coherent interface. Large strains and a lattice rotation formulation can be developed by utilizing approaches outlined in Refs. [16,19,36].

Similar approaches and results applicable for various phenomena are described by the phase field approach, such as various electromagnetic phase transformations [42], diffusive transformations and chemical reactions described by Cahn–Hilliard theory [43], twinning [4,10,44], evolution of multigrain structure [45], dislocation evolution [46–48], fracture in crystalline and amorphous solids and void nucleation [49], cavitation in liquids [50], and interaction cracks and dislocations with phase transformations [48,51,52].

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Appendix A

1. *Evaluating integrals for the interface energy γ .* According to definition (41)

$$\begin{aligned} \gamma := & \frac{\rho_0}{k} \int_{-\infty}^0 \psi d\zeta + \frac{\rho_0}{k} \int_0^{\infty} (\psi - \Delta G(\theta)) d\zeta = \frac{\rho_0 A(\theta)}{k} \int_{-\infty}^{\infty} \eta_{in}^2 (1 - \eta_{in})^2 d\zeta \\ & + \frac{k\beta}{2} \int_{-\infty}^{\infty} \left(\frac{d\eta_{in}}{d\zeta} \right)^2 d\zeta + \frac{\rho_0 \Delta G(\theta)}{k} \left(\int_{-\infty}^0 \eta_{in}^3 (4 - 3\eta_{in}) d\zeta + \int_0^{\infty} (\eta_{in}^3 (4 - 3\eta_{in}) - 1) d\zeta \right). \end{aligned} \quad (96)$$

Utilizing Eq. (39) and omitting in some places subscript *in*, we evaluate:

$$\begin{aligned}
\int_{-\infty}^{\infty} \eta_{in}^2 (1 - \eta_{in})^2 d\zeta &= \int_0^1 \eta(1 - \eta) d\eta = \frac{1}{6}; \\
\int_{-\infty}^{\infty} \left(\frac{d\eta_{in}}{d\zeta} \right)^2 d\zeta &= \int_0^1 \eta(1 - \eta) d\eta = \frac{1}{6}; \\
\int_{-\infty}^0 \eta^3 (4 - 3\eta) d\zeta + \int_0^{\infty} (\eta^3 (4 - 3\eta) - 1) d\zeta \\
&= \int_0^{0.5} \frac{\eta^2 (4 - 3\eta)}{1 - \eta} d\eta + \int_{0.5}^1 \frac{\eta^3 (4 - 3\eta) - 1}{\eta(1 - \eta)} d\eta = -\frac{1}{2}.
\end{aligned} \tag{97}$$

2. *Ginzburg–Landau equation for a critical nucleus.* Following, for example, Ref. [10], let us simplify the Ginzburg–Landau Eq. (36) for a stationary one-dimensional case at zero elastic stresses (i.e. $\psi^e = 0$) and $\rho \simeq \rho_0$:

$$\rho_0 \frac{\partial f}{\partial \eta} = \beta \frac{d}{dx} \frac{d\eta}{dx}. \tag{98}$$

Designating $\eta_x := \frac{d\eta}{dx}$, we will transform the Laplacian:

$$\frac{d\eta_x}{dx} = \frac{d\eta_x}{d\eta} \frac{d\eta}{dx} = \eta_x \frac{d\eta_x}{d\eta} = 0.5 \frac{d(\eta_x^2)}{d\eta} = \frac{\rho_0}{\beta} \frac{d\psi^\nabla}{d\eta}. \tag{99}$$

After substitution of Eq. (99) into the Ginzburg–Landau Eq. (98), we obtain:

$$\frac{\partial f}{\partial \eta} = \frac{d\psi^\nabla}{d\eta}. \tag{100}$$

Integrating Eq. (100) over η , one obtains:

$$0.5\beta \left(\frac{d\eta}{dx} \right)^2 = \rho_0 (f(\theta, \eta) - f_0), \tag{101}$$

where f_0 is the integration constant. Let us consider for $\theta \leq \theta_e$ a critical M nucleus within an A matrix with the boundary conditions $\eta_c(\pm\infty) = 0$ [10]. Since $\frac{d\eta}{dx}(\pm\infty) = 0$ and $f(\theta, 0) = 0$, substituting the boundary condition in Eq. (101) results in $f_0 = 0$.

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