Full length article

Multiphase phase field theory for temperature-induced phase transformations: Formulation and application to interfacial phases

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A B S T R A C T

The main conditions for the thermodynamic potential for multiphase Ginzburg—Landau theory are formulated for temperature-induced phase transformations (PTs). Theory, which satisfies all these conditions for $n-$ phase material, is developed. The key point is a new penalizing term in the local energy that allows controlling absence or presence and the extent of the presence of the third phase within the interface between two other phases. A finite-element method is applied for studying PT between β and δ phases of HMX energetic crystal via intermediate melting more than $100°$C below melting temperature. Depending on material parameters (ratio of the width and energy of the solid—solid (SS) to solid—melt interface and the magnitude of the penalizing term), there are either two (meta)stable stationary interfacial nanostructures, corresponding to slightly and strongly disordered interfaces (in the limits, pure SS interface or complete melt within SS interface), or these nanostructures coincide. A parametric study of these nanostructures is presented. The developed requirements and approach are applicable to various PTs between multiple solid and liquid phases and can be elaborated for PTs induced by mechanical and electromagnetic fields, diffusive PTs, and the evolution of multi-grain and multi-twin microstructures.

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1. Introduction

While in this paper we focus on the temperature-induced multiphase PTs, we will mention some works which include stresses as well, because these theories reduce to the temperature-induced PTs at zero stresses. The main focus is on the description of the first-order PTs for the case when a PT completes and there are no structural changes after completing PT, like for melting, martensitic PTs, and some reconstructive PTs. The main problem is to develop a consistent phase field approach (PFA) for PTs between an arbitrary number of phases. There are two very different approaches with different goals developed by two different communities. The first one is favored within the community working on the description of PTs between the austenite (A) and any of the n martensitic variants M_i and between martensitic variants $M_j \leftrightarrow M_i$ (which represents twinning in most cases) [1—8]. It utilizes n independent order parameters η_i, each of which describes A$\leftrightarrow$M$_i$ PTs between $n + 1$ phases. In most papers, researchers work within this

approach at the actual spatial scales, rather than within coarse-grained theories for the microscale. Thus, typical actual interface width is on the order of nanometers and detail of distribution of all parameters within the interface are of interest. That is why all simulations are limited to submicron samples.

The second multiphase approach is developed within the community working on multiphase solidification (e.g., in eutectic and peritectic systems) and grain growth [9—18]. It operates with $n + 1$ order parameters η_i satisfying constraint $\sum \eta_i = 1$, similar to phase concentrations. In most of these theories interface width artificially increased by several orders of magnitude (see, e.g. Refs. [11,16,17], or microscale theories [19,20]), and detail of variation of material parameters and fields across an interface are unrealistic but this is not important for the chosen objectives. This is done in order to be able to treat much larger samples comparable to those relevant for studying solidification of actual materials.

Each of these approaches satisfies some important requirements formulated to achieve some specific goals and have their advantages and drawbacks. They will be analyzed in Appendix A and it will be shown that none of them meets all the desired requirements. Two of the requirements, which were imposed in the

second approach and ignored in the first approach, are that each of the two-phase PTs should be described by a single order parameter and that an interface between any of the two phases should not contain the third phase [16–18,21]. These conditions are, in particular, required in order to have the possibility to obtain an analytical solution for a propagating interface, which can be used to calibrate parameters of the thermodynamic potential in terms of interface energy, width, and mobility that are assumed to be known. In the coarse-grained approach computational interface width is usually used, which may be larger than the physical width by several orders of magnitude, but keeps the same (i.e., independent of the interface width) energy and mobility. If the order parameter corresponding to the third phase appears within an interface between two other phases, then (as it follows from the thin-interface consideration [16,17,22,23]) a solution depends on the interface width, which due to unphysical width leads to incorrect results. Thus, PT between each of the two phases should occur along the straight line (or any line, which is independent of temperature, e.g., circle [8,24–27]) in the order parameter space. Since a single constraint $\sum \eta_i = 1$ does not lead to such a transformation path, additional efforts are made to satisfy these two conditions [16–18]. These efforts, however, do not completely solve the problem either. Note that the requirement that PT criteria should follow from the thermodynamic instability conditions accepted in Refs. [1,2,8] for the first approach was never used for the second approach [9,11,16–18]. Hyperspherical order parameters and a nonlinear constraint were suggested in Refs. [8,28] for multivariant martensitic PTs.

In the paper, we explicitly formulate all requirements, which we want to satisfy, first for two-phase PFA, then for an arbitrary number of phases. Then we develop a theory, which satisfies all these requirements. Instead of imposing constraints on the order parameter, we introduce simple terms penalizing deviation of the paths in the order parameter space from the straight lines connecting *each of the two phases*. By controlling these terms, we can either fully avoid a third phase within an interface between two other phases or allow it in order to describe the actual physical situation [24–27,29–31]. Comparison with previous requirements is performed. A number of model problems for a solid–solid PT via intermediate melting (*IM*) in HMX energetic material are solved and analyzed. Note that a similar approach, but without proper justification and with emphases on stress-induced PTs and twinning, when the third phase is excluded from the interface between two other phases, was presented in Ref. [32]. Detailed comparison of existing model with present model was presented in Appendix A.

2. Two-phase model

2.1. Ginzburg–Landau equation

The free energy ψ, dissipation rate D (both per unit mass), and Ginzburg–Landau equation for a single order parameter η have the form

$$\psi = \psi^{\theta}(\theta, \eta) + 0.5\beta\left|\nabla\eta\right|^2; \quad D = X\dot{\eta} \geq 0; \tag{1}$$

$$\dot{\eta} = LX = -L\frac{\delta\psi}{\delta\eta} = L\left(-\frac{\partial\psi^{\theta}}{\partial\eta} + \beta\nabla^2\eta\right), \tag{2}$$

where ψ^{θ} is the local thermal (chemical) energy, $\beta > 0$ and $L > 0$ are the gradient energy and kinetic coefficients, X is the thermodynamic driving force conjugate to $\dot{\eta}$, and $\frac{\delta}{\delta}$ is the variational derivative. Our goal is to formulate requirements to $\psi^{\theta}(\theta, \eta)$ and some interpolation functions and find the simplest function that satisfies

these requirements. Since all requirements are for homogeneous states, the gradient-related term in X can be omitted.

2.2. Conditions for free energy for bulk phases

1. We would like to enforce that $\eta = 0$ corresponds to the phase P_0 and $\eta = 1$ corresponds to the phase P_1. It is convenient to express any material property M (energy, entropy, specific heat, and when mechanics is included, also elastic moduli and thermal expansion) in the form

$$M(\eta, \theta) = M_0(\theta) + (M_1(\theta) - M_0(\theta))\varphi_m(\eta), \tag{3}$$

where M_0 and M_1 are values of the property M in phases P_0 and P_1, respectively, and $\varphi_m(\eta)$ is the corresponding interpolation function, which satisfies evident conditions

$$\varphi_m(0) = 0, \quad \varphi_m(1) = 1. \tag{4}$$

In application to free energy, we obtain

$$\psi^{\theta}(\theta, 0) = \psi_0^{\theta}(\theta), \quad \psi^{\theta}(\theta, 1) = \psi_1^{\theta}(\theta), \tag{5}$$

where $\psi_0^{\theta}(\theta)$ and $\psi_1^{\theta}(\theta)$ are the free energies of the bulk phases P_0 and P_1. However, it is not sufficient to verbally impose that $\eta = 0$ corresponds to the phase P_0 and $\eta = 1$ corresponds to the phase P_1. This should directly follow from the thermodynamic equilibrium conditions, because bulk phases should be thermodynamic equilibrium solutions of the Ginzburg–Landau Eq. (2).

2. Values $\eta = 0$ and $\eta = 1$ should satisfy the thermodynamic equilibrium conditions

$$X = -\frac{\partial\psi^{\theta}(\theta, 0)}{\partial\eta} = -\frac{\partial\psi^{\theta}(\theta, 1)}{\partial\eta} = 0 \tag{6}$$

for *any temperature* θ. Otherwise, thermodynamic equilibrium values of the order parameters obtained from condition $X = 0$ will depend on temperature. Substituting them in Eq. (3) will introduce artificial temperature dependence of the property M and will not allow us to obtain known properties M_0 and M_1 for bulk phases P_0 and P_1. It also follows from Eq. (6) that for any material property which participates in ψ^{θ}, one has

$$\frac{d\varphi_m(0)}{d\eta} = \frac{d\varphi_m(1)}{d\eta} = 0. \tag{7}$$

3. The free energy should not possess unphysical minima for any temperature. Any minimum in the free energy that does not correspond to the desired minima for phases P_0 and P_1 represents a spurious (unphysical) phase. It cannot be interpreted as a "discovery" of a new phase, because it is just consequence of chosen polynomial approximation rather than any physical knowledge. In particular, one can "discover" as many new phases as he/she wishes, if some periodic function of the order parameters is added to the potential.

The smallest degree potential that satisfies all these properties is the fourth degree. Thus, starting with the full fourth degree polynomial $\varphi = h + g\eta + a\eta^2 + b\eta^3 + c\eta^4$ and applying conditions 1–3, one obtains: