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Phase field modeling of solidification under stress

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We consider a phase field model that includes a stress field during nonisothermal phase transformation of a single-component system. The model is applied to the solidification and melting of confined spherical volumes, where sharp interface solutions can be obtained and compared with the results of the phase field simulations. Numerical solutions to the phase field model for a spherically symmetric geometry have been obtained, with particular emphasis on the computation of surface energy, surface stress, and surface strain. The analysis of the equilibrium states for the phase field model allows us to obtain the value of the surface energy in the presence of stress, which can then be compared to the analogous calculation of the energy of a planar liquid-solid interface. It is also demonstrated that modeling the liquid as a solid with zero shear modulus is realistic by comparing the long-range stress fields in phase field calculations with those calculated using sharp interface models of either a coherent or a relaxed liquid-solid interface.

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I. INTRODUCTION

Transformations between crystalline and amorphous states in nanovolumes are basic mechanisms of modern phase-change recording technology. This process exploits an amorphous-to-crystalline phase change to record information onto electronic media such as DVDs. Due to the density difference between phases, transformations in confined volumes are accompanied by internal stresses; thus, it is necessary to take into account the effect of internal stress during phase-change recording. In this paper we propose to study this "writing" process by drawing an analogy to the related process of melting and solidification in a confined volume. We employ a phase field model, which is an effective approach for the analysis and prediction of the evolution of complex microstructures during phase transformations. This approach has been particularly successful when it has been applied to solidification problems (see, e.g., Refs. 1–4). For a single-component system the phase field method requires solving two equations: the time-dependent Ginsburg-Landau phase field equation and the equation of heat transfer.

Another area of the successful application of phase field modeling is solid-solid phase transformations. In this case isothermal conditions are usually considered, and the problem is reduced to solving the phase field equation together with equations of elasticity for the strain and stress fields. Most of the published work in this area considers a homogeneous solid, neglecting the difference between the elastic properties of the phases (see, e.g., Refs. 5–7). Including elastic inhomogeneity in a phase field model presents an additional challenge. In Ref. 8 this was accomplished for systems in which the elastic inhomogeneity does not evolve with time.

The main goal of this paper is to study a phase field model that includes a stress field to describe the nonisothermal solidification of a single-component system. The stresses can be external or internal, i.e., they can arise as a result of boundary conditions at the external surface or they can be the result of elastic interactions between the phases. Thus, the phase field model should take into account the simultaneous evolution of three fields: a phase field (or an order parameter), a temperature field, and a stress-strain field. We place particular emphasis on the formulations of surface energy, surface stress, and surface strain that arise in phase field models of this type.

To demonstrate this approach we consider the solidification and melting of a confined sphere. For this simple system complete numerical solutions taking into account the time-space evolution of temperature, order parameter, and stress-strain field are obtained. The simulations show that, for some initial conditions and boundary conditions, the evolution of a spherically symmetric system results in a steady state corresponding to a uniform temperature and a time-independent distribution of the order parameter. Comparison of the results of the phase field model to the thermodynamic analysis of a sharp interface model shows that these steady states are equilibria representing phase transformations in a system with fixed volume. The analysis of these equilibrium states allows us to estimate the value of surface energy, which is then verified by a phase field calculation of the energy of a planar liquid-solid interface. The model represents the liquid-solid system as a coherent mixture, with the liquid phase approximated as an elastic solid with zero shear modulus. This type of treatment has been used before,[9–11] but here we provide an additional justification: we argue that the liquid in a two-phase solid-liquid system may be modeled as a solid with complete relaxation of shear stresses. A sharp interface model of a completely relaxed solid inclusion has been considered by Nabarro[12] and Kroner.[13] In recent work Hoyt[14] considers the related problem of the effects of stress on the equilibrium melting point of liquids confined to nanosized pores. Using a sharp interface model, he considers a hydrostatic state consisting of a liquid pore that also contains a spherical solid inclusion, and demonstrates that an elevation of melting point can be obtained that is consistent with recent experimental observations. The effect of plastic relaxation on the stress state and equilibrium of an incoherent solid inclusion was considered in Refs. 15 and 16 and it has been demonstrated that these characteristics are different from those of a coherent one.[17] The treatment of a liquid-solid system as a coherent mixture assumes that the stress fields in a coherent system and in a relaxed system are the same if the shear modulus of the liquid phase in the coherent system approaches zero. Consideration of the solidification and melting of a confined spherical volume with a sharp interface between the phases allows us to validate this assumption. We also verify that modeling the liquid as a coherent solid with zero shear modulus is reasonable by comparing the long-range stress fields in phase field calculations with those calculated using sharp interface models of either a coherent or a relaxed liquid-solid interface.

The plan of the paper is as follows. In the next section we give the general development of the phase field model. In Sec. III we describe the planar equilibrium state for our model and define appropriate surface quantities. The formulation of the model in a spherical geometry is given in Sec. IV. Numerical solutions for the spherical geometry are presented in Sec. V. A discussion is provided in Sec. VI, with concluding comments in Sec. VII. The sharp interface version of the spherical problem is summarized in the Appendix for comparison with the phase field approach.

II. GENERAL DEVELOPMENT OF THE PHASE FIELD MODEL

In this section we develop and discuss a phase field model describing the solidification and melting of a single-component system in the presence of stress. The system is characterized by an order parameter $\eta(x_i,t)$, temperature $T(x_i,t)$, and displacement field $u_j(x_i,t)$, which are functions of the spatial coordinates x_i and time t, for $i=1,2,3$. The free energy of the two-phase system is given by the functional

$$\mathcal{F}=\int_V\Bigg(f(\eta(x_i,t),T(x_i,t))+\frac{\beta}{2}[\boldsymbol{\nabla}\eta(x_i,t)]^2 + e(\boldsymbol{\nabla}u_j(x_i,t),\eta(x_i,t))\Bigg)dV. \tag{1}$$

Here $f(\eta,T)$ is a double-well free-energy density with two minima at $\eta=0$ and 1 corresponding to the bulk liquid and solid phases, respectively. The difference in energy between the two minima, Δf, depends on temperature, and vanishes at the equilibrium temperature T_0 defined by the state $f(0,T_0)=f(1,T_0)$ (see Fig. 1). Note that, due to the presence of stress, T_0 will in general be different from the stress-free bulk melting temperature. The second term in Eq. (1) is the gradient energy, associated with interfaces, where β is termed the gradient energy coefficient. The third term is an elastic energy density of the two-phase system, depending on η and the gradient of the displacement field u_j.

The order parameter is assumed to satisfy the time-dependent Ginsburg-Landau equation (relaxational dynamics)

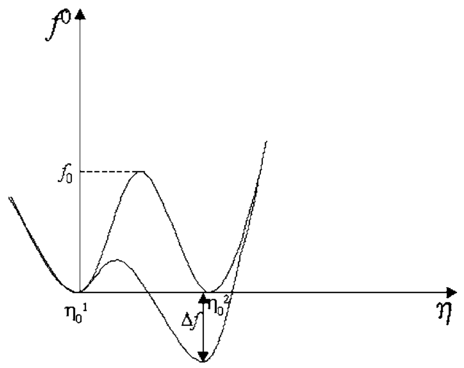

FIG. 1. Dependence of the free energy on temperature. If the temperature T differs from the equilibrium phase temperature T_0, the free energies of the initial phase at η_0^1 and the product phase at η_0^2 are unequal. For $T=T_0$, the difference in free energies vanishes, $\Delta f=0$.

$$\frac{\partial\eta}{\partial t}=-M_\eta\frac{\delta\mathcal{F}}{\delta\eta} \tag{2}$$

where M_η is a mobility coefficient. The temperature field satisfies the equation of heat conduction with a source term[1]

$$\frac{\partial T}{\partial t}=\boldsymbol{\nabla}\cdot(k\,\boldsymbol{\nabla}\,T)+\frac{L_V}{c}\frac{\partial\eta}{\partial t} \tag{3}$$

where k is the thermal diffusivity coefficient, L_V is the latent heat per unit volume, and c is the heat capacity.

For simplicity we assume that elastic equilibrium is maintained during the evolution of the order parameter. However, we note that the mobility M_η can be related to interface attachment kinetics, which is often estimated to be on the order of the speed of sound in the material, so the approximation of elastic equilibrium may be inapplicable in some cases. Nevertheless, with this assumption, the displacement field is determined by the equations of mechanical equilibrium,

$$0=\frac{\delta\mathcal{F}}{\delta u_i}=\frac{\partial}{\partial x_j}\frac{\delta\mathcal{F}}{\delta\varepsilon_{ij}}=\frac{\partial\sigma_{ij}}{\partial x_j}, \tag{4}$$

where ε_{ij} is the total strain tensor, and σ_{ij} is the stress tensor, defined by

$$\varepsilon_{ij}=\frac{1}{2}\left(\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}\right),\quad \sigma_{ij}=\frac{\delta\mathcal{F}}{\delta\varepsilon_{ij}}. \tag{5}$$

The stress and strain are related though a constitutive law, typically Hooke's law:

$$\sigma_{ij}=C_{ijlm}(\eta)[\varepsilon_{lm}-\varepsilon^0_{lm}(\eta)], \tag{6}$$

where $C_{ijlm}(\eta)$ is the elastic modulus tensor. In general C_{ijlm} will be different in the two phases and is thus a function of η. Here, $\varepsilon^0_{lm}(\eta)$ is the stress-free strain tensor associated with the phase transition, and therefore $[\varepsilon_{lm}-\varepsilon^0_{lm}(\eta)]$ is the elastic strain tensor. The elastic energy density e_{el} can be expressed through the strains as

$$e_{el} = \frac{1}{2}[\varepsilon_{ij} - \varepsilon^0_{ij}(\eta)]C_{ijlm}(\eta)[\varepsilon_{lm} - \varepsilon^0_{lm}(\eta)]. \tag{7}$$

For an isotropic material C_{ijlm} depends solely on the bulk modulus K and shear modulus μ, so we can write

$$e_{el} = \frac{K}{2}[\varepsilon_{ll} - \varepsilon^0_{ll}(\eta)]^2 + \mu\left([\varepsilon_{ik} - \varepsilon^0_{ik}(\eta)] - \frac{1}{3}\delta_{ik}[\varepsilon_{ll} - \varepsilon^0_{ll}(\eta)]\right)^2. \tag{8}$$

Solving Eqs. (2)–(4) with appropriate boundary and initial conditions, one can find the evolution of the order parameter, temperature, and stress-strain during the transformation.

To apply this model we chose the following form for the bulk free-energy density:

$$f(\eta,T) = f^0(\eta) + \Delta f p(\eta), \quad \Delta f = L_V\frac{(T-T_0)}{T_0}, \tag{9}$$

where

$$f^0(\eta) = 16 f_0 \eta^2(1-\eta)^2, \tag{10}$$

$$p(\eta) = \eta^3(10 - 15\eta + 6\eta^2). \tag{11}$$

Here T_0 is the bulk melting temperature of the unstressed material, q is the latent heat of solidification per unit volume, f_0 characterizes the height of the energy barrier between liquid and solid for $T=T_0$, and $p(\eta)$ is a smooth interpolation function with $p(0)=0$ and $p(1)=1$. The specific form of the function $p(\eta)$ ensures that the positions of the minima remain at $\eta=0$ and 1 for all temperatures.[1]

To model the effects of stress on liquid-solid coexistence, we assume the shear modulus of the liquid is equal to zero, i.e., $\mu(\eta)=\mu_S p(\eta)$, where μ_S is the shear modulus of the solid with the function $p(\eta)$ used to preserve the location of the minima at $\eta=0$ and 1 for all stresses as well as all temperatures. The bulk modulus K is assumed to be equal in the liquid and solid. The stress-free strain, which arises when the volume changes during the phase transition, is modeled as a pure dilatation,

$$\varepsilon^0_{ij}(\eta) = \varepsilon^0(\eta)\delta_{ij} = \varepsilon_0[1 - p(\eta)]\delta_{ij}, \tag{12}$$

so that the stress-free strain is isotropic, vanishes in the solid, and is ε_0 in the liquid. The unstressed solid phase is taken as the reference state.

Having specified our model, we now examine its properties in one-dimensional geometries. First, we analytically compute steady-state solutions for a planar geometry, and then examine the problem of solidification and melting of a confined sphere. The time-dependent phase field model is used to find the steady states (i.e., as $t\to\infty$), which are then compared with sharp interface results of the same system.

III. PLANAR EQUILIBRIUM AND SURFACE QUANTITIES

We first consider the phase field description of a stationary planar interface described by the one-dimensional phase field profile $\eta=\eta(z)$, where the bulk liquid region with $\eta\approx 0$ corresponds to $z\to\infty$ and the solid region with $\eta\approx 1$ corresponds to $z\to-\infty$; the interfacial region where $\eta(z)$ varies between zero and unity is assumed to be localized near $z=0$.

A. Axial stress and biaxial strain

Elastic equilibrium solutions can be found by assuming a uniform axial stress field $\sigma_{zz}=\tau_0$, and a uniform biaxial strain field $\varepsilon_{xx}=\varepsilon_{yy}=\varepsilon_S$, where τ_0 and ε_S are constants. This state is useful for making comparisons with more general curved geometries, where the local axial stress and biaxial strain relative to the interface normal can be used to define surface excess quantities such as surface energy and surface strain.

In the planar geometry, the transverse coordinates x and y and the axial coordinate z are principal axes of the system. By examining the stress-strain relation $\sigma_{jk}=\lambda(\eta)\varepsilon_{ll}\delta_{jk}+2\mu(\eta)\varepsilon_{jk}-[3\lambda(\eta)+2\mu(\eta)]\varepsilon^0(\eta)\delta_{jk}$, where $\lambda(\eta)=K-2\mu(\eta)/3$ and $\mu(\eta)$ are the Lamé coefficients, the remaining components of the stress and strain fields are given by

$$\sigma_{xx} = \sigma_{yy} = \frac{\lambda}{[\lambda+2\mu]}\tau_0 + Y(\varepsilon_S - \varepsilon^0), \tag{13}$$

$$\varepsilon_{zz} = \frac{1}{[\lambda+2\mu]}\tau_0 + \frac{[3\lambda+2\mu]}{[\lambda+2\mu]}\varepsilon^0 - \frac{2\lambda}{[\lambda+2\mu]}\varepsilon_S \tag{14}$$

where $Y=Y(\eta)$ is given by

$$Y = \frac{2\mu(3\lambda+2\mu)}{(\lambda+2\mu)} = \frac{18\mu K}{(3K+4\mu)}. \tag{15}$$

The corresponding elastic energy density e_{el} is given by

$$e_{el}(\eta) = \frac{1}{2[\lambda(\eta)+2\mu(\eta)]}\tau_0^2 + Y(\eta)[\varepsilon_S - \varepsilon^0(\eta)]^2. \tag{16}$$

To describe the phase equilibrium of the planar elastic system considered here, we consider the thermodynamic potential defined by[18]

$$\psi = (f + e_{el}) - \sigma_{zz}\varepsilon_{zz}. \tag{17}$$

This potential satisfies

$$d\psi = -s\,dT + \sigma_{xx}d\varepsilon_{xx} + \sigma_{yy}d\varepsilon_{yy} - \varepsilon_{zz}d\sigma_{zz}, \tag{18}$$

and is therefore the appropriate choice for the conditions of uniform axial stress and biaxial strain; this potential is uniform at equilibrium in the situation we consider here. The relation $\psi^{(S)}=\psi^{(L)}$ for our model leads to the equation

$$\frac{L_V(T-T_0)}{T_0} = \left[\frac{-\tau_0^2}{2(\lambda+2\mu)} + Y(\varepsilon_S - \varepsilon^0)^2 - \frac{(3\lambda+2\mu)}{(\lambda+2\mu)}\tau_0\varepsilon^0 + \frac{2\lambda}{(\lambda+2\mu)}\varepsilon_S\tau_0\right]_S^L, \tag{19}$$

where $[B]_S^L=B_L-B_S$ is the jump from liquid to solid bulk values. This expression gives the change in equilibrium temperature due to the various elastic effects.

The surface energy can be viewed as a surface excess of the potential ψ, and is defined by

$$\gamma = \int_{-\infty}^{\infty} \left(\frac{\beta}{2}\eta_z^2 + [(f + e_{el}) - (f^L + e_{el}^L)] - \sigma_{zz}[\varepsilon_{zz} - \varepsilon_{zz}^L] \right) dz. \tag{20}$$

The surface energy is a function of the control parameters T, τ_0, and ε_S. These parameters are not all independent, but are related by the equilibrium condition $\psi^{(S)}=\psi^{(L)}$, which leads to the relation

$$0 = -[s^{(S)} - s^{(L)}]\delta T + 2[\sigma_{xx}^{(S)} - \sigma_{xx}^{(L)}]\delta\varepsilon_S - [\varepsilon_{zz}^{(S)} - \varepsilon_{zz}^{(L)}]\delta\tau_0. \tag{21}$$

Following the procedures by Cahn *et al.* in Refs. 19–21, we can derive an expression for the variation of surface energy with the applied axial stress and biaxial strain,

$$d\gamma = 2\delta\varepsilon_S \int_{-\infty}^{\infty} \left[[\sigma_{xx}(z) - \sigma_{xx}^{(L)}] - \left(\frac{\sigma_{xx}^{(S)} - \sigma_{xx}^{(L)}}{s^{(S)} - s^{(L)}} \right) [s(z) - s^{(L)}] \right] dz - \delta\tau_0 \int_0^L \left[[\varepsilon_{zz}(z) - \varepsilon_{zz}^{(L)}] - \left(\frac{\varepsilon_{zz}^{(S)} - \varepsilon_{zz}^{(L)}}{s^{(S)} - s^{(L)}} \right) [s(z) - s^{(L)}] \right] dz, \tag{22}$$

in which we have eliminated the thermal variation δT by using Eq. (21). The coefficients that multiply $2\delta\varepsilon_S$ and $\delta\tau_0$ in Eq. (22) are the appropriate definitions of the surface excess biaxial stress and the surface excess axial strain for our case, which are independent of dividing surface conventions.

B. Biaxial strain with no axial stress

We next consider in more detail the case with no axial stress, $\tau_0=0$; the elastic energy is then due solely to the applied biaxial strain. The stress is then given by

$$\sigma_{xx} = \sigma_{yy} = Y(\eta)[\varepsilon_S - \varepsilon^0(\eta)], \tag{23}$$

and the elastic energy density becomes

$$e = Y(\eta)[\varepsilon_S - \varepsilon^0(\eta)]^2. \tag{24}$$

The surface energy reduces to

$$\gamma = \int_{-\infty}^{\infty} \left[F(\eta,T) + \frac{1}{2}\beta\left(\frac{d\eta}{dx}\right)^2 \right] dx, \tag{25}$$

where F, the bulk free energy density including elastic contributions, is given by

$$F(\eta,T) = f^0(\eta) + L_V\frac{(T-T_0)}{T_0}p(\eta) + Y(\eta)[\varepsilon_S - \varepsilon^0(\eta)]^2. \tag{26}$$

The equilibrium equation

$$0 = \frac{\delta\mathcal{F}}{\delta\eta} = \frac{dF}{d\eta} - \beta\frac{d^2\eta}{dx^2} \tag{27}$$

then admits a first integral,

$$F(\eta,T) - \frac{1}{2}\beta\left(\frac{d\eta}{dx}\right)^2 = F(1,T) = F(0,T), \tag{28}$$

where the integration constant is given by either of the far-field values of $F(\eta,T)$, which must therefore be equal. Since in our model we have $f_0(0)=p(0)=Y(0)=0$, we have $F(0,T)=0$. The equilibrium temperature in the presence of biaxial strain then satisfies

$$L_V\frac{(T-T_0)}{T_0} = -\frac{18\mu_S K\varepsilon_S^2}{(3K+4\mu_S)} \tag{29}$$

where we have used $\varepsilon^0(1)=0$ and the definition of $Y(1)$ given by Eq. (15). Using the first integral in Eq. (28) with $F(0,T)=0$, the surface energy is then given explicitly by

$$\gamma = \int_{-\infty}^{\infty} \beta\left(\frac{d\eta}{dx}\right)^2 dx = \beta^{1/2}\int_0^1 \sqrt{2F(\eta,T)}d\eta, \tag{30}$$

and the solution for the phase field reduces to quadrature,

$$x - x_0 = \beta^{1/2}\int_{1/2}^{\eta} \frac{d\eta}{\sqrt{2F(\eta,T)}}. \tag{31}$$

By using Eq. (22) with $\tau_0=0$, or directly by differentiating Eq. (30), we find that

$$\frac{\partial\gamma}{\partial\varepsilon_S} = 2\int_{-\infty}^{\infty} [\sigma_{xx}(\eta) - \sigma_{xx}(1)p(\eta)]dx. \tag{32}$$

This integral is the appropriate definition of surface stress in our case and is independent of a dividing surface convention.

C. No biaxial strain or axial stress

In the absence of axial stress ($\tau_0=0$) and biaxial strain ($\varepsilon_S=0$), and with no stress-free stain ($\varepsilon_0=0$), the elastic energy vanishes and the phase field, surface energy, and interface width ℓ reduce to the forms

$$\eta(z) = \frac{1}{2}\left(1 - \tanh\left[\frac{z}{\ell}\right]\right), \tag{33}$$

$$\gamma = \frac{2}{3}\sqrt{2\beta f_0}, \tag{34}$$

$$\ell = \frac{1}{4}\sqrt{2\beta/f_0}. \tag{35}$$

IV. PHASE FIELD MODEL IN A SPHERICAL GEOMETRY

With spherical symmetry the displacement has only a radial component. In spherical coordinates the equations of equilibrium $\partial\sigma_{ik}/\partial x_i=0$ reduce to

$$\frac{1}{r^2}\frac{d}{dr}(r^2\sigma_{rr}) - \frac{2}{r}\sigma_{\varphi\varphi} = 0. \tag{36}$$

Using the relationships

$$\varepsilon_{rr}=\frac{du}{dr},\quad \varepsilon_{\varphi\varphi}=\varepsilon_{\theta\theta}=\frac{u}{r}, \tag{37}$$

where u is the radial displacement, the constitutive law for stress in the isotropic case takes the form

$$\sigma_{rr}=K[\varepsilon_{ll}-\varepsilon_{ll}^{0}(\eta)]+\frac{4}{3}\mu(\eta)[\varepsilon_{rr}-\varepsilon_{\varphi\varphi}],$$

$$\sigma_{\varphi\varphi}=\sigma_{\theta\theta}=K[\varepsilon_{ll}-\varepsilon_{ll}^{0}(\eta)]-\frac{2}{3}\mu(\eta)[\varepsilon_{rr}-\varepsilon_{\varphi\varphi}]. \tag{38}$$

The equilibrium stress equation (36) can therefore be rewritten in terms of the displacement:

$$\left(K+\frac{4}{3}\mu(\eta)\right)\frac{d}{dr}\left(\frac{du}{dr}+2\frac{u}{r}\right)+\frac{4}{3}\frac{d\mu(\eta)}{dr}\left(\frac{du}{dr}-\frac{u}{r}\right)=K\frac{d\varepsilon_{ll}^{0}(\eta)}{dr}. \tag{39}$$

This equation coincides with the equilibrium equation used in Ref. 14, where the radially stressed sphere was considered in the case that the shear modulus does not depend on the order parameter.

By using Eqs. (1), (8), and (37), the free energy for the spherical solid-liquid system including elastic energy can be written as

$$\mathcal{F}=4\pi\int_{0}^{R}\left[f(\eta,T)+\frac{\beta}{2}\left(\frac{d\eta}{dr}\right)^{2}+\frac{K}{2}\left(\frac{du}{dr}+\frac{2u}{r}-\varepsilon_{ll}^{0}(\eta)\right)^{2}+\frac{2}{3}\mu(\eta)\left(\frac{du}{dr}-\frac{u}{r}\right)^{2}\right]r^{2}dr. \tag{40}$$

Here, we are assuming that no external work is done at the surface $r=R$.

The order parameter η should satisfy the time-dependent Ginsburg-Landau evolution equation (2):

$$\frac{\partial\eta}{\partial t}=-M_{\eta}\left[\frac{\partial f}{\partial\eta}-\frac{\beta}{r^{2}}\frac{d}{dr}\left(r^{2}\frac{d\eta}{dr}\right)-K\left(\frac{du}{dr}+\frac{2u}{r}-\varepsilon_{ll}^{0}(\eta)\right)\frac{d\varepsilon_{ll}^{0}(\eta)}{d\eta}+\frac{2}{3}\frac{d\mu(\eta)}{d\eta}\left(\frac{du}{dr}-\frac{u}{r}\right)^{2}\right], \tag{41}$$

while the temperature field should satisfy the equation of heat conduction, which in spherical coordinates with constant conductivity becomes

$$\frac{\partial T}{\partial t}=k\left(\frac{\partial^{2}T}{\partial r^{2}}+\frac{2}{r}\frac{\partial T}{\partial r}\right)+\frac{L_V}{c}\frac{\partial\eta}{\partial t}. \tag{42}$$

V. NUMERICAL RESULTS

We next present some numerical solutions for Eqs. (39), (41), and (42), corresponding to the problems of solidification or melting of a confined sphere from the outer surface.

A. Kinetics of the solidification or melting of a confined sphere

We consider the solidification or melting of a confined sphere with zero displacement specified at the outer surface $r=R$. To initiate the transition we fix values of the temperature $T_S\equiv T(R)$ and the order parameter $\eta_S\equiv\eta(R)$. Imposing the fixed-order-parameter boundary condition directly allows us to avoid the issue of inducing nucleation of one phase within the other. This restriction, however, may prevent the system from reaching a lower-energy state that does not contain any of the phase imposed by the boundary condition. This will be discussed later in more detail.

The calculations were performed using a time-dependent finite-difference method with 1000 mesh points in the radial direction. The dimensionless gradient coefficient is given by $\beta/(R^2 f_0)=0.002$, and with the following elastic properties: dimensionless bulk modulus in both phases, $K\varepsilon_0^2/f_0=0.22$; Poisson ratio in the solid phase, $\nu=1/3$; latent heat $L_V/f_0=2.5$, $L_V/(cT_0)=0.3$. The simulations were performed with a time step of 10^{-6}, and relaxation time parameter $M=0.01$. For these parameters the planar interface width given by Eq. (35) is $\ell=0.016R$, so that the interface is well resolved by 1000 mesh points.

We first consider the melting of a solid sphere. The boundary conditions imposed at the surface are $\eta_S=0$ (liquid) and a surface temperature $T_S>T_0$. The initial temperature of the sphere is $T_{init}<T_0$. We analyze the process of melting for different choices of the surface temperature T_S. At each temperature, the numerical solutions of Eqs. (41) and (42) describe the time evolution of the order parameter and temperature in each point of the sphere. The location of the solid-liquid interface is determined as the radius where $\eta=1/2$.

Two cases with a fixed $T_{init}/T_0=0.7$ are shown in Figs. 2 and 3. At $T_S/T_0=1.3$, melting occurs, and a two-phase coexistence is established at late times. At the higher surface temperature $T_S/T_0=1.75$, the final state is all liquid. Our simulations show that two-phase equilibria can be found up to the temperature $T_S/T_0\approx 1.65$. The fraction of the liquid phase, α_0, gradually increases with temperature from 0 to 0.84 as $T_S/T_0\rightarrow 1.65$, whereafter α_0 jumps discontinuously to unity (Fig. 4).

We now consider the converse problem of solidification from the outer surface. Because the displacement at the surface is zero, the liquid will be under stress. We thus set $\eta_S=1$, and the results are shown in Figs. 5 and 6. For these cases the initial temperature is set above T_0, specifically $T_{init}/T_0=1.8$, for two different surface temperatures of $T_S/T_0=1.5$ and 1.2. For the case $T_S/T_0=1.5$, the final state exhibits two-phase coexistence (Fig. 5), while for $T_S/T_0=1.2$ the sphere is solidified completely (Fig. 6). Two-phase states exist at temperatures lower than $T_S/T_0\approx 1.7$, and the fraction of the liquid phase decreases to $\alpha=0.1$ at a temperature $T_S/T_0=1.25$. For lower temperatures the sphere solidifies completely ($\alpha=0$) as can be seen in Fig. 4. While the states obtained at long times appear to be equilibria, there is no direct means to demonstrate that other, lower-energy states do not exist. We can establish, however, that these states are truly the steady state by solving Eqs. (41) and (42) with the assumption that the thermal conductivity is infinitely large. These simulations lead to the same steady states, which have been obtained as a result of the nonisothermal transformation. These steady states are determined by the temperature and order parameter at the surface and do not depend on the initial temperature.

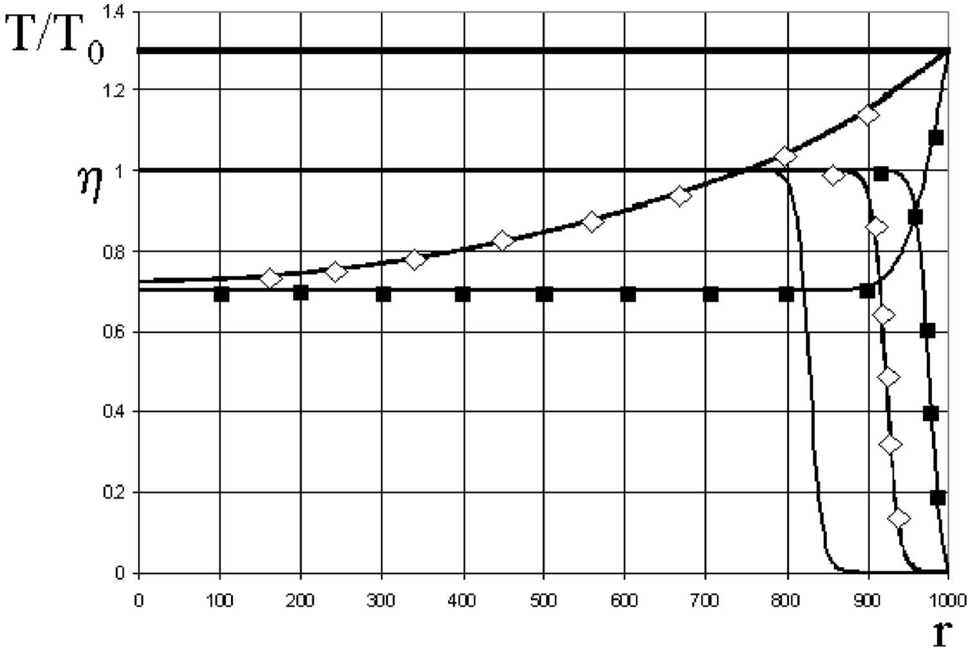

FIG. 2. Evolution of the order parameter η and the temperature T/T_0 during melting of the sphere. At the outer surface the temperature and order parameter are fixed, with $T_s/T_0=1.3$ and $\eta=0$, respectively. The initial temperature of the sphere is $T_{init}/T_0=0.7$, and the order parameter is initially unity. In the steady state (solid black lines), the temperature reaches T_s/T_0, and the two phases coexist. The symbols on the curves are an aid to the eye to indicate the time history of the evolution (curves with solid squares precede the curves with open diamonds, leading to the solid curves).

These simulations illustrate the significant effect that stress can have on two-phase systems in a confined geometry. In the absence of stress, there are unstable two-phase isothermal states that represent critical nuclei of either solid inclusions (with $T<T_0$) or liquid inclusions (with $T>T_0$). Perturbations of these unstable two-phase states generally lead to single-phase equilibria consistent with the specified wall temperature. Moreover, the unstable two-phase states do not coexist at a given temperature. In contrast, if stress is taken into account then (1) there is a temperature interval where equilibrium two-phase states exist during the solidification or melting of a confined sphere; (2) melting or solidification from the surface can lead to different equilibrium states at the same temperature; and (3) for either solid or liquid inclusions, as the temperature of the outer boundary is varied the two-phase states lose stability at finite phase fractions, leading to single-phase equilibria.

B. Analysis of equilibrium: Comparison of phase field calculations with a sharp interface model

We now develop a sharp interface model of a two-phase elastic system for comparison with our phase field model. This sharp interface model contains the equilibrium solutions equivalent to the two cases considered using phase field modeling in the previous section. The first problem describes the equilibrium states reachable during the melting from the surface. It considers the two-phase equilibrium in the sphere with zero displacements at the surface if the outer phase is a liquid and the inner phase is a solid. The second problem

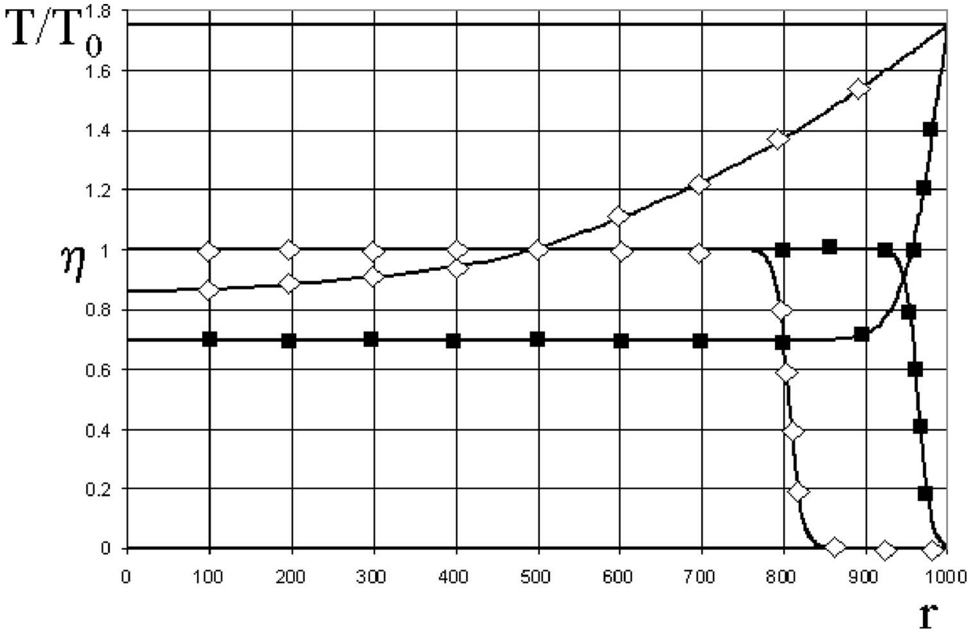

FIG. 3. Evolution of order parameter η and temperature T/T_0 during melting of the sphere. The temperature at the surface is fixed at $T_s/T_0=1.75$. The initial temperature of the sphere is $T_{init}/T_0=0.7$. In the steady state (solid black lines), the temperature reaches the fixed temperature at the surface, T_s/T_0, and there is no two-phase state.

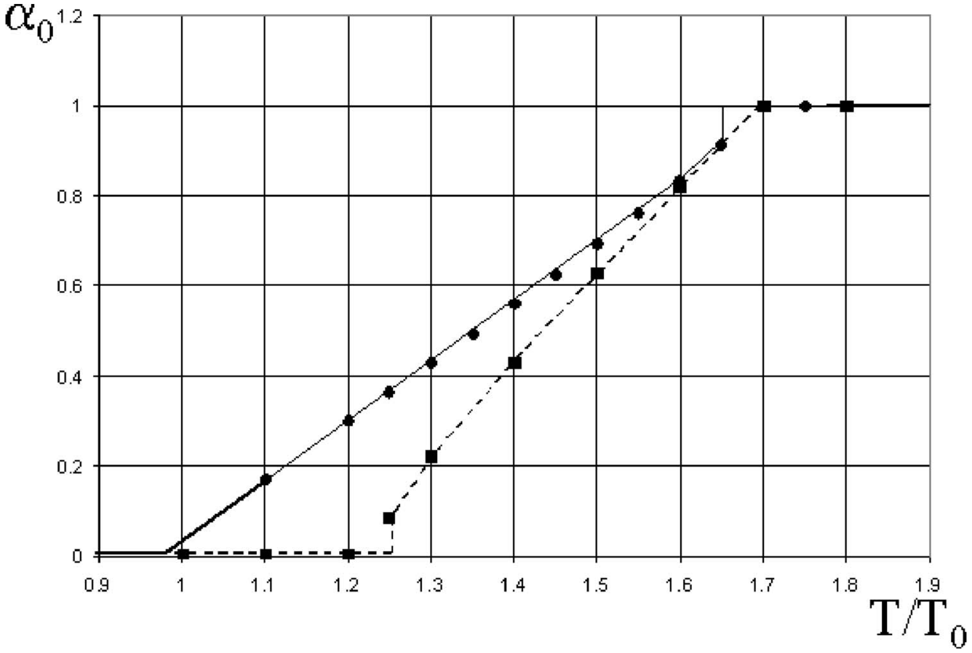

FIG. 4. The dependence of the equilibrium fraction of liquid on temperature following from steady-state results of phase field simulation. Solid line and solid circles: melting of the sphere from the surface. Dashed line and solid squares: solidification of the sphere from the surface.

describes the equilibrium states reachable during solidification from the outer surface of a confined sphere of liquid.

By minimizing the free energy in both cases the temperature dependence of the equilibrium fraction of liquid phase can be found and compared with the temperature dependence following from results of the phase field model. The sharp interface problem is a free-boundary problem, and posing the problem in the form of a variational principle provides the appropriate interface boundary conditions through the independent variations of the displacement field and the interface location in the reference state.

In a sharp interface model, surface energy effects are included explicitly by writing the total energy $\mathcal{F}$ as the sum of bulk energy and surface energy contributions, that is, $\mathcal{F}=\mathcal{F}_B+\mathcal{F}_S$. The bulk free energy $\mathcal{F}_B$ of the two-phase system for either a liquid or a solid inclusion can be written in the form

$$\mathcal{F}_B = 4\pi\int_0^{R_I} r^2 f^{(1)}(r,T,u^{(1)},u_r^{(1)})dr + 4\pi\int_{R_I}^{R} r^2 f^{(2)}(r,T,u^{(2)},u_r^{(2)})dr \tag{43}$$

where $u_r^{(\alpha)}=\partial u^\alpha/\partial r$, and the superscripts (1) and (2) refer to the inclusion phase and surrounding phase, respectively. Here R is the outer radius of the sphere, R_I is the radius at the interface in the reference state (see Fig. 7), and, for $\alpha=1,2$,

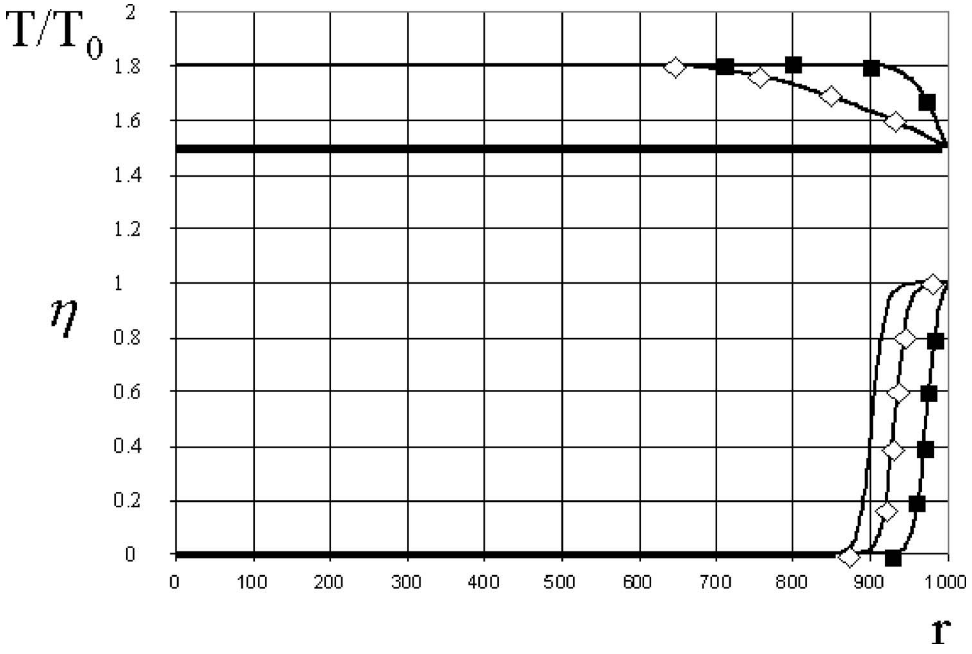

FIG. 5. Evolution of the order parameter η and temperature T/T_0 during solidification of a sphere. The temperature at the surface is fixed, $T_s/T_0=1.5$. The initial temperature of the sphere is $T_{init}/T_0=1.8$. In the steady state (solid black lines), the temperature reaches the fixed temperature at the surface, T_s/T_0, and the two-phase state exists.

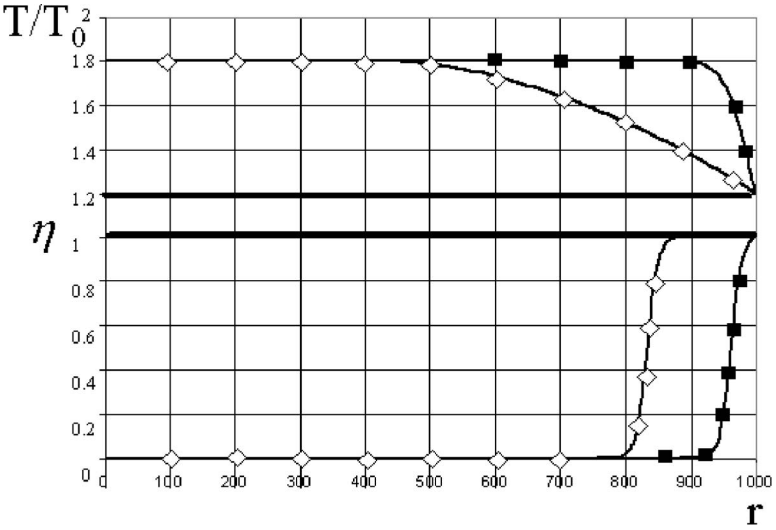

FIG. 6. Evolution of the order parameter η and temperature T/T_0 during solidification of a sphere. The temperature at the surface is fixed, $T_s/T_0=1.2$. The initial temperature of the sphere is $T_{init}/T_0=1.8$. In the steady state (solid black lines), the temperature reaches the fixed temperature on the outside surface, T_s/T_0 and there is no two-phase state.

$$f^{(\alpha)} = f(\eta^{\alpha},T) + \frac{1}{2}K[u_r^{(\alpha)} + 2u^{(\alpha)}/r - \varepsilon_{ll}^{0(\alpha)}]^2 + \frac{2}{3}\mu^{(\alpha)}[u_r^{(\alpha)} - u^{(\alpha)}/r]^2. \tag{44}$$

The liquid phase has $\eta^{(\alpha)}=0$, $\mu^{(\alpha)}=0$, and $\varepsilon_{ll}^{0(\alpha)}=3\varepsilon_0$, and the solid phase has $\eta^{(\alpha)}=1$, $\mu^{(\alpha)}=\mu_0$, and $\varepsilon_{ll}^{0(\alpha)}=0$. In this notation, the radial stress field in each phase is given by $\sigma_{rr}^{(\alpha)} = \partial f^{(\alpha)}/\partial u_r^{(\alpha)}$.

Following the development in Ref. 19, we let $\hat{\gamma}$ denote the interfacial energy per unit area in the reference state, so that the surface energy contribution is given by $\mathcal{F}_S=4\pi R_I^2\hat{\gamma}$. In order to include the effects of surface stress, the surface energy is generally assumed to depend on the tangential strain components $\varepsilon_{\theta\theta}$ and $\varepsilon_{\phi\phi}$, i.e., $\hat{\gamma}=\hat{\gamma}(\varepsilon_{\theta\theta},\varepsilon_{\phi\phi})$; since these components of strain are continuous across the interface the argument of $\hat{\gamma}$ is unambiguous. The surface stresses tangential to the interface are then given by[19] $\hat{\sigma}_{\theta\theta}=\partial\hat{\gamma}/\partial\varepsilon_{\theta\theta}$ and $\hat{\sigma}_{\phi\phi}=\partial\hat{\gamma}/\partial\varepsilon_{\phi\phi}$. For the case of a spherical geometry with isotropic material properties, we have $\varepsilon_{\theta\theta}=\varepsilon_{\phi\phi}=u(R_i)/R_I$, and $\hat{\sigma}_{\theta\theta}=\hat{\sigma}_{\phi\phi}$. A model with constant surface stress σ_S is therefore given by

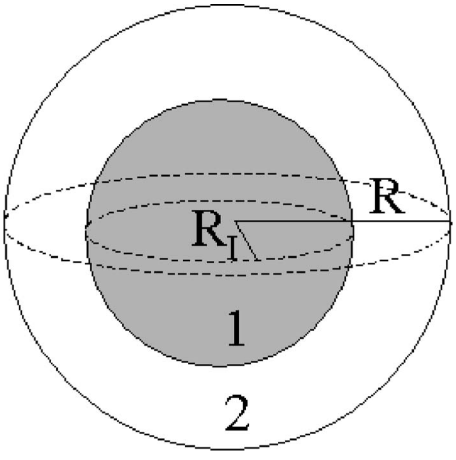

FIG. 7. The spherical inclusion in the sharp interface approximation. R is the outer radius of the spherical system, and R_I is the radius of the interface.

$$\hat{\gamma} = \gamma_0 + \sigma_S\varepsilon_{\theta\theta} + \sigma_S\varepsilon_{\phi\phi} = \gamma_0 + 2\sigma_S e_S, \tag{45}$$

where we have introduced the surface strain $e_S=u(R_I)/R_I$. More generally, for the case of spherical symmetry we write $\hat{\gamma}=\hat{\gamma}(e_S)$, and let $\sigma_S=2d\hat{\gamma}/de_S$ denote the surface stress, which will be strain dependent if $\hat{\gamma}(e_S)$ is nonlinear.

The equilibrium stress equation can be found by taking the variation of the total free energy $\mathcal{F}$ with respect to the displacement fields $u^{(\alpha)}$ in each phase, assuming the interface is coherent, $u^{(1)}(R_I)=u^{(2)}(R_I)$. This leads to bulk versions of the stress equation (39),

$$0 = \frac{d}{dr}\left(\frac{du^{(\alpha)}}{dr} + 2\frac{u^{(\alpha)}}{r}\right), \tag{46}$$

which states that the dilation $\varepsilon_{ll}^{(\alpha)}=u_r^{(\alpha)}+2u^{(\alpha)}/r$ is uniform in each phase.

To find the equilibrium position of an interface, the additional variation of the free energy with respect to R_I and $u^{(1)}(R_I)=u^{(2)}(R_I)$ leads to generalized versions of the Weierstrass-Erdmann conditions at the interface,[22]

$$0 = [f^{(1)} - u_r^{(1)}\sigma_{rr}^{(1)}] - [f^{(2)} - u_r^{(2)}\sigma_{rr}^{(2)}] + \frac{2}{R_I}[\hat{\gamma} - \sigma_S e_S], \tag{47}$$

$$0 = \sigma_{rr}^{(1)} - \sigma_{rr}^{(2)} + \frac{2\sigma_S}{R_I}. \tag{48}$$

The first condition relates the jump in the potential ψ in Eq. (17) across the interface to the interface curvature $2/R_I$, with a coefficient that depends on the free energy $\hat{\gamma}$ and the work done by surface stress (see, e.g., Ref. 23). This condition is the analog of the equilibrium Gibbs-Thomson equation in solidification theory. The appearance of the coefficient $\hat{\gamma} - \sigma_S e_S$ is consistent with the interfacial Eshelby relation, as discussed by Gurtin.[24] The second condition expresses mechanical equilibrium, and relates the jump in the normal

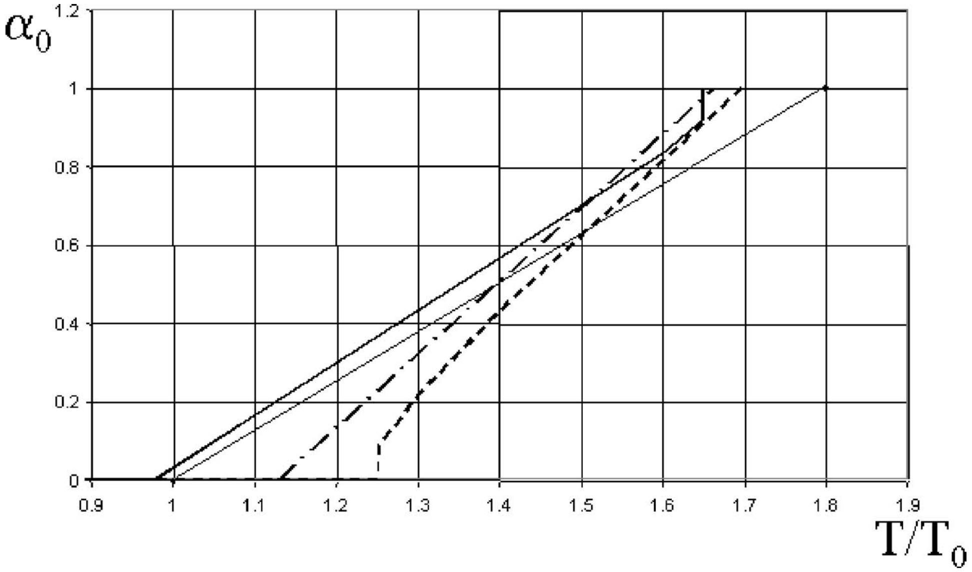

FIG. 8. The temperature dependence of the equilibrium liquid fraction α_0 for the two configurations. For the case that the outer phase is liquid, the upper thick solid curve shows the phase field results, and the lower thin solid curve shows the sharp interface results. For the case that the outer phase is solid, the lower dashed curve shows the phase field results, and the upper dot-dashed curve shows the sharp interface results. Here the effects of capillarity are neglected in the sharp interface results.

stress to the force due to surface stress; it is analogous to the Laplace-Young equation in fluid systems.

From the equation of interface equilibrium (47), we determine the temperature dependence of the equilibrium fraction of liquid, α, and compare it with the results of the phase field model. The calculation is outlined in the Appendix. The numerical results for the phase field model show a small jump in the radial component of the bulk stress, indicating the presence of surface stress in the model. Since the effect is small, however, we neglect it in comparison with the sharp interface model to simplify the presentation, and assume the surface energy is constant.

If liquid is the outer phase, the free energy of the two-phase sphere is

$$f = \frac{F}{V} = \frac{9}{2}K\varepsilon_0^2\alpha^2 + \Delta f(1-\alpha) + \frac{3\hat{\gamma}}{R}(1-\alpha)^{2/3} \qquad (49)$$

where α is the fraction of liquid, $\alpha = 1 - R_I^3/R^3$. The first term represents the elastic energy of the two-phase sphere, the second term represents the internal energy, and the last term is the surface energy. If the solid is an outer phase the free energy is

$$f = \frac{F}{V} = K\varepsilon_0^2\left(\frac{9}{2}\alpha^2 + \frac{3}{2}\alpha(1-\alpha)\right) + \Delta f(1-\alpha) + \frac{3\hat{\gamma}}{R}\alpha^{2/3} \qquad (50)$$

where the liquid fraction is now given by $\alpha = R_I^3/R^3$.

1. Comparison with $\hat{\gamma}=0$

We first compare the phase field results to the sharp interface results with $\hat{\gamma}=0$. If liquid is the outer phase, the stress states in the inner and outer phases are hydrostatic,

$$p^{(1)} = p^{(2)} = p = -3\varepsilon_0 K\alpha. \qquad (51)$$

(Hereafter we use the Poisson ratio $\nu = 1/3$ and $\mu/\mathrm{K} = 0.375$.) The equilibrium fraction of liquid is

$$\alpha_0 = \frac{\Delta f}{9K\varepsilon_0^2} = \frac{L_V}{9K\varepsilon_0^2}\frac{(T-T_0)}{T_0}. \qquad (52)$$

The liquid phase grows from $\alpha=0$ at temperature T_0 to $\alpha=1$ at temperature $T/T_0 = 1 - K\varepsilon_0^2/q$. The dependence of the equilibrium fraction of liquid on temperature corresponds to the Clausius-Clapeyron temperature dependence on pressure in a system with fixed volume:

$$\frac{dT}{dp} = \frac{d\alpha_0/dp}{d\alpha_0/dT} = \frac{3\varepsilon_0 T}{L_V}, \qquad (53)$$

where p is the pressure in the inner and outer phases given in Eq. (51).

If the inner phase is liquid and the outer phase is solid, there is a hydrostatic stress state in the liquid and a nonhydrostatic stress state in the solid. The pressures in the inner and outer phases are uniform,

$$p^{(inside)} = 2K\varepsilon_0^2(\alpha-1), \quad p^{(outside)} = K\varepsilon_0^2(3+2\alpha). \qquad (54)$$

The equilibrium fraction of liquid is

$$\alpha_0 = \frac{\Delta f}{6K\varepsilon_0^2} - \frac{1}{4} = \frac{q(T-T_0)}{6T_0K\varepsilon_0^2} - \frac{1}{4}. \qquad (55)$$

The liquid fraction decreases from $\alpha=1$ at temperature $T/T_0 = 1 + 15K\varepsilon_0^2/2q$ to $\alpha=0$ at temperature $T/T_0 = 1 + 3K\varepsilon_0^2/2q$. Thus, the liquid disappears at a temperature higher than T_0.

The dependence of the equilibrium fraction of liquid on temperature obtained from a sharp interface model together with the dependence following from the results of the phase field model are shown in Fig. 8. The difference in temperature dependence for the two configurations (the outer phase is either liquid or solid) is a result of elastic interactions between the phases in the case when the liquid is formed inside the solid phase. The sharp interface limit without capillarity qualitatively explains the coexistence of the two equi-

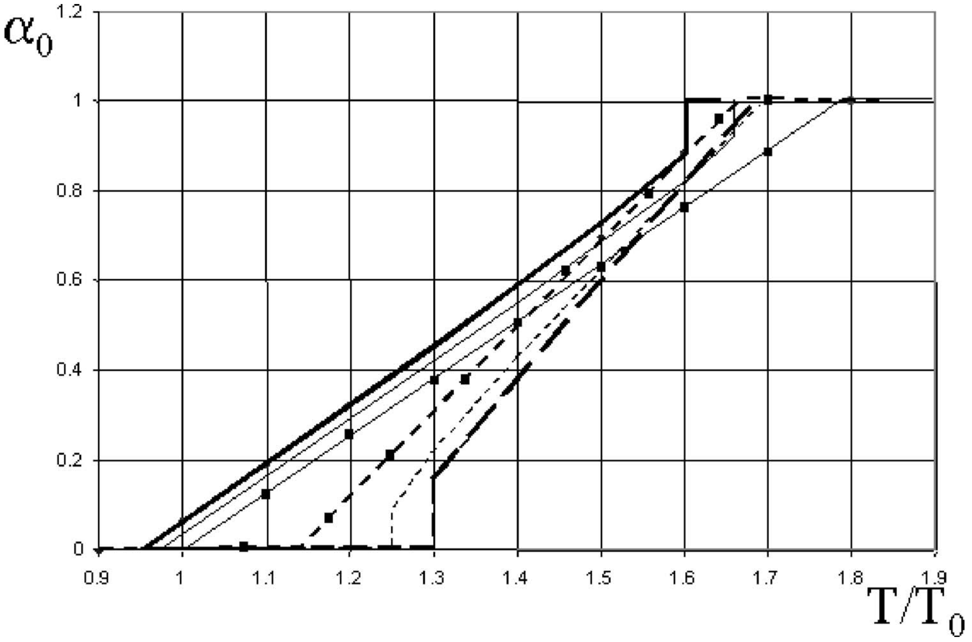

FIG. 9. The temperature dependence of the equilibrium liquid fraction α_0 for the sharp interface model with various values of the surface energy γ. The three solid curves correspond to the case of a liquid outer phase with (from left to right) $\gamma/(Rf_0)=0.053$ (thicker curve), $\gamma/(Rf_0)=0.043$, and $\gamma=0$. The three broken curves correspond to the case of a solid outer phase with (from right to left) $\gamma/(Rf_0)=0.053$ (thicker curve), $\gamma/(Rf_0)=0.043$, and $\gamma=0$.

librium liquid-solid phase states over a range of temperatures, but does not show the loss of the two-phase stability demonstrated by the phase field model.

2. Comparison with $\hat{\gamma}\neq 0$

With capillary effects included, Eqs. (49) and (50) have two extrema in α, one of them a minimum corresponding to the equilibrium two-phase state, and the other one a maximum corresponding to a critical nucleus. The two-phase equilibrium disappears at a critical temperature T_{cr}, where the minimum of the free energy coincides with the maximum. The dependence of the equilibrium fraction of liquid on temperature for various values of the surface energy is shown in Fig. 9. With increasing surface energy, the critical temperature where the two-phase state becomes unstable decreases in the case of a solid inner phase and increases in the case of a liquid inner phase.

From the comparison of the free energies [Eqs. (49) and (50)] it follows that the free energy in the problem where the outer phase is a liquid is always lower than the free energy in the problem where the outer phase is a solid. Thus, the equilibria reached when solidification starts from the surface are metastable to interchanging the inner and outer phases.

To estimate the value of surface energy in terms of the phase field parameters, we examine the surface energy's dependence on the equilibrium liquid fraction for phase field calculations with equilibrium fractions given by minimization of Eqs. (49) and (50). In the sharp interface approximation the surface energy $\gamma/(Rf_0)$ does not depend on the fraction of the equilibrium phase; thus, it can be used as a fitting parameter. The value of $\gamma/(Rf_0)=0.043$ gives agreement between the sharp interface and phase field calculations for both solidification and melting of the sphere.

Using the analytic result for the planar interface,

$$\frac{\gamma}{Rf_0} = \int_0^1 \left[2\frac{\beta}{R^2 f_0}\left(16\eta^2(1-\eta)^2 + \frac{K\epsilon_0^2}{f_0}\frac{18\mu_0 p(\eta)}{3+4\mu_0 p(\eta)}[1-p(\eta)]^2\right)\right]^{1/2} d\eta, \qquad (56)$$

we can also compute the surface energy. With the parameters used in the phase field calculations, $\beta/(R^2 f_0)=0.002$ and $K\varepsilon_0^2/f_0=0.22$, we obtain the value $\gamma/(Rf_0)=0.043$ for the surface energy, which coincides with the value obtained from phase field calculations. As can be seen from Eq. (56) the effect of elastic energy on surface energy is small [the surface energy $\gamma/(Rf_0)$ increases by about 0.001]. However, even if the elastic energy affects the surface energy insignificantly, it significantly affects the equilibrium states. The value of surface energy as well as surface stress increases with increasing elastic energy, e.g., ε_0. The value of the surface stress is computed to be $f_{xx}/(Rf_0)=f_{yy}/(Rf_0)=1.5\times 10^{-3}$.

In Fig. 10 the stress fields obtained by the phase field calculations for solidification and melting of the sphere are compared with Eqs. (A13) and (A10) in the Appendix. The phase field calculations coincide with the sharp interface model away from the interface, while near the interface the diffuse nature of the interface and the surface stresses influence the stress fields.

VI. DISCUSSION

As shown above, the equilibrium two-phase states established during phase field evolution are described adequately in terms of the thermodynamics of two-phase systems with sharp interfaces between phases. However, the phase field approach imposed a special constraint on the system that makes these equilibrium states dependent on the kinetic path of a transformation.

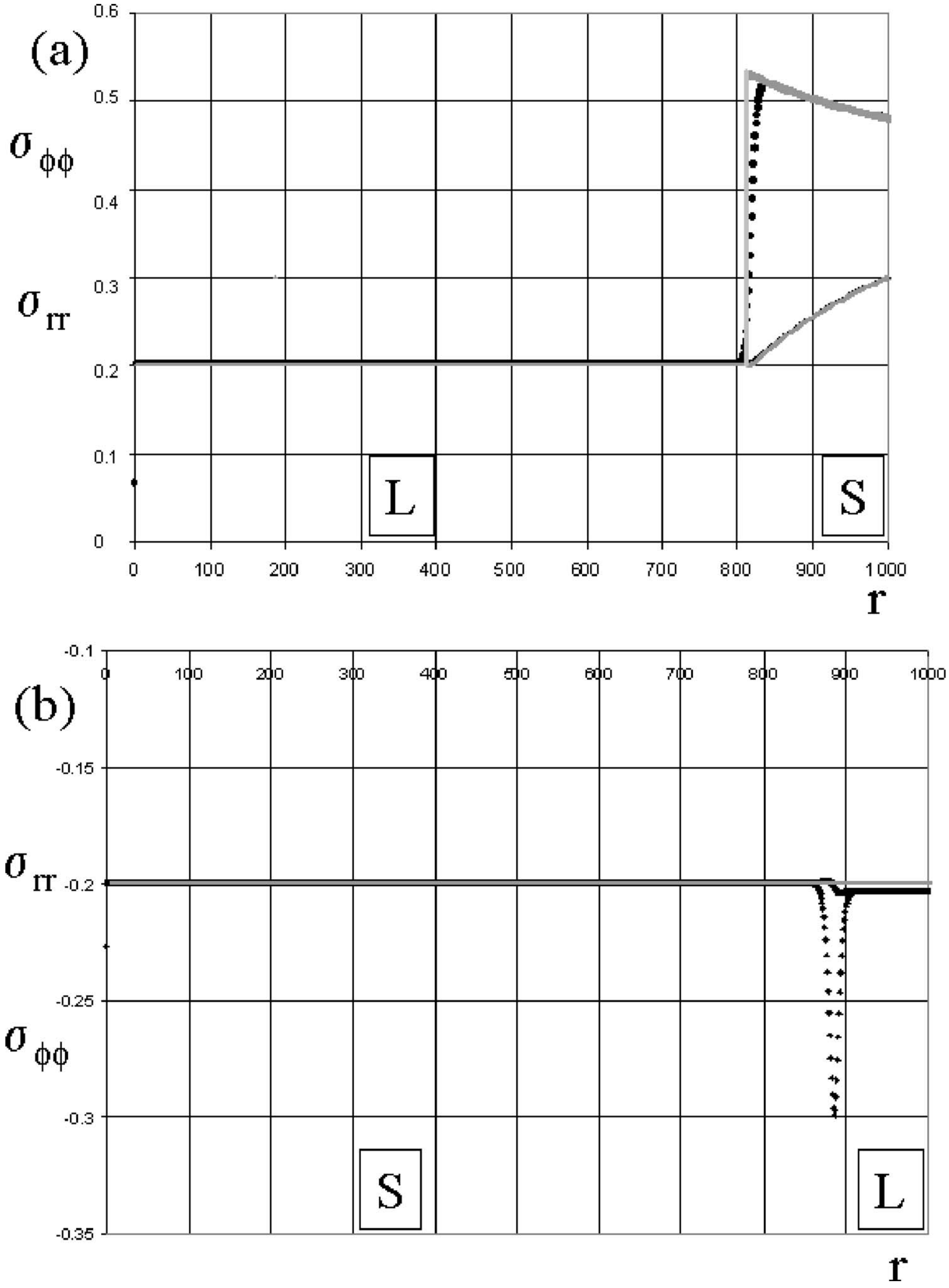

FIG. 10. The stresses σ_{rr} and $\sigma_{\phi\phi}$ from the phase field calculations (black dots) and sharp interface model (gray lines). (a) The case of a solid outer phase. The curves for $\sigma_{\phi\phi}$ lie above those for σ_{rr}. (b) The case of a liquid outer phase. The curves for $\sigma_{\phi\phi}$ lie below those for σ_{rr}.

Assuming that the order parameter at the surface is fixed ($\eta=0$ or 1), we have eliminated the necessity for nucleation of a new phase, but simultaneously have introduced an additional condition for accessibility of the equilibrium state. Thus, by requiring solidification to develop from the surface, we keep the system in a metastable state (because its energy is higher than the energy of the configuration with a solid phase inside of a liquid phase). The complete solidification under these conditions results in the formation of an unstressed solid at a temperature higher than the melting temperature T_0. However, this contrived situation can correspond to a realizable physical process if the solidification of a liquid inclusion in the solid is considered. For example, the inclusion can be the result of a local thermal heating (e.g., due to radiation). The kinetics of the solidification in this case is adequately described by our phase field simulation, and the final overheated solid state is stable with respect to the internal melting.

This example shows that for analysis of a realistic process, the boundary conditions at the surface in the phase field equations should be based on consideration of surface properties, including the surface's mechanical and thermodynamic states. From this point of view, the surface boundary conditions can be more complex during the melting of a confined sphere than during solidification of a liquid inclusion, because more information on the energy of an interface between liquid and constraining walls is required. Thus, in comparison with the classical problems of melting and solidification, where only temperature conditions at the surface are given (the so-called Stefan problems), the phase field approach contains an additional degree of freedom (order parameter at the surface), which needs to be specified. Comparison of the phase field model and the sharp interface model shows that the continuity of strain in the former and compatibility of strain in the latter lead to the same stress fields except in a small vicinity of the liquid-solid interface (Fig. 10). Therefore, the validity of coherency (continuity of displacement) of the liquid-solid mixture can be verified by analysis of the stress fields in the sharp interface model. This calculation is presented in the Appendix.

A system with a liquid inner phase is necessarily coherent because the elastic solutions for coherent and incoherent inclusions for this case are the same: the stress state in the inner phase is the hydrostatic pressure and this stress cannot be relaxed for any shear modulus of the inner phase. On the other hand, a system with a liquid outer phase that is considered to be coherent with the solid contains shear strains in the liquid which do not create shear stress, because of the zero shear modulus of a liquid. If we view this system as a mixture of incoherent phases,[14] then we should not employ the assumption of continuity of displacement, but should instead allow the shear strain in the liquid to relax by imposing a conservation of volume constraint that the sum of the volume change of the liquid phase, ΔV_L, and volume change of the solid phase, ΔV_S, should be equal to zero. Since $\Delta V_L = \alpha V_0 \varepsilon_L$ and $\Delta V_S = (1-\alpha) V_0 \varepsilon_S$, where V_0 is the total volume of the sphere, ε_L and ε_S are the total dilations in a liquid and a solid, we come to the equation

$$\alpha V_0\left(\varepsilon_0 + \frac{p}{3K}\right) + (1-\alpha) V_0 \frac{p}{3K} = 0, \tag{57}$$

where elastic dilations in the phases are determined by the uniform hydrostatic pressure p. We then have

$$p = -3K\varepsilon_0\alpha, \tag{58}$$

which coincides with the results following from a coherent model [Eq. (29)]. Thus, in the problem under consideration the coherent model of a liquid-solid system leads to the same results as an incoherent one if the shear modulus of liquid is assumed to be zero. The justification for treating the liquid as a coherent phase in more general cases will be considered elsewhere.

VII. CONCLUSIONS

A phase field model that incorporates the simultaneous time evolution of the phase, temperature, and displacement fields has been applied to the problem of solidification and melting of a confined sphere. The simulations have demonstrated that there are temperature intervals where equilibrium states are established in a liquid-solid mixture. These equilibrium states have also been obtained analytically using a sharp interface model of the two-phase sphere. Comparing the thermodynamic results of the two models allows one to evaluate the relative stability of the equilibrium states during both solidification and melting and estimate the surface energy. The resulting surface energy coincides with that calculated from the phase field model of a planar liquid-solid interface. The long-range stress fields are identical in the sharp interface and the phase field models. The sharp interface model has shown that the coherent and incoherent (relaxed) states of spherical two-phase system have the same stress fields. This identity of elastic fields justifies the assumption of coherency between the phases for our calculation of long-range elastic fields within the presented phase field modeling of liquid-solid transformations.

ACKNOWLEDGMENTS

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APPENDIX: SHARP INTERFACE CALCULATION

A sharp interface calculation for a spherically symmetric two-phase system can be based on the thermodynamics of a stressed solid.[25,26] From the equilibrium equation in spherical coordinates (r, φ, θ) and the symmetry of the model, it follows that the displacement has only a radial component $u = u(r)$ which, in the inner phase 1 and the outer phase 2, has the form

$$u^{(1)} = a_1 r, \quad u^{(2)} = a_2 r + \frac{b}{r^2}. \tag{A1}$$

The reference stress-free state is the solid phase. The strains and stresses are

$$\varepsilon_{rr}^{(1)} = \varepsilon_{\varphi\varphi}^{(1)} = \varepsilon_{\theta\theta}^{(1)} = a_1, \tag{A2}$$

$$\varepsilon_{rr}^{(2)} = a_2 - \frac{2b}{r^3}, \quad \varepsilon_{\varphi\varphi}^{(2)} = \varepsilon_{\theta\theta}^{(2)} = a_2 + \frac{b}{r^3}, \tag{A3}$$

$$\sigma_{rr}^{(1)} = \sigma_{\varphi\varphi}^{(1)} = \sigma_{\theta\theta}^{(1)} = 3K[a_1 - \varepsilon_0^{(1)}], \tag{A4}$$

$$\sigma_{rr}^{(2)} = 3K[a_2 - \varepsilon_0^{(2)}] - 4\mu^{(2)}\frac{b}{r^3}, \tag{A5}$$

$$\sigma_{\varphi\varphi}^{(2)} = \sigma_{\theta\theta}^{(2)} = 3K[a_2 - \varepsilon_0^{(2)}] + 2\mu^{(2)}\frac{b}{r^3}, \tag{A6}$$

where $\mu^{(2)}$ is the shear modulus of phase 2, and $\varepsilon_0^{(1)}$ and $\varepsilon_0^{(1)}$ are the stress-free strains associated with volume change in each phase. The bulk modulus K is assumed to be the same in both phases, the shear modulus in the liquid is assumed to vanish, and, since the stress-free solid phase is chosen as the reference state, the stress-free strain in the solid vanishes as well.

The coefficients a_1, a_2, and b are found from the boundary conditions. Mechanical equilibrium at the phase interface $r = R_I$ takes the form

$$\sigma_{rr}^{(1)}(R_I) = \sigma_{rr}^{(2)}(R_I) \tag{A7}$$

if we neglect the effects of surface stress. Continuity of displacement at the phase interface and zero displacement at the outer boundary $r = R$ have the forms

$$u^{(2)}(R_I) = u^{(1)}(R_I), \quad u^{(2)}(R) = 0. \tag{A8}$$

If the outer phase is liquid, we find

$$a_1 = -\left(1 - \frac{R_I^3}{R^3}\right)\varepsilon_0, \quad a_2 = \frac{R_I^3}{R^3}\varepsilon_0,$$

$$b = -R_I^3\varepsilon_0, \tag{A9}$$

where $\varepsilon_0=\varepsilon_0^{(2)}$ is the stress-free strain in the liquid. The stress fields are given by

$$\sigma_{rr}^{(1)} = \sigma_{\varphi\varphi}^{(1)} = \sigma_{\theta\theta}^{(1)} = \sigma_{rr}^{(2)} = \sigma_{\varphi\varphi}^{(2)} = \sigma_{\theta\theta}^{(2)} = -3K\varepsilon_0\left(1 - \frac{R_I^3}{R^3}\right). \tag{A10}$$

The total energy is then given by Eq. (49), and the relation between temperature and the radius R_I is

$$\frac{(T-T_0)}{T_0} = \frac{9K\varepsilon_0^2}{L_V}\left(1 - \frac{R_I^3}{R^3}\right) - \frac{2\hat{\gamma}}{L_V R}\left(\frac{R_I}{R}\right)^{-1}. \tag{A11}$$

If the outer phase is solid, we find

$$a_1 = k\left(1 - \frac{R_I^3}{R^3}\right)\varepsilon_0, \quad a_2 = -k\left(\frac{R_I^3}{R^3}\right)\varepsilon_0,$$

$$b = -kR_I^3\varepsilon_0, \tag{A12}$$

where $k=3K/(3K+4\mu)$, $\varepsilon_0=\varepsilon_0^{(2)}$ is again the stress-free strain in the liquid, and μ is the shear modulus of the solid. The stress fields are given by

$$\sigma_{rr}^{(1)} = \sigma_{\varphi\varphi}^{(1)} = \sigma_{\theta\theta}^{(1)} = -9K\varepsilon_0\frac{K(R_I^3 - R^3)}{R^3(3K+4\mu)}, \tag{A13}$$

$$\sigma_{rr}^{(2)} = 3K\varepsilon_0\frac{(3KR^3 - 3KR_I^3 + 4\mu R^3)}{R^3(3K+4\mu)} - 12\mu K\varepsilon_0\frac{R_I^3}{(3K+4\mu)r^3}, \tag{A14}$$

$$\sigma_{\varphi\varphi}^{(2)} = \sigma_{\theta\theta}^{(2)} = 3K\varepsilon_0\frac{(3KR^3 - 3KR_I^3 + 4\mu R^3)}{R^3(3K+4\mu)} + 6\mu K\varepsilon_0\frac{R_I^3}{(3K+4\mu)r^3}. \tag{A15}$$

The total energy is then given by Eq. (49), and the relation between temperature and the radius R_I is

$$\frac{(T-T_0)}{T_0} = \frac{9K\varepsilon_0^2}{2L_V} + \frac{9K\varepsilon_0^2}{2L_V}(2\alpha-1)k + \frac{2\hat{\gamma}}{L_V R}\alpha^{-1/3}, \tag{A16}$$

where $\alpha=R_I^3/R^3$ is the liquid fraction. If $\mu/K=3/8$ (Poisson ratio $\nu=1/3$), then $k=2/3$ and we have

$$\frac{(T-T_0)}{T_0} = \frac{15K\varepsilon_0^2}{2L_V} - \frac{6K\varepsilon_0^2}{L_V}(\alpha-1) + \frac{2\hat{\gamma}}{L_V R}\alpha^{-1/3}. \tag{A17}$$

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[1] W. Boettinger, J. Warren, C. Beckermann, and A. Karma, Annu. Rev. Mater. Res. **32**, 163 (2002).

[2] G. McFadden, Contemp. Math. **306**, 107 (2002).

[3] M. Grujicic, G. Cao, and R. Miller, J. Mater. Synth. Process. **10**, 191 (2002).

[4] H. Udaykumar and L. Mao, Int. J. Heat Mass Transfer **45**, 4793 (2002).

[5] K. Rasmussen, T. Lookman, A. Saxena, A. Bishop, R. Albers, and S. R. Shenoy, Phys. Rev. Lett. **87**, 055704 (2001).

[6] A. Artemev, Y. Wang, and A. Khachaturyan, Acta Mater. **48**, 2503 (2000).

[7] J. Slutsker, A. Artemev, and A. Roytburd, J. Appl. Phys. **91**, 9049 (2002).

[8] Y. Wang, Y. Jin, and A. Khachaturyan, Appl. Phys. Lett. **80**, 4513 (2002).

[9] J. Muller and M. Grant, Phys. Rev. Lett. **82**, 1736 (1999).

[10] K. Kassner, C. Misbah, J. Muller, J. Kappey, and P. Kohlert, Phys. Rev. E **63**, 036117 (2001).

[11] J. Slutsker, A. Roytburd, G. McFadden, and J. Warren, in *Nanomechanics of Materials and Structures*, edited by T.-J. Chuang, P. Anderson, M.-K. Wu, and S. Hsieh (Springer, Dordrecht, 2006), pp. 33–43.

[12] F. Nabarro, Proc. R. Soc. London, Ser. A **175**, 519 (1940).

[13] E. Kroner, Acta Metall. **2**, 302 (1954).

[14] J. J. Hoyt, Phys. Rev. Lett. **96**, 045702 (2006).

[15] A. Roitburd and D. Temkin, Dokl. Akad. Nauk SSSR **288**, 111 (1986).

[16] I. Kaganova and A. Roitburd, Sov. Phys. JETP **67**, 1173 (1988).

[17] I. Kaganova and A. Roitburd, Sov. Phys. Solid State **31**, 545 (1989).

[18] W. C. Johnson, Acta Mater. **48**, 433 (2000).

[19] J. W. Cahn, in *Interfacial Segregation*, edited by W. Johnson and J. Blakely (ASM, Metals Park, Ohio, 1979), pp. 3–23.

[20] W. Johnson, Acta Mater. **49**, 3463 (2001).

[21] G. McFadden and A. Wheeler, Proc. R. Soc. London, Ser. A **458**, 1129 (2002).

[22] I. Gelfand and S. Fomin, *Calculus of Variations* (Dover, New York, 2000).

[23] P. Leo and R. Sekerka, Acta Metall. **37**, 3119 (1989).

[24] M. E. Gurtin, *Configurational Forces as Basic Concepts of Continuum Physics* (Springer-Verlag, New York, 2000).

[25] F. Larche and J. Cahn, Acta Metall. **26**, 1579 (1978).

[26] P. Voorhees and W. Johnson, in *Solid State Physics*, edited by H. Ehrenreich and F. Spaepen (Elsevier, Boston, 2004), Vol. 59, p. 1.