PHYSICAL REVIEW E **84**, 031601 (2011)

Unified derivation of phase-field models for alloy solidification from a grand-potential functional

Mathis Plapp
Physique de la Matière Condensée, École Polytechnique, CNRS, F-91128 Palaiseau, France

(Received 9 May 2011; published 2 September 2011)

In the literature, two quite different phase-field formulations for the problem of alloy solidification can be found. In the first, the material in the diffuse interfaces is assumed to be in an intermediate state between solid and liquid, with a unique local composition. In the second, the interface is seen as a mixture of two phases that each retain their macroscopic properties, and a separate concentration field for each phase is introduced. It is shown here that both types of models can be obtained by the standard variational procedure if a grand-potential functional is used as a starting point instead of a free energy functional. The dynamical variable is then the chemical potential instead of the composition. In this framework, a complete analogy with phase-field models for the solidification of a pure substance can be established. This analogy is then exploited to formulate quantitative phase-field models for alloys with arbitrary phase diagrams. The precision of the method is illustrated by numerical simulations with varying interface thickness.

DOI: 10.1103/PhysRevE.84.031601 PACS number(s): 81.10.Aj, 64.70.D−, 81.30.Fb, 05.70.Ln

I. INTRODUCTION

The development of the phase-field method has led to tremendous progress in the modeling of pattern formation during solidification, due to its capability to simulate complex time-dependent and three-dimensional morphologies with relatively simple numerical codes [1–4]. The general principle of this method is to describe a multiphase system by a set of phase fields which take constant values in each of the bulk phases and vary smoothly through interfaces of a characteristic thickness W. The equations of motion for the phase fields and their coupling to the local thermodynamic state variables (temperature, density, composition, etc.) can be obtained, following the basic principles of out-of-equilibrium thermodynamics, by taking a variational derivative of a free energy functional, which is generally of the Ginzburg-Landau type. Mean-field approximations can be used to relate the parameters that appear in this functional to microscopic quantities, and the phase fields can often be interpreted as order parameters.

Generally, the equations that result from the straightforward application of these principles are not suitable for obtaining quantitatively accurate simulation results on solidification microstructures. The reason is that the characteristic natural thickness of the diffuse solid-liquid interfaces is a few times the interatomic distance, whereas solidification patterns typically exhibit length scales ranging from 1 to 100 μm. Even with the help of modern computers and multiscale algorithms, both of these scales cannot be resolved at the same time. Therefore, in order to simulate solidification microstructures, the thickness of the diffuse interfaces in the phase-field model has to be artificially enlarged, sometimes by two or three orders of magnitude. Quantitative results can only be expected if both the equilibrium and kinetic properties of the interfaces remain unchanged under this procedure.

To achieve this goal, it is helpful to adopt a phenomenological point of view: The phase field is seen as a smoothed indicator function (as opposed to a physical order parameter or density), and all equilibrium quantities and transport coefficients are interpolated between the phases with smooth functions of the phase fields that can be freely chosen. This freedom can be exploited to construct phase-field models with special properties. In particular, rescaling of the interface thickness is greatly simplified in models where bulk thermodynamics and interfacial properties can be controlled separately.

The phase-field models for the solidification of a pure substance published in the literature are all quite similar [1,5–7], in the sense that they all use the same set of fundamental fields (a phase field and the temperature field) and that the structure of the equations is the same. One reason for this universality is that a simple and intuitive formulation of the model in terms of these fields yields indeed, as is detailed below, a model in which the separation of bulk and interface properties is achieved. Therefore, the development of the "thin interface limit" [1,8], which has paved the way to quantitative simulations of dendrites [1,9], did not require a change in the model formulation.

The situation is more complicated for alloy phase-field models. Two different approaches with quite distinct philosophies have been pursued in parallel. The first, which will be called the "coarse-graining" approach in the following, generalizes the pure substance model by introducing a concentration field in addition to the temperature field and by writing down a free energy functional that depends on the phase field, the temperature, and the concentration [10–12]. The local values of these three fields are—in principle—the coarse-grained counterparts of the microscopic structural order parameter, temperature, and concentration fields, and the interface is seen as a narrow region in space where all of these quantities can exhibit rapid spatial variations. In contrast, the second approach, called the "two-phase" approach in the following, treats the interfaces as a mixture of two phases, each of which retains its bulk properties even inside the interface, and a separate concentration field is defined for each phase. The model equations are then obtained following the spirit of volume-averaging methods [13], with the phase field representing the local volume fraction of one of the phases [14–16]. The "physical" concentration field is obtained by an average of the concentrations in each phase, which is weighted by the value of the phase field. The introduction of two separate concentration fields adds a supplementary degree of freedom which has to be removed from the problem; this is done either by a specific partition relation [14,15] or by the condition of local equilibrium between the coexisting phases [16].

In the models of the "coarse-graining" type, the model structure generally leads to an intrinsic coupling between bulk and interface properties, which makes simulation results dependent on the chosen interface thickness. Only for the case of dilute binary alloys, a specific interpolation of the thermodynamic properties through the interface has been developed [17,18] which overcomes this constraint and makes quantitative simulations possible. In the two-phase approach, which is more phenomonological from the outset, bulk and interfacial properties are decoupled by construction. However, the removal of the extra degree of freedom introduced by the model formulation generally requires the solution of a nonlinear equation in each point of the interface and thus adds significant computational complexity.

The purpose of the present paper is to show that the coarse-graining approach can be easily extended to more complex alloy systems if instead of a free energy functional a grand-potential functional is used to generate the equations of motion. Furthermore, an analysis of the resulting model shows that it is, in fact, perfectly equivalent to the two-phase model, which offers the possibility to reinterpret and simplify the latter. The fundamentals underlying these findings can be stated quite simply. The motion of interfaces is controlled by the transport of a conserved extensive quantity: energy for a pure substance and chemical species for isothermal alloy solidification. In sharp-interface models, this fact is expressed by two separate laws: a transport equation in the volume and a conservation law of Stefan type at the moving boundary. In contrast, the two-phase equilibrium at interfaces is controlled by the intensive quantity that is conjugate to the conserved one: temperature for pure substances and chemical potential for alloys. It turns out that the pure substance model has been formulated from the start in terms of a phase field and the intensive variable (temperature), whereas alloy phase-field models are traditionally formulated in terms of a phase field and the composition, which is a density of the extensive variable (number of solute atoms). To obtain a model for alloys that has properties analogous to those of the pure substance model, it is sufficient to choose a formulation in terms of a phase field and the chemical potential and to switch to the appropriate thermodynamic potential, which is the grand potential. Of course, the fact that the quantity analogous to the temperature is the chemical potential is well known [19] and has been extensively used in sharp-interface models as well as in a few specific phase-field models [20–22], but its general consequences have so far not been fully appreciated in the framework of phase-field models.

It should be mentioned that a second obstacle for obtaining quantitative results on alloys is the strong contrast of the solute diffusivities between solid and liquid, which generates spurious solute trapping when the interface thickness is scaled up. This problem was solved by the so-called antitrapping current, which was introduced first in the coarse-graining approach [17,23], but has also been incorporated in the two-phase model [4,24]. Since the results of the present paper do not introduce major changes on this point, the results of Ref. [17] will be taken over without a detailed discussion. After a change of variables, the model is almost identical to the model of Ref. [17], such that the asymptotic analysis developed for that model remains valid. This will be illustrated by numerical simulations that explicitly test the independence of simulation results of the interface thickness for the case of a lens-shaped phase diagram.

The remainder of the paper is structured as follows. In Sec. II, the standard phase-field model for the solidification of pure substances is reviewed for reference. Next, the grand-potential formulation is introduced and motivated in Sec. III and illustrated by several examples in Sec. IV: a model with two parabolic free energy functions, a dilute alloy, and an alloy with a lens-shaped phase diagram. The relation of this model to other phase-field models is clarified in Sec. V, and an example for numerical simulations is presented in Sec. VI. Finally, the implications of the present findings for the further developments of alloy phase-field models are discussed in Sec. VII.

II. SOLIDIFICATION OF A PURE SUBSTANCE

The minimal model of solidification is considered, which implies some standard simplifications: The densities of the solid and the liquid are taken to be equal, and heat transport is assumed to take place by diffusion only. As a consequence, no motion of matter needs to be considered, and the only transported extensive quantity is heat.

Under these assumptions, the state of an inhomogeneous two-phase system can be completely specified on a coarse-grained (mesoscopic) scale by two fields: a phase field ϕ which indicates the local state (liquid or solid) of matter and the internal energy density e. The conservation law corresponding to heat transport is the conservation of energy, which writes

$$\partial_t e = -\vec{\nabla} \cdot \vec{j}_e. \tag{1}$$

The heat current $\vec{j}_e$ is given by Fourier's law,

$$\vec{j}_e = -\kappa(\phi,e)\vec{\nabla}T, \tag{2}$$

where $\kappa(\phi)$ is the heat conductivity, which in general may depend on both variables, and T is the local temperature.

If e is chosen as a dynamic variable, the corresponding thermodynamic potential is the entropy. Consequently, the system is naturally described by an entropy functional,

$$\mathcal{S}[\phi,e] = \int_V s(\phi,\vec{\nabla}\phi,e,\vec{\nabla}e), \tag{3}$$

where the local entropy density s depends on the fields as well as their gradients. Using the thermodynamic definition of the temperature,

$$\frac{\delta \mathcal{S}}{\delta e} = \frac{1}{T}, \tag{4}$$

the evolution equations for the fields e and ϕ can be written in a variational form,

$$\partial_t \phi = M_\phi \frac{\delta \mathcal{S}}{\delta \phi}, \tag{5}$$

$$\partial_t e = \vec{\nabla} \cdot (\kappa(\phi)\vec{\nabla}T) = -\vec{\nabla} \cdot \left(\kappa(\phi)T^2\vec{\nabla}\frac{\delta \mathcal{S}}{\delta e}\right). \tag{6}$$

The first equation expresses the local maximization of the entropy, which occurs at a rate given by the constant M_ϕ; the second is identical to the conservation law, Eq. (1).

While this is a perfectly viable starting point which has been explored by several authors [25,26], this formulation is rarely used in practice. Simulations are almost always carried out with models formulated in the variables ϕ and T that can be obtained from free energy functionals. Besides historical reasons (the first phase-field models for solidification were formulated in this language [5,27,28]), there are also formal considerations which make this approach preferable. The main reason to choose the intensive variable T instead of the extensive variable e is that it directly controls the two-phase equilibrium, which makes it easier and more intuitive to identify the driving forces in the model.

This point is illustrated by obtaining the equations of motion from a free energy functional that is constructed using a purely phenomenological point of view. It is shown below that the standard phase-field model of solidification is easily obtained as a special case. Let $f_s(T)$ and $f_l(T)$ be the free energy densities of pure solid and liquid, respectively, and let the corresponding equilibrium values of the phase field be $\phi = \pm 1$. The free energy is given by

$$\begin{aligned}\mathcal{F}[\phi,T] = \int_V f(\phi,\vec{\nabla}\phi,T) = \int_V & f_{\text{int}}(\phi,\vec{\nabla}\phi) \\ & + g_s(\phi) f_s(T) + [1 - g_s(\phi)] f_l(T),\end{aligned} \tag{7}$$

where the weighting function $g_s(\phi)$ is given by

$$g_s(\phi) = \frac{1 + g(\phi)}{2}, \tag{8}$$

with $g(\phi)$ a function that satisfies $g(\pm 1) = 1$ and $g'(\pm 1) = 0$; hence, $g_s = 1$ in the solid and $g_s = 0$ in the liquid. The term f_{int} is given by

$$f_{\text{int}} = \tfrac{1}{2}\sigma(\vec{\nabla}\phi)^2 + H f_{\text{dw}}(\phi), \tag{9}$$

where σ and H are constants of dimension energy per unit length and energy per unit volume, respectively, and $f_{\text{dw}}(\phi)$ is a double-well function with minima at $\phi = \pm 1$.

The motivations for this formulation are easily understood and are common to many phase-field models. The term f_{int} creates domains where the phase field is close to its equilibrium values $\phi = \pm 1$ (the minima of the double-well function), separated by diffuse interfaces. Therefore, far from the interfaces, the free energy density reduces to the one of the corresponding bulk phase. The term f_{int} contributes to the free energy only inside the interfaces; this excess free energy represents the surface tension. The function $g_s(\phi)$ interpolates between the two free energy densities through the diffuse interface.

A variation of the free energy functional with respect to the two fields ϕ and T yields

$$\begin{aligned}\delta\mathcal{F} = \int_V & \Big\{ -\sigma\vec{\nabla}^2\phi + H f'_{\text{dw}}(\phi) \\ & + \frac{g'(\phi)}{2}[f_s(T) - f_l(T)] \Big\} \delta\phi(\vec{x}) \\ & + \Big\{ g_s(\phi)\frac{\partial f_s(T)}{\partial T} + [1 - g_s(\phi)]\frac{\partial f_l(T)}{\partial T} \Big\} \delta T(\vec{x}),\end{aligned} \tag{10}$$

where the prime stands for derivation with respect to ϕ.

The variation of $\mathcal{F}$ with respect to ϕ is the driving force for the phase transition. Two features are noteworthy: (i) the requirement that $g'(\pm 1) = 0$ ensures that the driving force vanishes outside of the interfacial regions and (ii) since, at the melting temperature $T = T_m$, $f_s(T_m) = f_l(T_m)$, the "thermodynamical" part of the driving force is identically zero, independently of the value of ϕ. The latter property implies that the equilibrium interface profile in ϕ can be calculated from the term f_{int} alone. This can be shown by seeking the equilibrium solution for a planar interface along the x direction, which can be obtained from the condition that the variation of $\mathcal{F}$ with respect to ϕ must vanish. At $T = T_m$, this condition yields

$$-\sigma\partial_{xx}\phi + H f'_{\text{dw}}(\phi) = 0, \tag{11}$$

which implies that the solution of this equation is independent of the free energies $f_s(T)$ and $f_l(T)$. As a consequence, the surface free energy γ (defined as the excess free energy due to the presence of the interface) is also independent of the bulk free energies and is given by

$$\gamma = I\sqrt{\sigma H} = IHW, \tag{12}$$

where I is a numerical constant that depends on the shape of the double well function f_{dw}, and the interface thickness W is defined by

$$W = \sqrt{\frac{\sigma}{H}}. \tag{13}$$

Therefore, the surface tension γ and the interface thickness W can be freely chosen by appropriately fixing the two constants σ and H, independently of the bulk properties. As stated in the Introduction, the interface properties can thus be controlled independently of the bulk thermodynamics.

The equation of motion for the phase field is obtained from the free energy functional by the standard variational procedure,

$$\partial_t\phi = -M_\phi\frac{\delta\mathcal{F}}{\delta\phi}, \tag{14}$$

which expresses the fact that the system seeks to minimize its local free energy at a rate which is controlled by the constant M_ϕ.

To obtain an evolution equation for the temperature field, the starting point is the observation that, by definition, the variation of $\mathcal{F}$ with respect to T is equal to the negative of the local entropy density,

$$s(T,\phi) = -\frac{\delta\mathcal{F}}{\delta T} = -g_s(\phi)\frac{\partial f_s(T)}{\partial T} - [1 - g_s(\phi)]\frac{\partial f_l(T)}{\partial T}. \tag{15}$$

Since f_{int} was chosen independent of temperature, s is a *local* function of ϕ and T (no gradients are involved) and can be simply seen as the interpolation of the bulk entropy densities,

$$s(\phi,T) = g_s(\phi)s_s(T) + [1 - g_s(\phi)]s_l(T). \tag{16}$$

The use of the thermodynamic identity $de = T ds$ (valid at constant density) yields

$$\partial_t e = T\partial_t s = T\left(\frac{\partial s(\phi,T)}{\partial\phi}\partial_t\phi + \frac{\partial s(\phi,T)}{\partial T}\partial_t T\right). \tag{17}$$

Note that in writing the second equality, it is assumed that there is no entropy production due to local dissipation, which is equivalent to the hypothesis that the transformations are reversible on the mesoscopic scale of a coarse-graining cell. Furthermore, the definition of the specific heat per unit volume is

$$C_p(\phi,T) = T\frac{\partial s(\phi,T)}{\partial T} = -T g_s(\phi)\frac{\partial^2 f_s(T)}{\partial T^2} - T[1-g_s(\phi)]\frac{\partial^2 f_l(T)}{\partial T^2}. \tag{18}$$

Equations (17) and (18) can be combined with the energy conservation law [Eq. (1)], where the heat conductivity κ now depends on the variables ϕ and T, to yield

$$C_p(\phi,T)\partial_t T = -T\frac{\partial s}{\partial \phi}\partial_t\phi + \vec{\nabla}[\kappa(\phi,T)\vec{\nabla}T], \tag{19}$$

which is the desired evolution equation for the temperature field. This equation can be further simplified by writing the heat conductivity as the product of the specific heat and the thermal diffusion coefficient D_T, and by using Eq. (16) for the entropy density. The result is

$$\partial_t T = \frac{1}{C_p(\phi,T)}\left\{\vec{\nabla}[C_p(\phi,T)D_T(\phi,T)\vec{\nabla}T] + T[s_l(T)-s_s(T)]\frac{g'(\phi)}{2}\partial_t\phi\right\}. \tag{20}$$

Note that all quantities that appear in this equation except for the thermal diffusivity can be obtained from the bulk free energy densities $f_s(T)$ and $f_l(T)$.

The free energy functional used in the standard formulation of the phase-field model can be obtained from Eq. (7) by linearizing the free energy density $f(\phi,\vec{\nabla}\phi,T)$ around the melting temperature T_m,

$$f(\phi,\vec{\nabla}\phi,T) = f(\phi,\vec{\nabla}\phi,T_m) + \left.\frac{\partial f}{\partial T}\right|_{T_m}(T-T_m). \tag{21}$$

Using the definition of the latent heat per unit volume, $L = T_m[s_l(T_m)-s_s(T_m)]$, as well as the fact that the free energies of solid and liquid are equal at T_m, $f_s(T_m) = f_l(T_m)$, this expansion yields

$$\mathcal{F} = \int_V \frac{1}{2}\sigma(\vec{\nabla}\phi)^2 + Hf_{\rm dw}(\phi) + \frac{L}{2T_m}g(\phi)(T-T_m), \tag{22}$$

where the constant $[s_s(T_m)+s_l(T_m)]/2$ has been disregarded for simplicity.

The equation of motion for the phase field is then obtained from this linearized functional by a variational derivative. To obtain an equation of motion for the temperature, it is usually assumed that the specific heat is independent of both temperature and the phase field, $C_p(\phi,T)\equiv C_p$. Then, it is easy to "guess" the correct equation by realizing that the latent heat released or consumed during the phase transformation appears as a source term in the diffusion equation for the temperature,

$$\partial_t T = \vec{\nabla}(D_T(\phi,T)\vec{\nabla}T) + \frac{L}{C_p}\frac{g'(\phi)}{2}\partial_t\phi. \tag{23}$$

This equation is indeed obtained from Eq. (20) when a constant specific heat is inserted and the approximation $T = T_m$ is made in the second term on the right-hand side. Note that, in contrast, the correct general form could not have been easily guessed from Eq. (23). The underlying reason is that the linearized free energy functional formally yields a specific heat which is zero since all second derivatives with respect to the temperature vanish; therefore, thermodynamic consistency between the linearized functional [Eqs. (22)] and the evolution equation for the temperature [Eq. (23)] has been lost. The equations are nevertheless correct, since for the case of constant specific heat and constant latent heat, that is $T[s_l(T)-s_s(T)] = T_m[s_l(T_m)-s_s(T_m)] = L$, the internal energy density and the temperature are linearly related,

$$e(\phi,T) = \frac{e_l(T_m)+e_s(T_m)}{2} + C_p(T-T_m) - \frac{g(\phi)}{2}L. \tag{24}$$

Then, Eq. (23) can be directly obtained by combining the time derivative of Eq. (24) with the energy conservation law [Eq. (1)].

III. ISOTHERMAL ALLOY SOLIDIFICATION

A binary alloy is a mixture of two pure substances A and B. For simplicity, it is assumed here that the atomic volume V_a of both pure substances and of the mixture are all the same, and that hence the total number density of the alloy is a constant and equal in solid and liquid. Then, the only new field needed is the local composition (atomic fraction) c of "solute" (B) atoms. Furthermore, for constant atomic volume the chemical potentials of A and B atoms are not independent since removal of an A atom implies the addition of a B atom. This means that the only new intensive variable that needs to be considered is the difference of the chemical potentials of A and B atoms, which is called μ in the following.

The starting point of the coarse-graining approach, as pioneered in Refs. [10–12], is a free energy functional that depends on the variables ϕ, T, and c. The chemical potential is then defined as the functional derivative of the free energy functional with respect to c. Since c is dimensionless, the chemical potential obtained by this procedure has the dimensions of energy per unit volume. This convention obscures the thermodynamic roles of the two variables: The relevant extensive variable from which a density should be defined is the number of B atoms. Therefore, the variable that is analogous to the internal energy density in the pure substance model is the number density of B atoms,

$$\rho = \frac{c}{V_a}, \tag{25}$$

where V_a is the atomic volume (the constant volume occupied by one A or B atom). Then, the chemical potential defined by

$$\mu = \frac{\delta\mathcal{F}}{\delta\rho} = V_a\frac{\delta\mathcal{F}}{\delta c} \tag{26}$$

has the dimension of an energy, as is standard in basic thermodynamics. Since the nature of the variables is important for establishing the analogy between pure substance and alloy models, this convention for the chemical potential is adopted for the remainder of the paper. However, since it is customary to express free energy densities in terms of the composition rather than the number density, both ρ and c will be used in the following for ease of presentation, keeping in mind that the two variables are simply related by Eq. (25).

The number density is a conserved quantity, which implies

$$\partial_t \rho = -\vec{\nabla} \cdot \vec{j}_\rho, \tag{27}$$

where j_ρ is the mass current. For isothermal solidification, where the only thermodynamic driving force for mass diffusion is the gradient of the chemical potential, the mass current is given by

$$\vec{j}_\rho = -M(\phi,T,c)\vec{\nabla}\mu, \tag{28}$$

where $M(\phi,T,c)$ is the atomic mobility. Combining these equations and the definition of μ yields the equation of motion for ρ,

$$\partial_t \rho = \vec{\nabla} \cdot \left(M(\phi,T,c)\vec{\nabla}\frac{\delta \mathcal{F}}{\delta \rho}\right). \tag{29}$$

It is now shown that this approach generally leads to a model in which bulk and interface properties do not decouple. To this end, it is useful to start again from the variation of the free energy functional, now in the variables ϕ and ρ. Since isothermal solidification is considered, there is no variation with respect to temperature. In order to simplify the notations, the variable T (which becomes a simple parameter for isothermal solidification) will be dropped from the free energy densities and the mobility from now on. The variation of $\mathcal{F}$ is

$$\begin{aligned} \delta\mathcal{F} = \int_V & \left\{ -\sigma\vec{\nabla}^2\phi + Hf'_{\rm dw}(\phi) \right. \\ & \left. + \frac{g'(\phi)}{2}\left[f_s(c) - f_l(c)\right]\right\}\delta\phi(\vec{x}) \\ & + V_a\left\{g_s(\phi)\frac{\partial f_s(c)}{\partial c} + [1-g_s(\phi)]\frac{\partial f_l(c)}{\partial c}\right\}\delta\rho(\vec{x}). \end{aligned} \tag{30}$$

A crucial difference with the pure substance case is obvious: there is no simple argument which ensures that the "thermodynamic driving force" term proportional to $f_s(c) - f_l(c)$ vanishes. Indeed, for two-phase equilibrium in an alloy, both the free energy density and the concentration vary across the interface. The values of all these quantities in the bulk phases at two-phase coexistence are obtained from two conditions: (i) The chemical potential must be the same in both phases, and (ii) the grand-potential density $\omega = f - \mu\rho$ must also be the same. Given the curves of free energy versus composition, the graphical interpretation of these two conditions is the well-known common tangent construction.

Let us examine the consequence of these conditions for the phase-field model outlined above. Since the two variables—phase field and concentration—vary through the interface, the equilibrium interface profile is given by two coupled nonlinear differential equations. One is obtained from the condition of constant chemical potential, which remains valid in the diffuse interface picture, and reads

$$\frac{\delta\mathcal{F}}{\delta\rho} = V_a g_s(\phi)\frac{\partial f_s(c)}{\partial c} + V_a[1-g_s(\phi)]\frac{\partial f_l(c)}{\partial c} = \mu_{\rm eq}(T), \tag{31}$$

where $\mu_{\rm eq}(T)$ is the equilibrium value obtained from the common tangent construction. This equation defines an implicit relation between the composition c and the phase field ϕ.

The equation for the phase field, obtained as before from the condition that the variation of $\mathcal{F}$ vanishes, is

$$-\sigma\partial_{xx}\phi + Hf'_{\rm dw}(\phi) + \frac{\delta f_{\rm th}}{\delta\phi} = 0, \tag{32}$$

where $f_{\rm th}(\phi,c) = g_s(\phi)f_s(c) + [1-g_s(\phi)]f_l(c)$ denotes the "thermodynamic part" of the free energy density. Obviously, this equation becomes identical to Eq. (11) only if the third term is identically zero. The physical meaning of this condition can be made transparent by remarking that, since the concentration and the phase field are not independent variables any more under the constraint of Eq. (31), the variation of $f_{\rm th}$ with respect to ϕ, taking into account the constraint of Eq. (31), is

$$\frac{\delta f_{\rm th}}{\delta\phi} = \frac{\partial f_{\rm th}}{\partial\phi} + \frac{\partial f_{\rm th}}{\partial c}\frac{dc}{d\phi} = \frac{\partial f_{\rm th}}{\partial\phi} + \frac{\mu_{\rm eq}}{V_a}\frac{dc}{d\phi}. \tag{33}$$

Therefore, if

$$\frac{\delta f_{\rm th}}{\delta\phi} = \frac{d}{d\phi}(f_{\rm th} - \mu_{\rm eq}\rho) \equiv 0, \tag{34}$$

the equation for the equilibrium phase-field profile reduces to Eq. (11); in other words, the quantity $f_{\rm th} - \mu_{\rm eq}\rho$ must be constant through the interface. Far from the interfaces, where $f_{\rm int}$ does not contribute, this quantity is equal to the grand-potential density. Note that the common tangent construction implies that the two *bulk* values of the grand potential must be equal. However, for a general choice of free energy functions, there is no reason for this condition to be valid *throughout the whole interface*. As a consequence, the interface equation and all quantities that are obtained from its solution (surface tension, kinetic coefficients etc.) depend on the bulk free energy densities. For realistic values of the interface thickness, this dependence is small, but when the interface thickness is upscaled, large errors can occur.

This fact has been recognized by several authors, and so far two different strategies have been followed to cure this problem. The first is to develop specifically designed free energy functionals that satisfy the condition of Eq. (34), but are valid only for certain choices of bulk free energies (see below). The second strategy is the one of the two-phase model [14–16], in which two separate concentration fields, one for each phase, are used; the supplementary degree of freedom is then eliminated in such a way that Eq. (34) is satisfied.

The new idea put forward here is that a general solution to this problem can also be obtained in the coarse-graining spirit (using a single concentration field) when the model is derived from a grand-potential functional instead of a free energy functional. Indeed, the model formulated in the variables ϕ and ρ is equivalent to the pure substance model formulated in terms of ϕ and e: It has the same variational structure [compare Eqs. (6) and (29)], and both ρ and e are densities of extensive variables. To obtain the equivalent of the more successful pure substance models formulated in the variables ϕ and T, alloy models should be formulated in the variables ϕ

and μ; the corresponding thermodynamic potential is the grand potential.

Grand-potential functionals have been used extensively in classical density functional theory (see [29] for a review). In the context of phase-field models, a grand-potential functional has been introduced to study solidification with density change [30,31]. However, in all the cited works, the density is retained as the fundamental field that is used to evaluate the functional. In contrast, the grand potential in its role as a thermodynamic potential depends on the chemical potential. If the goal is to have a complete formulation of the problem in terms of the dynamical variable μ, the grand-potential functional Ω should be a functional of the field μ. In thermodynamic equilibrium, this field is just a constant which is equal to the thermodynamic equilibrium chemical potential, but out of equilibrium μ can depend on space and time. Therefore, the field ρ that appears in the free energy density needs to be eliminated in favor of μ. This is simple if the values of ρ and μ are related by a local and invertible function. A free energy functional of the form of Eq. (7), taken with free energy densities that depend on T and c, is a good starting point since it contains no nonlocal terms in ρ such as $(\vec{\nabla}\rho)^2$. Moreover, for functions $f_s(c)$ and $f_l(c)$ that are convex in c, the relation between μ and c is monotonous and hence invertible. Thus, it is possible to switch from c to μ as the dynamic field. After this operation, the number density is not a fundamental free field any more, but is obtained as a local functional derivative of the grand-potential functional with respect to the local chemical potential,

$$\rho = -\frac{\delta\Omega[\phi,\mu]}{\delta\mu}. \tag{35}$$

Note that the above requirements (no square gradient terms in c and convex free energy functions) imply that the present method cannot be applied to systems that exhibit phase separation.

In analogy with Eq. (7), the grand-potential functional is

$$\begin{aligned}\Omega[\phi,\mu] &= \int_V \omega(\phi,\vec{\nabla}\phi,\mu)\\ &= \int_V \omega_{\rm int}(\phi,\vec{\nabla}\phi) + g_s(\phi)\omega_s(\mu) + [1-g_s(\phi)]\omega_l(\mu),\end{aligned} \tag{36}$$

where $\omega_{\rm int}$ is identical to $f_{\rm int}$, and the grand-potential densities of the bulk phases are obtained by a Legendre transform of the free energies,

$$\omega_\nu(\mu) = f_\nu(c) - \mu\rho, \qquad (\nu = s,l). \tag{37}$$

This procedure can be easily performed for any convex free energy function, either analytically or numerically. Note that this transformation implicitly uses the equivalence between statistical ensembles (canonical and grand canonical) on the mesoscopic scale. This is consistent with the general philosophy of the coarse-graining approach, which assumes that thermodynamic quantities can be defined on the scale of a coarse-graining cell.

The variation of the grand-potential functional (at constant temperature) is

$$\begin{aligned}\delta\Omega = \int_V &\left\{-\sigma\vec{\nabla}^2\phi + Hf'_{\rm dw}(\phi)\right.\\ &\left.+\frac{g'(\phi)}{2}[\omega_s(\mu)-\omega_l(\mu)]\right\}\delta\phi(\vec{x})\\ &+\left\{g_s(\phi)\frac{\partial\omega_s(\mu)}{\partial\mu} + [1-g_s(\phi)]\frac{\partial\omega_l(\mu)}{\partial\mu}\right\}\delta\mu(\vec{x}).\end{aligned} \tag{38}$$

Since, at solid-liquid coexistence, $\omega_s = \omega_l$, the equilibrium interface equation obtained from the condition of vanishing variation with respect to ϕ is identical to Eq. (11), as desired.

Furthermore, using Eq. (35), the variation of Ω with respect to μ yields

$$\rho(\phi,\mu) = -\frac{\delta\Omega}{\delta\mu} = -g_s(\phi)\frac{\partial\omega_s(\mu)}{\partial\mu} - [1-g_s(\phi)]\frac{\partial\omega_l(\mu)}{\partial\mu}, \tag{39}$$

which is the equivalent of Eq. (15) for the entropy density. Note that this can also be rewritten as

$$\rho(\phi,T,\mu) = g_s(\phi)\rho_s(T,\mu) + [1-g_s(\phi)]\rho_l(T,\mu), \tag{40}$$

with $\rho_\nu = \partial\omega_\nu/\partial\mu$ $(\nu = s,l)$. It is useful to restate this equation in terms of c for future use,

$$c(\phi,\mu) = V_a\rho(\phi,\mu) = g_s(\phi)c_s(\mu) + [1-g_s(\phi)]c_l(\mu), \tag{41}$$

where obviously $c_\nu(\mu) = V_a\partial\omega_\nu/\partial\mu$. Two-phase coexistence is characterized by a constant chemical potential, $\mu = \mu_{\rm eq}(T)$; the corresponding composition profile through a solid-liquid interface is

$$c_{\rm eq}(\phi) = c[\phi,\mu_{\rm eq}(T)] = g_s(\phi)c_s^{\rm eq}(T) + [1-g_s(\phi)]c_l^{\rm eq}(T). \tag{42}$$

The equations of motion for ϕ and μ are now formulated following the same steps as for the pure substance model. The phase field evolves toward a minimum of the grand potential,

$$\partial_t\phi = -M_\phi\frac{\delta\Omega}{\delta\phi} = M_\phi\left[\sigma\vec{\nabla}^2\phi - Hf'_{\rm dw} - \frac{g'(\phi)}{2}(\omega_s-\omega_l)\right]; \tag{43}$$

this equation shows that the thermodynamic driving force for the phase transition is the difference in grand-potential densities. The evolution equation for the chemical potential is obtained by taking the time derivative of Eq. (40), which yields

$$\partial_t\rho = \left(\frac{\partial\rho(\phi,\mu)}{\partial\phi}\partial_t\phi + \frac{\partial\rho(\phi,\mu)}{\partial\mu}\partial_t\mu\right). \tag{44}$$

It is useful to define the quantity

$$\chi(\phi,\mu) = \frac{\partial\rho(\phi,\mu)}{\partial\mu} = g_s(\phi)\frac{\partial\rho_s(\mu)}{\partial\mu} + [1-g_s(\phi)]\frac{\rho_l(\mu)}{\partial\mu}, \tag{45}$$

which will play a role similar to the specific heat in the pure substance model. The symbol χ is chosen here because this quantity can be seen as a generalized susceptibility [32]. Furthermore, the mobility can be written as the product of $\chi(\phi,\mu)$ and a solute diffusion coefficient $D(\phi,\mu)$. Indeed, in the bulk phases, for monotonous (and hence invertible) functions $\rho_{s,l}(\mu)$,

$$\chi_\nu(\mu) = \frac{\partial \rho_\nu(\mu)}{\partial \mu} = \frac{1}{\partial \mu_\nu(\rho)/\partial \rho} = \frac{1}{{V_a}^2 \partial^2 f_\nu(c)/\partial c^2}, \tag{46}$$

which is the well-known thermodynamic factor (Darken factor [33]). The combination of these definitions and Eq. (44) with the mass conservation law, Eq. (27), yields

$$\partial_t \mu = \frac{1}{\chi(\phi,\mu)} \left\{ \vec{\nabla} \cdot [D(\phi,\mu)\chi(\phi,\mu)\vec{\nabla}\mu] - \frac{g'(\phi)}{2} [\rho_s(\mu) - \rho_l(\mu)]\, \partial_t \phi \right\}, \tag{47}$$

an equation completely equivalent to Eq. (20) for the temperature in the pure substance model.

IV. EXAMPLES

The model is completely specified for *any* set of free energy functions for solid and liquid by the definitions of the grand-potential functional [Eqs. (36) and (37)] and the evolution equations (43) and (47). In order to illustrate some of its properties, it is useful to work out several explicit examples. First, it is shown that the equivalent of the linearized pure substance model is obtained from parabolic free energies. Next, it is shown that the dilute alloy model of Ref. [17] can be recovered using this formalism. Finally, the more general case of an ideal solution model is treated.

A. Parabolic free energies

The simplest phenomenological approximation for free energy functions for fixed equilibrium compositions c_s^{eq} and c_l^{eq} at some temperature T are two parabolas,

$$f_\nu(c) = \tfrac{1}{2}\epsilon_\nu \left(c - c_\nu^{\text{eq}}\right)^2, \qquad (\nu = s,l), \tag{48}$$

where ϵ_s and ϵ_l are constants with dimension energy per unit volume. The chemical potential in each phase is

$$\mu = \frac{\partial f_\nu}{\partial \rho} = V_a \epsilon_\nu (c - c_\nu), \tag{49}$$

which can, of course, be inverted to yield c as a function of μ in each phase,

$$c = \frac{\mu}{V_a \epsilon_\nu} + c_\nu^{\text{eq}}. \tag{50}$$

The grand-potential densities are then obtained from the Legendre transform, $\omega_\nu = f_\nu - \mu\rho$, where Eq. (50) is used to switch variables from c to μ,

$$\omega_\nu(\mu) = -\frac{1}{2}\frac{\mu^2}{{V_a}^2 \epsilon_\nu} - \frac{\mu}{V_a} c_\nu^{\text{eq}}. \tag{51}$$

Of course, the use of the definition $\rho = -\partial\omega/\partial\mu$ together with $c = V_a \rho$ yields again Eq. (50). The equilibrium chemical potential for two-phase coexistence is obtained by the condition $\omega_s(\mu_{\text{eq}}) = \omega_l(\mu_{\text{eq}})$. The solution $\mu_{\text{eq}} = 0$ corresponds to the common tangent between the bottoms of the parabolic wells, and the equilibrium compositions are equal to c_s^{eq} and c_l^{eq}. For $\epsilon_s \neq \epsilon_l$, a second solution exists which corresponds to a common tangent that is tilted and yields different values for the equilibrium compositions; this solution is not of interest here. Since $\mu_{\text{eq}} = 0$, we have $\mu = \mu - \mu_{\text{eq}}$; that is, in this model μ is directly the deviation from the equilibrium value of the chemical potential.

Inserting these grand-potential densities in Eqs. (41) and (45) yields the expressions for c and χ as a function of ϕ and μ,

$$c(\phi,\mu) = \left\{ \frac{1}{V_a \epsilon_s} g_s(\phi) + \frac{1}{V_a \epsilon_l}[1 - g_s(\phi)] \right\} \mu + c_s^{\text{eq}} g_s(\phi) + c_l^{\text{eq}}[1 - g_s(\phi)], \tag{52}$$

$$\chi(\phi,\mu) = \frac{1}{{V_a}^2 \epsilon_s} g_s(\phi) + \frac{1}{{V_a}^2 \epsilon_l}[1 - g_s(\phi)]. \tag{53}$$

It is easy to see that when $\epsilon_s = \epsilon_l \equiv \epsilon$, the resulting model is equivalent to the standard pure substance model. Indeed, in this case the difference between the compositions in the two phases is independent of μ and identical to $\Delta c = c_l^{\text{eq}} - c_s^{\text{eq}}$, and the susceptibility is just a constant, $\chi = 1/({V_a}^2 \epsilon)$. This corresponds to the approximations of constant latent heat and constant specific heat, respectively. It is easily verified that Eq. (52) becomes identical to Eq. (24), with Δc and χ replacing L and C_p, respectively. This analogy has been used in several phase-field models [20–22]. The present formalism makes it possible to generalize this model and to use $\epsilon_s \neq \epsilon_l$, that is, parabolas with different curvatures.

B. Dilute alloy

The phase-field model for a dilute alloy of Ref. [17] starts from the free energy densities

$$f_\nu(T,c) = f_\nu^A(T) + \epsilon_\nu c + \frac{k_B T}{V_a}(c \ln c - c), \qquad (\nu = s,l), \tag{54}$$

where $f_s^A(T)$ and $f_l^A(T)$ are the free energy densities of pure A, ϵ_s and ϵ_l are again constants with dimension energy per unit volume, k_B is Boltzmann's constant, and the last term in Eq. (54) is the dilute limit of the entropy of mixing.

The calculation of the grand-potential densities is straightforward and yields

$$\omega_\nu = f_\nu^A - \frac{k_B T}{V_a} \exp\left(\frac{\mu - V_a \epsilon_\nu}{k_B T}\right). \tag{55}$$

The compositions as a function of the chemical potential are given by

$$c_\nu = \exp\left(\frac{\mu - V_a \epsilon_\nu}{k_B T}\right). \tag{56}$$

It is obvious that these compositions satisfy, for any value of the chemical potential, the partition relation

$$c_s = k c_l, \tag{57}$$

with the partition coefficient k given by

$$k = \exp\left(\frac{V_a(\epsilon_l - \epsilon_s)}{k_B T}\right). \tag{58}$$

The equilibrium chemical potential for a given temperature is again obtained from the condition $\omega_s(T,\mu_{\rm eq}) = \omega_l(T,\mu_{\rm eq})$, which yields

$$f_s^A(T) - f_l^A(T) = \frac{k_BT}{V_a}\left[\exp\left(\frac{\mu_{\rm eq} - V_a\epsilon_s}{k_BT}\right) - \exp\left(\frac{\mu_{\rm eq} - V_a\epsilon_l}{k_BT}\right)\right]. \quad (59)$$

The left-hand side can be expanded for temperatures close to the melting temperature T_m; the right-hand side can be rewritten in terms of $c_l^{\rm eq} = c_l(\mu_{\rm eq})$ and the partition coefficient. The result is

$$\frac{L}{T_m}(T - T_m) = \frac{k_BT}{V_a}c_l^{\rm eq}(k-1). \quad (60)$$

If, on the right-hand side of this equation, T is approximated by T_m, which is justified in the limit $c \ll 1$, the standard dilute alloy phase diagram is obtained,

$$c_l^{\rm eq} = \frac{T_m - T}{m}, \quad (61)$$

where $m = k_BT_m^2(1-k)/(V_aL)$ is the liquidus slope.

When these expressions are now used in the complete grand-potential functional, the composition as a function of ϕ and μ becomes

$$c(\phi,\mu) = g_s(\phi)\exp\left(\frac{\mu - V_a\epsilon_s}{k_BT}\right) + [1 - g_s(\phi)]\exp\left(\frac{\mu - V_a\epsilon_l}{k_BT}\right). \quad (62)$$

A specific feature of the dilute alloy model is that this expression can be factorized into two functions that depend only on ϕ and μ, respectively. Moreover, the latter can again be rewritten in terms of the liquid composition, which yields

$$c(\phi,\mu) = c_l(\mu)\,[1 - (1-k)g_s(\phi)]\,. \quad (63)$$

As a result, the expression for the susceptibility is also quite simple and reads

$$\chi(\phi,\mu) = \frac{1}{V_ak_BT}\exp\left(\frac{\mu - V_a\epsilon_l}{k_BT}\right)[1 - (1-k)g_s(\phi)] = \frac{c(\phi,\mu)}{V_ak_BT}. \quad (64)$$

Inserting these expressions in Eqs. (43) and (47) leads to model equations identical to those of Ref. [17]. The difference of the grand-potential densities is

$$\omega_s(\mu) - \omega_l(\mu) = f_s^A(T) - f_l^A(T) - \frac{k_BT}{V_a}\left[\exp\left(\frac{\mu - V_a\epsilon_s}{k_BT}\right) - \exp\left(\frac{\mu - V_a\epsilon_l}{k_BT}\right)\right]. \quad (65)$$

The free energy difference can be expressed in terms of the equilibrium chemical potential using Eq. (59), and after some algebra one obtains

$$\omega_s(\mu) - \omega_l(\mu) = \frac{k_BT}{V_a}c_l^{\rm eq}(1-k)\left[\exp\left(\frac{\mu - \mu_{\rm eq}}{k_BT}\right) - 1\right]. \quad (66)$$

As in Ref. [17], two dimensionless variables are now introduced. The first,

$$u = \frac{\mu - \mu_{\rm eq}}{k_BT}, \quad (67)$$

is the dimensionless deviation of the chemical potential from its equilibrium value. This variable can also be expressed in terms of the composition and the equilibrium composition at two-phase coexistence using the definition of Eq. (42) as

$$u = \ln\frac{c(\phi,\mu)}{c_{\rm eq}(\phi)}. \quad (68)$$

The second dimensionless variable,

$$U = \frac{e^u - 1}{1 - k}, \quad (69)$$

is a dimensionless supersaturation. This can be seen by inserting the identity $e^u = c(\phi,\mu)/c_{\rm eq}(\phi)$ obtained from the preceding equation, which yields

$$U = \frac{c(\phi,\mu) - c_{\rm eq}(\phi)}{(1-k)c_{\rm eq}(\phi)}. \quad (70)$$

When the driving force (the grand-potential difference) is expressed in either of these variables, the same evolution equation for the phase field as in Ref. [17] is obtained.

Matters are slightly more complicated for the second evolution equation. Reference [17] uses an evolution equation for the composition (or, equivalently, for the dimensionless supersaturation U) rather than for the chemical potential. For the dilute alloy model, such an equation can be obtained starting from the general evolution equation of the chemical potential [Eq. (47)] or (more simply) from the original formulation of the mass conservation law [Eq. (27)]. For this purpose, the chemical potential has to be eliminated in favor of c or U. This is possible because Eqs. (67) and (69) can be inverted and combined with Eq. (63) to yield

$$\mu = \mu_{\rm eq} + k_BT\ln\frac{c}{c_l^{\rm eq}[1 - (1-k)g_s(\phi)]} \quad (71)$$

and

$$c = c_l^{\rm eq}[1 - (1-k)g_s(\phi)]\,[1 + (1-k)U]\,. \quad (72)$$

A straightforward calculation then yields the variational form (without the antitrapping current) of the evolution equation for the composition of Ref. [17]. These steps will be discussed in more detail later on; here, it is important to stress that the possibility to switch from an evolution equation for μ to one for c by an exact transformation is specific to the dilute alloy model: This procedure only works because the function $c(\phi,\mu)$ is easily inverted, which is not the case in more general models, as seen below.

C. Ideal solution model

In an ideal solution model, the free energy is a weighted average of the pure substance free energies of A and B plus an entropy of mixing term,

$$f_\nu(T,c) = (1-c)f_\nu^A(T) + cf_\nu^B(T) + \frac{k_BT}{V_a}[c\ln c + (1-c)\ln(1-c)]. \tag{73}$$

Contact with the notations of the previous examples can be made by setting $\epsilon_\nu = f_\nu^B - f_\nu^A$; the free energy becomes

$$f_\nu(T,c) = f_\nu^A(T) + c\epsilon_\nu(T) + \frac{k_BT}{V_a}[c\ln c + (1-c)\ln(1-c)]. \tag{74}$$

The chemical potential is

$$\mu = \frac{\partial f_\nu}{\partial \rho} = V_a\epsilon_\nu + k_BT\ln\frac{c}{1-c}. \tag{75}$$

This can be inverted to yield the concentration in each phase as a function of μ,

$$c_\nu(\mu) = \frac{\exp\left(\frac{\mu - V_a\epsilon_\nu}{k_BT}\right)}{1+\exp\left(\frac{\mu - V_a\epsilon_\nu}{k_BT}\right)}. \tag{76}$$

The grand-potential densities are

$$\omega_{s,l} = f_\nu^A + \frac{k_BT}{V_a}\ln(1-c) = f_\nu^A - \frac{k_BT}{V_a}\ln\left[1+\exp\left(\frac{\mu - V_a\epsilon_\nu}{k_BT}\right)\right]. \tag{77}$$

As before, these expressions can now be used to define the interpolated composition and the susceptibility,

$$c(\phi,\mu) = \frac{\exp\left(\frac{\mu - V_a\epsilon_s}{k_BT}\right)}{1+\exp\left(\frac{\mu - V_a\epsilon_s}{k_BT}\right)}g_s(\phi) + \frac{\exp\left(\frac{\mu - V_a\epsilon_l}{k_BT}\right)}{1+\exp\left(\frac{\mu - V_a\epsilon_l}{k_BT}\right)}[1-g_s(\phi)], \tag{78}$$

$$\chi(\phi,\mu) = \frac{c_s(\mu)[1-c_s(\mu)]g_s(\phi) + c_l(\mu)[1-c_l(\mu)][1-g_s(\phi)]}{V_ak_BT}, \tag{79}$$

where the latter has been expressed in terms of the functions $c_{s,l}(\mu)$ because this leads to a simpler expression.

The equations of motion for the ideal solution model are obtained by inserting these expressions in the general evolution equations [Eqs. (43) and (47)]. The equilibrium chemical potential and the phase diagram can be calculated analytically, but the resulting expressions are quite complicated and not of interest here. The important point here is that for this model it is not possible to transform the evolution equation for μ into one for the composition c: Whereas the functions $c_\nu(\mu)$ for the composition in each phase as a function of μ can be easily inverted, the same is not true for the interpolated composition given by Eq. (78). As a consequence, it is easy to obtain c from μ for given ϕ and T, but hard to obtain μ from c.

V. RELATIONS WITH OTHER PHASE-FIELD MODELS

A. Equivalence to the Kim-Kim-Suzuki model

In the two-phase model [16], the interface region is seen as a phenomenological superposition of the two bulk phases, with a weighting function $h_s(\phi)$ that interpolates between liquid ($h_s = 0$) and solid ($h_s = 1$). The main difference to the coarse-graining approach is that the two-phase model starts with two separate composition fields for the solid and the liquid, c_s and c_l. The free energy density and the "true" composition (in the coarse-graining sense) are then written as

$$f(\phi,c) = h_s(\phi)f_s(c_s) + [1-h_s(\phi)]f_l(c_l), \tag{80}$$

$$c = h_s(\phi)c_s + [1-h_s(\phi)]c_l. \tag{81}$$

Since there are two equations but three variables (ϕ, c_s, and c_l), an additional condition is needed to close the system: The chemical potentials of the two coexisting phases are required to be the same,

$$\mu \equiv \frac{\partial f_s(\phi,c_s)}{\partial c_s} = \frac{\partial f_l(\phi,c_l)}{\partial c_l}. \tag{82}$$

Taking this implicit relationship between c_s and c_l into account, the number of independent fields is reduced to two, and two evolution equations for, say, ϕ and c can be written.

This approach is completely equivalent to the grand-potential formalism outlined above, with the difference that the dynamical variable is c instead of μ. To see this, set $h_s(\phi) = g_s(\phi)$. Equation (81) becomes identical to Eq. (41). Furthermore, since the compositions c_s and c_l in Eq. (41) are defined as functions of the variable μ, Eq. (82) is automatically satisfied. Finally, since all the equations of Ref. [16] are developed by analogy with the pure substance model, it is not surprising that the evolution equations, Eqs. (31) and (32) of Ref. [16], are identical to the evolution equations (43) and (47) of the present paper once all the notations have been properly translated: The driving force for the phase transformation is the difference in grand-potential density, and the quantity f_{cc} that appears in the evolution equation for the concentration in Ref. [16] is identical to $1/({V_a}^2\chi)$ here.

In summary, the two-phase model can be obtained in a fully variational manner from a grand-potential functional. Note that, in this point of view, the introduction of two separate composition fields is not necessary anymore: The fundamental dynamical field is the chemical potential, and the two fields c_s and c_l are simply obtained as the derivatives of the bulk grand-potential densities with respect to μ, whereas the "real" composition at any space point is given by the functional derivative of the grand-potential functional.

B. Relation to the phenomenological two-phase model

At this point, it is useful to discuss the respective merits of the grand potential and the two-phase approaches. At first glance, the former seems to be more advantageous: The number of fundamental fields is equal to two (as compared to three for the two-phase model), and whereas μ has to be obtained from c_s and c_l in the two-phase model by solving Eq. (82), c_s and c_l are obtained from μ by simple derivatives in the grand-potential formalism. However, an analysis in terms of computation time reveals that matters are not so simple. For the sake of concreteness, consider the simplest case of constant but distinct solute diffusivities in the solid and the liquid. In this case, the evolution equation for the composition reduces, in the bulk phases, to the simple linear diffusion equation. In contrast, the evolution equation for μ has several nonlinearities (even in the bulk) due to the presence of the factors $\chi(\phi,\mu)$, which are, in general, nonlinear functions of μ. This means that the numerical effort to integrate the equation for μ in the bulk is higher that the one for integrating an equation for c. In the interfaces, the grand-potential formulation does not require much additional effort, whereas the nontrivial Eq. (82) has to be solved in the two-phase model. However, since the interface regions usually represent only a small fraction of all the grid points in a numerical simulation, the equation of motion for μ may not always be advantageous from a computational point of view.

The computational disadvantage of the grand-potential formalism in the bulk can be alleviated by an additional step, which also brings to light the direct relation of this approach to the phenomenological two-phase models that use a simple partition relation between the two concentration fields [14,15]. The idea is to make a change of variables and to replace the chemical potential field by another continuous field that plays the same role. In order to obtain the standard diffusion equation for this field in the liquid phase, the appropriate field is the density (or the composition) in the liquid, ρ_l or c_l. Indeed, under the hypothesis that $\mu = \partial f_l/\partial\rho$ is an invertible function of ρ, the function $\rho_l = \partial\omega_l/\partial\mu$ is just its inverse function, according to the properties of the Legendre transform. Furthermore, $\rho_s = \partial\omega_s/\partial\mu$ is also a function of μ and can therefore expressed as a function of ρ_l,

$$\rho_s(\rho_l) = \rho_s[\mu(\rho_l)]. \tag{83}$$

Eliminating μ in favor of ρ_l in Eq. (47) yields

$$\begin{aligned}\partial_t\rho_l = \frac{\chi_l(\rho_l)}{\chi(\phi,\rho_l)}\Bigg\{&\vec{\nabla}\cdot\left[D(\phi,\rho_l)\frac{\chi(\phi,\rho_l)}{\chi_l(\rho_l)}\vec{\nabla}\rho_l\right]\\ &+\frac{g'(\phi)}{2}[\rho_s(\rho_l)-\rho_l]\partial_t\phi\Bigg\},\end{aligned} \tag{84}$$

where $\chi_l = \partial^2\omega_l/\partial\mu^2 = \chi(-1,\mu)$ is the susceptibility of the liquid phase. Using the fact that $\chi(\phi,\mu) = \chi_s(\mu)g_s(\phi) + \chi_l(\mu)[1-g_s(\phi)]$ by definition, this equation can be rewritten as

$$\begin{aligned}\partial_t\rho_l = {}&\frac{1}{\chi_l(\rho_l)\{1-[1-g_s(\phi)\chi_s/\chi_l]\}}\\ &\times\Bigg\{\vec{\nabla}\cdot[D(\phi,\rho_l)\chi_l(\rho_l)[1-(1-g_s(\phi)\chi_s/\chi_l)]\vec{\nabla}\rho_l]\\ &+\frac{g'(\phi)}{2}\,[\rho_s(\rho_l)-\rho_l]\,\partial_t\phi\Bigg\}.\end{aligned} \tag{85}$$

For a dilute alloy, $\rho_s/\rho_l = k$ and $\chi_s/\chi_l = k$, according to Eqs. (58) and (64), and the above model becomes identical to the one of Refs. [14,15]. The grand-potential formalism thus indicates a path for the generalization of these models to arbitrary phase diagrams.

C. Local supersaturation approximation

Further progress can be made by a simple approximation. The crucial point is the relation between composition and chemical potential: Its nonlinearity penalizes the grand-potential formalism in the bulk and makes the resolution of Eq. (82) in the two-phase model nontrivial. The idea is thus to replace the exact relation between chemical potential and composition *in the interfaces* by an approximate one that will make it possible to write a simple equation for the composition. This approximation is called the *local supersaturation approximation*: It exploits the fact that, for slow solidification, the chemical potential in the interfaces is close to the value for two-phase equilibrium. This suggests to use a Taylor expansion of the composition around the equilibrium composition profile in the interface,

$$c - c_{\rm eq}(\phi) = \left.\frac{\partial c}{\partial\mu}\right|_{\mu_{\rm eq}}(\mu-\mu_{\rm eq}) = V_a\chi(\phi,\mu_{\rm eq})(\mu-\mu_{\rm eq}), \tag{86}$$

which can be easily inverted to yield

$$\mu = \mu_{\rm eq} + \frac{c-c_{\rm eq}(\phi)}{V_a\chi(\phi,\mu_{\rm eq})}. \tag{87}$$

Furthermore, an expansion of the driving force around the equilibrium chemical potential yields

$$\omega_s(\mu)-\omega_l(\mu) = \frac{c_l^{\rm eq}-c_s^{\rm eq}}{V_a}(\mu-\mu_{\rm eq}). \tag{88}$$

Inserting these expression in the evolution equation for the phase field and the mass conservation law yields a simple set of equations for ϕ and c,

$$\frac{1}{M_\phi}\partial_t\phi = \sigma\vec{\nabla}^2\phi - Hf'_{\rm dw} - \frac{g'(\phi)}{2}\Delta c\frac{c-c_{\rm eq}(\phi)}{{V_a}^2\chi(\phi,\mu_{\rm eq})}, \tag{89}$$

$$\partial_t c = \vec{\nabla}\left[D(\phi)\chi(\phi,\mu_{\rm eq})\vec{\nabla}\left(\frac{c-c_{\rm eq}(\phi)}{\chi(\phi,\mu_{\rm eq})}\right)\right]. \tag{90}$$

Note that the second equation can also be rewritten after applying the chain rule as

$$\begin{aligned}\partial_t c = {}&\vec{\nabla}D(\phi)\vec{\nabla}c\\ &+\vec{\nabla}\left[D(\phi)\frac{g'(\phi)}{2}\left(\Delta c+\frac{\chi_l^{\rm eq}-\chi_s^{\rm eq}}{\chi(\phi,\mu_{\rm eq})}\right)\vec{\nabla}\phi\right],\end{aligned} \tag{91}$$

where $\chi_{s,l}^{\rm eq} = \chi(\pm 1,\mu_{\rm eq})$. This latter form displays explicitly the two driving forces for solute diffusion that establish the equilibrium solute profile and that lead to solute redistribution out of equilibrium:composition gradients and differences between the thermodynamic potentials in the two phases.

Before proceeding further, it is useful to relate the quantities that appear in the above equations to the phase diagram of the binary alloy, characterized by the curves $c_s^{\rm eq}(T)$ and $c_l^{\rm eq}(T)$, or equivalently by the coexistence line $\mu_{\rm eq}(T)$. The quantities $\chi_\nu^{\rm eq}$ are related to the liquidus and solidus slopes, $m_\nu = dT/dc_\nu^{\rm eq}$,

$$\frac{1}{m_\nu} = \frac{dc_\nu^{\rm eq}}{dT} = \left.\frac{\partial c}{\partial\mu}\right|_{\mu_{\rm eq}}\frac{d\mu_{\rm eq}}{dT} = V_a\chi_\nu^{\rm eq}\frac{d\mu_{\rm eq}}{dT}. \tag{92}$$

Moreover, the quantity $d\mu_{\rm eq}/dT$ can be evaluated using a Clausius-Clapeyron relation for the μ-T coexistence line,

$$\frac{d\mu_{\rm eq}}{dT} = -\frac{L}{T\Delta\rho} = -\frac{LV_a}{T\Delta c}. \tag{93}$$

Combining these results yields

$$\chi_{s,l}^{\rm eq} = -\frac{T\Delta c}{V_a{}^2 L m_{s,l}}. \tag{94}$$

Thus, the susceptibilities are inversely proportional to the liquidus and solidus slopes, and therefore, $\chi_s^{\rm eq}/\chi_l^{\rm eq} = m_l/m_s$. Defining an effective partition coefficient by the ratio of the liquidus solpes $k_m = m_l/m_s$, the evolution equations of the phase-field model can be further simplified. Indeed, the susceptibility along the equilibrium profile is

$$\begin{aligned}\chi(\phi,\mu_{\rm eq}) &= \chi_s^{\rm eq} g_s(\phi) + \chi_l^{\rm eq}[1-g_s(\phi)]\\ &= \chi_l^{\rm eq}[1-(1-k_m)g_s(\phi)],\end{aligned} \tag{95}$$

and the evolution equations for ϕ and c become

$$\begin{aligned}\frac{1}{M_\phi}\partial_t\phi &= \sigma\vec{\nabla}^2\phi - Hf'_{\rm dw}\\ &\quad - \frac{g'(\phi)}{2}\frac{\Delta c}{V_a{}^2\chi_l^{\rm eq}}\frac{c-c_{\rm eq}(\phi)}{1-(1-k_m)g_s(\phi)},\end{aligned} \tag{96}$$

$$\begin{aligned}&\partial_t c\\ &= \vec{\nabla}\left[D(\phi)[1-(1-k_m)g_s(\phi)]\vec{\nabla}\left(\frac{c-c_{\rm eq}(\phi)}{1-(1-k_m)g_s(\phi)}\right)\right].\end{aligned} \tag{97}$$

These equations are very similar to the ones of the dilute alloy model, except that the partition coefficient k has been replaced by the effective partition coefficient k_m which depends on the temperature. In that sense, this approach bears some similarity with the method used in Ref. [34] to construct a quantitative phase-field model for arbitrary phase diagrams: The free energy curves are first approximated by a dilute alloy phase diagram with "effective" (temperature-dependent) partition coefficient, melting temperature, and liquidus slope; the equations of motion for the dilute alloy model are then applied with these effective parameters. Here the approximation is directly in the evolution equations and can be applied in a straightforward manner for arbitrary free energy functions. Also note that the two approximations are not completely equivalent. For instance, the effective partition coefficient in Ref. [34] is defined by the ratio of the compositions, $c_s^{\rm eq}/c_l^{\rm eq}$, which is equal to the ratio m_l/m_s only for a dilute alloy.

It should also be noted that this approximation is *not* equivalent to the approximation of constant concentration gap Δc (equivalent to parallel liquidus and solidus slopes) used in Refs. [20,22,35]. This can be easily seen from Eq. (86) by considering a constant chemical potential deviation $\delta\mu = \mu - \mu_{\rm eq}$ (generated, for example, by a local curvature of the interface): The shifts in concentration on the two sides of the interface are proportional to $\chi_{s,l}^{\rm eq}$, respectively, and hence inversely proportional to the liquidus slopes, as they should be.

The above approximation has been called "local" for two reasons. First, this emphasizes the fact that the approximation of the relationship between composition and chemical potential is needed only in the interfaces, while it leaves the bulk evolution equations unchanged. Second, it is anticipated that this method should be applicable to situations in which the temperature field varies slowly with time and over large length scales, such as in directional solidification or in thermosolutal models with realistic values of the Lewis number. For this purpose, it should be sufficient to apply the above equations with the *local* value of the temperature for each point of the interface, which implies that Δc, $\chi_{s,l}^{\rm eq}$, and k_m are not constants but vary between different interface points.

D. Nonvariational model and antitrapping current

The next step is to incorporate into the model two features that have been widely used to increase the precision and performance of phase-field models. The first is motivated by the fact that a nonvariational model can be more efficient for computational purposes than a strictly variational formulation. This was first highlighted by Karma and Rappel [1], and their method has since been used in many other models. In the terms of the present formulation, it amounts to keeping the interpolation function $g(\phi)$ in the evolution equation of the phase field, but using a different interpolation function for the number density and the susceptibility. Let $h(\phi)$ be a function that has the property $h(\pm 1) = \pm 1$, and let

$$h_s(\phi) = \frac{1+h(\phi)}{2}. \tag{98}$$

Then, the concentration is defined as

$$\rho(\phi,\mu) = \frac{c(\phi,\mu)}{V_a} = \rho_s(\mu)h_s(\phi) + \rho_l(\mu)[1-h_s(\phi)], \tag{99}$$

instead of Eq. (40); as a consequence, the equilibrium composition profile given by Eq. (42) is also modified and becomes

$$c_{\rm eq}(\phi) = c_s^{\rm eq} h_s(\phi) + c_l^{\rm eq}[1-h_s(\phi)]. \tag{100}$$

The susceptibility is still defined as the derivative of the number density with respect to the chemical potential and becomes

$$\begin{aligned}\chi(\phi,T,\mu) = \frac{\partial\rho(\phi,T,\mu)}{\partial\mu} &= h_s(\phi)\chi_s(T,\mu)\\ &\quad + [1-h_s(\phi)]\chi_l(T,\mu).\end{aligned} \tag{101}$$

The second feature is the so-called antitrapping current, which was developed in order to counterbalance spurious solute trapping [17,23]. Indeed, if the solute diffusivity in the solid is substantially lower than in the liquid, as is usually the case in alloy solidification, the upscaling of the interface thickness magnifies the solute trapping effect, whose magnitude is proportional to the interface thickness [36]. To restore local equilibrium at the interface, as appropriate for low-speed solidification, an additional solute current is introduced which "pushes" the solute out of the freezing material, and which is given by

$$\vec{j}_{\rm at} = aW[\rho_l(\mu) - \rho_s(\mu)]\hat{n}\partial_t\phi, \tag{102}$$

where $\hat{n} = -\vec{\nabla}\phi/|\vec{\nabla}\phi|$ is the unit normal vector pointing from the solid to the liquid, W is the interface thickness, and $a > 0$ is a constant to be determined by a matched asymptotic analysis [17]. The current thus defined is proportional to the interface velocity (*via* the factor $\partial_t\phi$) and to the composition difference between solid and liquid, and is directed from the solid to the liquid for a solidifying interface, for which $\partial_t\phi > 0$. The mass conservation law [Eq. (27)] reads now

$$\begin{aligned}\partial_t\rho &= -\vec{\nabla}(\vec{j}_\rho + \vec{j}_{\mathrm{at}})\\ &= \vec{\nabla}\{M(\phi,\mu)\vec{\nabla}\mu - aW[\rho_l(\mu) - \rho_s(\mu)]\hat{n}\partial_t\phi\}.\end{aligned} \tag{103}$$

Taking these modifications into account, the evolution equation for the chemical potential [Eq. (47)] is replaced by

$$\begin{aligned}\partial_t\mu = \frac{1}{\chi(\phi,\mu)}\Big\{&\vec{\nabla}\cdot[D(\phi,\mu)\chi(\phi,\mu)\vec{\nabla}\mu - aW[\rho_l(\mu)\\ &- \rho_s(\mu)]\hat{n}\partial_t\phi] - \frac{h'(\phi)}{2}[\rho_s(\mu) - \rho_l(\mu)]\partial_t\phi\Big\};\end{aligned} \tag{104}$$

the evolution equation for ϕ remains unchanged.

In the local supersaturation approximation, the composition difference in the expression for the antitrapping current is approximated by its equilibrium value, $\rho_l - \rho_s = (c_l^{\mathrm{eq}} - c_s^{\mathrm{eq}})/V_a = \Delta c/V_a$. The evolution equation for the composition [Eq. (97)] is then replaced by

$$\begin{aligned}\partial_t c = \vec{\nabla}\Bigg[&D(\phi)[1-(1-k_m)h_s(\phi)]\vec{\nabla}\left(\frac{c - c_{\mathrm{eq}}(\phi)}{1-(1-k_m)h_s(\phi)}\right)\\ &- aW\hat{n}\Delta c\partial_t\phi\Bigg].\end{aligned} \tag{105}$$

E. Relation to the quantitative dilute alloy model

As usual, the parameters of the phase-field model have to be related to the quantities that appear in the sharp-interface theories by matched asymptotic analysis. The complete asymptotic analysis for the general Eqs. (43) and (47) will be presented elsewhere. Here, only the behavior of the model in the local supersaturation approximation is discussed, because for its analysis the analogy to the dilute alloy model [17] can be exploited.

In order to apply directly the results of Ref. [17], it is useful to cast the evolution equations in dimensionless form. From Eqs. (89) and (90), it is clear that the dimensionless variable that generalizes the quantity U of the dilute alloy model defined by Eq. (69) is

$$U = \frac{\chi_l^{\mathrm{eq}}}{\chi(\phi,\mu_{\mathrm{eq}})}\frac{c - c_{\mathrm{eq}}(\phi)}{\Delta c} = \frac{c - c_{\mathrm{eq}}(\phi)}{\Delta c[1-(1-k_m)h_s(\phi)]}. \tag{106}$$

Indeed, this expression can be rewritten using the fact that $c_{\mathrm{eq}}(\phi) = c_l^{\mathrm{eq}}[1-(1-k)h_s(\phi)]$, where $k = c_s^{\mathrm{eq}}/c_l^{\mathrm{eq}}$ is the standard partition coefficient,

$$U = \frac{1}{1-k}\frac{1-(1-k)h_s(\phi)}{1-(1-k_m)h_s(\phi)}\frac{c - c_{\mathrm{eq}}(\phi)}{c_{\mathrm{eq}}(\phi)}, \tag{107}$$

which reduces to Eq. (70) for a dilute alloy, since $k = k_m$ in this case.

In terms of this variable, Eq. (90) becomes

$$\begin{aligned}[1-(1-k_m)h_s(\phi)]\partial_t U = \vec{\nabla}\big\{&D(\phi)[1-(1-k_m)h_s(\phi)]\vec{\nabla}U\\ &+ aW\hat{n}[1+(1-k_m)U]\partial_t\phi\big\}\\ &+ [1+(1-k_m)U]\partial_t h_s(\phi).\end{aligned} \tag{108}$$

A form formally identical to Eq. (69) in Ref. [17] is obtained by choosing a particular interpolation for the diffusion coefficient $D(\phi)$, namely, by setting

$$D(\phi)[1-(1-k_m)h_s(\phi)] \equiv D_l q(\phi), \tag{109}$$

where D_l is the solute diffusivity in the liquid, supposed to be constant. Note that, since the left-hand side is actually the product of the diffusivity and the susceptibility, strictly speaking the function $q(\phi)$ is an interpolation of the *mobility* rather than of the diffusion coefficient. The final result for the evolution equation is

$$\begin{aligned}&[1-(1-k_m)h_s(\phi)]\partial_t U\\ &\quad = \vec{\nabla}\{D_l q(\phi)\vec{\nabla}U + aW\hat{n}[1+(1-k_m)U]\partial_t\phi\}\\ &\qquad + [1+(1-k_m)U]\partial_t h_s(\phi).\end{aligned} \tag{110}$$

This equation is indeed identical to the one used in the asymptotics of the dilute alloy model, except that the dilute alloy partition coefficient k is replaced by the ratio of the solidus and liquidus slopes k_m. This is very natural, since this quantity controls how the composition difference between solid and liquid depends on the chemical potential at the interface.

The replacement of c by U in the evolution equation for the phase field leads to

$$\frac{1}{M_\phi}\partial_t\phi = \sigma\vec{\nabla}^2\phi - Hf'_{\mathrm{dw}} - \frac{g'(\phi)}{2}\frac{(\Delta c)^2}{V_a\chi_l^{\mathrm{eq}}}U. \tag{111}$$

This equation is now divided by the constant H, which amounts to nondimensionalizing the free energy and grand-potential densities (since H has dimension of energy per unit volume). Furthermore, the function g is now chosen to be the standard fifth-order polynomial $g(\phi) = 15(\phi - 2\phi^3/3 + \phi^5/5)/8$, the function $h(\phi) = \phi$, and the double-well function to be $f_{\mathrm{dw}} = 1/4 - \phi^2/2 + \phi^4/4$. The resulting equation reads

$$\tau\partial_t\phi = W^2\vec{\nabla}^2\phi + \phi - \phi^3 - (1-\phi^2)^2\lambda U, \tag{112}$$

where $\tau = 1/(M_\phi H)$ is the relaxation time for the phase field, $W = \sqrt{\sigma/H}$ is the interface thickness defined by Eq. (13), and the constant λ is given by

$$\lambda = \frac{15}{16}\frac{(\Delta c)^2}{HV_a{}^2\chi_l^{\mathrm{eq}}}. \tag{113}$$

Equation (112) is identical to the standard evolution equation for the phase field [1,17].

As announced previously, the results of the asymptotic analysis of Ref. [17] can now be exploited since Eqs. (110) and (112) are identical to the model analyzed in this reference. Therefore, the variable U obeys, in the liquid, the free boundary problem

$$\partial_t U = D_l \vec{\nabla}^2 U, \tag{114}$$

$$U_{\rm int} = -d_0 \mathcal{K} - \beta V_n, \tag{115}$$

$$[1 + (1 - k_m) U_{\rm int}] V_n = -D_l \partial_n U|_{\rm int}, \tag{116}$$

where $\mathcal{K}$ and V_n are the local curvature and interface velocity, respectively, d_0 is the capillary length, and β the kinetic coefficient. Equation (115) is the generalized Gibbs-Thomson equation, and Eq. (116) is the Stefan boundary condition that describes mass conservation at the phase boundary.

In terms of the phase-field parameters, the capillary length and the kinetic coefficient are given by

$$d_0 = a_1 \frac{W}{\lambda}, \tag{117}$$

$$\beta = a_1 \frac{\tau}{\lambda W} \left(1 - a_2 \frac{\lambda W^2}{\tau D_l} \right), \tag{118}$$

with $a_1 = 5\sqrt{2}/8$ and $a_2 = 0.6267$; these values are identical to those obtained by Karma and Rappel [1].

In terms of physical quantities, this expression for the capillary length is, in fact, identical to the standard thermodynamic definition [32]. Indeed, the number $a_1 = 5\sqrt{2}/8$ quoted above is equal to $(15/16)I$, where I, the numerical constant defined in Eq. (12), is equal to $2\sqrt{2}/3$ for the standard fourth-order double well potential used here. With the help of these relations, Eq. (117) can be rewritten as

$$d_0 = \frac{I W H {V_a}^2 \chi_l^{\rm eq}}{(\Delta c)^2}. \tag{119}$$

Then, the use of Eqs. (12) and (46) yields

$$d_0 = \frac{\gamma {V_a}^2 \chi_l^{\rm eq}}{(\Delta c)^2} = \frac{\gamma}{(\Delta c)^2 \left. \frac{\partial^2 f_l(c)}{\partial c^2} \right|_{c_l}}. \tag{120}$$

VI. NUMERICAL TESTS

The relations found in the preceding section are now used to perform some illustrative simulations on a concrete model system. The ideal solution model is chosen, with the same parameters as those used in Ref. [12] to model the nickel-copper alloy. This alloy exhibits a typical lens-shape phase diagram with a rather narrow coexistence zone. Concretely, the free energy densities given by Eq. (73) are used; the free energy differences (between solid and liquid) of the pure substances are given by

$$f_s^{Ni}(T) - f_l^{Ni}(T) = \frac{L^{Ni}}{T_m^{Ni}} (T - T_m^{Ni}), \tag{121}$$

$$f_s^{Cu}(T) - f_l^{Cu}(T) = \frac{L^{Cu}}{T_m^{Cu}} (T - T_m^{Cu}), \tag{122}$$

with the melting temperatures $T_m^{Ni} = 1728$ K and $T_m^{Cu} = 1358$ K and the latent heats $L^{Ni} = 2350\ {\rm J/cm^3}$ and $L^{Cu} = 1728\ {\rm J/cm^3}$. The molar volume is taken to be 7.42 cm^3, and the surface tension $\gamma = 3.3 \times 10^{-5}\ {\rm J/cm^2}$.

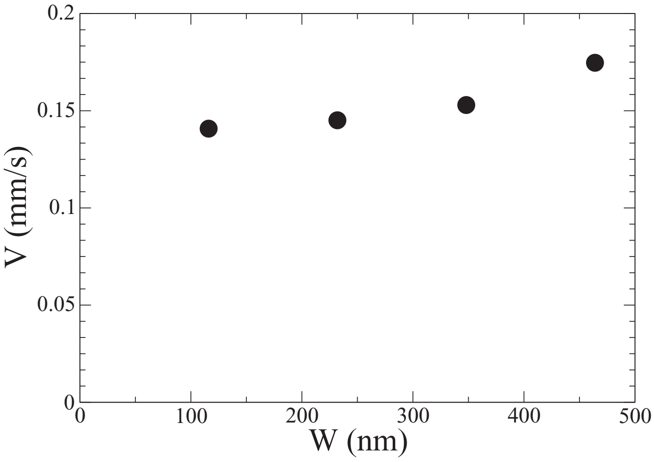

FIG. 1. Growth velocity of a two-dimensional dendrite in the Ni-Cu alloy at 1710 K, for different choices of the interface width W.

For a temperature of 1710 K, the equilibrium concentrations are $c_s^{\rm eq} = 0.045\,988$ and $c_l^{\rm eq} = 0.058\,098$, the partition coefficient is $k = 0.7916$, the ratio of the liquidus slopes is $k_m = 0.8017$, and the capillary length calculated by Eq. (120) is $d_0 = 6{,}426 \times 10^{-6}$ cm. Isothermal dendritic solidification is simulated in two dimensions. The anisotropy needed to obtain stable dendritic growth is introduced in the standard way [1,17,23] by making the surface tension dependent on the angle θ between the interface normal and a crystallographic axis, here chosen to coincide with the x direction. A standard fourfold anisotropy, $\gamma(\theta) = \bar{\gamma}[1 + \epsilon_4 \cos(4\theta)]$, is used, with $\epsilon_4 = 0.025$. The initial composition of the liquid is chosen as $(c_s^{\rm eq} + c_l^{\rm eq})/2$, which corresponds to a supersaturation of 0.5.

Four simulations are carried out with the equations of motion in the local supersaturation approximation, with $\lambda = 1.596, 3.192, 4.788$, and 6.384, which corresponds to interface widths of $W = 116, 232, 348$, and 464 nm. For each simulation, the relaxation time of the phase-field equation is chosen such as to eliminate interface kinetics ($\beta = 0$ for all orientations). The steady-state growth velocity of the dendrites is measured as described in Ref. [1], and the result is displayed in Fig. 1. It exhibits the behavior that is typical for quantitative phase-field models: The simulation results converge to a constant value with decreasing interface thickness W, and the convergence is roughly quadratic in W, which can be expected since all terms linear in W have been eliminated by the model formulation. It is not surprising to find such behavior, since the model used here is essentially identical to the dilute alloy model for which rapid convergence with W has been demonstrated [17,23]. Moreover, the parameters chosen here are in a region of the phase diagram in which the dilute approximation should still work quite well. However, this is not a limitation of the approach: Simulations at $T = 1410$ K, where the ratio of the liquidus slopes $k_m = 1.2609$ is very different from the partition coefficient $k = 0.9590$, yield a similar convergence plot. This shows that the model can be applied to alloys with arbitrary phase diagram.

VII. SUMMARY AND PERSPECTIVES

The most important conclusions of the present work can be summarized as follows.

(i) A phase-field model for alloy solidification has been obtained in a completely variational framework, starting from a phenomenological grand-potential functional that is a simple sum of bulk and interface contributions. In this model, the two dynamic variables are the phase field and the chemical potential field. A complete analogy can be established with the standard phase-field model for the solidification of a pure substance, in which the variables are the phase field and the temperature field. The main difference between the two sets of equations is that the relation between the composition and the chemical potential (the extensive and the intensive variable) is nonlinear, whereas the relation between temperature and internal energy is usually assumed to be linear.

(ii) The resulting model is shown to be completely equivalent to the model of Kim, Kim, and Suzuki [16], with the chemical potential replacing the composition as the dynamic field. As a result, in the present model no "partitioning" of the solute into coexisting phases is necessary; the (auxiliary) compositions in each of the phases can be simply obtained from the chemical potential. With an additional change of variables, the simpler models with constant partition coefficient [14,15] can also be recovered and extended to general alloy phase diagrams. These developments show that these two-phase models, despite a seemingly quite different starting point, can, in fact, also be obtained by a coarse-graining procedure if the appropriate thermodynamic potential is used.

(iii) The equations of the new model can also be written in terms of a phase field and the composition field. They thus have essentially the same computational complexity as the original phase-field models for alloy solidification [10,11] derived in the coarse-graining framework. However, in contrast to the latter models, they have a decisive property which is required for quantitative simulations: Bulk and interface thermodynamic properties can be adjusted independently. This difference in behavior is due to the different interpolations of the relevant thermodynamic potentials (free energies in Refs. [10,11], grand potentials here).

(iv) With an additional approximation—a linearization of the relation between chemical potential and composition inside the interfaces—the model becomes equivalent to the quantitative dilute alloy model studied in Refs. [17,23]. This feature makes it possible to include the additional antitrapping current as in that model and to apply the detailed asymptotic analysis of Ref. [17]. As demonstrated for one particular case here, efficient and accurate simulations are thus possible for arbitrary alloy phase diagrams.

Numerous interesting perspectives for future work arise from the present results. First, the model has been worked out here for isothermal solidification only, but it can be easily extended to nonisothermal situations: coupled equations for the phase field, the temperature field, and the chemical potential field can be developed by following the same steps as done here for each transport field separately, taking also into account off-diagonal elements in the Onsager matrix of transport coefficients as well as cross-derivatives of the thermodynamic potentials. This is anticipated to yield a generalization of the thermosolutal model of Ref. [18].

Moreover, the generalization of the formalism to multicomponent systems should be straightforward. This is particularly interesting because general models for multicomponent multiphase solidification have been developed in the two-phase framework [4,24,37]. In these models, the determination of the compositions in the individual phases for given global composition requires to solve a generalization of Eq. (82), which represents a set of coupled nonlinear equations (one for each component). A formulation in terms of the chemical potential would completely avoid this problem and thus potentially offer important gains in computational performance.

It should also be mentioned that the two-phase approach has been used in other contexts. One example is the treatment of fluid flow in solidification [15] and two-phase flows [38,39], where two separate velocity fields, one for each phase, are introduced, in contrast to "coarse-graining" models in which a single velocity field is used [40]. It would be interesting to reassess the relations between these different models in the light of the present findings.

ACKNOWLEDGMENTS

I thank Abhik Choudhury, who has independently pursued research along similar lines, for stimulating discussions.

[1] A. Karma and W.-J. Rappel, Phys. Rev. E **57**, 4323 (1998).

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

[3] M. Plapp, J. Cryst. Growth **303**, 49 (2007).

[4] I. Steinbach, Modell. Simul. Mater. Sci. Eng. **17**, 073001 (2009).

[5] J. S. Langer, in *Directions in Condensed Matter Physics*, edited by G. Grinstein and G. Mazenko (World Scientific, Singapore, 1986), p. 165.

[6] G. Caginalp, Phys. Rev. A **39**, 5887 (1989).

[7] R. Kobayashi, Physica D **63**, 410 (1993).

[8] A. Karma and A. Sarkissian, Metall. Mater. Trans. A **27**, 635 (1996).

[9] A. Karma, Y. H. Lee, and M. Plapp, Phys. Rev. E **61**, 3996 (2000).

[10] A. A. Wheeler, W. J. Boettinger, and G. B. McFadden, Phys. Rev. A **45**, 7424 (1992).

[11] G. Caginalp and W. Xie, Phys. Rev. E **48**, 1897 (1993).

[12] J. A. Warren and W. J. Boettinger, Acta Metall. Mater. **43**, 689 (1995).

[13] J. Ni and C. Beckermann, Metall. Trans. B **22**, 349 (1991).

[14] J. Tiaden, B. Nestler, H.-J. Diepers, and I. Steinbach, Physica D **115**, 73 (1998).

[15] C. Beckermann, H.-J. Diepers, I. Steinbach, A. Karma, and X. Tong, J. Comput. Phys. **154**, 468 (1999).

[16] S. G. Kim, W. T. Kim, and T. Suzuki, Phys. Rev. E **60**, 7186 (1999).

[17] B. Echebarria, R. Folch, A. Karma, and M. Plapp, Phys. Rev. E **70**, 061604 (2004).

[18] J. C. Ramirez, C. Beckermann, A. Karma, and H.-J. Diepers, Phys. Rev. E **69**, 051607 (2004).
[19] J. S. Langer, Rev. Mod. Phys. **52**, 1 (1980).
[20] W. Losert, D. A. Stillman, H. Z. Cummins, P. Kopczyński, W.-J. Rappel, and A. Karma, Phys. Rev. E **58**, 7492 (1998).
[21] M. Plapp and M. Dejmek, Europhys. Lett. **65**, 276 (2004).
[22] R. Folch and M. Plapp, Phys. Rev. E **72**, 011602 (2005).
[23] A. Karma, Phys. Rev. Lett. **87**, 115701 (2001).
[24] S. G. Kim, Acta Mater. **55**, 4391 (2007).
[25] O. Penrose and P. C. Fife, Physica D **43**, 44 (1990).
[26] S.-L. Wang, R. F. Sekerka, A. A. Wheeler, B. T. Murray, S. R. Coriell, R. J. Braun, and G. B. McFadden, Physica D **69**, 189 (1993).
[27] G. J. Fix, in *Free Boundary Problems: Theory and Applications*, edited by A. Fasano and M. Primicerio (Piman, Boston, 1983), p. 580.
[28] J. B. Collins and H. Levine, Phys. Rev. B **31**, 6119 (1985).
[29] R. Evans, Adv. Phys. **28**, 143 (1979).
[30] M. Conti, Phys. Rev. E **64**, 051601 (2001).
[31] M. Conti and M. Fermani, Phys. Rev. E **67**, 026117 (2003).
[32] J. S. Langer, in *Solids Far From Equilibrium*, edited by C. Godrèche (Edition Aléa Saclay, Cambridge, UK, 1992), p. 297.
[33] L. S. Darken, Trans. AIME **175**, 184 (1948).
[34] C. Tong, M. Greenwood, and N. Provatas, Phys. Rev. B **77**, 064112 (2008).
[35] R. Folch and M. Plapp, Phys. Rev. E **68**, 010602(R) (2003).
[36] M. J. Aziz, J. Appl. Phys. **53**, 1158 (1982).
[37] J. Eiken, B. Böttger, and I. Steinbach, Phys. Rev. E **73**, 066122 (2006).
[38] Y. Sun and C. Beckermann, Physica D **198**, 281 (2004).
[39] Y. Sun and C. Beckermann, Physica D **237**, 3089 (2008).
[40] D. M. Anderson, G. B. McFadden, and A. A. Wheeler, Physica D **135**, 175 (2000).