

Phase-field and sharp-interface alloy models

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We consider a phase-field model of a binary mixture or alloy which has a phase boundary. The model identifies all macroscopic parameters and the interface thickness ϵ . In the limit as ϵ approaches zero, an alternative two-phase alloy solidification model (with a sharp interface) is obtained. For small concentrations, we recover the classical sharp-interface problems, the theory of which is reviewed. We obtain, in the simplest phase-field system, a new (nonlinear) interface relation for concentration c which is discontinuous across the interface and subject to $[\ln[c/(1-c)]]^\pm = -2M$, coupled with $-\sigma(\alpha v + \kappa) = [s]_E \{ T - T_B - [(T_A - T_B)/2M] \ln[(1-c^+)/ (1-c^-)] \}$, where σ is surface tension, v is (normal) velocity of the interface, κ is the curvature, $[s]_E$ is the jump in entropy density between phases, T_A and T_B are the melting temperatures of the two materials, M is related to the phase diagram, and α is a dynamical constant.

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I. INTRODUCTION

The study of free boundaries in recent years can be grouped broadly into two categories: (a) sharp-interface problems in which one or more variables (or their derivatives) are typically discontinuous across an interface; and (b) systems of parabolic equations in which the interface is specified by a level set of one of the variables. In the 1980s a close relationship was established between these types of models [1,2]. Similar issues have also been discussed for a broad spectrum of free boundary problems (see [3] for a survey).

An important example of (a) is the surface tension and kinetics model (or modified Stéfán model) which describes solidification. The material, which occupies a spatial region $\Omega \subset \mathbb{R}^d$, may be either of two phases, e.g., liquid and solid, separated by an interface $\Gamma(t) \subset \mathbb{R}^{d-1}$, and is described by the equations

$$C_v T_t = K_1 \Delta T \quad \text{in } \Omega \setminus \Gamma(t), \tag{1.1}$$

$$lv = -K_1 [\nabla T \cdot \hat{n}]^\pm \quad \text{on } \Gamma(t), \tag{1.2}$$

$$T - T_M = -\frac{\sigma}{[s]_E} (\kappa + \alpha v) \quad \text{on } \Gamma(t), \tag{1.3}$$

where T is (absolute) temperature, C_v the specific heat per mass, K_1 the thermal conductivity divided by density, l the latent heat per mass, σ the surface tension, α the relaxation scaling, s the entropy per unit volume, and $[s]^\pm$ the difference between the solid and liquid phases. The unit normal is \hat{n} and the (normal) velocity to the interface $\Gamma(t)$ at (x, t) is denoted v while the sum of principle curvatures at (x, t) on $\Gamma(t)$ is denoted $\kappa(x, t)$ or κ . Thus the sharp-interface problem can be stated as finding $T(x, t)$ and $\Gamma(t)$ in suitable spaces subject to initial and boundary conditions.

A special case of (1.1)–(1.3), known as the classical Stéfán model, is obtained by setting $\sigma=0$, so that $T - T_M = 0$ at the interface. We note that the difference

between the two models ($\sigma \neq 0$ and $\sigma = 0$) is actually quite profound for two reasons. Setting $\sigma = 0$ has the effect of (1) eliminating an important length scale in the problem, which is crucial in terms of the stability of the interface, and (2) enabling the sign $T(x, t)$ to determine the phase of the material, i.e., $T > 0$ implies the material is in the liquid phase.

An alternative formulation of phase boundary problems along the lines of (b) is the phase-field model in which a phase or “order” parameter $\phi(x, t)$ is employed. In the distinguished limit of the surface tension and kinetics model, (1.1)–(1.3), one can write the parabolic system for (T, ϕ) as

$$C_v T_t + \frac{l}{2} \phi_t = \frac{K_1}{\rho} \Delta T, \tag{1.4}$$

$$\alpha \epsilon^2 \phi_t = \epsilon^2 \Delta \phi + \frac{1}{2} (\phi - \phi^3) + \epsilon \frac{[s]_E}{3\sigma} (T - T_M), \tag{1.5}$$

where ϵ represents the thickness of the interfacial layer and all other variables are the same as previously defined. The interface in (1.4) and (1.5) is now defined implicitly as the level curve where ϕ vanishes. Equation (1.5) arises from a dynamical “model-A-type” equation (see, e.g., [4]) of the form $\phi_t = -\delta F / \delta \phi$, with F as free-energy density, while (1.4) is an energy balance equation.

The theoretical link between the phase field model (1.4) and (1.5) and sharp-interface models such as (1.1)–(1.3) was established using formal matched asymptotics in [1,2] and proven rigorously under various conditions in [5,6]. A number of theorems have also been proven for the special case in which the phase equation (1.5) is considered independently for fixed T (see [7] and references therein). While the theoretical results are concerned with the limit $\epsilon \rightarrow 0$, computations have shown that the phase-field equations exhibit an interface which is close to the sharp interface problem even when ϵ is relatively large [8].

In the present paper, we discuss a generalization of this

model to the case of alloys. A related approach has been used in the isothermal case in [9]. We will use a simplified set of equations which are derived in [10] and studied in mathematical detail in [11]. Our aim is to write the simplest system of equations of phase field type which has the characteristic behavior of alloys and can be shown through asymptotic analysis to have the appropriate scaling and coefficients. Furthermore, the analysis then leads to a new sharp-interface alloy problem that generalizes equations which are currently studied.

II. THE ALLOY PROBLEM

The problem of phase boundaries involving a mixture of two materials (e.g., alloys or impurities) is of great practical interest and presents challenging theoretical issues which we review briefly in this section. We consider a substance (e.g., a binary alloy) comprised of a mixture of material A and material B , with concentration $c(x,t) \in (0,1)$ denoting the fraction of material A in the mixture. Two aspects of this problem are particularly interesting from a physical perspective. (a) There is a jump in the concentration itself, and not just in the gradient, as in temperature. (b) The diffusion of material is generally much smaller in the solid phase compared with the liquid, and leads to partly degenerate equations in the limit of zero diffusion in the solid.

An understanding of (a) is best accomplished by means of the (c,T) phase diagram (Fig. 1). A clearly written reference is [12]. We focus on the $c=0$ side of the diagram. A complete phase diagram for an "ideal" mixture or alloy [13] is shown in Fig. 2. The intriguing aspect of this phase diagram is that liquid and solid are not separated by a single curve, but by two curves (called liquidus and solidus), which merge at the melting temperature T_B of the pure B material ($c=0$). To a reasonable approximation for small c , one may assume these two curves are linear. To be specific, we will discuss the

phase diagram displayed in Fig. 1(a). At a fixed temperature $T_E < T_B$ the liquidus line intersects with $T=T_E$ at a point c_L while the solidus intersects at c_S . Thus one expects an interface at equilibrium at temperature T_E to exhibit concentration c_L on the liquidus side and c_S on the solid. That is, the concentration is a piecewise constant function with a jump between c_L and c_S at the phase boundary.

While the (equilibrium) phase diagram explains (a), it is irrelevant to (b) since the latter is a dynamical phenomena, exhibited in the (concentration) diffusion equation below. The dynamical modeling of the alloy problem is typically accomplished by means of a (sharp-interface) free-boundary problem which often accounts for only the liquid phase ("one-phase problem") thereby neglecting the diffusion of impurities in the solid which is small. Also, the concentration of impurities is assumed to be sufficiently small that one does not need to regard the thermodynamic variables, such as latent heat, as a function of c .

A. The two-phase (sharp-interface) problem

A reasonable two-phase description of the dilute binary alloy may be written by expanding on the usual discussion of the one-phase problem (e.g., [12]) as follows.

The (dilute) two-phase alloy model

We consider the coupled system for (T,c,Γ) satisfying (1.1), (1.2), and

$$c_t = K_2^\pm \Delta c \quad \text{in } \Omega \setminus \Gamma(t), \quad (2.1)$$

$$-v[c]^\pm = K_2[\nabla c \cdot \hat{\mathbf{n}}]^\pm \quad \text{on } \Gamma(t), \quad (2.2)$$

$$T - T_B = -\frac{\sigma}{[s]_E}(\kappa + \alpha v) + \frac{1}{2}(m_l c^+ + m_s c^-) \quad \text{on } \Gamma(t), \quad (2.3)$$

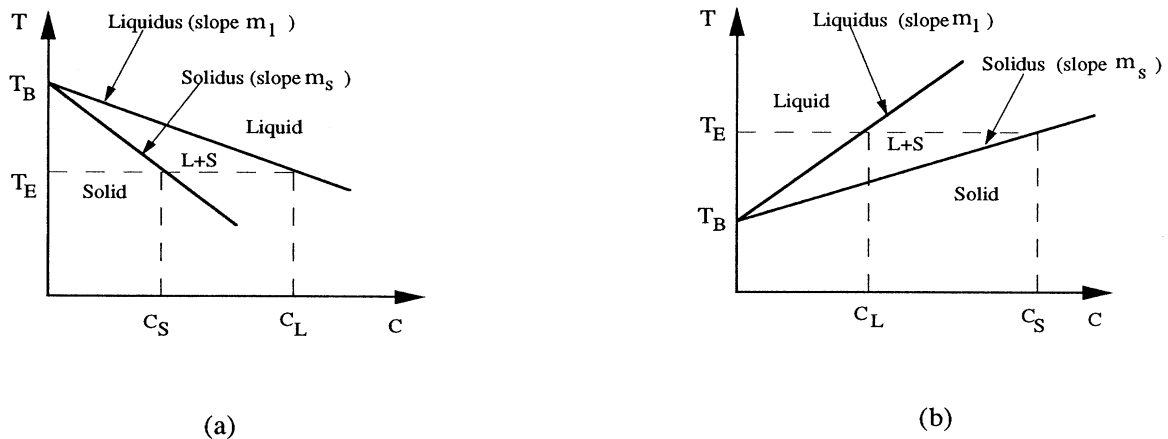


FIG. 1. Idealized phase diagrams in the neighborhood of $(c,T)=(0,T_B)$ which display linear liquidus and solidus lines which separate the single-phase regions from the coexistence region. This idealization is inherent in typical sharp-interface alloy models (one-phase or two-phase) and represents a local approximation to the phase diagram displayed in Fig. 2. Case (a) assumes negative slopes for the liquidus and solidus lines while (b) assumes they are positive. The sign of the slopes determines which phase has higher solute concentration. In (a), solute from the liquid must be rejected as the material freezes. The phase-field alloy model we discuss is not restricted to constant slopes, but asymptotically approaches constant slopes in the neighborhood of small c .

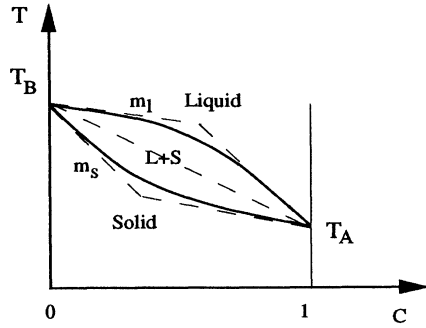


FIG. 2. The phase diagram for the range of c values displaying the melting temperatures T_A and T_B for the pure materials A and B . The liquidus is given by the upper curve while the solidus is given by the lower curve. The extent to which the liquidus and solidus are separated from the line connecting $(0, T_B)$ and $(1, T_A)$ is determined by the jump in entropy. The phase diagram can be obtained from the free energy through the phase-field alloy model (in equilibrium) so that the liquidus is $c^+(T)$ and the solidus is $c^-(T)$.

$$m_l c^+ = m_s c^- \quad \text{on } \Gamma(t), \quad (2.4)$$

where T_B is the melting temperature of the pure B material [i.e., T_M in (1.3)] and c^+ represents the limit of c from the liquid side (and c^- the solid side) while $[\]^\pm$ is the difference between the limits from the liquid and solid sides. Also, K_2^\pm are the diffusivity of the solute in the liquid and solid phases, respectively, and all other parameters are as defined in Sec. I.

We note that the last term in (2.3) has been written to reflect the symmetry of the situation since clearly (in equilibrium) one has $m_l c^+ = m_s c^-$ ($c^+ = c_L$, $c^- = c_S$ in equilibrium). In fact, Eq. (2.3), which is a generalization of the interface relation (1.3), can be understood very simply in terms of the basic phase diagram (Fig. 1). If we consider a stationary planar interface, then $\kappa = v = 0$ in (2.3) so that the value of T is given by

$$T - T_B = \frac{1}{2}(m_l c^+ + m_s c^-) = m_l c_L = m_s c_S. \quad (2.5)$$

This means that a temperature T is compatible with the coexistence of liquid and solid phases if the liquid has concentration c_L and the solid c_S , as shown by the horizontal line in Fig. (1a) or (1b). Thus (2.3) represents a modification of (1.3) in which the equilibrium alloy effects are combined linearly with the Gibbs-Thomson (namely the $\sigma\kappa$ term) and the kinetic undercooling ($\alpha\sigma v$ term) effects.

B. The one-phase (sharp-interface) problem

The single-phase version of (2.1)–(2.4) is obtained by suppressing the role of concentration in the solid while maintaining some of the key relationships in the phase diagram. In particular, the relation (2.3) is replaced by the single-phase version

$$T - T_B = -\frac{\sigma}{[s]_E}(\kappa + \alpha v) + m_l c \quad \text{on } \Gamma(t) \quad (2.3')$$

where we can unambiguously write c (rather than c^+ or c^-) since we are only concerned with concentration in the liquid. Furthermore, by making the approximation that the jump in c for the dynamics $[c]^\pm$ is equal to that of the statics, i.e., $[c]^\pm = c_L - c_S$, and using the relations

$$j \equiv \frac{c_S}{c_L} \quad (2.5a)$$

or

$$c_L - c_S = (1 - j)c_L, \quad (2.5b)$$

one can write the analog of (2.2) as

$$-(1 - j)v\kappa = K_2^+ \nabla c \cdot \hat{n} \quad \text{on } \Gamma(t) \quad (2.2')$$

where c again denotes concentration in the liquid (i.e., c^+ on the interface). The right-hand side of (2.2') has been further simplified by assuming that the limit of ∇c on the interface from the solid side can be neglected. The rationale for this would be that the physical effect of diffusion and conservation of mass are adequately represented. In other words, Eq. (2.2) expresses the idea that the excess concentration, which is deposited (or absorbed) at the interface as a result of different concentrations in the two phases, must diffuse into the material in order to conserve mass. The modification to (2.2') implies the hope that allowing this excess to diffuse into the liquid alone will not change the physical picture drastically. Thus the issues involved in a "one-phase alloy" problem are similar to those in the "one-phase Stéfan" problems, and the difficulties demonstrated in [14] are also similar. Nevertheless, our objective is not to endorse the "one-phase" approach but merely to demonstrate its relationship to the other models, and mention that its use leads to some exact solutions and stability calculations (see, for example, [15,12]). The problem is usually written as a system which is coupled to a two-phase temperature system, but can easily be modified so that a system with truly one-phase results.

The (dilute) one-phase alloy model

Consider a system for (T, c, Γ) satisfying (1.1), (1.2), (2.2'), (2.3'), and

$$c_t = K_2^+ \Delta c \quad \text{in liquid}. \quad (2.1')$$

This model accounts for heat conduction in liquid and solid, but impurity diffusion only in liquid. For the *completely one-phase problem*, consider (1.1) also to be valid in the liquid only, while (1.2) is modified to

$$-lv = K_1 \nabla T \cdot \hat{n} \quad \text{on } \Gamma(t). \quad (1.2')$$

Thus the completely one-phase model involves a time-dependent domain, with part of the boundary consisting of $\Gamma(t)$.

In addition to the similarities between the one-phase alloy and one-phase Stéfan models, there are significant differences. In terms of thermal diffusion, the differences between the two phases is usually not vast, so that the neglecting of one of the two phases is a mathematical convenience, and any degeneracies which may arise are mathematical artifacts. For the alloy problem, however,

there usually is a large difference in the diffusivity of solute, i.e., $K_2^- \ll K_2^+$, and K_2^- is generally close to zero. Thus, at least part of the degeneracy, embodied in (2.1) as K_2^- vanishes, is generic to the physical problem, and presents a fundamental issue which is independent of the particular mathematical approach.

It is worth noting that both the one-phase and two-phase models defined above are based on a linearized phase diagram such as Fig. 1 and do not incorporate the physics of Fig. 2.

In the subsequent section, we consider a phase-field approach to this problem in which K_2 has a transition layer between the values K_2^- in the solid to K_2^+ in the liquid, and $K_2^- \neq 0$. The model embodies the entire phase diagram shown in Fig. 2.

III. A PHASE-FIELD MODEL FOR AN ALLOY WITH THERMAL PROPERTIES

We consider a relatively simple model of phase-field type which incorporates the physics of binary alloys and thermal properties. A detailed derivation of a more comprehensive system is presented in [10]. Our objective here is to study the simplest set of equations which (a) exhibit the characteristic behavior as the interface thickness ϵ approaches zero, and (b) identify all of the material parameters.

The free energy of the binary mixture can be written essentially as a sum of the free energies of the two parts [with concentration c in the A material, and $(1-c)$ in the B material], so that using $\mathcal{F} = \int_{\Omega} F dx$ one can write

$$\begin{aligned} \mathcal{F}\{\phi, T, c\} = \int_{\Omega} dx \left\{ \left[\frac{\xi_A^2}{2} c + \frac{\xi_B^2}{2} (1-c) \right] |\nabla\phi|^2 + \left[\frac{c}{8a_A} + \frac{1-c}{8a_B} \right] (1-\phi^2)^2 \right. \\ \left. - \frac{1}{2} \{ [s]_A (T - T_A) c + [s]_B (T - T_B) (1-c) \} \phi + Vc(1-c) \right. \\ \left. + RT [c \ln c + (1-c) \ln(1-c)] - C_v T \ln T \right\}. \end{aligned} \quad (3.1)$$

The logarithmic terms arise from the entropy of mixing while the $Vc(1-c)$ is due to the differences in interaction energies between similar atoms compared to distinct atoms [16]. In particular, $V=0$ corresponds to an ideal mixture. The parameters ξ_A , a_A , etc. are microscopic parameters which will be related to macroscopic values.

A calculation similar to that of [2] shows that the surface tension $\sigma(c)$ is given by

$$\sigma(c) = \frac{2}{3} [\xi_A^2 c + \xi_B^2 (1-c)]^{1/2} \left[\frac{c}{a_A} + \frac{1-c}{a_B} \right]^{1/2} \quad (3.2)$$

while the interface width $\epsilon_w(c)$ is given by

$$\epsilon_w(c) = [\xi_A^2 c + \xi_B^2 (1-c)]^{1/2} \left[\frac{c}{a_A} + \frac{1-c}{a_B} \right]^{-1/2}. \quad (3.3)$$

Note that if $\xi_A = \xi_B$ and $a_A = a_B$, then σ and ϵ_w are the constants of the pure model [2].

We describe the dynamics of this system by augmenting the phase-field equations with an equation in conservation form, so that one has, with u as internal energy density

$$\tau_1 \phi_t = - \frac{\delta F}{\delta \phi}, \quad (3.4)$$

$$u_t = \nabla \cdot K_1 \nabla T, \quad (3.5)$$

$$\tau_2 c_t = \nabla \cdot K_2(\phi, T) c(1-c) \nabla \left[\frac{\delta F}{\delta c} \right]. \quad (3.6)$$

Here τ_1 and τ_2 are relaxation parameters (which will be identified in terms of the macroscopic parameters) and K_2 is the solute diffusivity. This formulation of the alloy

phase-transition problem concludes that there is a need for both ϕ and c variables. In pure equilibrium, the variables ϕ and T are adequate to determine c ; however, this is no longer possible in nontrivial geometries or dynamical situations (see [10] for further discussion). A study of the isothermal alloy problem based on (3.4) and (3.6) has been carried out in [9]. However, our scaling and asymptotics differ from theirs. A fourth-order concentration has also been coupled with a phase equation in a recent paper [17].

Our approach in studying (3.4)–(3.6) will involve simplifying the equations by considering the idealization that a number of variables such as surface tension σ , entropy difference between phases $[s]_E$, the latent heat l , the interface thickness ϵ_w are identical for both materials, A and B , and that $V=0$. In this way we can focus on the crucial aspects of the alloy phase diagram and dynamics which are preserved by considering different melting temperatures ($T_A \neq T_B$) and solute diffusivities ($K_2^- \neq K_2^+$). Under these conditions, substitution of the free energy (3.1) into the governing equations (3.4)–(3.6) results in the system

$$\begin{aligned} \alpha \epsilon^2 \phi_t = \epsilon^2 \Delta \phi + \frac{1}{2} (\phi - \phi^3) \\ + \frac{\epsilon}{3\sigma} [s]_E \{ T - T_A c - T_B (1-c) \}, \end{aligned} \quad (3.7)$$

$$C_v T_t + \frac{l}{2} \phi_t - \frac{Q}{2} c_t = \nabla \cdot K_1 \nabla T, \quad (3.8)$$

$$c_t = \nabla \cdot K_2(\phi, T) c(1-c) \nabla \left[N\phi + RT \ln \frac{c}{1-c} \right], \quad (3.9)$$

where ϵ is a measure of the interface width, α is defined

by $\alpha \equiv \tau_1/\epsilon^2$, and Q and N are defined by

$$Q \equiv 2(T_B - T_A) \left[C_v + \frac{s^s + s^l}{2} \right], \quad (3.10)$$

$$N \equiv \frac{1}{2}[s]_E(T_A - T_B).$$

Here s^s and s^l are the entropy densities of the solid and liquid phases. Note that τ_2 has been incorporated into K_2 .

Thus the form of (3.7)–(3.10) shows that all of the constants are identified as macroscopic material parameters with the exception of ϵ . From the asymptotic analysis it will be clear that the interface has a transition layer of the form $\tanh(r/2\epsilon)$ so that the interface width is approximately 10ϵ . Thus, setting $10\epsilon \simeq 10^{-8}$ cm would be physically reasonable. In order to extract further information from these equations, however, it is important to examine (a) what the equations imply in the limit $\epsilon \rightarrow 0$ (with all other parameters held fixed), and (b) to what extent the solutions vary as ϵ is made much larger. Objective (a) is accomplished through asymptotic analysis and leads to key relationships between variables at the interface. Objective (b) is essential to quantitatively reliable numerical computations, since the use of the true value of ϵ would necessitate a grid which has far too many node points to be practical. For the pure phase-field equations, it was shown [8] that the interface could be stretched out (within the limits of the geometry to be resolved) to a practical value which is several orders of magnitude higher. Note that the system (3.7)–(3.9) can easily be modified along the lines of [5] by multiplying $[s]_E$ by a term proportional to $(1-\phi^2)^2$ if preserving the pure phases at exactly ± 1 is convenient mathematically.

IV. BASIC IDEAS AND EQUILIBRIUM DIAGRAM

We present a preliminary analysis of these equations in order to (1) demonstrate the basic ideas with a minimum of technical detail, (2) show that the transition layer in concentration c has a logarithmic relationship to the transition in the order parameter ϕ , and (3) derive the equilibrium phase diagram from the equations so that the macroscopic parameters in the equations are related to those of the phase diagram.

Initially we consider a stationary one-dimensional interface and let r be the coordinate which measures the distance to the interface, i.e., $\phi=0$. Using the *stretched* or *inner* coordinate $z=r/\epsilon$, we can define $\hat{\phi}(z,t) \equiv \phi(r,t)$, $\hat{c}(z,t) \equiv c(r,t)$, etc. Then the phase equation (3.7) can be written as

$$0 = \hat{\phi}_{zz} + \frac{1}{2}(\hat{\phi} - \hat{\phi}^3) + \frac{\epsilon[s]_E}{3\sigma} [\hat{T} - T_A \hat{c} - T_B(1 - \hat{c})]. \quad (4.1)$$

We look for an asymptotic solution of the form $\hat{\phi} = \hat{\phi}^0 + \epsilon \hat{\phi}^1 + \epsilon^2 \hat{\phi}^2 + \dots$ (to be made precise in Sec. V), so that substituting this identity into (4.1) and formally equating terms with similar powers of ϵ leads to the $O(1)$ equation

$$\hat{\phi}_{zz}^0 + \frac{1}{2}[\hat{\phi}^0 - (\hat{\phi}^0)^3] = 0. \quad (4.2)$$

This has a solution $\hat{\phi}^0(z) = \tanh(z/2)$, assuming solid on the left [$\hat{\phi}(-\infty) = -1$] and liquid on the right [$\hat{\phi}(\infty) = 1$]. For stationary profiles, the concentration equation (3.9) implies

$$\left[N \hat{\phi}^0 + R \hat{T}^0 \ln \frac{\hat{c}^0}{1 - \hat{c}^0} \right]_z = 0 \quad (4.3)$$

or

$$N \hat{\phi}_z^0 = -R \hat{T}^0 \frac{\hat{c}_z^0}{\hat{c}^0(1 - \hat{c}^0)} \quad (4.4)$$

where we assume \hat{T}^0 is independent of z (as shown in Sec. V, even in the dynamical situation). Integration of (4.3) with respect to z implies

$$N \hat{\phi}^0 + R \hat{T}^0 \ln \frac{\hat{c}^0}{1 - \hat{c}^0} = A \quad (4.5)$$

where A is independent of z but may depend on other variables. Subtracting (4.5) at $z = -\infty$ from the same equation at $z = \infty$, one has to leading order

$$\left[\ln \frac{c}{1 - c} \right]_{-}^{+} = -\frac{2N}{RT}. \quad (4.6)$$

Here we have used the values of $\hat{\phi}$ at $\pm \infty$ as well as the standard asymptotic result that $\lim_{z \rightarrow \infty} \hat{c}^0 = \lim_{r \rightarrow 0^+} c^0$. Thus (4.6) is one of the equations which relate c^+ , c^- , and T to form the solidus and liquidus lines as shown in Figs. 1 and 2. The second is obtained through the phase equation (3.7) [or (4.1)] which provides the Gibbs-Thomson relation for a pure material.

Subtracting (4.2) from (4.1) results in

$$\begin{aligned} \mathcal{L} \hat{\phi}^1 &\equiv \hat{\phi}_{zz}^1 + \frac{1}{2}[1 - 3(\hat{\phi}^0)^2] \hat{\phi}^1 \\ &= -\frac{[s]_E}{3\sigma} [\hat{T}^0 - T_A \hat{c}^0 - T_B(1 - \hat{c}^0)] \equiv H. \end{aligned} \quad (4.7)$$

Since $\hat{\phi}_z^0$ is a solution to the homogeneous equation $\mathcal{L} \psi = 0$, the Fredholm alternative theorem implies that a necessary condition for the solution of (4.7) is that $\hat{\phi}_z^0$ be orthogonal to H , i.e.,

$$\int_{-\infty}^{\infty} \hat{\phi}_z^0 [\hat{T}^0 - T_A \hat{c}^0 - T_B(1 - \hat{c}^0)] dz = 0. \quad (4.8)$$

[Note that in this special case Fredholm's alternative is obtained simply by differentiating (4.2), multiplying by $\hat{\phi}^1$ and subtracting from it (4.7) multiplied by $\hat{\phi}_z^0$. One obtains (4.8) upon integration and using integration by parts.]

In order to evaluate (4.8), we utilize (4.4) to substitute for $\hat{\phi}_z^0$ and write the integral as

$$2(T_B - \hat{T}^0) = -\frac{R}{N}(T_B - T_A) \hat{T}^0 \int_{-\infty}^{\infty} \frac{\hat{c}_z^0}{1 - \hat{c}^0} dz \quad (4.9)$$

or, in terms of the usual variables, with c^+ and c^- denoting the limits of c from the two directions,

$$2(T_B - T) = \frac{R}{N}(T_B - T_A) T \ln \frac{1 - c^+}{1 - c^-}. \quad (4.10)$$

Thus (4.10) along (4.6) determines the phase diagram, i.e., the complete liquidus curve $c^+(T)$ and solidus curve $c^-(T)$ as follows.

Lemma 4.1. For any $N_1(T)$ (e.g., $N_1 = N/(RT)$) $= [s]_E (T_A - T_B)/(2RT)$ the system of equations

$$\ln \frac{c^+}{1-c^+} - \ln \frac{c^-}{1-c^-} = -2N_1, \quad (4.11)$$

$$2N_1(T - T_B) = (T_A - T_B) \ln \frac{1-c^+}{1-c^-}. \quad (4.12)$$

has a unique solution $(c^+(T), c^-(T))$ given by

$$c^+(T) = \frac{1 - \tilde{N}_1}{1 - e^{2N_1}}, \quad c^-(T) = \frac{1 - \tilde{N}_1}{\tilde{N}_1 e^{-2N_1(1 - e^{2N_1})}} \quad (4.13)$$

with $\tilde{N}_1 \equiv e^{2N_1(T - T_B)/(T_A - T_B)}$ (see Fig. 2). The derivatives are given by

$$(c^+)'(T) = \frac{-2N_1}{(1 - e^{2N_1})(T_A - T_B)} e^{[2N_1/(T_A - T_B)](T - T_B)} + O(T - T_B), \quad (4.14)$$

$$(c^-)'(T) = \frac{-2N_1 e^{2N_1}}{(1 - e^{2N_1})(T_A - T_B)} e^{[-2N_1/(T_A - T_B)](T - T_B)} + O(T - T_B)$$

so that the derivatives evaluated at $T = T_B$ are

$$(c^+)'(T_B) = \frac{-2N_1(T_B)}{(1 - e^{2N_1(T_B)})(T_A - T_B)}, \quad (4.15)$$

$$(c^-)'(T_B) = \frac{-2N_1(T_B) e^{2N_1(T_B)}}{(1 - e^{2N_1(T_B)})(T_A - T_B)}.$$

The linearization of (4.14) obtained from the Taylor expansion near $c^\pm \sim 0$ and $T - T_B \sim 0$ is

$$c^- \simeq \frac{1}{m_s} (T - T_B), \quad m_s = \frac{(1 - e^{2N_1(T_B)})(T_A - T_B)}{-2N_1(T_B) e^{2N_1(T_B)}}, \quad (4.16)$$

$$c^+ \simeq \frac{1}{m_l} (T - T_B), \quad m_l = \frac{(1 - e^{2N_1(T_B)})(T_A - T_B)}{-2N_1(T_B)}.$$

The slopes m_l and m_s thereby satisfy

$$\frac{m_l}{m_s} = e^{2N_1(T_B)}. \quad (4.17)$$

Discussion of Lemma 4.1

The identity (4.17) establishes a one-to-one relationship between $N_1(T_B)$ and the ratio of slopes of $c^-(T)$ and $c^+(T)$ near T_B (see Fig. 1). In the context of the full phase diagram (Fig. 2), the lemma implies the following. (1) The linear superposition of free energies for an ideal mixture [$V=0$ in (3.1)] results in liquidus and solidus curves which have a particular symmetry about the

straight line connecting $(0, T_B)$ and $(1, T_A)$. Furthermore the particular logarithmic-exponential relationships between c^\pm and T expressed by (4.13) are a direct consequence of the fundamental ingredients of the theory: (a) the entropy of mixing term in the free energy \mathcal{F} , (b) the linear superposition of the free energies of the pure A and B materials, and (c) the form of the concentration equation which involves $\nabla(\delta F/\delta c)$. In particular the linear interpolation in (c) between the melting temperatures T_A and T_B combined with the entropy of mixing term results in the crucial equation (4.3) by which the transition layer in ϕ forces a transition layer in c .

Given T_A and T_B an "average" or base-line slope due to the line from $(0, T_B)$ to $(1, T_A)$ is established [i.e., $m_{av} = (T_A - T_B)/(1 - 0) = T_A - T_B$]. This base-line slope is evident in (4.16) and (4.15). The extent of spreading between the $c^+(T)$ and $c^-(T)$ is determined by the ratio m_l/m_s , which, by (4.17), is determined by N_1 . As N_1 approaches zero, (4.16) implies m_l/m_s approaches 1. Also, we have for $N_1 \sim 0$ approximation that

$$c^+(T) = c^-(T) \sim \frac{T - T_B}{T_A - T_B}. \quad (4.18)$$

As N_1 becomes larger the gulf between liquidus and solidus widens.

The results above are stated for an arbitrary $N_1(T)$. Upon substitution of the value of N_1 derived from the free energy (namely $N_1 = [s]_E (T_A - T_B)/(2RT)$), one has, from (4.16),

$$m_l = - \frac{RT_B}{[s]_E} (1 - e^{([s]_E/RT_B)(T_A - T_B)}), \quad (4.19)$$

$$m_s = - \frac{RT_B}{[s]_E} \frac{1 - e^{([s]_E/RT_B)(T_A - T_B)}}{e^{([s]_E/RT_B)(T_A - T_B)}}.$$

Here the slopes of the liquidus and solidus lines in the phase diagram are related directly to the macroscopic parameters. As discussed above, m_l and m_s converge when N_1 approaches zero, which means that $[s]_E \gg R$, i.e., the term which arises from the shift in melting temperatures $\epsilon([s]_E/3\sigma)[T - T_A c - T_B(1 - c)]$ is large in comparison with the entropy of mixing $RT[c \ln c + (1 - c) \ln(1 - c)]$. In other words, as the entropy difference between the phases vanishes, the distinction between solid and liquid vanishes, so that the equilibrium values of concentration are the same in both phases, i.e., $c^+(T) - c^-(T) \rightarrow 0$ as $[s]_E \rightarrow 0$. The comparison of $[s]_E$ with R arises since these two quantities, both with entropy density units, are the coefficients of the two key quantities relating to two different sources of entropy, namely, phase and concentration.

It will be shown in Sec. V that Eqs. (4.6) and (4.10) apply to a moving interface with nontrivial geometry provided that the left-hand side of (4.10) is supplemented by the terms $-\sigma(av + \kappa)$. The two equations together supersede the Gibbs-Thomson condition (1.3), and also reduce to this condition in appropriate limits as concentration approaches 0 and 1.

The concentration profile (see Fig. 3)

Returning to the integrated equation (4.5), we see that a solution can be obtained to leading order as

$$c \simeq \frac{e^{A/(RT)} e^{-(N/RT)\phi}}{1 + e^{A/(RT)} e^{-(N/RT)\phi}} \quad (4.20)$$

where we use the original (c, ϕ) so that $\phi \simeq \tanh(r/2\epsilon)$. If we consider (4.20) in the approximation $T \sim T_B$, then

$$\begin{aligned} c^-(T_B) &= \frac{e^{A/(RT_B)} e^{N/(RT_B)}}{1 + e^{A/(RT_B)} e^{N/(RT_B)}}, \\ c^+(T_B) &= \frac{e^{A/(RT_B)} e^{-N/(RT_B)}}{1 + e^{A/(RT_B)} e^{-N/(RT_B)}}, \end{aligned} \quad (4.21)$$

and the integration constant A must depend upon T . It is also evident that setting the integration constant to zero, so that one considers $\delta F/\delta c = 0$ instead of $\nabla(\delta F/\delta c) = 0$ in equilibrium results in an immediate contradiction, since c^- and c^+ do not tend to zero as T approaches T_B .

In fact, examining (4.3) with $\hat{\phi}^0$ fixed as $\tanh(r/2\epsilon)$, it is clear that one boundary condition is needed in order to solve for \hat{c}^0 . This boundary condition can be the values of \hat{c}^0 at $-\infty$ (that is, c^-) or at $+\infty$ (that is, c^+). Of course, in equilibrium, the value c^- is the value of the concentration which corresponds to a particular temperature on the solidus line in the phase diagram. Hence the boundary condition for the basic concentration profile, (4.3), which is defined as A in (4.5), necessarily involves the temperature. At a fixed temperature in equilibrium, knowing any one of the triple (c^-, c^+, A) thereby determines the other two. Our treatment avoids the calculation of A , since (4.4) is valid for any value of the integration constant, and, along with the phase equation (4.1), leads to (4.6) and (4.10), which determine $c^+(T)$ and $c^-(T)$. Hence the constant A is determined partly through the phase equation.

A simplification of the dynamical system of equation

The discussion above demonstrates the role of the basic concentration profile equation in determining the transition layer of c as a function of ϕ . The role of the coefficient RT is less significant since an energy conservation equation such as (3.8) will prevent transition layers in T . Then T is essentially a constant for the inner expansion equations. However, the presence of T in (3.9) results in T derivatives which are mixed with the c derivatives in the pure phases. Under the assumption that $\nabla T \cdot \nabla c$ and $c \Delta T$ terms are not significant in comparison with the remaining terms in (3.9) one may make the following simplifications which also serve as a generalization of the model.

Consider instead of $\nabla\{N\phi + RT \ln[c/(1-c)]\}$ in (3.9) the term $\nabla\{M\phi + \ln[c/(1-c)]\}$ where M is a constant independent of T , so that RT is absorbed into K_2 and the derivatives of T ignored. The constant M can be evaluated based on the asymptotics as discussed above and the phase diagram with the result

$$M = \frac{1}{2} \ln \frac{m_l}{m_s}. \quad (4.22)$$

Then the concentration equation is rewritten as

$$c_t = \nabla \cdot K_2(\phi, T) c(1-c) \nabla \left[M\phi + \ln \frac{c}{1-c} \right], \quad (4.23)$$

where M is defined by (4.22), and coupled with a simplified heat equation

$$C_v T_t + \frac{l}{2} \phi_t = \nabla \cdot K_1 \nabla T \quad (4.24)$$

and the phase equation (3.7), to form the simplest phase-field alloy system [(3.7), (4.23), and (4.24)].

V. ASYMPTOTIC ANALYSIS OF PHASE-FIELD ALLOY MODELS

In this section, an asymptotic analysis for small ϵ will be carried out for layered solutions of the system (3.7), (4.23), and (4.24). A complete determination of the solution will involve initial and boundary conditions; however, they will be left unspecified here, as our primary attention is rather on the laws of motion of the interface. A supplementary discussion in some special cases will be presented in Sec. VI. (We will specify the boundary and initial conditions at that time.) Our analysis here treats motion of interface as a moving internal layer of width $O(\epsilon)$. The interfacial curve Γ is defined as the set of points in domain Ω at which $\phi = 0$. Setting $x = (x_1, x_2)$, we define $r(x, t, \epsilon)$ in a neighborhood of Γ to be the signed distance from x to Γ , with the convention that $+$ is the direction of positive ϕ and $-$ is the direction of negative ϕ . Note that for any small $\epsilon > 0$, the system (3.7), (4.23), and (4.24) is parabolic and has regular solutions [11]. It is reasonable to suppose that r is a smooth function in a neighborhood of Γ . The interface Γ itself may be represented by the equation

$$r(x, t, \epsilon) = 0, \quad |\nabla r| = 1, \quad \Delta r = \kappa \quad (5.1)$$

on interface Γ , where κ is the curvature of Γ .

We define a function $s(x, t, \epsilon)$ so that (r, s) is a local orthogonal coordinate system in the neighborhood of Γ , such that on Γ , s measures arc length from some point depending smoothly on t . We set up outer expansions for the functions c , T , and ϕ , i.e.,

$$\begin{aligned} c(x, t, \epsilon) &= c^0(x, t) + \epsilon c^1(x, t) + \dots, \\ T(x, t, \epsilon) &= T^0(x, t) + \epsilon T^1(x, t) + \dots, \\ \phi(x, t, \epsilon) &= \phi^0(x, t) + \epsilon \phi^1(x, t) + \dots \end{aligned} \quad (5.2)$$

The terms on the right-hand sides of these expansions may be discontinuous at $r = 0$.

The inner expansion proceed by using the stretching transformation $z \equiv r/\epsilon$ and considering c , T , and ϕ as functions of the variables z , s , and t and $c(x, t, \epsilon) = \hat{c}(z, s, t, \epsilon)$, etc. Thus

$$\begin{aligned}\hat{c}(z,s,t,\epsilon) &= \hat{c}^0(z,s,t) + \epsilon \hat{c}^1(z,s,t) + \dots, \\ \hat{T}(z,s,t,\epsilon) &= \hat{T}^0(z,s,t) + \epsilon \hat{T}^1(z,s,t) + \dots, \\ \hat{\phi}(z,s,t,\epsilon) &= \hat{\phi}^0(z,s,t) + \epsilon \hat{\phi}^1(z,s,t) + \dots.\end{aligned}\quad (5.3)$$

By the definition of r , we have

$$\hat{\phi}(0,s,t,\epsilon) \equiv 0. \quad (5.4)$$

In the following, we will use the notation $f|_{\Gamma_{\pm}}$ to denote the limiting values of f as Γ is approached from the side where $r > 0$ or $r < 0$, respectively. The notation $f_r|_{\Gamma_{\pm}}$ is defined similarly. The variables ϕ and c will exhibit transition layers as shown in Fig. 3, while $\nabla T \cdot \hat{\mathbf{n}}$ exhibits a similar transition layer behavior.

The main results in this section are the following (see Fig. 4).

Proposition 5.1. In limit as $\epsilon \rightarrow 0$, there exists a formal asymptotic solution (ϕ, T, c) of the phase-field alloy model (3.7), (4.23), and (4.24), which is governed by the following sharp-interface model:

$$\begin{aligned}C_v T_t &= K_1 \Delta T \quad \text{in } \Omega \setminus \Gamma(t), \\ c_t &= K_2^{\pm} \Delta c \quad \text{in } \Omega \setminus \Gamma(t), \\ [T]_{\pm}^{\pm} &= 0 \quad \text{on } \Gamma(t), \\ [K_1 \nabla T \cdot \hat{\mathbf{n}}]_{\pm}^{\pm} &= -lv \quad \text{on } \Gamma(t), \\ \left[\ln \frac{c}{1-c} \right]_{\pm}^{\pm} &= -2M \quad \text{on } \Gamma(t), \\ [K_2 \nabla c \cdot \hat{\mathbf{n}}]_{\pm}^{\pm} &= -[c]_{\pm}^{\pm} v \quad \text{on } \Gamma(t), \\ \alpha v + \kappa &= \frac{[s]_E}{-\sigma} \left[T - T_B - \frac{T_A - T_B}{2M} \ln \frac{1-c^+}{1-c^-} \right] \quad \text{on } \Gamma(t).\end{aligned}\quad (5.5)$$

Thus (5.5) is a new sharp-interface alloy problem which describes the entire (c, T) phase diagram, unlike the alloy models described in Sec. II. Of course, the asymptotics leading to (5.5) are valid for any value of M , but would not correspond to the phase diagram if (4.22) is not satisfied.

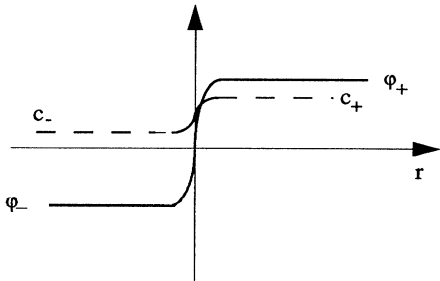


FIG. 3. Profiles of ϕ and c across the interface. In phase-field models, a phase change corresponds to a transition layer in the order parameter ϕ while temperature T has a transition layer in its gradient and the concentration c has a transition layer which is similar to that of ϕ . However, while ϕ always has a transition from (approximately) -1 to 1 , the transition in c (between the two positive values c_S and c_L) depends on the temperature, in accordance with the phase diagram of Fig. 2.

Proposition 5.2. In limit as $\epsilon \rightarrow 0$ and for small concentration c , there exists a formal asymptotic solution (ϕ, T, c) (with linearization for concentration c) of the phase field alloy model (3.7), (4.23), and (4.24), which is governed by the two-phase alloy problem

$$\begin{aligned}C_v T_t &= K_1 \Delta T \quad \text{in } \Omega \setminus \Gamma(t), \\ c_t &= K_2^{\pm} \Delta c \quad \text{in } \Omega \setminus \Gamma(t), \\ [T]_{\pm}^{\pm} &= 0 \quad \text{on } \Gamma(t), \\ [K_1 \nabla T \cdot \hat{\mathbf{n}}]_{\pm}^{\pm} &= -lv \quad \text{on } \Gamma(t), \\ \frac{c^+}{c^-} &= e^{-2M} \quad \text{on } \Gamma(t), \\ [K_2 \nabla c \cdot \hat{\mathbf{n}}]_{\pm}^{\pm} &= -[c]_{\pm}^{\pm} v \quad \text{on } \Gamma(t), \\ \alpha v + \kappa &= \frac{[s]_E}{-\sigma} \left[T - T_B - \frac{T_A - T_B}{2M} (c^- - c^+) \right] \quad \text{on } \Gamma(t).\end{aligned}\quad (5.6)$$

Verification of Proposition 5.1

To obtain the first two equations, we use the outer expansion (5.2). Setting (5.2) into (3.7), (4.23), and (4.24) and equating coefficients of corresponding powers of ϵ , we obtain the $O(1)$ system

$$\begin{aligned}\phi^0 - (\phi^0)^3 &= 0, \\ C_v T_t^0 &= K_1 \Delta T^0, \\ c_t^0 &= \nabla \cdot K_2^{\pm} c^0 (1 - c^0) \nabla \left[\ln \frac{c^0}{1 - c^0} \right]\end{aligned}\quad (5.7)$$

where we take $\phi_-^0 = -1$ and $\phi_+^0 = 1$, and the $O(\epsilon)$ system

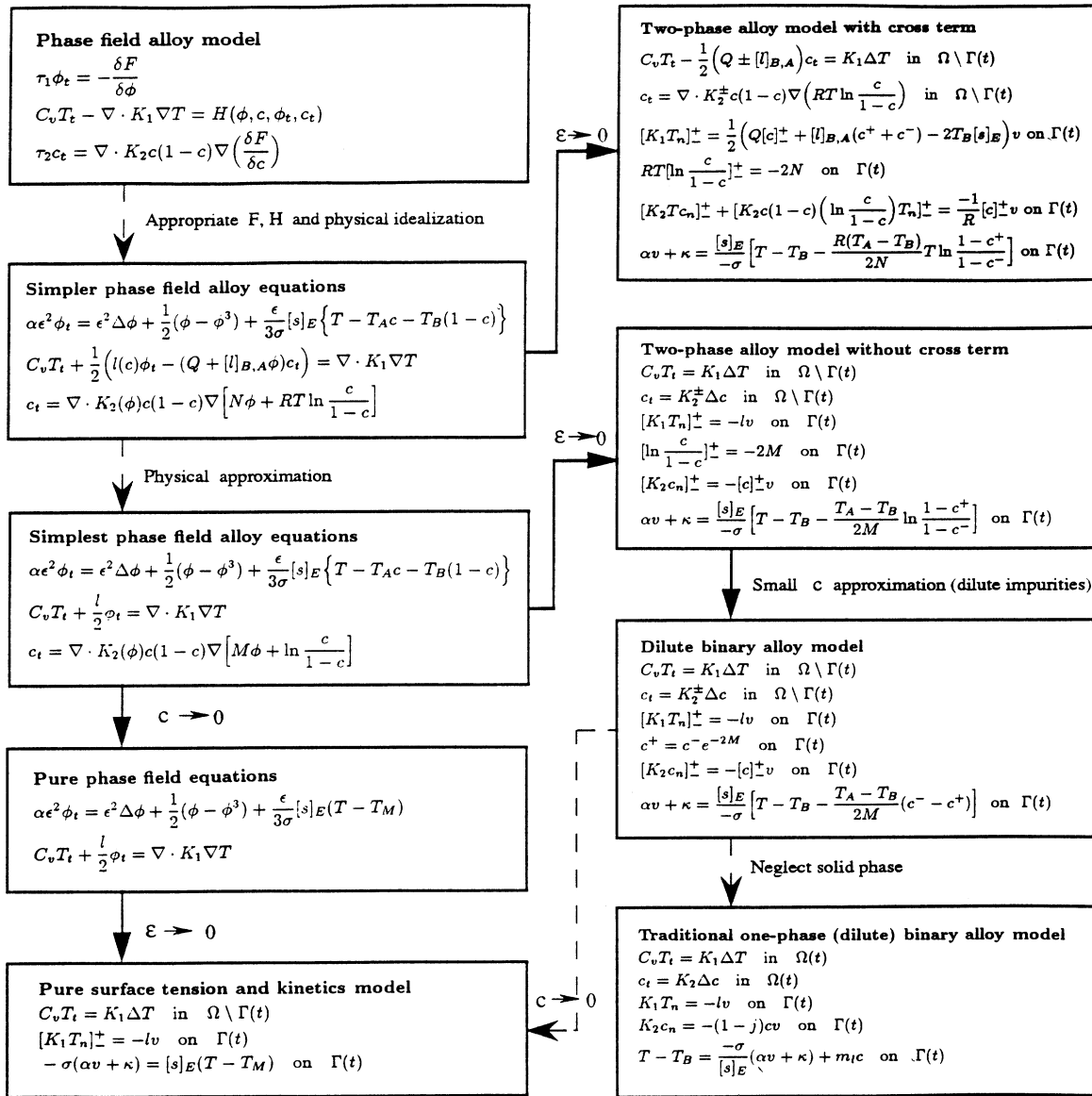
$$\begin{aligned}[1 - 3(\phi^0)^2] \phi^1 + \frac{2[s]_E}{3\sigma} \{ T^0 - T_A c^0 - T_B (1 - c^0) \} &= 0, \\ C_v T_t^1 + \frac{l}{2} \phi_t^1 &= K_1 \Delta T^1, \\ c_t^1 &= \nabla \cdot K_2^{\pm} c^0 (1 - c^0) \nabla \left[M \phi^1 + \frac{c^1}{c^0 (1 - c^0)} \right] \\ &+ \nabla \cdot K_2^{\pm} c^1 (1 - 2c^0) \nabla \left[\ln \frac{c^0}{1 - c^0} \right] \\ &+ \nabla \cdot K_2' (\phi^0) \phi^1 c^0 (1 - c^0) \nabla \left[\ln \frac{c^0}{1 - c^0} \right].\end{aligned}\quad (5.8)$$

Thus the first two equations follow from the $O(1)$ system of the outer solution.

To obtain the interface conditions, we need to use the stretched inner expansion (5.3). Using the (r, s) coordinate system one may write the Laplacian as

$$\Delta u = u_{rr} + \Delta r u_r + |\nabla s|^2 u_{ss} + \Delta s u_s \quad (5.9)$$

and the time derivative u_t as $u_t + r_t u_r + s_t u_s$. One writes the system (3.7), (4.23), and (4.24) in terms of (r, s, t) as follows:



$$l(c) = (T_{Ac} + T_B(1-c)) [s]_E$$

$$[l]_{B,A} = (T_B - T_A) [s]_E$$

$$Q = 2(T_B - T_A) \left(C_v + \frac{s^s + s^l}{2} \right)$$

$$j = \frac{m_l}{m_s}, \quad M = \frac{1}{2} \ln \frac{m_l}{m_s}$$

$$N = \frac{1}{2} [s]_E (T_A - T_B)$$

$$T_n \equiv \nabla T \cdot n, \text{ etc.}, \quad [T_n]^\pm \equiv \text{jump in } T_n, \text{ etc.}$$

FIG. 4. Relationship between different alloy models. The most general phase-field model (upper left box) leads to a number of different limiting sets of equations, some of which are classical, e.g., the traditional one-phase alloy model (dilute binary alloy), and some are introduced in this paper, e.g., the two-phase alloy model without cross terms, in which the conditions involving c^+ and c^- are the new interface relations replacing the Gibbs-Thomson condition. With various simplifications and idealization, we obtain the "simplest" phase-field alloy model which retains the key characteristics of an alloy. These idealizations consist of fixing, for example, the surface tension σ , for the mixture, an assumption which is accurate for pairs of materials with similar surface tension between phases, or for small concentrations of one material in another. The solid lines and arrows between the boxes indicate a mathematical relationship in the sense of a theorem for simpler geometries and matched asymptotic for more complicated geometries. The dashed lines indicate physical idealizations or approximations.

The inner expansion is

$$\alpha \epsilon^2 [\phi_t + \phi_r r_t + \phi_s s_t] = \epsilon^2 [\phi_{rr} + |\nabla s|^2 \phi_{ss} + \Delta r \phi_r + \Delta s \phi_s] + \frac{1}{2}(\phi - \phi^3) + \epsilon \frac{[s]_E}{3\sigma} \{T - T_A c - T_B(1-c)\}, \tag{5.10}$$

$$C_v [T_t + r_t T_r + s_t T_s] + \frac{l}{2} [\phi_t + r_t \phi_r + s_t \phi_s] = K_1 [T_{rr} + |\nabla s|^2 T_{ss} + \Delta r T_r + \Delta s T_s], \tag{5.11}$$

$$[c_t + r_t c_r + s_t c_s] = K_2(\phi)c(1-c) \{F_{1rr} + |\nabla s|^2 F_{1ss} + \Delta r F_{1r} + \Delta s F_{1s}\} + \{K_2(\phi)c(1-c)\}_r F_{1r} + |\nabla s|^2 \{K_2(\phi)c(1-c)\}_s F_{1s}, \tag{5.12}$$

where

$$F_1(\phi, c) \equiv M\phi + \ln \frac{c}{1-c}.$$

Scaling the r variable by use of $z = r/\epsilon$, one may write (5.10)–(5.12) as follows:

$$\hat{\phi}_{zz} + \frac{1}{2}(\hat{\phi} - \hat{\phi}^3) + \epsilon \left[-\alpha r_t \hat{\phi}_z + \Delta r \hat{\phi}_z + \frac{[s]_E}{3\sigma} [\hat{T} - T_A \hat{c} - T_B(1-\hat{c})] \right] + \epsilon^2 [|\nabla s|^2 \hat{\phi}_{ss} + \Delta s \hat{\phi}_s - \alpha \hat{\phi}_t - \alpha s_t \hat{\phi}_s] = 0, \tag{5.13}$$

$$K_1 \hat{T}_{zz} + \epsilon \left[K_1 \Delta r \hat{T}_z - \frac{l}{2} r_t \hat{\phi}_z - C_v r_t \hat{T}_z \right] + \epsilon^2 \left[K_1 (|\nabla s|^2 \hat{T}_{ss} + \Delta s \hat{T}_s) - C_v (\hat{T}_t + s_t \hat{T}_s) - \frac{l}{2} (\hat{\phi}_t + s_t \hat{\phi}_s) \right] = 0, \tag{5.14}$$

$$\{K_2(\hat{\phi})\hat{c}(1-\hat{c})(F_1(\hat{\phi}, \hat{c}))_z\}_z + \epsilon [\Delta r K_2(\hat{\phi})\hat{c}(1-\hat{c})(F_1(\hat{\phi}, \hat{c}))_z - r_t \hat{c}_z] + \epsilon^2 [K_2(\hat{\phi})\hat{c}(1-\hat{c})(|\nabla s|^2 F_{1ss} + \Delta s F_{1s}) + |\nabla s|^2 (K_2(\hat{\phi})\hat{c}(1-\hat{c}))_s F_{1s} - \hat{c}_t - s_t \hat{c}_s] = 0. \tag{5.15}$$

Substituting (5.3) into (5.13)–(5.15), we obtain the $O(1)$ system:

$$\hat{\phi}_{zz}^0 + \frac{1}{2}[\hat{\phi}^0 - (\hat{\phi}^0)^3] = 0, \tag{5.16}$$

$$\hat{T}_{zz}^0 = 0, \tag{5.17}$$

$$\left\{ K_2(\hat{\phi}^0)\hat{c}^0(1-\hat{c}^0) \left[M\hat{\phi}^0 + \ln \frac{\hat{c}^0}{1-\hat{c}^0} \right]_z \right\}_z = 0. \tag{5.18}$$

We seek to construct bounded solutions of the $O(1)$ equations (5.17) and (5.18) above with $0 < \hat{c}^0 < 1$. The solutions to (5.17) and (5.18) which satisfy this requirement are

$$\hat{T}^0(z, s, t) = c_1(s, t), \tag{5.19}$$

$$M\hat{\phi}^0 + \ln \frac{\hat{c}^0}{1-\hat{c}^0} = c_2(s, t), \tag{5.20}$$

where $c_1(s, t)$ and $c_2(s, t)$ are constants with respect to the variable z , so that c_2 may also depend on \hat{T}^0 . Next, one has the $O(\epsilon)$ system:

$$\begin{aligned} \hat{\phi}_{zz}^1 + \frac{1}{2}[1 - 3(\hat{\phi}^0)^2]\hat{\phi}^1 \\ = -\alpha r_t^0 \hat{\phi}_z^0 + \Delta r^0 \hat{\phi}_z^0 + \frac{[s]_E}{3\sigma} \{ \hat{T}^0 - T_A \hat{c}^0 - T_B(1-\hat{c}^0) \}, \end{aligned} \tag{5.21}$$

$$K_1 \hat{T}_{zz}^1 - \frac{l}{2} r_t^0 \hat{\phi}_z^0 = 0, \tag{5.22}$$

$$\left\{ K_2(\hat{\phi}^0)\hat{c}^0(1-\hat{c}^0) \left[M\hat{\phi}^1 + \frac{\hat{c}^1}{\hat{c}^0(1-\hat{c}^0)} \right]_z \right\}_z = r_t^0 \hat{c}_z^0, \tag{5.23}$$

where the equalities (5.19) and (5.20) have been used.

Note that Eq. (5.16) and conditions $\hat{\phi}^0(-\infty) = -1$, $\hat{\phi}^0(0) = 0$, and $\hat{\phi}^0(\infty) = 1$ imply that

$$\hat{\phi}^0(z) = \tanh \frac{z}{2}. \tag{5.24}$$

Integrating Eqs. (5.22) and (5.23), one obtains

$$K_1 \hat{T}_z^1 + \frac{l}{2} r_t^0 \hat{\phi}^0 = c_3(s, t), \tag{5.25}$$

$$K_2(\hat{\phi}^0)\hat{c}^0(1-\hat{c}^0) \left[M\hat{\phi}^1 + \frac{\hat{c}^1}{\hat{c}^0(1-\hat{c}^0)} \right]_z = r_t^0 \hat{c}^0 + c_4(s, t). \tag{5.26}$$

After using the matching conditions (see, e.g., [18]), we obtain from Eqs. (5.20), (5.25), and (5.26) that

$$K_1 T_r^0|_{\Gamma_{\pm}} \pm \frac{l}{2} r_t^0 \Big|_{\Gamma_{\pm}} = c_3(s, t), \tag{5.27}$$

$$\pm M + \ln \frac{c^0}{1-c^0} \Big|_{\Gamma_{\pm}} = c_2(s, t), \tag{5.28}$$

$$K_2^{\pm} c_r^0|_{\Gamma_{\pm}} = r_t^0 c^0|_{\Gamma_{\pm}} + c_4(s, t). \tag{5.29}$$

Noticing also that the normal velocity v (dropping the superscript) is given by $-r_t$, we may write $-r_t^0 = v^0$ in Eqs. (5.27)–(5.29). Subtracting the equation with the minus sign from that with the plus sign from (5.27)–(5.29), respectively, we obtain the interface conditions to lowest order. These are

$$K_1 [T_r^0]_{\pm}^{\pm} = -lv^0, \tag{5.30}$$

$$\left[\ln \frac{c^0}{1-c^0} \right]_{-}^{+} = -2M, \quad (5.31)$$

$$[K_2 c_r^0]_{\pm}^{\pm} = -v^0 [c^0]_{\pm}^{\pm}. \quad (5.32)$$

These give the interface conditions for first-order approximation of the solution [except the last interface condition in (5.5)].

To obtain this last condition, we note that $\hat{\phi}_z^0$ satisfies

$$\hat{\phi}_{zz}^1 + \frac{1}{2}[1-3(\hat{\phi}^0)^2]\hat{\phi}^1 = 0,$$

i.e., $\hat{\phi}_z^0$ is an eigenfunction of the linear operator $\mathcal{L}\psi \equiv \psi_{zz} + \frac{1}{2}[1-3(\hat{\phi}^0)^2]\psi = 0$ corresponding to the eigenvalue 0, and it is simple, so that the solvability condition gives

$$-(\alpha v^0 + \Delta r^0) \int_{R^1} (\hat{\phi}_z^0)^2 dz = \int_{R^1} \frac{[s]_E}{3\sigma} [\hat{T}^0 - T_A \hat{c}^0 - T_B(1-\hat{c}^0)] \hat{\phi}_z^0 dz. \quad (5.33)$$

By using Eq. (5.20), we can calculate the integral of the right-hand side in (5.33), that is,

$$\int_{R^1} \frac{[s]_E}{3\sigma} [\hat{T}^0 - T_A \hat{c}^0 - T_B(1-\hat{c}^0)] \hat{\phi}_z^0 dz = \frac{[s]_E}{3\sigma} \left[2\hat{T}^0 - 2T_B - \frac{1}{M}(T_A - T_B) \ln \frac{1-\hat{c}^0(\infty)}{1-\hat{c}^0(-\infty)} \right]. \quad (5.34)$$

From (5.33), (5.34), and the matching conditions, we may obtain, by use of $\Delta r^0 = \kappa^0$, the interface relation which generalizes Gibbs-Thomson,

$$-(\alpha v^0 + \kappa^0) = \frac{[s]_E}{2\sigma} \left[2T^0 - 2T_B - \frac{1}{M}(T_A - T_B) \ln \frac{1-c_+^0}{1-c_-^0} \right] \quad (5.35)$$

on $\Gamma(t)$, where we have used $\int_{R^1} (\hat{\phi}_z^0)^2 dz = \frac{2}{3}$. This completes verification of Proposition 5.1.

Verification of Proposition 5.2

Note that for small values of c_+^0 and c_-^0 , one has

$$\left[\ln \frac{c^0}{1-c^0} \right]_{-}^{+} = \ln \frac{c_+^0(1-c_-^0)}{c_-^0(1-c_+^0)} \approx \ln \frac{c_+^0}{c_-^0}$$

and

$$\ln \frac{1-c_+^0}{1-c_-^0} \approx c_-^0 - c_+^0.$$

Then Proposition 5.2 follows immediately from the proof of Proposition 5.1.

Finally, a more detailed phase-field alloy model, with

cross terms in the temperature and concentration equations, can be stated as

$$\begin{aligned} \alpha \epsilon^2 \phi_t &= \epsilon^2 \Delta \phi + \frac{1}{2}(\phi - \phi^3) \\ &+ \frac{\epsilon}{3\sigma} [s]_E \{ T - T_A c - T_B(1-c) \}, \\ C_v T_t + \frac{1}{2} \{ l(c) \phi_t - (Q + [l]_{B,A} \phi) c_t \} &= \nabla \cdot K_1 \nabla T, \\ c_t &= \nabla \cdot K_2(\phi) c(1-c) \nabla \left[N \phi + RT \ln \frac{c}{1-c} \right], \end{aligned} \quad (5.36)$$

where

$$\begin{aligned} l(c) &= [T_A c + T_B(1-c)] [s]_E, \\ [l]_{B,A} &= (T_B - T_A) [s]_E, \\ N &= \frac{1}{2} [s]_E (T_A - T_B), \\ Q &= 2(T_B - T_A) \left[C_v + \frac{s^l + s^s}{2} \right], \end{aligned} \quad (5.37)$$

and R is Boltzmann's constant, the other parameters are the same as in (3.7), (4.23), and (4.24), and s^s and s^l are the entropy densities in solid and liquid, respectively.

By the same method as employed in verification of proposition 5.1, we have the following asymptotic result.

Proposition 5.3. In limit as $\epsilon \rightarrow 0$, there exists a formal asymptotic solution (ϕ, T, c) of the phase-field alloy model (5.36), which is governed by the following two-phase sharp-interface alloy model

$$\begin{aligned} C_v T_t - \frac{1}{2}(Q \pm [l]_{B,A}) c_t &= K_1 \Delta T \quad \text{in } \Omega \setminus \Gamma(t), \\ c_t &= \nabla \cdot K_2^{\pm} c(1-c) \nabla \left[RT \ln \frac{c}{1-c} \right] \quad \text{in } \Omega \setminus \Gamma(t) \end{aligned} \quad (5.38)$$

and on the interface $\Gamma(t)$

$$\begin{aligned} [T]_{\pm}^{\pm} &= 0, \\ [K_1 \nabla T \cdot \hat{n}]_{\pm}^{\pm} &= \frac{1}{2} \{ Q [c]_{\pm}^{\pm} + [l]_{B,A} (c^+ + c^-) - 2T_B [s]_E \} v, \\ RT \left[\ln \frac{c}{1-c} \right]_{-}^{+} &= -2N, \end{aligned} \quad (5.39)$$

$$\begin{aligned} [K_2 RT \nabla c \cdot \hat{n}]_{\pm}^{\pm} &+ \left[RK_2 c(1-c) \left[\ln \frac{c}{1-c} \right] \nabla T \cdot \hat{n} \right]_{-}^{+} \\ &= -[c]_{\pm}^{\pm} v, \\ \alpha v + \kappa &= \frac{[s]_E}{-\sigma} \left[T - T_B - \frac{R(T_A - T_B)}{2N} T \ln \frac{1-c^+}{1-c^-} \right]. \end{aligned}$$

Note that equations in (5.36) differ from the simplest version (3.7), (4.23), and (4.24) in that all equilibrium constants including N are obtained from free-energy considerations and cross terms in c and T are present. The two equations agree in the small c or $1-c$ limit. In particular, if we write the concentration equation

$$\begin{aligned}
 c_t &= \nabla \cdot \frac{K_2(\phi, T)}{RT} c(1-c) \nabla \left[N\phi + RT \ln \frac{c}{1-c} \right] \\
 &= \nabla \cdot \frac{K_2 N}{RT} c(1-c) \nabla \phi + \nabla \cdot K_2 \nabla c \\
 &\quad + \nabla \cdot \left[K_2 \frac{\nabla T}{T} c(1-c) \ln \frac{c}{1-c} \right],
 \end{aligned}$$

then it is clear that the first term will vanish in the pure phases (as shown by the asymptotics) while the third term will be smaller than $c \ln c \nabla T$. For small c , this last term is consequently small compared with terms in the heat equation.

VI. A PDE SYSTEM WITH CONSTANT TEMPERATURE

In this section, we state a rigorous result for a system of ϕ and c (neglecting the temperature equation). It is convenient mathematically to replace, without loss of generality, the physical parameters by constants a and b . We then consider the following system:

$$\phi_t = \Delta \phi + \frac{2}{\epsilon^2} \{ \phi(1-\phi^2) + \epsilon(a + bc) \}, \tag{6.1}$$

$$c_t = \nabla \cdot \left\{ c(1-c) \nabla \left[M\phi + \ln \frac{c}{1-c} \right] \right\}, \tag{6.2}$$

in $Q_T \equiv \Omega \times (0, T)$, subject to the suitable boundary and initial conditions. In particular, if we let Ω be a one-dimensional domain, e.g., $\Omega = (-1, 1)$, then we impose the following boundary and initial conditions:

$$\begin{aligned}
 \phi(x, 0) &= \tanh(x/\epsilon), \quad x \in (-1, 1) \\
 \phi(\pm 1, t) &= \tanh(\pm 1/\epsilon), \quad t \in (0, T) \\
 c(x, 0) &= c_0(x), \quad x \in (-1, 1) \\
 c_x(\pm 1, t) &= 0, \quad t \in (0, T)
 \end{aligned} \tag{6.3}$$

where a , b , and M (with $bM < 0$) are constants, one has $c_0(x) \in C^1[0, 1]$ with $0 < c_0(x) < 1$ and $c_{0x}(\pm 1) = 0$, and $\epsilon > 0$ is a small parameter.

The main results in this section are the following two theorems. The proof can be found in [11].

Theorem 6.1. Let $c_0(x) \in C^1[0, 1]$ with $0 < c_0(x) < 1$ and $c_{0x}(\pm 1) = 0$. Then for any $\epsilon > 0$ there exists a unique solution $(\phi^\epsilon(x, t), c^\epsilon(x, t))$ to the problem (6.1)–(6.3). The solution is smooth in Q_T .

Theorem 6.2. In limit $\epsilon \rightarrow 0+$, there exists a pair of functions $(S(t), c(x, t))$ defined on $(0, T_*)$ with $S(t) \in H^1(0, T_*)$ and $c(x, t) \in L^\infty(Q_{T_*})$, such that the limit function $c(x, t)$ of $c^\epsilon(x, t)$ and $S(t)[(\phi^\epsilon(x, t), c^\epsilon(x, t))]$ is the unique solution to the problem (6.1)–(6.3) as stated in Theorem 6.1.] satisfy

$$c_t = c_{xx} \quad \text{in } Q_{T_*} \setminus \{(S(t), t) \mid 0 < t < T_*\}$$

with boundary and interface conditions

$$\begin{aligned}
 c(x, 0) &= c_0(x), \quad x \in (-1, 1) \\
 c_x(\pm 1, t) &= 0, \quad t \in (0, T_*) \\
 [c_x]^\pm &= -[c]^\pm S'(t), \quad t \in (0, T_*) \\
 \frac{2}{3} S'(t) &= -2a - \frac{b}{M} \ln \frac{1-c^+}{1-c^-}, \quad t \in (0, T_*) \\
 \left[\ln \frac{c}{1-c} \right]^\pm &= -2M, \quad t \in (0, T_*)
 \end{aligned}$$

and

$$\phi^\epsilon(x, t) \rightarrow \begin{cases} -1 & \text{if } -1 < x < S(t) \\ +1 & \text{if } 1 > x > S(t) \end{cases}$$

as $\epsilon \rightarrow 0+$, where $T_* > 0$ is the first time such that one of the following occurs: either $T_* = T$, $S(T_*) = -1$, or $S(T_*) = 1$. Other approaches to alloy problems have been used in [19,20].

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