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G. B. McFadden
A. A. Wheeler

U. S. DEPARTMENT OF COMMERCE
Technology Administration
Mathematical and Computational
Sciences Division
National Institute of Standards
and Technology
Gaithersburg, MD 20899

Faculty of Mathematical Studies
University of Southampton
Highfield, Southampton So17 1BJ UK



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Dr. Karen H. Brown, Acting Director

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G. B. McFadden

National Institute of Standards and Technology
Gaithersburg, MD 20899-8910, USA

and

A.A. Wheeler

Faculty of Mathematical Studies
University of Southampton
Highfield, Southampton SO17 1BJ UK

Abstract

In this paper we discuss some applications of the classical Gibbs adsorption equation to specific diffuse interface models that are based on conserved and non-conserved order parameters. Such models are natural examples of the general methodology developed by J.W. Gibbs in his treatment of the thermodynamics of surfaces. We employ the methodology of J.W. Cahn, which avoids the use of conventional dividing surfaces to define surface excess quantities. We show that the Gibbs adsorption equation holds for systems with gradient energy coefficients, provided the appropriate definitions of surface excess quantities are used. We consider in particular the phase field model of a binary alloy with gradient energy coefficients for solute and the phase field. We derive a solute surface excess quantity that is independent of a dividing surface convention, and find that the adsorption in this model is influenced by the surface free energies of the pure components of the binary alloy, as well as the solute gradient energy coefficient. We present one-dimensional numerical solutions for this model corresponding to a stationary planar interface and show the consistency of the numerical results with the Gibbs adsorption equation. We also discuss the Gibbs adsorption equation in the context of other diffuse interface models that arise in spinodal decomposition and order-disorder transitions.

1 Introduction

Diffuse interface models of phase transitions were first employed to describe a liquid near its critical point. Subsequently, they were developed for a variety of other situations including spinodal decomposition and anti-phase boundaries in solids. The diffuse interface description of an interface envisages that the interface has a small finite thickness over which the material undergoes a smooth transition from one physical state to another, e.g., solid to liquid. The state of the system at each point in space is characterized by one or more order parameters. In an alloy the composition may play the role of an order parameter, which therefore varies continuously within the interfacial region between its value in each of the bulk phases. Consequently other thermodynamic quantities such as the pressure and Helmholtz free-energy density also vary through the interface. The associated variation of the free energy density in the interfacial region gives rise to the surface energy associated with the interface.

Gibbs (1957) in his treatment of interfaces did not explicitly address their internal structure. Rather, he introduced the notion of a dividing surface which separates the two bulk phases and accounts for the physical properties of the interface through additional excess quantities such as composition. In this treatment he derived the Gibbs adsorption equation which relates changes in the surface energy of an interface to corresponding changes in intensive thermodynamic variables, such as temperature and chemical potential, and involves the excess quantities associated with the interface. These ideas have been more recently developed by Cahn (1979).

In this paper we focus on a phase-field model of a binary alloy developed by Wheeler, Boettinger & McFadden (1993), hereafter denoted by WBM. This model employs a phase-field variable $\phi(\mathbf{x}, t)$ to describe the phase of the system as well as a composition $c(\mathbf{x}, t)$. The governing equations are derived from a free energy functional that contains square gradient terms in both the composition and phase field. It may be shown that for a planar interface in equilibrium the chemical potential is continuous across the interface and the bulk solid and liquid compositions satisfy a common tangent construction. For an ideal solution, this gives a lens-shaped phase diagram. Charach and Fife (1998) have investigated an extensive range of asymptotic limits of this model. Related phase-field models of a simple binary alloy have been also developed by Lin and Rogers (1992), Lowen, Bechhoefer & Tuckerman (1992), Caginalp & Xie (1993), Wheeler, Boettinger & McFadden (1992), Warren & Boettinger (1995), Kim, Kim & Suzuki (1999), and Bi & Sekerka (1998). In addition, phase-field models have been extended to more complex alloys, such as eutectic alloys by Karma (1994) and Wheeler, McFadden & Boettinger

(1996), as well as Steinbach et al. (1996).

Other diffuse models that involve alloy systems include spinodal decomposition (Cahn & Hilliard 1958) and antiphase boundaries (Allen & Cahn 1979), as well as multiple order parameter models of order-disorder transitions in body-centered-cubic (BCC) alloys (Cahn & Novick-Cohen 1996), face-centered-cubic (FCC) alloys (Braun, Cahn, McFadden & Wheeler 1997), and hexagonal-close-packed (HCP) alloys (Cahn, Han, & McFadden 1999).

In this paper we show that the phase-field model of a simple binary alloy satisfies the Gibbs adsorption equation when we make a suitable definition of the excess composition. We present numerical calculations which illustrate that the component of the alloy with the lower surface energy preferentially adsorbs on the interface, as well as how the surface energy depends on both temperature and the solute gradient energy coefficient. We go on to show that the Gibbs adsorption equation may also be derived for other diffuse interface models of alloys, including spinodal decomposition and interphase and antiphase boundaries in a multiple-order-parameter diffuse interface model of order-disorder transitions of an FCC alloy.

2 The Gibbs-Adsorption Equation for a Binary Alloy

In this section we review the classical description of the equilibrium surface free energy for a binary alloy, including J.W. Cahn's formulation of the Gibbs adsorption equation. The modifications to this treatment for a phase-field model of a binary alloy are described in the following section.

2.1 Thermodynamic Equilibrium

We consider an isothermal binary alloy system comprised of two species, A and B . As in our previous treatments (Wheeler et al. 1992, 1993), we assume a constant molar volume throughout the system, which allows us to neglect the effects of volume change on solidification. In this situation the Helmholtz free energy density, f , may be considered to depend only on the composition c , representing the mole fraction of component B , and the temperature of the system, T , and satisfies the relation

$$df = -s dT + \mu dc, \tag{1}$$

where s is the entropy per unit volume and $\mu = \partial f / \partial c$ is the chemical potential¹. The pressure $p(c, T)$ is given by

$$p = -f + c\mu, \quad (2)$$

and satisfies the Gibbs-Duhem equation,

$$dp = s dT + c d\mu. \quad (3)$$

For equilibrium of a spatially heterogeneous system, these thermodynamic relations are assumed to apply locally at each point, though f , s , c , and p may vary from point to point. Gibbs (1957) provides a description of the equilibrium properties of phase boundaries that apply in general, without requiring a detailed model of the interfacial region itself.

We consider a planar solid-liquid interface at temperature T that is at equilibrium, with a semi-infinite solid region extending to $x \rightarrow -\infty$, and a semi-infinite liquid region extending to $x \rightarrow +\infty$. We consider a control volume consisting of a cylinder of uniform cross-sectional area A and length $2W$ extending over the interval $-W < x < W$. The solid-liquid interface is assumed to be located near $x = 0$, and the cylinder is assumed to be long enough that the material near $x = -W$ consists of bulk solid phase and that near $x = W$ is bulk liquid phase. We assume the equilibrium solute profile is described by a function $c(x)$ which tends to bulk equilibrium values in regions far from the solid-liquid interface.

The total Helmholtz free energy of the control volume, F_W , is given by

$$F_W = A \int_{-W}^W f(c, T) dx, \quad (4)$$

and we also define a total entropy S_W , total composition C_W , and volume V_W ,

$$S_W = A \int_{-W}^W s dx, \quad C_W = A \int_{-W}^W c dx, \quad V_W = A \int_{-W}^W dx = 2AW. \quad (5)$$

For a given temperature, T , the system within the control volume is at equilibrium if F_W is a minimum for given values of C_W and V_W . Introducing constant Lagrange multipliers $\tilde{\mu}$ and \tilde{p} ,

¹Strictly speaking, a more accurate term for μ is the diffusion potential, proportional to the difference between the chemical potentials of species B and A , but for brevity we will simply refer to μ as the chemical potential.

the condition for equilibrium is

$$0 = \delta \{F_W - \tilde{\mu}C_W + \tilde{p}V_W\}, \quad (6)$$

where the minimum is taken with respect to variations in solute, $c(x) + \delta c(x)$, and the end points $x = -W + \delta W_S$ and $x = W + \delta W_L$, for a fixed value of A . This gives

$$0 = A \int_{-W}^W [f_c(c, T) - \tilde{\mu}] \delta c dx + [f(c_L, T) - \tilde{\mu}c_L + \tilde{p}] \delta W_L - [f(c_S, T) - \tilde{\mu}c_S + \tilde{p}] \delta W_S, \quad (7)$$

where $c_L = c(W)$ and $c_S = c(-W)$ are the equilibrium bulk concentrations in the liquid and solid phases, respectively. The equilibrium concentration profile is thus characterized by a uniform chemical potential. The pressures $p_L = c_L\mu - f(c_L, T)$ and $p_S = c_S\mu - f(c_S, T)$ in the bulk liquid and solid phases are equal and satisfy $p_L = p_S = \tilde{p}$. At equilibrium, then, we have uniform values of μ and T , but only that $p_L = p_S$ in the bulk phases; f , c , s , and p generally vary through the interface.

The equilibrium conditions imply that the common tangent construction holds, as given by

$$f_c(c_L, T) = f_c(c_S, T) = \frac{f(c_L, T) - f(c_S, T)}{c_L - c_S}. \quad (8)$$

These conditions define the liquidus and solidus concentrations, $c_L(T)$ and $c_S(T)$, as functions of temperature. The chemical potential $\mu(T)$ is also a function of temperature at equilibrium. Prescription of the value of C_W serves to specify the position of the interfacial region within the control volume, so that a variation in C_W for a given temperature changes the relative amounts of solid and liquid in the control volume.

An explicit example for $f(c, T)$ is provided by the ideal solution model considered in Wheeler et al. (1992), where

$$f(c_L, T) = f_L(c_L, T) = \frac{RT}{v_m} I(c_L), \quad (9)$$

and

$$f(c_S, T) = f_S(c_S, T) = c_S \frac{L_B(T - T_B)}{T_B} + (1 - c_S) \frac{L_A(T - T_A)}{T_A} + \frac{RT}{v_m} I(c_S), \quad (10)$$

where T_A and T_B are the bulk melting points of components A and B , respectively, L_A and L_B are the latent heats per unit volume of A and B , R is the ideal gas constant, and v_m is the

molar volume, which is assumed to be uniform throughout the system. Here

$$I(c) = c \ln c + (1 - c) \ln(1 - c) \quad (11)$$

is proportional to the ideal entropy of mixing. These free energies lead to a lens-shaped phase diagram, as illustrated in Fig. 1 for a model of the Cu-Ni system with properties listed in Table 1.

2.2 The Surface Free Energy

The surface free energy γ_W can be introduced through the expression

$$\begin{aligned} F_W &= A \int_{-W}^W f(c, T) dx = A \int_{-W}^W \{[f(c, T) - f(c_L, T)] - f_c(c_L, T)[c - c_L]\} dx \\ &+ f_c(c_L, T)A \int_{-W}^W c dx + [f(c_L, T) - c_L f_c(c_L, T)]V_W = A\gamma_W + \mu C_W - p_L V_W, \end{aligned} \quad (12)$$

where

$$\gamma_W = \int_{-W}^W \{[f(c, T) - f(c_L, T)] - f_c(c_L, T)[c - c_L]\} dx. \quad (13)$$

Using the relation $p = c\mu - f(c, T)$, we may also write

$$F_W = \mu C_W - A \int_{-W}^W p(x) dx, \quad (14)$$

where the contribution to the free energy from the pressure $p(x)$ appears explicitly. Comparing Eq. (12) and Eq. (14), we see that the surface free energy γ_W can be interpreted as the free energy associated with the variation of pressure through the interfacial region. We note that F_W , S_W , and C_W all vary strongly with the width W , since their integrands tend to non-zero limits as $x \rightarrow \pm\infty$. In contrast, γ_W has a well-defined finite limit for large W given by

$$\gamma = \int_{-\infty}^{\infty} \{[f(c, T) - f(c_L, T)] - \mu[c - c_L]\} dx, \quad (15)$$

where convergence of the integral is made possible by the common tangent construction, Eq. (8), satisfied by the integrand.

2.3 The Gibbs Adsorption Equation

The equilibrium surface energy for a binary alloy can be considered to be a function of T alone, and the Gibbs adsorption equation in this context describes the variation of surface energy with temperature, $d\gamma/dT$. Gibbs' original treatment was described in terms of a dividing surface which is introduced to define surface excess quantities that account for local variation in the interfacial region; for example, a surface excess entropy S_{xs} can be defined by

$$S_W = A \int_{-W}^W s(x) dx = s_S A \int_{-W}^{X_0} dx + s_L A \int_{X_0}^W dx + S_{xs} A, \quad (16)$$

where $x = X_0$ is the location of the dividing surface. In this description the bulk entropy densities s_L and s_S in the liquid and solid are extended to either side of the dividing surface, and the excess quantity S_{xs} is introduced to account for the actual variation of $s(x)$ near the interface. One similarly defines an adsorption, or surface excess concentration, C_{xs} , and relates $d\gamma/dT$ to the excess quantities C_{xs} and S_{xs} ,

$$d\gamma = -S_{xs} dT - C_{xs} d\mu. \quad (17)$$

Although C_{xs} and S_{xs} depend on the location of the dividing surface, the resulting expression for $d\gamma/dT$ does not, consistent with the fact that $d\gamma/dT$ represents a measurable quantity, unlike S_{xs} and C_{xs} . We note that γ_W itself can be interpreted as the surface excess of the quantity $f - cf_c = -p$; in this case, however, γ_W is independent of the location of the dividing surface by virtue of the common tangent construction.

Cahn (1979) gives an elegant discussion of the Gibbs adsorption equation which proceeds without the introduction of a dividing surface. We provide a short summary of Cahn's formulation for the special case of a binary alloy in the next section. This description is then generalized to treat the case of a phase-field model with gradient energy coefficients appearing in the free energy function.

2.4 Cahn's Formulation of the Gibbs Adsorption Equation

In terms of the thermodynamic description given in the previous section, if we perturb an equilibrium system that is at temperature T and composition C_W by $T \rightarrow T + \delta T$ and $C_W \rightarrow C_W + \delta C_W$, the local composition of the resulting equilibrium state will also be changed, with

$c(x) \rightarrow c(x) + \delta c(x)$, where

$$\delta C_W = A \int_{-W}^W \delta c(x) dx. \quad (18)$$

The variations δT and δC_W represent independent variations; for example, a variation in C_W at a given temperature can result from a translation in x of the system that changes the relative amounts of solid and liquid within the control volume.

The corresponding free energy change is given by

$$\delta F_W = A \int_{-W}^W \delta f dx = A \int_{-W}^W [f_c \delta c(x) - s \delta T] dx = \mu \delta C_W - S_W \delta T, \quad (19)$$

which is the system-wide version of equation (1). On the other hand, from the relation $F_W = A\gamma_W - p_L V_W + \mu C_W$ in Eq. (13), a variation at fixed A and W gives

$$\delta F_W = A\delta\gamma_W - V_W \delta p_L + \mu \delta C_W + C_W \delta \mu, \quad (20)$$

where $\delta \mu$ and δp_L are the changes in μ and p_L that result from the variations δT and δC_W . Comparing Eq. (19) and Eq. (20) leads to the following version of the Gibbs adsorption equation:

$$A\delta\gamma_W = V_W \delta p_L - C_W \delta \mu - S_W \delta T. \quad (21)$$

Note, however, that the quantities V_W , C_W , and S_W are all strongly-varying functions of the width W . To obtain an invariant form for this equation, we follow Cahn's treatment by appending the two Gibbs-Duhem equations for the bulk phases,

$$0 = \delta p_L - s_L \delta T - c_L \delta \mu, \quad (22)$$

$$0 = \delta p_S - s_S \delta T - c_S \delta \mu, \quad (23)$$

which also represent the increments to Eq. (21) that result from changes of the endpoints at $x = W$ and $x = -W$. If we note that $\delta p_L = \delta p_S$ at equilibrium, we may then write (21 - 23) as the linear system

$$\begin{pmatrix} 1 & V_W & -C_W \\ 0 & 1 & -c_L \\ 0 & 1 & -c_S \end{pmatrix} \begin{pmatrix} -A\delta\gamma_W \\ \delta p_L \\ \delta \mu \end{pmatrix} = \begin{pmatrix} S_W \\ s_L \\ s_S \end{pmatrix} \delta T, \quad (24)$$

and use Kramer's rule to solve for $A\delta\gamma_W$. This gives

$$\delta\gamma_W = -\delta T \int_{-W}^W \left\{ (s - s_L) - \frac{(s_S - s_L)}{(c_S - c_L)}(c - c_L) \right\} dx. \quad (25)$$

This expression has well-defined limits for large W , leading to the expression

$$\begin{aligned} \frac{d\gamma}{dT} &= - \int_{-\infty}^{\infty} \left\{ (s - s_L) - \frac{(s_S - s_L)}{(c_S - c_L)}(c - c_L) \right\} dx \\ &= - \frac{d\mu}{dT} \int_{-\infty}^{\infty} \left\{ (c - c_L) - \frac{(c_S - c_L)}{(s_S - s_L)}(s - s_L) \right\} dx. \end{aligned} \quad (26)$$

The term $(s_S - s_L)/(c_S - c_L)$ is seen from (22) and (23) to equal $-d\mu/dT$, and Eq. (25) equivalently results from Eq. (21) by using this expression and Eq. (22) to eliminate p_L . It is also easily seen that the expression (25) is equivalent to the Gibbs adsorption equation (17) by using the appropriate definitions for $d\mu/dT$ and the definitions of the surface excess quantities.

3 The Phase Field Model for a Binary Alloy

We next consider the phase-field model of a simple binary alloy discussed by Wheeler et al. (1992), which is based upon a gradient Helmholtz free energy functional given by

$$F_W = \int_V \left\{ f(c, T, \phi) + \frac{\epsilon^2}{2} |\nabla\phi|^2 + \frac{\kappa^2}{2} |\nabla c|^2 \right\} dV, \quad (27)$$

where ϵ and κ are constant gradient energy coefficients; we denote the solute gradient energy coefficient by κ rather than δ , the more common notation, to avoid confusion with variational quantities. This model has also been studied by a number of other authors as well, including Charach & Fife (1998, 1999) and Cahn & Novick-Cohen (2000).

The free energy density considered by Wheeler et al. (1992) is given by an ideal solution model

$$f(c, T, \phi) = r(\phi)f_S(c, T) + [1 - r(\phi)]f_L(c, T) + \frac{W(c)}{4}g(\phi), \quad (28)$$

where $W(c) = cW_B + (1 - c)W_A$ is a linear combination of the double well heights for the pure components, and

$$g(\phi) = \phi^2(1 - \phi^2), \quad r(\phi) = \phi^2(3 - 2\phi). \quad (29)$$

The phase-field variable ϕ , which labels the liquid and solid phases in our model, is analogous

to an order parameter in solid-state order-disorder transitions (Allen & Cahn 1979). In this context, the liquid phase in our model is analogous to a disordered phase with $\phi = 0$, and the solid phase is analogous to the ordered phase with $\phi = 1$. The phase-field variable can also be interpreted in terms of the density of atoms in the solid-liquid system. In the solid phase, the density varies periodically on the scale of the crystal lattice, whereas the mean density is uniform in the liquid phase, with a smooth transition between the two states in the interfacial region. The phase-field variable can then be regarded as characterizing the amplitude of the density modulation. With the convention that $\phi = 0$ represents the liquid phase and $\phi = 1$ represents the solid phase, the above functions $g(\phi)$ and $r(\phi)$ satisfy $g(0) = g(1) = 0$, $r(0) = 0$, and $r(1) = 1$, resulting in $f(c, T, 1) = f_S(c, T)$ and $f(c, T, 0) = f_L(c, T)$.

An equivalent expression for the free energy density is

$$f(c, T, \phi) = cf_B(\phi, T) + [1 - c]f_A(\phi, T) + \frac{RT}{v_m}I(c), \quad (30)$$

where $I(c)$ is given in Eq. (11). Here f_A and f_B are the free energy densities of components A ($c = 0$) and B ($c = 1$), respectively, and are given by

$$f_A(\phi, T) = \frac{L_A(T - T_A)}{T_A}r(\phi) + \frac{W_A}{4}g(\phi), \quad f_B(\phi, T) = \frac{L_B(T - T_B)}{T_B}r(\phi) + \frac{W_B}{4}g(\phi), \quad (31)$$

cf. Eq. (10). At the melting points of the pure components, the equilibrium surface energies and widths of the solid-liquid interface can be related to the double well heights and gradient energy coefficient, viz. (Wheeler et al. 1992)

$$\gamma_A = \frac{\epsilon}{6}\sqrt{W_A/2}, \quad \gamma_B = \frac{\epsilon}{6}\sqrt{W_B/2}, \quad (32)$$

and

$$\ell_A = \frac{\epsilon}{\sqrt{W_A/2}}, \quad \ell_B = \frac{\epsilon}{\sqrt{W_B/2}}. \quad (33)$$

3.1 Thermodynamic Equilibrium for the Phase-Field Model

Equilibrium inside the control volume of length $2W$ is described by the Euler equations

$$\kappa^2 c_{xx} = f_c(c, T, \phi) - \tilde{\mu}, \quad (34)$$

$$\epsilon^2 \phi_{xx} = f_\phi(c, T, \phi), \quad (35)$$

where $\tilde{\mu}$ is again a Lagrange multiplier representing the constraint on the total concentration C_W , which is defined by Eq. (5) in this case as well. Neumann boundary conditions $c_x(W) = c_x(-W) = 0$ and $\phi_x(W) = \phi_x(-W) = 0$ arise naturally if the energy is minimized in the control volume with respect to c and ϕ ; if the width W is large enough compared to the interfacial region, the solute and phase fields will be uniform far from the interfacial region. In that case the generalized chemical potential $f_c - \kappa^2 c_{xx} = \tilde{\mu}$ reduces to the classical chemical potential in the bulk solid and liquid phases.

The Euler equations admit a first integral

$$\frac{\epsilon^2}{2} \phi_x^2 + \frac{\kappa^2}{2} c_x^2 = [f(c, T, \phi) - f(c_L, T, 0)] - \tilde{\mu}[c - c_L], \quad (36)$$

and by examining the far field values of equations (34) and (36) we see that the common tangent conditions (8) relating c_L , c_S , and T also apply in this case.

3.2 Surface Free Energy for the Phase-Field Model

The surface free energy in the phase-field model includes the gradient energy terms, and is defined by writing

$$\begin{aligned} F_W &= A \int_{-W}^W \left\{ f(c, T, \phi) + \frac{\epsilon^2}{2} \phi_x^2 + \frac{\kappa^2}{2} c_x^2 \right\} dx \\ &= A \int_{-W}^W \left\{ \frac{\epsilon^2}{2} \phi_x^2 + \frac{\kappa^2}{2} c_x^2 + [f(c, T, \phi) - f(c_L, T, 0)] - f_c(c_L, T, 0)[c - c_L] \right\} dx \\ &\quad + f_c(c_L, T, 0) A \int_{-W}^W c dx + [f(c_L, T, 0) - c_L f_c(c_L, T, 0)] V_W \\ &= A \gamma_W + \tilde{\mu} C_W - p_L V_W, \end{aligned} \quad (37)$$

where we have assumed that $c_{xx}(W)$ is negligible in replacing $f_c(c_L, T, 0)$ by $\tilde{\mu}$ in the last equation. This expression has the same form as in Eq. (12), but now instead of the definition (13) we have

$$\gamma_W = \int_{-W}^W \left\{ \frac{\epsilon^2}{2} \phi_x^2 + \frac{\kappa^2}{2} c_x^2 + [f(c, T, \phi) - f(c_L, T, 0)] - f_c(c_L, T, 0)[c - c_L] \right\} dx. \quad (38)$$

3.3 Gibbs Adsorption Equation for the Phase-Field Model

A derivation for the Gibbs adsorption relation corresponding to this phase-field model follows the same lines as given above; for brevity we simply compute $d\gamma/dT$ by varying the temperature only. A variation in temperature causes variations in γ_W , $\tilde{\mu}$ and p_L , as well as the functions $c(x)$ and $\phi(x)$. From Eq. (37) we have

$$\frac{dF_W}{dT} = A \frac{d\gamma_W}{dT} + \frac{d\tilde{\mu}}{dT} C_W + \tilde{\mu} \frac{dC_W}{dT} - \frac{dp_L}{dT} V_W. \quad (39)$$

We also have

$$\begin{aligned} \frac{dF_W}{dT} &= A \frac{d}{dT} \int_{-W}^W \left\{ f(c, T, \phi) + \frac{\epsilon^2}{2} \phi_x^2 + \frac{\kappa^2}{2} c_x^2 \right\} dx \\ &= A \int_{-W}^W \left\{ f_c c_T + f_T + f_\phi \phi_T + \epsilon^2 \phi_x \phi_{xT} + \kappa^2 c_x c_{xT} \right\} dx \\ &= A \int_{-W}^W \left\{ (f_c - \kappa^2 c_{xx}) c_T - s + (f_\phi - \epsilon^2 \phi_{xx}) \phi_T \right\} dx, \\ &= \tilde{\mu} \frac{dC_W}{dT} - S_W, \end{aligned} \quad (40)$$

where we have integrated by parts and used the Euler equations to obtain the final expression. Comparing Eq. (39) and Eq. (40) gives

$$\frac{d\gamma_W}{dT} = -\frac{d\tilde{\mu}}{dT} C_W - S_W + \frac{dp_L}{dT} V_W. \quad (41)$$

Using

$$\frac{dp_L}{dT} = s_L + c_L \frac{d\mu}{dT} \quad (42)$$

and

$$\frac{dp_S}{dT} = s_S + c_S \frac{d\mu}{dT} \quad (43)$$

and following Cahn's treatment as before, leads again to the expression

$$\frac{d\gamma_W}{dT} = -\frac{d\mu}{dT} \int_{-W}^W \left\{ (c - c_L) - \frac{(c_S - c_L)}{(s_S - s_L)} (s - s_L) \right\} dx; \quad (44)$$

thus the addition of gradient energy terms does not alter the form (25) of the classical Gibbs adsorption equation. However, the gradient terms do affect the profiles that comprise the integrands in (44) as will be illustrated numerically in a specific example below.

4 Numerical Calculations

In this section we describe numerical calculations for the model binary alloy considered by Wheeler et al. (1992). Numerical solutions were computed by discretizing the Euler equations (34) and (35) and using second-order-accurate finite differences on a uniform grid of $2N + 1$ points, with a mesh spacing of $h = W/N$. Neumann boundary conditions were applied at $x = \pm W$, resulting in $2N + 4$ nonlinear equations in the $2N + 4$ unknowns $c_j \approx c(jh)$ and $\phi_j \approx \phi(jh)$, for $j = -N, \dots, N$. In addition, the Lagrange multiplier $\tilde{\mu}$ is computed by specifying a value for the total solute C_W . An alternative possibility is to specify the condition $\phi(0) = 1/2$ instead of the solute constraint; both conditions serve to locate the position of the interfacial region inside the box. The resulting set of nonlinear equations is solved using the package SNSQ (Powell 1970). Acceptable accuracy is obtained using 200 grid points provided that the width W is an order of magnitude wider than the interfacial region.

4.1 The Phase-Field Model without Solute Gradient Energy Terms ($\kappa = 0$)

We first set $\kappa = 0$ and study the effect on interface adsorption of varying the surface free energies of the pure components, γ_A and γ_B . Some interface profiles for $T = 1700K$ are shown in Fig. 2. The dashed curve corresponds to the choice $\gamma_A = \gamma_B$; Table 2 contains the resulting values of γ , normalized by γ_A , and the quantity $d\gamma/dT$, normalized by γ_A/T_A . This temperature is near the pure A side of the phase diagram, and the concentrations and surface free energies are near those of component A.

If γ_A is fixed and γ_B is increased (lower curves), the equilibrium profile is characterized by depletion of B in the interfacial region, consistent with the minimization of the free energy by reducing the amount of the higher-energy component in the interface. The surface free energy increases with increasing γ_B , and $d\gamma/dT$ becomes increasingly negative.

If γ_B is fixed and γ_A is increased (upper curves), the situation is reversed, and the lowest energy state has preferential incorporation of component B in the interfacial region, which is also reflected in the trends shown in Table 2.

We next show in Fig. 3 the dependence of γ on temperature for $\gamma_A = \gamma_B = 3.7(10^{-5})$ J/cm². Although the surface free energy of the pure components are equal, the surface energy is larger for intermediate values of the system temperature, reflecting the influence of the solute

contribution to the surface free energy.

The corresponding surface adsorption is shown in Fig. 4. Here we define a dimensionless surface adsorption

$$\Gamma_{xs} = \frac{1}{2l_A} \int_{-W}^W \left\{ (c - c_L) - \frac{(c_S - c_L)}{(s_S - s_L)} (s - s_L) \right\} dx. \quad (45)$$

The derivative of the surface free energy γ_W with respect to temperature is proportional to $-\Gamma_{xs}d\mu/dT$. The ‘s-shaped’ adsorption curve reflects the change in sign of $d\gamma/dT$, which is non-monotonic in this case. We emphasize that Γ_{xs} is independent of a dividing surface convention, and generalizes the adsorption coefficient that was displayed in Fig. 3 of WBM; Γ_{xs} includes contributions from both the solute and the entropy profiles.

We next show in Fig. 5 the dependence of γ on temperature for $\gamma_A = 3.7(10^{-5})$ J/cm² and $\gamma_B = 2.8(10^{-5})$ J/cm². In this case the surface free energy is a monotonic function of temperature, as the contribution to the surface free energy from solute is less than the variation that is associated with the different values for the pure components.

The corresponding adsorption is shown in Fig. 6. The adsorption Γ_{xs} is positive, with a maximum at an intermediate temperature near the middle of the phase diagram.

4.2 The Phase-Field Model with Solute Gradient Energy Terms ($\kappa \neq 0$)

We next present numerical calculations with a non-zero solute gradient energy coefficient κ . We take $\gamma_A = 3.7(10^{-5})$ J/cm² and $\gamma_B = 2.8(10^{-5})$ J/cm², with $\epsilon = 3.3(10^{-6})$ (J/cm)^{1/2}; the case $\kappa = 0$ therefore corresponds to Figs. 5 and 6. In Fig. 7 we show the surface free energy for $\kappa = \epsilon = 3.3(10^{-6})$ (J/cm)^{1/2}, $\kappa = 1.0(10^{-5})$ (J/cm)^{1/2}, $\kappa = 2.0(10^{-5})$ (J/cm)^{1/2}, and $\kappa = 3.3(10^{-5})$ (J/cm)^{1/2}. The curve for $\kappa = \epsilon = 3.3(10^{-6})$ (J/cm)^{1/2}, indicated by a dashed line, is almost indistinguishable from the case $\kappa = 0$ shown in Fig. 5. As κ increases, the surface free energy also increases due to the enhancement of the free energy from the solute gradient energy contribution. For the value $\kappa = 3.3(10^{-5})$ (J/cm)^{1/2}, the maximum surface free energy occurs at an intermediate temperature in the interior of the phase diagram. The corresponding adsorption coefficients are shown in Fig. 8. For larger values of κ , the adsorption adopts an ‘s-shaped’ profile with both positive and negative values, which is consistent with the observations in Fig. 3 of WBM, which corresponded to a limiting case $\epsilon/\kappa \ll 1$ (in WBM, κ was

denoted by δ). For $\epsilon/\kappa \ll 1$ the width of the transition layer for the solute profile is much larger than that for the phase field, as discussed in WBM and Charach & Fife (1999). The surface free energy curve shown in Fig. 4 of WBM for $\kappa = 3.3(10^{-5}) \text{ J/cm}^{1/2}$ shows a non-monotonic temperature dependence that is similar to the present calculations with $\epsilon = 3.3(10^{-6}) \text{ J/cm}^{1/2}$ and $\kappa = 3.3(10^{-5}) \text{ J/cm}^{1/2}$.

5 Discussion

We next mention some variations of this procedure, which apply to special cases and generalizations of the solidification model that we have discussed above. We start with two examples, given by the Cahn-Hilliard equation and the binary alloy model of Kim, Kim, and Suzuki (1999), where analytic solutions allow the Gibbs adsorption equation to be verified explicitly. We then discuss an example with multiple order parameters that illustrates the dependence of the Gibbs adsorption equation on the thermodynamic degrees of freedom in the system.

5.1 Cahn-Hilliard Equation

The Cahn-Hilliard equation is a special case of the binary alloy phase-field model that results from setting $\epsilon = 0$ and taking a special form of the free energy density that is independent of ϕ . A simple model for spinodal decomposition near the critical temperature T_{cr} and critical composition c_{cr} is obtained by assuming

$$f(c, T) = a(T - T_{\text{cr}})(c - c_{\text{cr}})^2 + b(c - c_{\text{cr}})^4, \quad (46)$$

where a and b are positive constants. If $T < T_{\text{cr}}$, a solute profile of the form

$$c(x) = c_{\text{cr}} + \left[\frac{a(T_{\text{cr}} - T)}{2b} \right]^{1/2} \tanh \frac{x}{2\xi} \quad (47)$$

satisfies the Cahn-Hilliard equation, where the width ξ of the interface is given by

$$\xi^2 = \frac{\kappa^2}{4a(T_{\text{cr}} - T)}. \quad (48)$$

The surface energy of the interface is given by

$$\gamma(T) = \int_{-\infty}^{\infty} \left\{ \frac{\kappa^2}{2} c_x^2 + f(c, T) \right\} dx = \frac{2\kappa a^{3/2} (T_{\text{cr}} - T)^{3/2}}{3b}. \quad (49)$$

This model is symmetric about the point $c = c_{\text{cr}}$, so that the chemical potential μ is zero for the planar system for all T . The resulting form of the Gibbs adsorption equation,

$$\frac{d\gamma}{dT} = - \int_{-\infty}^{\infty} [s(x) - s(\infty)] dx = \frac{-\kappa a^{3/2} (T_{\text{cr}} - T)^{1/2}}{b} \quad (50)$$

can be verified directly, where the entropy density is $s = -f_T = -a(c - c_{\text{cr}})^2$.

5.2 Kim, Kim, and Suzuki's Model of a Binary Alloy

A model for the solidification of a binary alloy that has a very simple description of the equilibrium phase field and solute profiles across the solid-liquid interface was given by Kim, Kim, and Suzuki (1999). In their model, ϕ is interpreted as a solid fraction, and solute concentrations $c_L(x)$ and $c_S(x)$ in the liquid and solid are defined throughout the system; the solute concentration at each point in space is then given by

$$c = r(\phi)c_S + [1 - r(\phi)]c_L, \quad (51)$$

where $r(\phi)$ is a smooth function of ϕ with $r(0) = 0$ and $r(1) = 1$; e.g., $r(\phi) = \phi$ or $r(\phi) = \phi^2(3 - 2\phi)$. The concentrations $c_L(x)$ and $c_S(x)$ are also assumed to satisfy a parallel tangent construction at each point, with

$$\frac{\partial f_L(c_L, T)}{\partial c_L} = \frac{\partial f_S(c_S, T)}{\partial c_S}, \quad (52)$$

where f_L and f_S are the prescribed bulk free energy densities in each phase. Eqns. (51) and (52) are inverted to give the relations $c_L = c_L(c, T, \phi)$ and $c_S = c_S(c, T, \phi)$, and the free energy density $f(c, T, \phi)$ is then defined as

$$f(c, T, \phi) = r(\phi)f_S(c_S(c, T, \phi)) + [1 - r(\phi)]f_L(c_L(c, T, \phi)) + \frac{W(T)}{4}g(\phi), \quad (53)$$

which differs from the form used in Eq. (28) in that c_S and c_L appear in the arguments of f_S and f_L rather than the concentration c itself. Kim, Kim, and Suzuki (1999) assume a constant

double well height W , but we assume here that the height depends on temperature as a means of allowing different surface free energies at $T = T_A$ and $T = T_B$.

The free energy functional of the system has the form (27) with $\kappa = 0$, and the equilibrium equations

$$f_c = \tilde{\mu}, \quad f_\phi - \epsilon^2 \phi_{xx} = 0, \quad (54)$$

have particularly simple solutions because of the specific form chosen for $f(c, T, \phi)$. By using (51) and (52) we find that $f_\phi(c, T, \phi) = W(T)g'(\phi)/4$, so that the phase field is given by the profile $\phi(x) = [1 - \tanh(x/2\ell)]/2$, where $\ell(T) = \epsilon/\sqrt{W(T)}$. In addition, the equilibrium equations imply that the common tangent construction holds, which in this case results in $c_L(x)$ and $c_S(x)$ being constants that are given by the liquidus and solidus values at the given temperature T ; the solute profile $c(x)$ in (51) is then simply an interpolation by $r(\phi)$ between the liquidus and solidus values.

The derivative of the surface free energy is

$$\begin{aligned} \frac{d\gamma}{dT} &= \frac{d}{dT} \int_{-\infty}^{\infty} \left\{ \frac{\epsilon^2}{2} \phi_x^2 + \frac{W(T)}{4} g(\phi) \right\} dx \\ &= \frac{W'(T)}{4} \int_{-\infty}^{\infty} g(\phi) dx + \int_{-\infty}^{\infty} \left\{ \epsilon^2 \phi_x \phi_{xT} + \frac{W}{4} g'(\phi) \phi_T \right\} dx = \frac{W'(T)}{4} \int_{-\infty}^{\infty} g(\phi) dx, \end{aligned} \quad (55)$$

where an integration by parts again simplifies the final expression. On the other hand, we have

$$s(x) = -f_T = r(\phi)s_S + [1 - r(\phi)]s_L - \frac{W'(T)}{4} g(\phi), \quad (56)$$

where $s_S = -\partial f_S(c_S, T)/\partial T$ and $s_L = -\partial f_L(c_L, T)/\partial T$ are the bulk entropy densities in each phase, so that the Gibbs adsorption equation gives

$$\frac{d\gamma}{dT} = - \int_{-\infty}^{\infty} \left\{ [s(x) - s_L] - \frac{[s_S - s_L]}{[c_S - c_L]} [c(x) - c_L] \right\} dx = \frac{W'(T)}{4} \int_{-\infty}^{\infty} g(\phi) dx \quad (57)$$

in agreement with (55).

5.3 Diffuse Interface Model of FCC Alloys

Adsorption also arises in models of interphase boundaries (IPBs) and antiphase boundaries (APBs) that are based on diffuse interface descriptions; examples include face-centered-cubic alloys (Braun et al. 1997) and hexagonal-close-packed alloys (Cahn, Han, & McFadden 1999). In

numerical computations for an FCC system performed by Tonaglu (2000), adsorption is observed in the concentration profiles associated with APBs. This model provides a good illustration of the appropriate degrees of freedom that appear in the Gibbs adsorption equation, and we provide a brief summary of the governing equations here.

The FCC model is based on four order parameters that describe how the two species are distributed on the FCC lattice, corresponding to the corners and faces of the unit cell. The overall concentration in the system is denoted by c , a conserved order parameter, and there are, in addition, three non-conserved order parameters, denoted by X , Y , and Z . The disordered phase is characterized by $X = Y = Z = 0$, and ordered states have one or more non-zero values of X , Y , and Z . There is an associated free energy density $f(c, X, Y, Z, T)$. The free energy functional for the system includes three gradient energy coefficients A , B , and κ , and takes the form

$$F = \int_V \left\{ \frac{A}{2}(X_x^2 + Y_y^2 + Z_z^2) + \frac{B}{2}(X_y^2 + X_z^2 + Y_x^2 + Y_z^2 + Z_x^2 + Z_y^2) + \frac{\kappa^2}{2}|\nabla c|^2 + f(c, X, Y, Z, T) \right\} dV \quad (58)$$

For a planar system with unit normal $\vec{n} = (n_x, n_y, n_z)$, a one-dimensional solution depends only on the variable $\zeta = \vec{n} \cdot (x, y, z)$ that measures distance from the interface. The system has the associated free energy

$$F_W = A \int_{-W}^W \left\{ \frac{\alpha_x^2}{2} X_\zeta^2 + \frac{\alpha_y^2}{2} Y_\zeta^2 + \frac{\alpha_z^2}{2} Z_\zeta^2 + \frac{\kappa^2}{2} c_\zeta^2 + f(c, X, Y, Z, T) \right\} d\zeta, \quad (59)$$

where

$$\alpha_x^2 = An_x^2 + Bn_y^2 + Bn_z^2, \quad \alpha_y^2 = Bn_x^2 + An_y^2 + Bn_z^2, \quad \alpha_z^2 = Bn_x^2 + Bn_y^2 + An_z^2. \quad (60)$$

The Euler equations are

$$f_c - \kappa^2 c_{\zeta\zeta} = \tilde{\mu}, \quad (61)$$

where the Lagrange multiplier $\tilde{\mu}$ again is equal to the chemical potential, and the non-conserved order parameters satisfy

$$\alpha_x^2 X_{\zeta\zeta} - f_X = 0, \quad \alpha_y^2 Y_{\zeta\zeta} - f_Y = 0, \quad \alpha_z^2 Z_{\zeta\zeta} - f_Z = 0. \quad (62)$$

A first integral of the system is given by

$$0 = \frac{\alpha_x^2}{2} X_\zeta^2 + \frac{\alpha_y^2}{2} Y_\zeta^2 + \frac{\alpha_z^2}{2} Z_\zeta^2 + \frac{\kappa^2}{2} c_\zeta^2 \quad (63)$$

$$+ [f(c, X, Y, Z, T) - f(c(\infty), X(\infty), Y(\infty), Z(\infty), T)] - \tilde{\mu}[c - c(\infty)].$$

5.3.1 Interphase Boundaries

An IPB connecting the disordered bulk phase with concentration c_{dis} and an ordered bulk phase with concentration c_{or} and associated order parameters $(X_0, Y_0, Z_0) \neq (0, 0, 0)$ is described by the above Euler equations, with solutions that satisfy the far-field boundary conditions

$$[c(\zeta), X(\zeta), Y(\zeta), Z(\zeta)] \rightarrow \begin{cases} [c_{or}, X_0, Y_0, Z_0] & \text{as } \zeta \rightarrow -\infty, \\ [c_{dis}, 0, 0, 0] & \text{as } \zeta \rightarrow \infty, \end{cases} \quad (64)$$

say. The situation is analogous to our previous treatment of the binary alloy solidification problem, with the disordered phase playing the role of the liquid phase, and the ordered phase playing the role of the ordered phase. The Euler equations again imply that the common tangent construction holds, which in this case is given by

$$f_c(c_{dis}, 0, 0, 0, T) = f_c(c_{or}, X_0, Y_0, Z_0, T) = \frac{f(c_{dis}, 0, 0, 0, T) - f(c_{or}, X_0, Y_0, Z_0, T)}{c_{dis} - c_{or}} = \tilde{\mu}, \quad (65)$$

and

$$f_X(c_{dis}, 0, 0, 0, T) = f_Y(c_{dis}, 0, 0, 0, T) = f_Z(c_{dis}, 0, 0, 0, T) = 0, \quad (66)$$

$$f_X(c_{or}, X_0, Y_0, Z_0, T) = f_Y(c_{or}, X_0, Y_0, Z_0, T) = f_Z(c_{or}, X_0, Y_0, Z_0, T) = 0. \quad (67)$$

Employing a control volume of uniform cross-sectional area A as before, extending over the interval $-W < \zeta < W$ in this case, leads to a corresponding surface free energy γ_W given by

$$\begin{aligned} \gamma_W = \int_{-W}^W \left\{ \frac{\kappa^2}{2} c_\zeta^2 + \frac{\alpha_x^2}{2} X_\zeta^2 + \frac{\alpha_y^2}{2} Y_\zeta^2 + \frac{\alpha_z^2}{2} Z_\zeta^2 \right. \\ \left. + [f(c, X, Y, Z, T) - f(c_{dis}, 0, 0, 0, T)] - \tilde{\mu}[c - c_{dis}] \right\} d\zeta, \end{aligned} \quad (68)$$

in terms of which we have

$$F_W = A\gamma_W + \tilde{\mu}C_W - p_{dis}V_W, \quad (69)$$

where p_{dis} , the pressure in the bulk disordered phase, is given by $p_{dis} = c_{dis}f_c(c_{dis}, 0, 0, 0, T) - f(c_{dis}, 0, 0, 0, T)$. The bulk equilibrium concentrations are then functions of the temperature, $c_{dis}(T)$ and $c_{or}(T)$, whose loci form curves in the phase diagram analogous to the liquidus and solidus curves in the solidification case. The temperature is the sole thermodynamic degree of freedom for an IPB, and the Gibbs adsorption equation

$$\frac{d\gamma_W}{dT} = - \int_{-W}^W \left\{ (s - s_{dis}) - \frac{(s_{or} - s_{dis})}{(c_{or} - c_{dis})} (c - c_{dis}) \right\} d\zeta \quad (70)$$

for this diffuse interface system can be derived as before, in this case by making use of the Euler equations (61) and (62) to simplify the result. Here the entropy density is given by $s = -f_T(c, X, Y, Z, T)$.

5.3.2 Antiphase Boundaries

An APB connects variants of an ordered bulk phase. The variants have the same bulk concentrations c_{or} and free energy; but the composition and temperature of the ordered phase are independent thermodynamic degrees of freedom, in contrast to the case of an IPB. The non-conserved order parameters assume different values in the two variants; examples include an APB connecting two $L1_0$ variants with $X = X_0 \neq 0, Y = Z = 0$ and $X = -X_0, Y = Z = 0$, or an APB connecting two $L1_2$ variants with $X = Y = Z = X_0 \neq 0$ and $X = -Y = -Z = X_0$.

The boundary conditions for the Euler equations (61) and (62) in this case are $c \rightarrow c_{or}$ as $\zeta \rightarrow \pm\infty$; the far-field values of the non-conserved order parameters are denoted by $X(\infty), X(-\infty)$, etc. The variants have equal energy,

$$f(c_{or}, X(-\infty), Y(-\infty), Z(-\infty), T) = f(c_{or}, X(\infty), Y(\infty), Z(\infty), T), \quad (71)$$

which follows from the first integral (63) for this case.

The surface adsorption and surface excess entropy for the APB are well-defined quantities, with no need for a dividing surface convention, and are given by

$$C_{xs} = \int_{-\infty}^{\infty} (c - c_{or}) d\zeta, \quad S_{xs} = \int_{-\infty}^{\infty} (s - s_{or}) d\zeta, \quad (72)$$

where $s_{or} = -f_T(c_{or}, X(\infty), Y(\infty), Z(\infty), T)$ is the entropy density of the bulk ordered phase.

In the control volume we define the surface free energy γ_W by

$$\begin{aligned} \gamma_W = \int_{-W}^W & \left\{ \frac{\kappa^2}{2} c_\zeta^2 + \frac{\alpha_x^2}{2} X_\zeta^2 + \frac{\alpha_y^2}{2} Y_\zeta^2 + \frac{\alpha_z^2}{2} Z_\zeta^2 \right. \\ & \left. + [f(c, X, Y, Z, T) - f(c_{or}, X(\infty), Y(\infty), Z(\infty), T)] - \tilde{\mu}[c - c_{or}] \right\} d\zeta. \end{aligned} \quad (73)$$

For a fixed control volume, we consider changes $\delta\gamma_W$ due to variations δT in temperature and δc_{or} in the bulk composition; there are also associated changes in the local profiles of the concentration and the non-conserved order parameters, as well as in the total concentration C_W , the chemical potential $\tilde{\mu}$, and the bulk pressure p_{or} . The variations δC_W and $\delta c(x)$ are related as in Eq. (18). Note that a translation of the system within the control volume does not cause an appreciable change in C_W provided W is large enough; therefore we do not assume that δC_W can be varied independently of T and c_{or} .

The free energy of the control volume is $F_W = A\gamma_W + \tilde{\mu}C_W - p_{or}V_W$, and examination of its variation again leads to the familiar equation

$$A\delta\gamma_W = V_W\delta p_{or} - C_W\delta\tilde{\mu} - S_W\delta T, \quad (74)$$

where the Euler equations can be used to eliminate the contributions from the gradient energy terms as before. For an APB there is a single Gibbs-Duhem equation that holds in the bulk for both variants,

$$\delta p_{or} = s_{or}\delta T + c_{or}\delta\tilde{\mu}, \quad (75)$$

which leads to the result

$$\delta\gamma_W = -\delta T \int_{-W}^W [s(x) - s_{or}] d\zeta - \delta\tilde{\mu} \int_{-W}^W [c(x) - c_{or}] d\zeta = -S_{xs}\delta T - C_{xs}\delta\tilde{\mu}. \quad (76)$$

Here

$$\delta\tilde{\mu} = f_{cc}(c_{or}, X(\infty), Y(\infty), Z(\infty), T) \delta c_{or} + f_{cT}(c_{or}, X(\infty), Y(\infty), Z(\infty), T) \delta T \quad (77)$$

which allows the calculation of $d\gamma_W/dT$ and $d\gamma_W/dc_{or}$ directly in terms of S_{xs} , C_{xs} , and second derivatives of the free energy density.

6 Conclusion

In this paper we have shown that diffuse interface models of alloy systems satisfy the Gibbs adsorption equation. In particular, we have investigated in detail a phase-field model of a binary alloy involving gradient energy terms in both the phase-field and composition. Numerical solutions of a planar interface using this model exhibit the component with the lower surface energy preferentially adsorbing onto the interface as well as the surface energy being enhanced through the presence of the solute gradient energy term. We also considered examples using models of spinodal decomposition and order-disorder transitions in binary alloys. In each case we have verified that the Gibbs adsorption equation holds for systems that feature gradient energy coefficients and combinations of conserved and non-conserved order parameters, provided that the appropriate definitions of surface excess quantities are used.

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L_A	2350 J/cm ³
L_B	1725 J/cm ³
T_A	1728 K
T_B	1358 K
v_m	7.4 cm ³ /mole
R	8.314 J/mole K

Table 1: Material parameters used in phase diagram calculations.

γ_A (J/cm ²)	γ_B (J/cm ²)	γ/γ_A	$(T_A/\gamma_A)d\gamma/dT$
11.2(10 ⁻⁵)	2.8(10 ⁻⁵)	0.952673	2.9194647
8.4(10 ⁻⁵)	2.8(10 ⁻⁵)	0.959877	2.4917755
5.6(10 ⁻⁵)	2.8(10 ⁻⁵)	0.969577	1.8930718
2.8(10 ⁻⁵)	2.8(10 ⁻⁵)	1.006204	-0.363581
2.8(10 ⁻⁵)	5.6(10 ⁻⁵)	1.115590	-6.733671
2.8(10 ⁻⁵)	8.4(10 ⁻⁵)	1.261922	-14.490109
2.8(10 ⁻⁵)	11.2(10 ⁻⁵)	1.417201	-22.055166

Table 2: Material parameters used in adsorption calculations. Here $T = 1700$ K, $\epsilon = 3.3(10^{-6})$ (J/cm)^{1/2}, $l_A = \epsilon^2/6\gamma_A$.

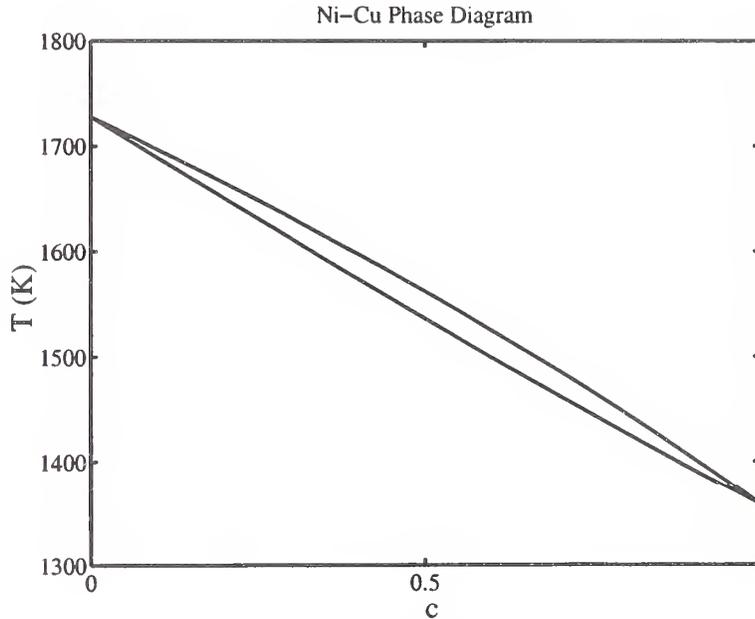


Figure 1: Phase diagram using the parameters in Table 1.

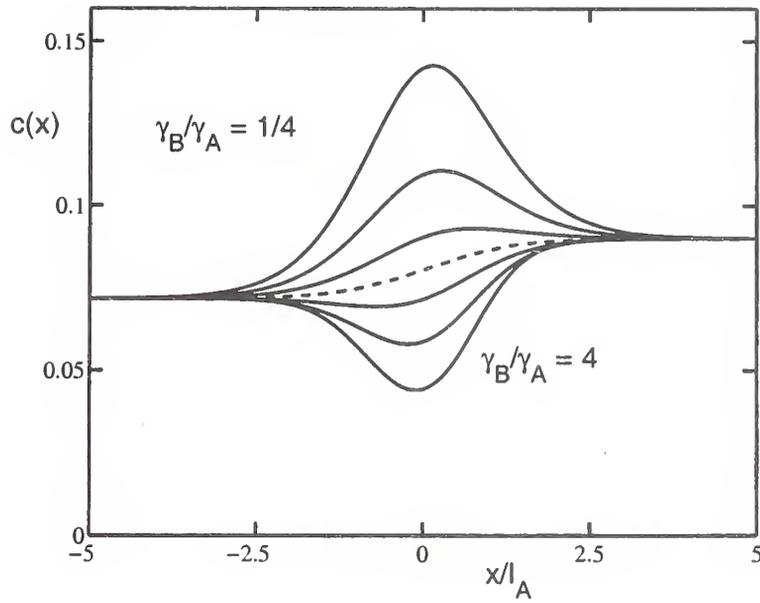


Figure 2: Concentration profiles using the parameters in Table 2.

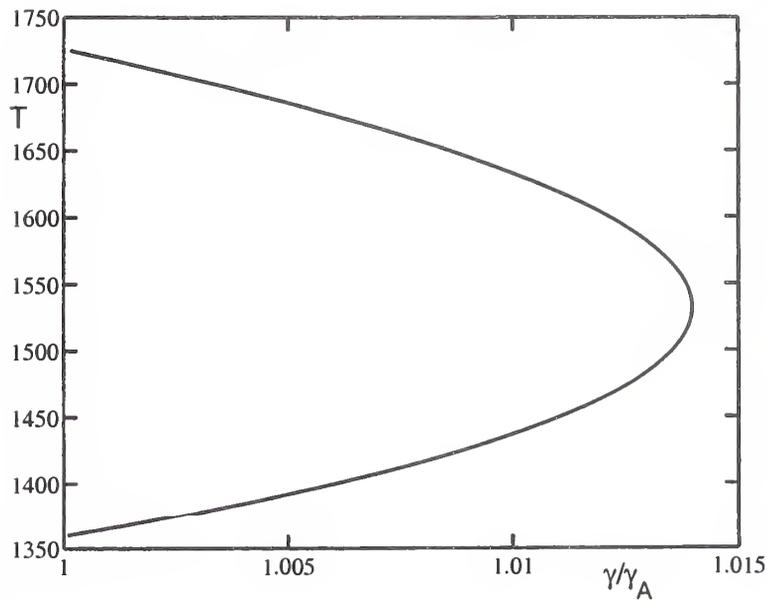


Figure 3: The dependence of γ on temperature for $\gamma_A = \gamma_B = 3.7(10^{-5}) \text{ J/cm}^2$.

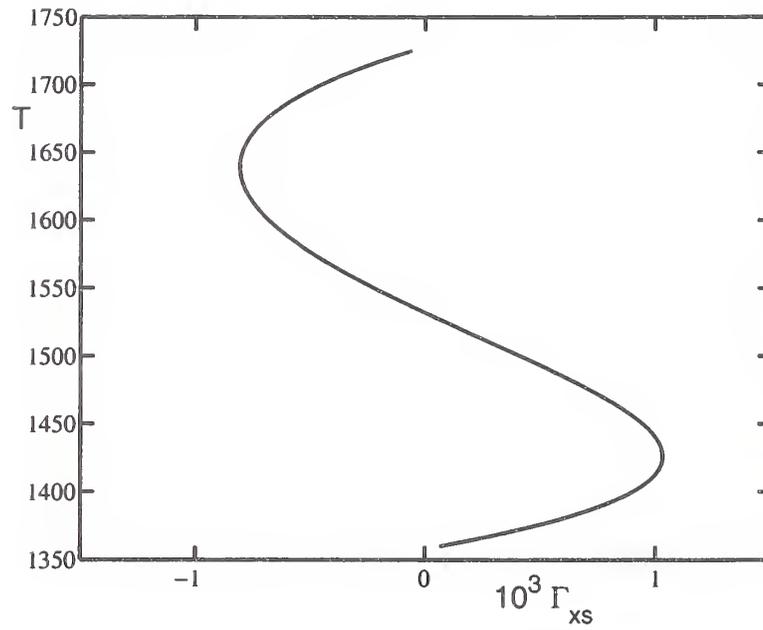


Figure 4: The dependence of the dimensionless surface adsorption Γ_{xs} on temperature for $\gamma_A = \gamma_B = 3.7(10^{-5}) \text{ J/cm}^2$.

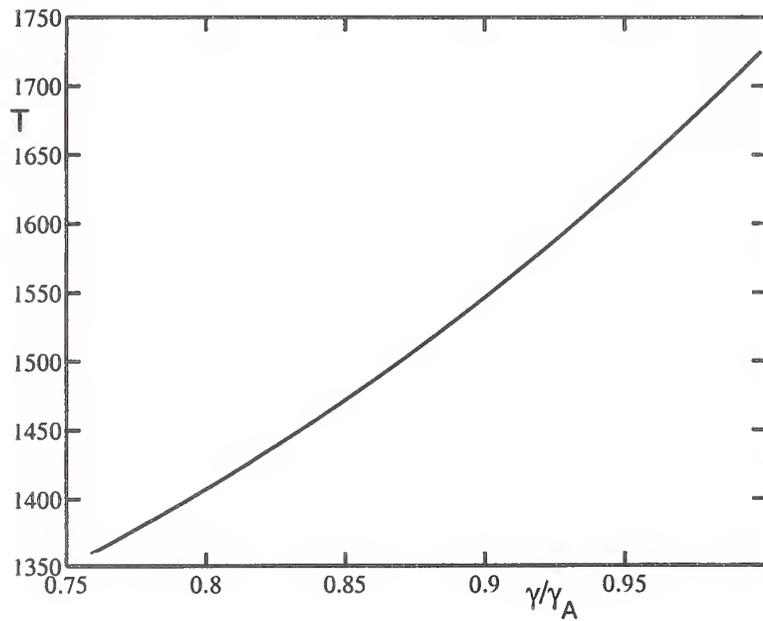


Figure 5: The dependence of γ on temperature for $\gamma_A = 3.7(10^{-5}) \text{ J/cm}^2$ and $\gamma_B = 2.8(10^{-5}) \text{ J/cm}^2$.

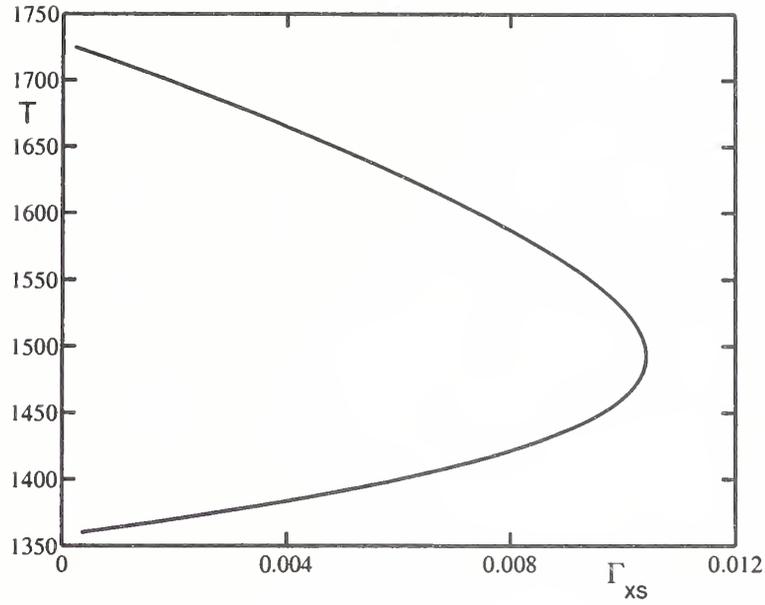


Figure 6: The dependence of the dimensionless surface adsorption Γ_{xs} on temperature for $\gamma_A = 3.7(10^{-5})$ J/cm² and $\gamma_B = 2.8(10^{-5})$ J/cm².

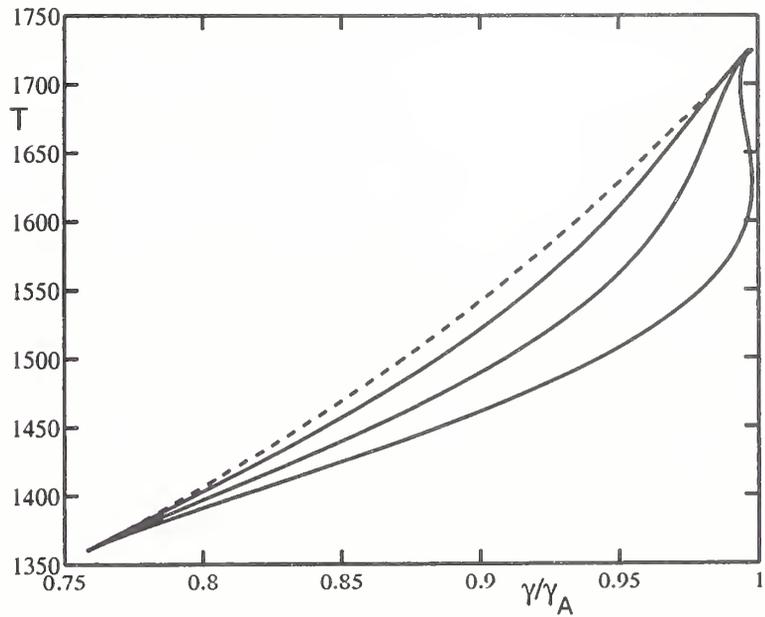


Figure 7: The surface free energy for $\kappa = \epsilon = 3.3(10^{-6})$ (J/cm)^{1/2} [dashed curve], $\kappa = 1.0(10^{-5})$ (J/cm)^{1/2}, $\kappa = 2.0(10^{-5})$ (J/cm)^{1/2}, and $\kappa = 3.3(10^{-5})$ (J/cm)^{1/2}.

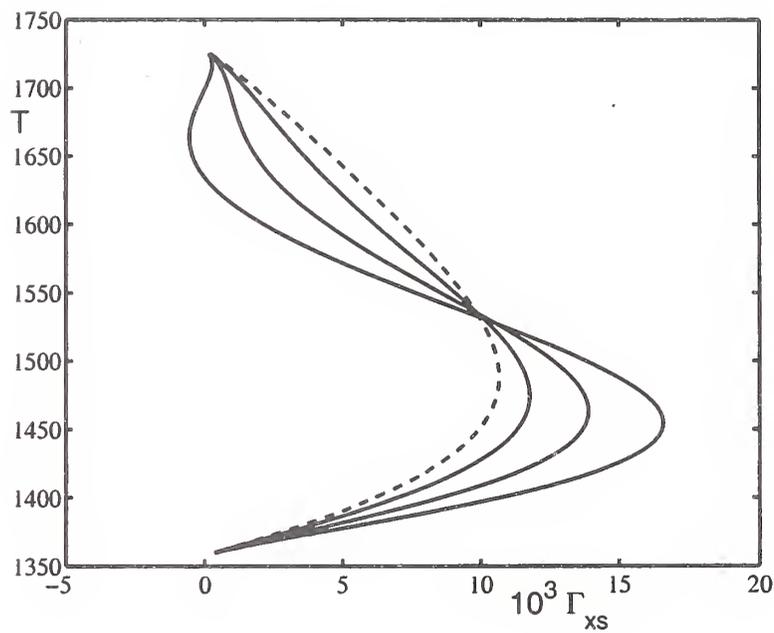


Figure 8: The surface adsorption for $\kappa = \epsilon = 3.3(10^{-6}) \text{ (J/cm)}^{1/2}$ [dashed curve], $\kappa = 1.0(10^{-5}) \text{ (J/cm)}^{1/2}$, $\kappa = 2.0(10^{-5}) \text{ (J/cm)}^{1/2}$, and $\kappa = 3.3(10^{-5}) \text{ (J/cm)}^{1/2}$.

