THEORY OF DEPARTURE FROM LOCAL EQUILIBRIUM AT THE INTERFACE OF A TWO-PHASE DIFFUSION COUPLE*

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A simple model is developed to calculate the departure from local equilibrium at a moving two-phase interface in a binary diffusion couple. The model is based on the solution of a generalized diffusion equation derived by assuming that the diffusion flux of a species is proportional to the gradient of the functional derivative, with respect to concentration, of the total Helmholtz free energy. This total free energy is composed of the integral of two terms, a coarse-grained free energy per unit volume that reflects the bulk thermodynamic properties of the material and an energy density proportional to the square of the concentration gradient. Final results are conveniently represented by replacing the actual concentration profile with another having a jump discontinuity at a plane whose position is judiciously chosen within the region of high concentration gradient; values of composition and its derivative at the discontinuity are chosen such that the bulk solutions, when extrapolated to these values, are the same as for the complete profile. The composition deviations from thermodynamic equilibrium in each phase at the interface are found to be proportional to an assumed large interfacial resistivity; they contain a term proportional to the interface velocity and a second independent term proportional to the flux of one atomic species through the interface. Fluxes of A and B atoms, measured in the interface frame, are found to be related linearly to differences in chemical potential across the interface by a symmetric matrix which guarantees a decrease of net free energy but allows a given species to move contrary to its chemical potential gradient, thus giving rise to trapping in some circumstances.

THEORIE DES ECARTS PAR RAPPORT A L'EQUILIBRE LOCAL A L'INTERFACE D'UN COUPLE DE DIFFUSION BIPHASÉ

On développe un modèle simple pour calculer l'écart par rapport à l'équilibre local à un interface entre deux phases, mobile dans un couple de diffusion binaire. Le modèle repose sur la résolution d'une équation de diffusion généralisée obtenue en admettant la proportionnalité entre le flux de diffusion d'une espèce et le gradient de la dérivée de l'énergie libre totale par rapport à la concentration. Cette énergie libre totale est composée de l'intégrale de deux termes: une énergie libre spécifique de métal à gros grains qui reflète les propriétés thermodynamiques du métal massif et une densité d'énergie proportionnelle au carré du gradient de concentration. Les résultats finals sont convenablement représentés en remplaçant le véritable profil de concentration par un autre profil présentant une discontinuité sur un plan dont la position est judicieusement choisie dans la région de fort gradient de concentration. On choisit les valeurs de la composition et de sa dérivée à la discontinuité de manière à ce que l'extrapolation jusqu'à ces valeurs des solutions dans le métal massif soient les mêmes que pour le profil complet. On a trouvé que les écarts de composition par rapport à l'équilibre thermodynamique dans chacune des phases à l'interface sont proportionnels à une résistivité interfaciale supposée grande; ils contiennent un terme proportionnel à la vitesse de l'interface et un second terme indépendant, proportionnel au flux d'un des types d'atomes à travers l'interface. On a trouvé que les flux d'atomes A et B, mesurés par référence à l'interface, dépendaient linéairement des différences du potentiel chimique de part et d'autre de l'interface par l'intermédiaire d'une matrice symétrique. Ceci garantit la décroissance de l'énergie libre, mais permet à un type d'atomes de se déplacer dans le sens contraire du gradient de potentiel chimique, entraînant ainsi parfois un certain piègeage.

THEORIE DER ABWEICHUNG VOM LOKALEN GLEICHGEWICHT AN DER GRENZFLÄCHE EINES ZWEIPHASIGEN DIFFUSIONSPAARES

Ein einfaches Modell wird entwickelt, um die Abweichung vom lokalen Gleichgewicht zu berechnen, die in einem binären Diffusionspaar an einer sich bewegenden Zwei-Phasen-Grenzfläche auftreten. Das Modell basiert auf der Lösung einer generalisierten Diffusionsgleichung. Diese wurde mit der Annahme abgeleitet, daß die Diffusionsstromdichte einer Spezies proportional zum Gradienten der Ableitung der totalen freien Energie nach der Konzentration ist. Diese totale freie Energie besteht aus dem Integral über zwei Terme, einer freien Energie pro Volumeneinheit, welche die thermodynamischen Eigenschaften des Materials zum großen Teil widerspiegelt, und einer Energiedichte proportional zum Quadrat des Konzentrationsgradienten. Die endgültigen Ergebnisse werden günstigerweise dargestellt, indem das tatsächliche Konzentrationsprofil durch eines ersetzt wird, welches einen Sprung aufweist in einer Ebene, deren Lage zweckmäßig innerhalb des Gebietes hoher Konzentrationsänderungen gewählt wird. Die Werte für die Zusammensetzung und deren Ableitung an dem Sprung werden so gewählt, daß die Lösungen im Materialinnern bei Extrapolation zu diesen Werten denjenigen für das vollständige Profil gleichen. Man findet, daß die Abweichung der Zusammensetzung vom thermodynamischen Gleichgewicht an der Grenzfläche in jeder Phase proportional sind zu einem angenommenen großen Grenzflächenwiderstand; sie enthalten einen Term, der proportional zur Geschwindigkeit der Grenzfläche ist, und einen unabhängigen zweiten, der proportional zur Flußdichte einer Atomsorte durch die Grenzfläche hindurch ist. Die Flußdichten der A- und B-Atome in der Grenzfläche hängen über eine symmetrische Matrix linear mit Differenzen im chemischen Potential über der Grenzfläche zusammen. Dieser Zusammenhang garantiert eine Abnahme der gesamten freien Energie, erlaubt aber, daß eine bestimmte Spezies entgegen dem chemischen Potential wandert, welches unter gewissen Umständen zum Einfangen führen kann.

INTRODUCTION

Our overall objective in this paper is to calculate, for a simple explicit model, the departure from local equilibrium at a moving two-phase interface in a binary diffusion couple. Consistent with this objective, we shall show how the principles of irreversible thermodynamics, when applied via this model, can lead to an explicit expression for the interface mobility

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and an unambiguous definition of the relevant interface fluxes and conjugate driving forces. This model will be generalized in subsequent publications to multicomponent systems and to less-idealized interfaces such as encountered in the joining of dissimilar materials.

We consider a two-phase diffusion couple in a binary alloy system. At a temperature high enough for significant diffusion to occur, there will be a redistribution of solute generally accompanied by motion of the interface that separates the phases. The situation is depicted schematically in Fig. 1 where the α phase is assumed to be forming at the expense of the β phase.

The usual analytical description of this phenomenon consists of solving standard diffusion equations in the α and β phases and joining their solutions at a hypothetical moving interface of infinitesimal thickness located at $x = x_i$. The boundary conditions which permit joining these solutions at the moving interface are (1) the conservation of diffusing species and (2) the condition that the concentrations (of, say, B atoms) in α and β, respectively, tend to determinable values $C_B{}^{\alpha\beta}$ and $C_B{}^{\beta\alpha}$ as the interface is approached from the respective phases. Once a definite 'rule' has been established to determine $C_B{}^{\alpha\beta}$ and $C_B{}^{\beta\alpha}$, the problem is mathematically well-set and the time evolution of the concentration profile and the interface motion are, at least in principal, determinable.

A tractable and often fruitful choice of $C_B{}^{\alpha\beta}$ and $C_B{}^{\beta\alpha}$ is based on the assumption that their values are given by a phase diagram which supposedly records the concentrations of bulk α and β in thermodynamic equilibrium with one another; denote these values by $C_{B0}{}^{\alpha\beta}$ and $C_{B0}{}^{\beta\alpha}$. This assumption is sometimes called the assumption of 'local equilibrium' or 'diffusion control,' the latter name stemming from the fact that the interface concentrations are fixed and the rate of phase boundary motion is controlled solely by diffusion in the bulk. On the other hand, the
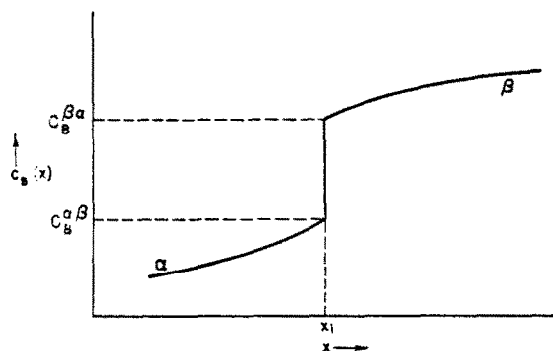

FIG. 1. Concentration, $c_B(x)$, of B atoms as a function of distance, x, corresponding to the classical description of a two-phase binary diffusion couple. There is a discontinuity in composition from $C_B{}^{\alpha\beta}$ to $C_B{}^{\beta\alpha}$ at position x_i.

assumption opposite to 'diffusion control' is 'interface control' wherein $C_B{}^{\alpha\beta}$ and $C_B{}^{\beta\alpha}$ tend, respectively, to the compositions of α and β far from the interface, i.e. to the bulk compositions of these phases. In this case of interface control, the chemical potential difference of atoms at compostions $C_B{}^{\alpha\beta}$ (in α) and $C_B{}^{\beta\alpha}$ (in β) is assumed to be consumed by some irreversible process that takes place entirely at the interface and is necessary to incorporate atoms from α into β.

Intermediate to the extreme of 'diffusion control' and 'interface control' is 'mixed control' of some sort. In fact, every real case is undoubtedly "mixed control" with the two extremes being just a matter of degree. Quantitative evaluation of this degree, however, is of great importance since it leads to a well-set problem as mentioned above. Nevertheless, there are presently few general theoretical guidelines for determining both of the needed differences $C_B{}^{\alpha\beta}-C_{B0}{}^{\alpha\beta}$ and $C_B{}^{\beta\alpha}-C_{B0}{}^{\beta\alpha}$. Some workers[1,2] have made the assumption that one of the species, say B, of the binary $A-B$ system is much more mobile than the other at the $\alpha-\beta$ interface. Consequently, they assume that the chemical potential of B atoms is continuous across the $\alpha-\beta$ interface whereas the corresponding difference for A atoms is not; in fact, they further assume, or deduce on the basis of a model, that the chemical potential difference $\mu_A{}^\beta-\mu_A{}^\alpha$ is some definite function, say $g(v)$, of the phase boundary velocity $v = dx_i/dt$. Taken together, the assumptions $\mu_B{}^\alpha = \mu_B{}^\beta$ and $\mu_A{}^\beta-\mu_A{}^\alpha = g(v)$ constitute two equations from which both unknown quantities $C_B{}^{\alpha\beta}-C_{B0}{}^{\alpha\beta}$ and $C_B{}^{\beta\alpha}-C_{B0}{}^{\beta\alpha}$ can be determined as functions of v. However, the assumption that $\mu_B{}^\alpha = \mu_B{}^\beta$ is quite arbitrary and unnecessarily restrictive.

A number of other models of the departure from local equilibrium at moving interfaces have been reviewed, in the context of the thermodynamics of solidification, by Baker and Cahn.[3] These researchers apply the principles of irreversible thermodynamics to the isothermal transformation, at a solid–liquid interface, of a binary liquid solution to a solid. While they are able to map out, (see their Fig. 8) on a graph of solid and liquid interfacial compositions, a region wherein the total free energy of transformation decreases, they are able to say very little about the relationships of the fluxes of A and B atoms to the differences of chemical potentials, $\mu_A{}^S-\mu_A{}^L$ and $\mu_B{}^S-\mu_B{}^L$ across the solid liquid interface. In fact, Baker and Cahn conclude that irreversible thermodynamics, as applied to interfacial processes, is ambiguous with respect to a proper choice of fluxes and reference frames. There is also some freedom of choice as to how these fluxes are related to chemical potential differences via phenomenological coefficients

which might conceivably obey the Onsager relations. Of particular interest is the possibility of so-called 'trapping' of one of the species ('solute trapping' or 'solvent trapping'), which is said to occur when a species flows 'up' its own chemical potential gradient. This can occur by means of interaction with the chemical potential difference of the other species, the whole free energy, of course, decreasing in the process. Baker and Cahn further emphasize the ambiguities of application of irreversible thermodynamics to interfacial processes by pointing out that theories of Borisov[4] and Boralis[5] prohibit trapping while those by Aptekar–Kamenetskaya[6] and Jindal–Tiller[7] allow trapping.

In the present paper, we shall show how a simple model can lead to the unambiguous determination of the manner in which the total driving force for the transformation is distributed among bulk diffusion processes and various processes local to the two-phase interface. In effect we remove the ambiguities of application of irreversible thermodynamics, associated with choices of fluxes and reference frames, by formulating the problem in terms of a model sufficiently complete to describe dynamical phenomena in both bulk phases and the interfacial region in terms of a single formalism. In this model we view the system on a much finer scale than that of Fig. 1 and account for details of concentration profile, energetics, and transport in the interfacial region. However, since such fine details of the concentration profile are not generally reported and are doubtless rather dependent on the aspects of any specific model, we report our results in terms of the values of slope and intercept to which the composition profiles in the bulk α and β phases must appear to extrapolate, at a suitable hypothetical infinitesimally thin interface, in order for the solutions in the bulk phases to agree with those of the complete model.

1. DESCRIPTION OF THE MODEL

The model which we shall consider is the standard semi-phenomenonological picture of a two-phase system which has been used extensively by Cahn[8] and Hilliard,[9] and which has roots traceable to Van der Waals. We assume that the system, at each position $\mathbf{r}$, can be described adequately by a single scalar variable $c_B(\mathbf{r})$. For present purposes, we can think of $c_B(\mathbf{r})$ as being the local concentration† (moles/unit vol of B

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† In a later publication, we shall treat multicomponent systems with variable molar volume where the appropriate variables for the diffusion equations are necessarily concentrations. Therefore, we have formulated the present problem in terms of the concentration of B atoms. c_B, instead of the atom fraction. c, as used by Hilliard.[9] Both the present model and Hilliard's model are restricted to constant molar volume, $1/n$, where n is the constant number of moles/unit vol. Therefore, $c_B = nc$ and our K_B is $2/n^2$ times the K of Hilliard.

atoms) in an A–B binary solid solution whose molar volume, $1/n$, is independent of composition throughout the two-phase system. For each $c_B(\mathbf{r})$, we assume the existence of a coarse-grained[10] free-energy functional of the form

$$F\{c_B(\mathbf{r})\} = \int d\mathbf{r} \left[\frac{K_B}{2} (\nabla c_B)^2 + f(c_B) \right]. \qquad (1.1)$$

Here, $f(c_B)$ is the Helmholtz free energy per unit volume computed subject to the constraint that the average concentration is equal to c_B in every subregion of the system of volume ξ^3, where ξ is a microscopic length to be defined later. Because of the constraint, $f(c_B)$ is not exactly the true thermodynamic free energy, which must be a convex function of c_B, but can exhibit two distinct minima characterizing the two coexisting phases. Note that we have included the gradient energy in equation (1.1), but have omitted strain energies or lattice anisotropies. For simplicity, we shall assume the gradient energy coefficient, K_B, to be a constant, independent of c_B. This assumption is not at all essential to our main results and will be dispensed with in our later publication dealing with a more general formulation of this theory.

The systems which we shall consider will be characterized by a function $f(c_B)$ having two minima and a common tangent of slope μ_0, as shown in Fig. 2. The concentrations corresponding to the points of common tangency are denoted by $C_{B0}{}^{\alpha\beta}$ and $C_{B0}{}^{\beta\alpha}$ consistent with the fact that these are the concentrations of B atoms for bulk α and β phases in equilibrium with one another.

Stationary solutions to equation (1.1) subject to the constraint of overall conservation of B atoms can be handled conveniently by the method of Lagrange multipliers as demonstrated by Hilliard.[9] We are interested in solutions of the form sketched in Fig. 3.
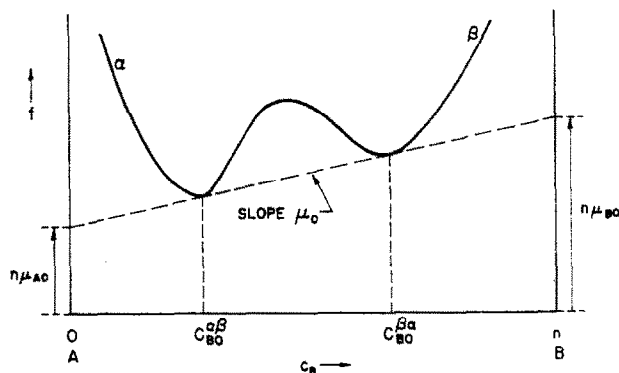

FIG. 2. Typical free energy per unit volume, f, as a function of concentration c_B. The dashed line has slope μ_0 and is tangent at concentrations $C_{B0}{}^{\alpha\beta}$ and $C_{B0}{}^{\beta\alpha}$.
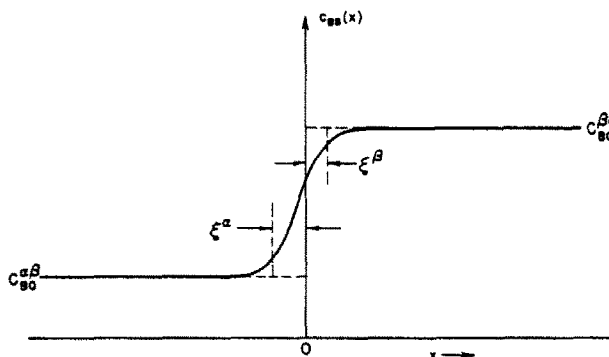
FIG. 3. Typical shape of stationary concentration, $c_{BS}(x)$, vs distance, x, profile for an equilibrium interface as seen on a scale of the correlation lengths ξ^α and ξ^β.

These shall be denoted by $c_{BS}(x)$ and obey the equation

$$-K_B \frac{d^2 c_{\bar{B}S}}{dx^2} + \frac{df}{dc_{\bar{B}S}} = \mu_0. \qquad (1.2)$$

In the simple case where f has two parabolic minima characterized by constant values of $d^2f/dc_B{}^2$, the decay of this interface profile is exponential and is described by the correlation lengths ξ^α and ξ^β, where

$$(\xi^\alpha)^2 = K_B/(d^2f/dc_B{}^2)\big|_{c_B = c_{B0}{}^{\alpha\beta}}$$
$$(\xi^\beta)^2 = K_B/(d^2f/dc_B{}^2)\big|_{c_B = c_{B0}{}^{\beta\alpha}}. \qquad (1.3)$$

The length ξ which occurs in the coarse graining constraint must be of the order of, but not larger than, either ξ^α or ξ^β in order that well developed phase separation will not occur in the cells over which the average concentration is defined.

It should be emphasized that the assumption of a coarse-grained $f(c_B)$ varying smoothly between $C_{B0}{}^{\alpha\beta}$ and $C_{B0}{}^{\beta\alpha}$ does not necessarily imply that the two phases have identical crystal structures.† In computing $f(c_B)$ via a constrained partition sum, one presumably will find well-defined crystal symmetries for compositions near $C_{B0}{}^{\alpha\beta}$ and $C_{B0}{}^{\beta\alpha}$. However, for some intermediate values of c_B near the maximum of $f(c_B)$, the constrained system may not have any strong statistical preference for one symmetry or the other. That is, the interfacial region may be, in some sense, amorphous. Clearly, we are not going to be able to discuss singular interfaces, where the crystal symmetry changes abruptly across a single-lattice spacing. Nor are we going to discuss phase transformations in which the lattice structure changes without a change in composition.

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† If the phases do not have identical crystal structures, the assumption of constant and uniform partial molar volume is unlikely to be valid; however, we shall relax this assumption in future publications.

It is important at the outset, however, to distinguish clearly between our use of equation (1.1) and that of Cahn et al.[11] in their theory of interface motion. In the one-dimensional theory of Cahn, it is presumed that c_B can be defined on each lattice plane such that any given concentration profile $c_B(x)$ will lead to a value of F calculable via the finite difference equivalent of equation (1.1). From this, it is found that the value of F will be given by a constant plus a periodic function of the distance between the origin of x and a given lattice place. The periodic variations of F above its constant value are then presumed to be barriers to interface advancement which, when combined with the driving force for the transformation, as calculated by a difference in bulk free energies, serve to determine the mechanism of growth. However, in the present paper, the authors use equation (1.1) with c_B presumed to be defined only on a coarse-grained scale of length of the order of ξ, as mentioned previously. Therefore, a variation over a lattice spacing of the position of $x = 0$ relative to a given lattice plane will make a necessarily negligible contribution to F given by equation (1.1). Hence, in the present theory, the interface mobility must be introduced in a purely phenomenological fashion and the role of equation (1.1) will only be to apportion the total available free energy of transformation between interfacial and bulk processes.

Dynamical aspects of our model will be described by formulation of a diffusion equation in a manner described by Hilliard.[9] Thus, the flux of B atoms is

$$J_B = -J_A = -nM \frac{\partial}{\partial x}\left(\frac{\delta F}{\delta c_B}\right), \qquad (1.4)$$

where $\delta F/\delta c_B$ is the functional derivative of F with respect to c_B and M is exactly the mobility of Hilliard. From equation (1.1),

$$J_B = -nM \frac{\partial}{\partial x}\left(\frac{df}{dc_B} - K_B \frac{\partial^2 c_B}{\partial x^2}\right). \qquad (1.5)$$

Taken together with the conservation equation

$$\frac{\partial c_B}{\partial t} = -\frac{\partial J_B}{\partial x}, \qquad (1.6)$$

equation (1.5) leads to the fourth order nonlinear equation

$$\frac{\partial c_B}{\partial t} = \frac{\partial}{\partial x}\left[nM \frac{\partial}{\partial x}\left(\frac{df}{dc_B} - K_B \frac{\partial^2 c_B}{\partial x^2}\right)\right] \qquad (1.7)$$

which is well known in the theory of spinodal decomposition and nucleation but, to our knowledge, has

never been used as the basis for a theory of interface motion. This subject is taken up in the next section.

2. DETAILED DESCRIPTION OF A MOVING INTERFACE

In principle, equation (1.7) can be used to provide a complete description of what goes on in a two-phase diffusion couple. That is, given an initial configuration such as two uniform systems in contact with a sharp discontinuity in c_B at the interface, we can integrate equation (1.7) to obtain a unique prediction of the subsequent behavior. Such a procedure is perfectly feasible using modern high-speed computers; but numerical techniques will not give us the physical insight that we can obtain from some simple analysis.

We shall proceed to show that an approximate analytical solution to this problem can be found by piecing together an approximate analytical solution that is valid in the interfacial region with other approximate solutions that are valid far from the interfacial region. This is possible because there are two very different scales of length which enter into this problem. First, there is the microscopic correlation length ξ introduced above, which we presume to have the same order of magnitude as the interface thickness itself. Second, there is the much larger† diffusion length, say l_D, which we can identify roughly with the total displacement of the interface or with the distance across which the components of the system have diffused into the adjoining bulk phases. Associated with each of these lengths is a characteristic time, essentially the time required for diffusion across the corresponding distance. Because ξ is small, we may assume that the time $\tau_\xi \sim \xi^2/D$ required for relaxation of composition fluctuations of size ξ or smaller is short compared to the time $\tau_D \sim l_D{}^2/D$ required for other processes of interest to us.‡ In particular, we assume that the smoothing of an initially sharp interface profile will take place in a time much shorter than that required for an appreciable displacement of the interface. Since the latter time is ξ/v, we require $\tau_\xi \ll \xi/v$ which is equivalent to $v\xi/D \ll 1$. Accordingly, we shall assume that the interface profile is very nearly but not quite equal to the stationary value $c_{BS}(x)$, which is a solution to equation (1.2), right from the beginning of the process; we further assume that the only important deviations from $c_{BS}(x)$ are those which are driven by the slow diffusion which is taking place in the environment of this interface.

We therefore proceed to transform equation (1.7) into a frame of reference† moving with the—as yet undetermined—interfacial velocity v. Thus,

$$\frac{\partial c_B}{\partial t} - v\frac{\partial c_B}{\partial x} = \frac{\partial}{\partial x}\left[nM\frac{\partial}{\partial x}\left(\frac{df}{dc_B} - K_B\frac{\partial^2 c_B}{\partial x^2}\right)\right]. \quad (2.1)$$

Then, in regions of the sytem well away from the interface, it is appropriate to linearize equation (2.1) about the equilibrium concentrations $C_{B0}{}^{\alpha\beta}$ and $C_{B0}{}^{\beta\alpha}$. The last term on the right-hand side (the one that comes from the gradient energy) can be neglected because $c_B(x)$ will vary only on the scale of the diffusion length. Far from the interfacial region, we therefore obtain a diffusion equation of the form‡

$$\frac{\partial u}{\partial t} - v\frac{\partial u}{\partial x} = D\frac{\partial^2 u}{\partial x^2}, \quad (2.2)$$

where $u = c_B - C_{B0}{}^{\alpha\beta}$ or $c_B - C_{B0}{}^{\beta\alpha}$, depending upon which side of the interface we are considering, and D is the corresponding diffusivity given by

$$D = nM\left.\frac{d^2f}{dc_B{}^2}\right|_{c_B = C_{B0}{}^{\alpha\beta}\text{ or }C_{B0}{}^{\beta\alpha}}. \quad (2.3)$$

The situation is quite different in the interfacial region. Here we may linearize equation (2.1) about $c_{BS}(x)$; i.e.

$$u(x, t) = c_B(x, t) - c_{BS}(x), \quad (2.4)$$

which is consistent with the above definition of the function u in the exterior regions. We obtain

$$\frac{\partial}{\partial x}\left[nM_S(x)\frac{\partial}{\partial x}\left(-K_B\frac{\partial^2 u}{\partial x^2} + W_S(x)u\right)\right]$$

$$\cong -v\frac{dc_{BS}}{dx} + \frac{\partial u}{\partial t} - v\frac{\partial u}{\partial x}, \quad (2.5)$$

where

$$M_S(x) = M(c_B)\big|_{c_B = c_{BS}(x)} \quad (2.6)$$

and

$$W_S(x) = \left.\frac{d^2f}{dc_B{}^2}\right|_{c_B = c_{BS}(x)}. \quad (2.7)$$

Because spatial variations in the interfacial region occur on the scale of ξ, the left-hand side of (2.5) has the order of magnitude $D'u/\xi^2$. Here, $D' \sim nM_S(x)W_S(x)$ has the dimensions and approximate

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† For very small times, this diffusion length might be much smaller than the correlation length and the theory would have to be modified to take such details into account.

‡ D is to be regarded as a typical diffusion coefficient. See Eq. (2.3).

† We define this frame of reference by the equation $x' = x - \int_0^t v(t')\,dt'$ and then drop the primes on x'.

‡ Note that when equation (2.2) is transformed back to the fixed reference frame, it becomes just the standard form of Fick's second law.

magnitude of a diffusion constant, but may be appreciably smaller than D, the diffusion coefficient for regions far from the interface, in cases where the interfacial mobility is low. The leading term on the right-hand side of (2.5) is the inhomogeneous term, $-v \, dc_{BS}/dx$. This is of the order of $v \, \Delta C_{B0}/\xi$ where $\Delta C_{B0} = C_{B0}{}^{\beta\alpha} - C_{B0}{}^{\alpha\beta}$; and therefore,

$$u \sim \frac{\xi v \, \Delta C_{B0}}{D'} . \qquad (2.8)$$

It then follows that*

$$\frac{\partial u}{\partial t} \sim \frac{u}{\tau_D} \sim \left(\frac{\xi^2}{l_D{}^2}\right)\left(\frac{D}{D'}\right)\frac{v \, \Delta C_{B0}}{\xi} \ll \frac{v \, \Delta C_{B0}}{\xi} , \quad (2.9)$$

and

$$v\frac{\partial u}{\partial x} \sim \frac{vu}{\xi} \sim \left(\frac{v\xi}{D}\right)\left(\frac{D}{D'}\right)\frac{v \, \Delta C_{B0}}{\xi} \ll \frac{v \, \Delta C_{B0}}{\xi} . \quad (2.10)$$

Thus, we can self-consistently neglect these last two terms in equation (2.5).

The resulting version of equation (2.5) contains the time only *via* the slowly varying function $v(t)$. No time derivatives remain. Thus, this equation determines the slighly deformed profile of the moving interface; it, of course, is valid only in a microscopically small region containing the interface. Our strategy is to use the solution of this equation to determine the interfacial boundary conditions for diffusion in the external regions.

To obtain a solution of the truncated version of (2.5), we first integrate twice. The result is

$$-K_B \frac{d^2 u}{dx^2} + W_S(x)u$$

$$= -\int_0^x \frac{1}{nM_S(x')}[J + vc_{BS}(x')] \, dx' + a, \quad (2.11)$$

where J and a are constants of integration. It should be obvious that J is a flux of some kind which we shall identify later.

We now have an inhomogeneous, second order differential equation for $u(x)$ that we should be able to solve by inverting the linear operator which appears on the left-hand side. We have to be careful, however, because this operator is singular. That is, if we look for a complete set of eigenfunctions $U_n(x)$ satisfying

$$\left[-K_B \frac{d^2}{dx^2} + W_S(x)\right]U_n(x) = \lambda_n U_n(x), \quad (2.12)$$

and require that $U_n(x)$ be bounded at $x = \pm\infty$, we discover that one of the eigenvalues λ_n vanishes. Specifically, differentiating equation (1.2) with respect to x and comparing the resulting equation to (2.12) we find

$$U_0(x) \propto \frac{dc_{BS}}{dx} ; \quad \lambda_0 = 0. \qquad (2.13)$$

This result is a direct consequence of the translational symmetry of our model, which requires that $F\{c_{BS}\}$ be invariant under displacements of the interface position. For an infinitesimal displacement Δx, the displaced interface profile is

$$c_{BS}(x + \Delta x) \cong c_{BS}(x) + \frac{dc_{BS}}{dx}\Delta x. \qquad (2.14)$$

The operator on the left-hand side of (2.12) is just the second variational derivative of F with respect to c_B evaluated at $c_B = c_{BS}$ and must therefore lead to a vanishing result when applied to the displacement function dc_{BS}/dx. Thus, dc_{BS}/dx is an uninteresting homogeneous solution of (2.11) and corresponds to a shift of the interface position; this solution can always be eliminated by proper choice of the origin of the moving frame of reference. We also know that, because it has a zero eigenvalue, the operator in question has no inverse in the space of the bounded functions $u(x)$.

Another way of stating the significance of this vanishing eigenvalue is to point out that, in general, the inhomogeneous solutions of equation (2.11) will contain exponentially growing terms at infinity. If we allow such terms, the solution is not even unique. The clue to a satisfactory solution is the fact we can choose a special value of the integration constant "a" for which these terms disappear. To see this, note that we can solve a modified Green's function equation,

$$\left(-K_B \frac{d^2}{dx^2} + W_S(x)\right)\tilde{G}(x, x')$$

$$= \delta(x - x') - U_0(x)U_0(x'), \quad (2.15)$$

Where $U_0(x)$ is understood here to be a normalized eigenfunction of the operator $(-K_B(d^2/dx^2) + W_S)$ with eigenvalue zero (i.e. $U_0 \propto dc_{BS}/dx$) and $\tilde{G}$ is required to remain finite as either x or x' go to infinity. The formal solution of (2.15) is

$$\tilde{G}(x, x') = \sum_{n \neq 0} \frac{U_n(x)U_n(x')}{\lambda_n} , \qquad (2.16)$$

---

* We assume that D/D' is not so large as to offset the smallness of $\xi^2/l_D{}^2$ or $v\xi/D$; this is consistent with equation (2.8) and the fact that we are treating u as a perturbation in the sense that $u/\Delta C_{B0} \ll 1$.

which is well defined because none of the λ_n vanish. Now denote the right-hand side of (2.11) by the symbol $Y(x)$:

$$Y(x) \equiv a - \int_0^x \frac{1}{nM_S(x')} [J + vc_{BS}(x')] \, \mathrm{d}x'. \quad (2.17)$$

If we then form the integral*

$$u(x) = \int_{-\infty}^{\infty} \tilde{G}(x, x') Y(x') \, \mathrm{d}x', \quad (2.18)$$

we see by application of (2.15) that u will satisfy (2.11) provided that we introduce the constraint

$$\int_{-\infty}^{\infty} Y(x) \frac{\mathrm{d}c_{BS}}{\mathrm{d}x} \, \mathrm{d}x = 0. \quad (2.19)$$

We are free to require (2.19) by choice of the constants of integration J and a; whereas, physically, this choice actually defines precisely the position of an interface, in relation to the compositional discontinuity, whose velocity v appears in our equations and was left undefined at the time we introduced equation (2.1). As we shall see, the combination of equation (2.18) subject to the special condition, equation (2.19) provides us with just enough information to deduce the interfacial boundary conditions that we are seeking.

For present purposes, we do not need the complex function $u(x)$ inside the interface. What we are really interested in is $u(x)$ for values of x in the ranges $|\xi| \ll |x| \ll l_D$, i.e. just inside the interface as seen on a macroscopic scale, e.g. in Fig. 4(a). In these regions, the solution of (2.15) is trivial, because $W_S(x)$ is a constant and $U_0(x)$ vanishes. Thus,

$$\tilde{G}(x, x') \approx \frac{\xi}{2K_B} \exp \left(- \frac{1}{\xi} |x - x'| \right)$$

$$\approx \frac{1}{W_S} \delta(x - x'), \quad (2.20)$$

where ξ and W_S are given by the versions of equations (1.3) and (2.7) appropriate for whichever phase is present on the side of the interface being considered. The final form of (2.20) is a $\xi \to 0$ limit appropriate for use in (2.19) when $Y(x)$ is very slowly varying on the scale of ξ. Inserting (2.20) into (2.18), we find

$$u(x) \approx \frac{1}{W_S} Y(x); \quad |\xi| \ll x \ll l_D. \quad (2.21)$$

FIG. 4. Concentration, $c_B(x)$, vs distance, x, profiles for a non-equilibrium interface which is possibly moving. (a) The interface is viewed on a scale of the diffusion lengths, $l_D{}^\alpha$ and $l_D{}^\beta$, and there appears to be a discontinuity in concentration at the interface. (b) The interface is viewed on a scale of the correlation lengths, ξ^α and ξ^β, where the extrapolated concentration slopes and intercepts are evident. The relative positions of $C_B{}^{\alpha\beta}$ to $C_{B_0}{}^{\alpha\beta}$ and $C_B{}^{\beta\alpha}$ to $C_{B_0}{}^{\beta\alpha}$ are purely schematic.

Evidently, equations (2.17), (2.19) and (2.21) can be used to calculate the values of concentration, slope and intercept as the interface is approached from either bulk phase; see Fig. 4(b) which is just Fig. 4(a) on a microscopic scale where the actual interface concentration profile and its extrapolated values are evident. We shall now proceed to calculate these extrapolated values which constitute our central results.

3. RESULTS

A. Extrapolated slopes and intercepts

The extrapolated slopes,

$$C_B{}^{\beta'} \equiv \left(\frac{\mathrm{d}c_B{}^\beta}{\mathrm{d}x} \right)_{\text{interface}} \quad \text{and} \quad C_B{}^{\alpha'} \equiv \left(\frac{\mathrm{d}c_B{}^\alpha}{\mathrm{d}x} \right)_{\text{interface}},$$

are easily obtained by differentiation of equations (2.21) with the aid of equation (2.17). Thus,

$$\begin{aligned}
C_B{}^{\alpha'} &= - \frac{1}{D^\alpha} (J + vC_{B0}{}^{\alpha\beta}); \\
C_B{}^{\beta'} &= - \frac{1}{D^\beta} (J + vC_{B0}{}^{\beta\alpha}).
\end{aligned} \quad (3.1)$$

Equation (3.1) expresses the extrapolated concentration slopes in terms of the constant* of integration J which can only be determined by solution of a specific

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* In these and other equations applicable to the interfacial region, it is to be understood that infinite limits of integration mean distances large compared to ξ but not large compared to l_D.
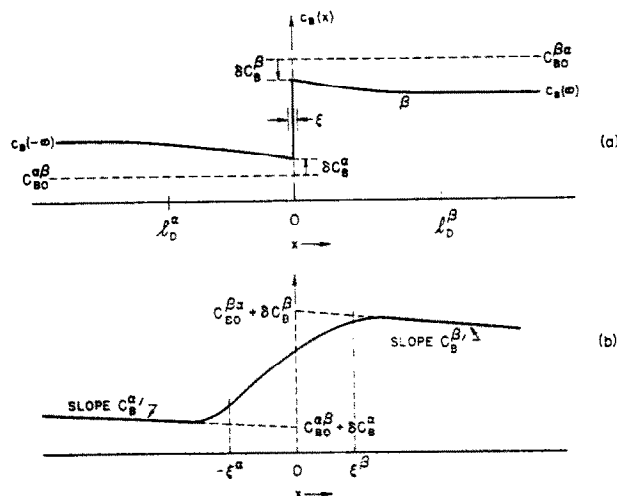
* Of course, the 'constant' of integration J is independent of x but is a function of time. J only varies over times sufficiently long to change significantly the concentration profile in the regions external to the interfacial region.

initial value problem for u in regions outside the interface. In other words, equations (3.1) are actually equivalent to a boundary condition which, upon elimination of J, takes the familiar form

$$D^\beta C_B^{\beta'} - D^\alpha C_B^{\alpha'} = -v(C_{B0}{}^{\beta\alpha} - C_{B0}{}^{\alpha\beta})$$
$$= -v\,\Delta C_{B0}. \qquad (3.2)$$

We shall see later that the actual extrapolated interface concentrations differ from $C_{B0}{}^{\beta\alpha}$ and $C_{B0}{}^{\alpha\beta}$ by terms proportional to v; therefore, equation (3.2) is just the familar interface flux condition for the conservation of B atoms to the extent that terms of order v^2 can be neglected consistent with our former approximations. Furthermore, equations (3.1) yield

$$J = -D^\alpha C_B^{\alpha'} - vC_{B0}{}^{\alpha\beta} = -D^\beta C_B^{\beta'} - vC_{B0}{}^{\beta\alpha}$$

$$= -\tfrac{1}{2}\,(D^\alpha C_B^{\alpha'} + D^\beta C_B^{\beta'}) - \frac{v}{2}\,(C_{B0}{}^{\alpha\beta} + C_{B0}{}^{\beta\alpha}), \quad (3.3)$$

from which it can be deduced that J is the flux of B atoms which passes through the interface as measured in a reference frame in which the interface is at rest.

The extrapolated values of the interface concentrations are much more interesting than equations (3.1) and can be found from equation (2.21) as follows: Extrapolation from the α phase gives*

$$\delta C_B^\alpha \equiv C_B^{\alpha\beta} - C_{B0}{}^{\alpha\beta} = \lim_{x \ll -\xi\alpha} \frac{1}{W_S}\left[Y(x) - x\frac{dY}{dx}\right]$$

$$= \frac{a}{W_S{}^\alpha} + \frac{J}{nW_S{}^\alpha}\int_{-\infty}^0 \left[\frac{1}{M_S(x)} - \frac{1}{M_0{}^\alpha}\right]dx \qquad (3.4)$$

$$+ \frac{v}{nW_S{}^\alpha}\int_{-\infty}^0 \left[\frac{c_{BS}(x)}{M_S(x)} - \frac{C_{B0}{}^{\alpha\beta}}{M_0{}^\alpha}\right]dx,$$

where $W_S{}^\alpha$ and $M_0{}^\alpha$ are values of W_S and M_S at $c_B = C_{B0}{}^{\alpha\beta}$. Similarly, extrapolation from the β phase gives

$$\delta C_B^\beta \equiv {}_B{}^{\beta\alpha} - C_{B0}{}^{\beta\alpha} = \lim_{x \gg \xi\beta} \frac{1}{W_S}\left[Y(x) - x\frac{dY}{dx}\right]$$

$$= \frac{a}{W_S{}^\beta} - \frac{J}{nW_S{}^\beta}\int_0^\infty \left[\frac{1}{M_S(x)} - \frac{1}{M_0{}^\beta}\right]dx \qquad (3.5)$$

$$- \frac{v}{nW_S{}^\beta}\int_0^\infty \left[\frac{c_{BS}(x)}{M_S(x)} - \frac{C_{B0}{}^{\beta\alpha}}{M_0{}^\beta}\right]dx.$$

---

* Here again, infinite limits of integration are to be understood in the sense of equation (2.18).

The equation for the constant 'a', obtained from equation (2.19), can be written in the explicit form

$$a = \frac{1}{\Delta C_{B0}}$$

$$\times \left\{\int_0^\infty \frac{dx}{nM_S(x)}[C_{B0}{}^{\beta\alpha} - c_{BS}(x)][J + vc_{BS}(x)]\right.$$

$$\left. - \int_{-\infty}^0 \frac{dx}{nM_S(x)}[c_{BS}(x) - C_{B0}{}^{\alpha\beta}][J + vc_{BS}(x)]\right\}. $$
$$(3.6)$$

Note that these equations refer only to the actual stationary interface profile $c_{BS}(x)$ and the mobility $M_S(x)$, and not to the more detailed ingredients of $F\{c_B\}$. Thus, we can estimate δC_B^α and δC_B^β in terms of purely phenomenological characteristics of the interface—its effective thickness and interior mobility. It will be easier to see how this works out, however, after we have examined some simple specific models in the next subsection.

B. Specific simple models

In order to illustrate and interpret the results of subsection A, we shall now calculate the extrapolated slopes and intercepts for several simple specific models.

(i) *Continuous symmetric model.* A very simple and conventional model to which we might apply our theory is one for which

$$f(c_B) = f_0 + \mu_0 c_B + \frac{W}{2(\Delta C_{B0})^2}$$
$$\times (c_B - C_{B0}{}^{\alpha\beta})^2(c_B - C_{B0}{}^{\beta\alpha})^2, \quad (3.7)$$

where f_0 and W are constants. For this specific $f(c_B)$, the corresponding stationary concentration profile is

$$c_{BS}(x) = C_0 + \tfrac{1}{2}\Delta C_{B0}\tanh\left(\frac{x}{2\xi}\right), \qquad (3.8)$$

where $\xi^2 = K_B/W$ and $C_0 = \tfrac{1}{2}(C_{B0}{}^{\alpha\beta} + C_{B0}{}^{\beta\alpha})$. A plausible mobility function is

$$\frac{1}{M_S(x)} = \frac{1}{M_0}\left(1 + \rho\operatorname{sech}^2\left(\frac{x}{2\xi}\right)\right), \qquad (3.9)$$

where M_0 is a constant mobility far from the interface and ρ is a parameter which, if positive, accounts for an extra resistivity, proportional to the gradient of $c_{BS}(x)$, in the interfacial region. This excess resistivity is localized within, but extends smoothly throughout, the interfacial region.

The corresponding values of δC_B^α and δC_B^β may be found from substitution into equations (3.4) and (3.5)

with the results

$$\delta C_B{}^\alpha = - \frac{v\,\Delta C_{B0}\xi\rho}{3D} + \frac{2\xi\rho}{D}J_0; \qquad (3.10)$$

$$\delta C_B{}^\beta = - \frac{v\,\Delta C_{B0}\xi\rho}{3D} - \frac{2\xi\rho}{D}J_0, \qquad (3.11)$$

where $D = nM_0W$ and

$$J_0 \equiv J + vC_0 = -\frac{D}{2}\left(C_B{}^{\alpha'} + C_B{}^{\beta'}\right) \quad (3.12)$$

is the arithmetic mean of the fluxes of B atoms in α and β at the interface as measured in the laboratory frame. An additional term $v\,\Delta C_{B0}\xi/D$ has been omitted from the right-hand sides of both (3.10) and (3.11) because its retention would be inconsistent with other approximations. The order of magnitude of this term is

$$\frac{v\,\Delta C_{B0}\xi}{D} = \xi(C_B{}^{\beta'} - C_B{}^{\alpha'}) \sim \frac{\xi}{l_D}\Delta C_B, \quad (3.13)$$

where ΔC_B might be, for example, $C_B(\infty) - C_{B0}{}^{\beta\alpha}$ (see Fig. 4(a)). This term is therefore sensitive to the precise choice of the point $x = 0$ within the interfacial thickness of ξ. The other terms in (3.10) and (3.11) are larger than (3.13) by the factor ρ. Thus, our theory predicts measurable values of $\delta C_B{}^\alpha$ and $\delta C_B{}^\beta$ only when ρ is very large, say, at least a few per cent of the ratio l_D/ξ.

(ii) *Discontinuous asymmetric model.* Results equivalent to those stated above can be obtained by using for $c_{BS}(x)$ the triangular profile shown in Fig. 5(a) without trying to relate this profile to a specific free-energy function $f(c_B)$. Note that we have chosen the interfacial region to extend from $x = -2\xi$ to $x = +2\xi$ in order to match dc_{BS}/dx at $x = 0$ with its value obtained from equation (3.8). For this example, we shall adopt the slightly more general mobility function shown in Fig. 5(b) and thus allow for different constants in the different phases. Specifically, we take

$$c_{BS}(x) = \begin{cases} C_{B0}{}^{\alpha\beta}, & x < -2\xi \\ C_0 + \dfrac{\Delta C_{B0}}{4\xi}x, & -2\xi < x < 2\xi \\ C_{B0}{}^{\beta\alpha}, & x > 2\xi \end{cases} \quad (3.14)$$

$$\frac{1}{M_S(x)} = \begin{cases} \dfrac{1}{M^\alpha}, & x < -2\xi. \\ \dfrac{\rho}{M_0}, & -2\xi < x < 2\xi \\ \dfrac{1}{M^\beta}, & x > 2\xi. \end{cases} \quad (3.15)$$

The corresponding composition deviations are

$$\delta C_B{}^\alpha = - \frac{v\,\Delta C_{B0}\xi\rho^\alpha}{3D^\alpha} + \frac{2\xi\rho^\alpha}{D^\alpha}J_0 \quad (3.16)$$

$$\delta C_B{}^\beta = - \frac{v\,\Delta C_{B0}\xi\rho^\beta}{3D^\beta} - \frac{2\xi\rho^\beta}{D^\beta}J_0 \quad (3.17)$$

where $\rho^\alpha = \rho M^\alpha/M_0$, $\rho^\beta = \rho M^\beta/M_0$. Here again we have omitted negligible and unreliable terms $2\xi C_B{}^{\alpha'}$ and $-2\xi C_B{}^{\beta'}$ from the right-hand sides of (3.16) and (3.17), respectively. Note that even the numerical factors in the remaining terms agree with the previous results given by equations (3.10) and (3.11)

(iii) *Symmetrical spiked mobility model.* To see which specific features of the interface *do* affect the final results, we return to our model and use, instead of the $M_S(x)$ given in equation (3.9) the function

$$\frac{1}{M_S(x)} = \frac{1}{M_0}\left[1 + 2\rho\delta\left(\frac{x}{2\xi}\right)\right]. \quad (3.18)$$

That is, we assume that the excess resistivity is concentrated in an infinitesimally small region near $x = 0$. The integral of M_S^{-1} across the whole interface remains the same; however, the resulting composition deviations are

$$\delta C_B{}^\alpha = \frac{2\xi\rho}{D}J_0 \quad (3.19)$$

$$\delta C_B{}^\beta = - \frac{2\xi\rho}{D}J_0. \quad (3.20)$$

Therefore, the first terms in equations (3.10), (3.11), (3.16) and (3.17) are sensitive to the detailed shape of the interface mobility.
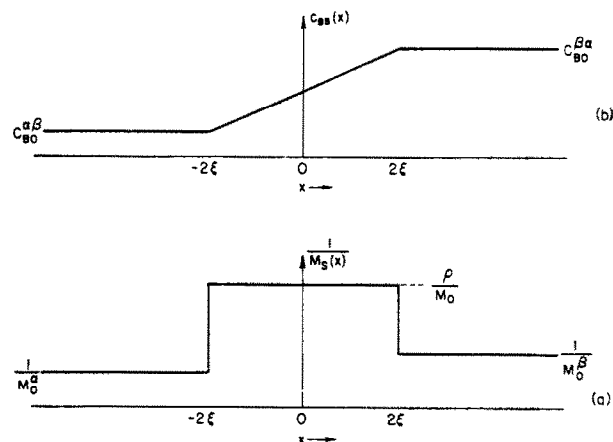

FIG. 5. Stationary concentration, $c_{BS}(x)$, vs distance, x, profile and assumed reciprocal mobility function $1/M_S(x)$, for the discontinuous asymmetric model (Section 3Bii).

C. *Interface Fluxes and chemical potential differences*

Our results in subsections A and B are presented in terms of deviations of the extrapolated interface concentrations from their equilibrium values. While these values of $\delta C_B{}^\alpha$ and $\delta C_B{}^\beta$ are the quantities which must be known operationally to provide boundary conditions for a well-set initial-value diffusion problem, it is the chemical potential deviations at the interface and their relationship to fluxes of atoms that cross the interface that are of fundamental importance insofar as the thermodynamics of irreversible interfacial processes is concerned. In this subsection, we recast our results in terms of such fundamental quantities.

Figure 6 illustrates the relationship of the relevant chemical potentials to the function $f(c_B)/n$. The solid line is the common tangent (tangent at $C_{B0}{}^{\alpha\beta}$ and $C_{B0}{}^{\beta\alpha}$) and intersects the axes of $c_B = 0$ and $c_B = n$ at $\mu_{A0} \equiv \mu_{A0}{}^\beta = \mu_{A0}{}^\alpha$ and $\mu_{B0} \equiv \mu_{B0}{}^\beta = \mu_{B0}{}^\alpha$, respectively. The dashed line is tangent to the f/n-curve at the extrapolated interface concentration $C_B{}^{\beta\alpha}$ and has intercepts on the verticals at $\mu_A{}^\beta$ and $\mu_B{}^\beta$. Similarly, the dotted line is tangent at the extrapolated interface concentration $C_B{}^{\alpha\beta}$. The relevant chemical potential differences across the interface are

$$\Delta\mu_A \equiv \mu_A{}^\beta - \mu_A{}^\alpha = \delta\mu_A{}^\beta - \delta\mu_A{}^\alpha \quad (3.21)$$

and

$$\Delta\mu_B \equiv \mu_B{}^\beta - \mu_B{}^\alpha = \delta\mu_B{}^\beta - \delta\mu_B{}^\alpha, \quad (3.22)$$

where $\delta\mu_A{}^\beta$, $\delta\mu_A{}^\alpha$, $\delta\mu_B{}^\beta$ and $\delta\mu_B{}^\alpha$ are as shown in Fig. 6 i.e., $\delta\mu_A{}^\beta \equiv \mu_A{}^\beta - \mu_{A0}{}^\beta$, etc.

From equation (2.7) we have, for small $\delta C_B{}^\alpha$,

$$W_S{}^\alpha \, \delta C_B{}^\alpha = \left[\frac{d}{dc_B}(\mu_B{}^\alpha - \mu_A{}^\alpha)\right]\delta C_B{}^\alpha$$

$$= (\mu_B{}^\alpha - \mu_A{}^\alpha) - (\mu_{B0}{}^\alpha - \mu_{A0}{}^\alpha)$$

$$= \delta\mu_B{}^\alpha - \delta\mu_A{}^\alpha. \quad (3.23)$$

We also have the Gibbs–Duhem equation

$$\left(1 - \frac{C_{B0}{}^{\alpha\beta}}{n}\right)\delta\mu_A{}^\alpha + \frac{C_{B0}{}^{\alpha\beta}}{n}\delta\mu_B{}^\alpha = 0. \quad (3.24)$$

Simultaneous solution of (3.23) and (3.24) yields

$$\delta\mu_A{}^\alpha = -\frac{C_{B0}{}^{\alpha\beta}}{n}W_S{}^\alpha \, \delta C_B{}^\alpha$$

$$\delta\mu_B{}^\alpha = \left(1 - \frac{C_{B0}{}^{\alpha\beta}}{n}\right)W_S{}^\alpha \, \delta C_B{}^\alpha. \quad (3.25a)$$

Similarly, for the β phase we have

$$\delta\mu_A{}^\beta = -\frac{C_{B0}{}^{\beta\alpha}}{n}W_S{}^\beta \, \delta C_B{}^\beta$$

$$\delta\mu_B{}^\beta = \left(1 - \frac{C_{B0}{}^{\beta\alpha}}{n}\right)W_S{}^\beta \, \delta C_B{}^\beta. \quad (3.25b)$$

Substitution of (3.25a) and (3.25b) in (3.21) and (3.22) then yields

$$\Delta\mu_A = -\frac{C_{B0}{}^{\beta\alpha}}{n}W_S{}^\beta \, \delta C_B{}^\beta + \frac{C_{B0}{}^{\alpha\beta}}{n}W_S{}^\alpha \, \delta C_B{}^\alpha \quad (3.26)$$

$$\Delta\mu_B = \left(1 - \frac{C_{B0}{}^{\beta\alpha}}{n}\right)W_S{}^\beta \, \delta C_B{}^\beta$$

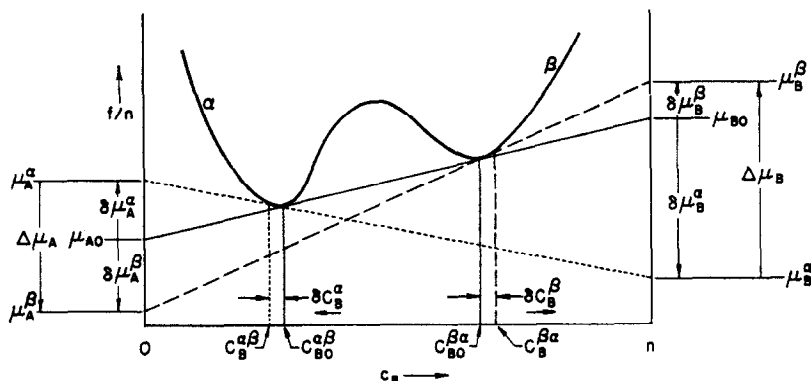$$- \left(1 - \frac{C_{B0}{}^{\alpha\beta}}{n}\right)W_S{}^\alpha \, \delta C_B{}^\alpha. \quad (3.27)$$

FIG. 6. Relationship of relevant chemical potential differences to free energy/mole, f/n, as a function of concentration, c_B. The solid line is tangent to the f/n curve at the equilibrium concentrations $C_B{}^{\alpha\beta}$ and $C_B{}^{\beta\alpha}$. The dashed line is tangent to the f/n curve at the concentration $C_B{}^{\beta\alpha}$ extrapolated from the β phase while the dotted line is tangent at $C_B{}^{\alpha\beta}$ extrapolated from the α phase. $\Delta\mu_A$ and $\Delta\mu_B$ are the chemical potential differences of A and B atoms, respectively, across the interface and are composed from the partial differences $\delta\mu_B{}^\alpha$, $\delta\mu_A{}^\beta$, $\delta\mu_B{}^\alpha$ and $\delta\mu_B{}^\beta$. The relative positions of $C_B{}^{\alpha\beta}$ to $C_{B0}{}^{\alpha\beta}$ and $C_B{}^{\beta\alpha}$ to $C_{B0}{}^{\beta\alpha}$ are purely schematic.

Equations (3.26) and (3.27) constitute the desired relationship between the chemical potential differences across the interface and the concentration deviations at the interface. For equations (3.16) and (3.17), which describe the most general of our specific models, we have

$$\Delta\mu_A = \frac{\xi\rho}{M_0}\left\{\frac{v}{3}\left(\frac{\Delta C_{B0}}{n}\right)^2 + 4\frac{J_0}{n}\frac{C_0}{n}\right\} \qquad (3.28)$$

$$\Delta\mu_B = \frac{\xi\rho}{M_0}\left\{\frac{v}{3}\left(\frac{\Delta C_{B0}}{n}\right)^2 - 4\frac{J_0}{n}\left(1 - \frac{C_0}{n}\right)\right\}. \quad (3.29)$$

Equations (3.28) and (3.29) are the desired chemical potential difference across the interface; they will become particularly enlightening if recast in terms of the fluxes j_A^{int} and j_B^{int} of A and B atoms that *cross* the interface, i.e., fluxes calculated in a reference frame in which the interface is at rest. We have already seen, from equation (3.3), that

$$j_B^{\mathrm{int}} = J. \qquad (3.30)$$

Moreover,

$$\begin{aligned} j_A^{\mathrm{int}} &= D^\alpha C_B^{\alpha'} - v(n - C_{B0}^{\alpha\beta}) \\ &= D^\beta C_B^{\beta'} - v(n - C_{B0}^{\beta\alpha}) \qquad (3.31) \\ &= -J - nv. \end{aligned}$$

Thus, for a moving interface, the fluxes of A and B atoms in the interface frame are not equal in magnitude and opposite in direction as was the case for the fluxes in equation (1.4). In fact, j_A^{int} and j_B^{int} can be treated as independent quantities which can replace the pair J and v or J_0 and v in our description of interfacial processes. In terms of interfacial fluxes, equations (3.28) and (3.29) take the form

$$\begin{pmatrix} \Delta\mu_A \\ \Delta\mu_B \end{pmatrix} = -\frac{\xi\rho}{nM_0}\begin{pmatrix} R_{AA} & R_{AB} \\ R_{BA} & R_{BB} \end{pmatrix}\begin{pmatrix} j_A^{\mathrm{int}} \\ j_B^{\mathrm{int}} \end{pmatrix}, \quad (3.32)$$

where

$$R_{AA} = 4\left(\frac{C_0}{n}\right)^2 + \frac{1}{3}\left(\frac{\Delta C_{B0}}{n}\right)^2$$

$$R_{BB} = 4\left(1 - \frac{C_0}{n}\right)^2 + \frac{1}{3}\left(\frac{\Delta C_{B0}}{n}\right)^2 \qquad (3.33)$$

$$R_{AB} = R_{BA} = -4\frac{C_0}{n}\left(1 - \frac{C_0}{n}\right) + \frac{1}{3}\left(\frac{\Delta C_{B0}}{n}\right)^2.$$

Algebra yields

$$R_{AA}R_{BB} - R_{AB}^2 = \frac{4}{3}\left(\frac{\Delta C_{B0}}{n}\right)^2. \qquad (3.34)$$

Thus, the R-matrix in equation (3.32) is symmetric and positive definite.

D. Discussion

Our most general results consist of formulas, equations (3.4) and (3.5), for the deviations of interface concentrations in the α and β phases from their equilibrium values. These concentration deviations may be related to chemical potential differences across the interface via equations (3.26) and (3.27); this can be done most meaningfully in terms of the interface fluxes j_B^{int} and j_A^{int} given by equations (3.30) and (3.31).

Of course, the actual evaluation of equations (3.4) and (3.5) requires a specification of the mobility function $M_S(x)$ and a stationary concentration profile $c_{BS}(x)$ consistent with some $f(c_B)$. The specific models considered in Section 3B lead to explicit expressions for the interfacial composition deviations in terms of interface velocities and atomic fluxes (see, e.g. equations (3.10) and (3.11)). Presumably one could determine experimentally these concentration deviations provided that concentration profiles could be measured on a fine scale (order ξ) and extrapolated to the interface. In fact, Eifert et al.[13] have determined, via extrapolation of electron microprobe data from bulk phases, the apparent deviations from interface equilibrium concentrations at moving α–β interfaces in Cu–Al alloys. Moreover, Powell and Schuhmann[14] have shown that such concentration deviations are of the order of magnitude of those to be expected if the system is considered as a ternary with vacancies being the third component, the concentrations of Cu and Al being those in equilibrium with an assumed non-equilibrium concentration of vacancies. However, concentration deviations as predicted, e.g. by our equations (3.10) and (3.11) are also a possibility. Nevertheless, no quantitative comparison will be attempted here because the microprobe beam size of Eifert et al.[13] is too large to lead to reliable extrapolated data on a scale of ξ and, in addition, our theory provides no quantitative knowledge of the mobility enhancement factor ρ.

It should be emphasized, however, that the present theory predicts deviations from equilibrium concentrations even for static interfaces ($v = 0$) provided that there is a flux through the interface. Thus for $v = 0$, any of the specific models of Section 3B are consistent with the results

$$\delta C_B^\alpha = \frac{2\xi\rho^\alpha}{D^\alpha}J, \qquad (3.35)$$

$$\delta C_B^\beta = -\frac{2\xi\rho^\beta}{D^\beta}J. \qquad (3.36)$$
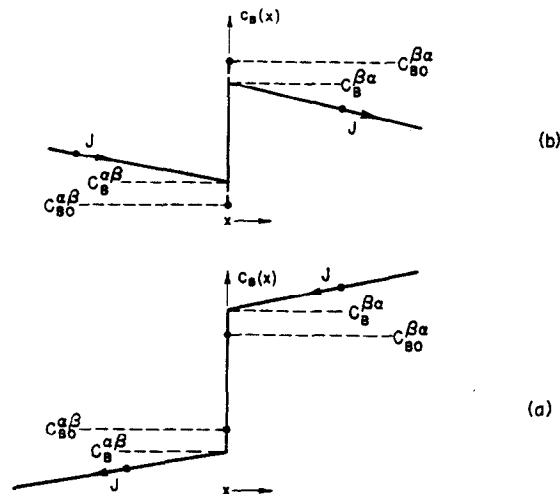
FIG. 7. Concentration, $c_B(x)$, vs distance, x, profiles for a stationary interface in a non-equilibrium situation where there is a net diffusion flux J, of B atoms. (a) J is to the right, (b) J is to the left. In both cases, the extrapolated concentrations $C_B{}^{\alpha\beta}$ and $C_B{}^{\beta\alpha}$ are shifted from $C_{B_0}{}^{\alpha\beta}$ and $C_{A_0}{}^{\beta\alpha}$ in such a direction as to reduce $|J|$ for a given set of external boundary conditions.

The corresponding concentration profiles are shown in Fig. 7(a and b) for positive and negative values of J, respectively. This clearly indicates the independent role of J and v in determining interfacial concentration deviations.

We now turn to discuss the significance of our equation (3.32) which relates the interface fluxes j_A^{int} and j_B^{int}, measured in a reference frame in which the interface is at rest, to the chemical potential differences, $\Delta\mu_A$ and $\Delta\mu_B$, across the interface. As equation (3.33) shows, the matrix in equation (3.32) obeys the symmetry relations of Onsager.[15] This demonstrates explicitly that the fluxes j_A^{int} and j_B^{int} and the respective conjugate generalized forces $\Delta\mu_A$ and $\Delta\mu_B$ are a proper set for the application of the classical principles of irreversible thermodynamics to problems that involve moving interfaces.

The positive definite nature of the R-matrix, as demonstrated by equation (3.34), guarantees that the interfacial processes described by equation (3.32) will result in a net rate of reduction of free energy. Thus, the rate of free energy change, due to interface fluxes, per unit area of interface is

$$\frac{d\Delta f}{dt} = j_A^{\text{int}}\Delta\mu_A + j_B^{\text{int}}\Delta\mu_B$$

$$= -\frac{\xi\rho}{nM_0}[R_{AA}(j_A^{\text{int}})^2$$
$$+ 2R_{AB}j_A^{\text{int}}j_B^{\text{int}} + R_{BB}(j_B^{\text{int}})^2]. \quad (3.37)$$

The quantity in brackets is positive via equation (3.34), thus making $d(\Delta f)/dt$ negative for any j_A^{int} and j_B^{int}.

On the other hand, this model allows solute or solvent trapping, in the sense of Baker and Cahn,[3] as discussed in the Introduction. This should be obvious because the off diagonal terms in (3.32) can always be exploited to make, say, $\Delta\mu_A$ and j_A^{int} have opposite signs. A simple example is provided by the case where initial conditions are arranged such that $C_B{}^{\beta'} = 0$. Then equation (3.1) yields $J = -vC_{B0}{}^{\beta\alpha}$ and, from equations (3.30) and (3.31), we obtain

$$j_A^{\text{int}} = -v(n - C_{B0}{}^{\beta\alpha})$$
$$j_B^{\text{int}} = -vC_{B0}{}^{\beta\alpha}. \quad (3.38)$$

We also find $J_0 = -v\,\Delta C_{B0}/2$ in which case equations (3.28) and (3.29) yield

$$\Delta\mu_A = -\frac{\xi\rho\,\Delta C_{B0}v}{M_0n^2}[\tfrac{2}{3}C_{B0}{}^{\beta\alpha} + \tfrac{4}{3}C_{B0}{}^{\alpha\beta}] \quad (3.40)$$

$$\Delta\mu_B = \frac{\xi\rho\,\Delta C_{B0}v}{M_0n^2}[\tfrac{1}{3}\Delta C_{B0} + 2(n - C_0)]. \quad (3.41)$$

Evidently j_B^{int} and $\Delta\mu_B$ have opposite signs, whereas j_A^{int} and $\Delta\mu_A$ have the same sign, irrespective of the sign of v. Therefore, this set of initial conditions demonstrates a case in which A atoms are trapped. From the form of equation (3.32), there are obviously ranges of fluxes where trapping will occur; A atoms will be trapped for $R_{AA}j_A^2 > -R_{AB}j_Aj_B$ and B atoms will be trapped for $R_{BB}j_B^2 > -R_{AB}j_Aj_B$.

CONCLUSIONS

1. A model can be formulated, consistent with the principles of irreversible thermodynamics, to account for departures from equilibrium in a two-phase binary system containing a mobile diffuse interface.

2. Deviations of interface concentrations from their equilibrium values can be calculated for small departures from equilibrium and are found to contain a term proportional to interface velocity and a second independent term proportional to a flux of either species of atoms through the interface, measured in a reference frame in which the interface is at rest.

3. Deviations of interface concentrations from their equilibrium values are found to be proportional to an assumed reduction of atomic mobility in the interfacial region.

4. When the fluxes of A and B atoms across the interface are expressed in a reference frame in which the interface is at rest, they are found to be linearly related to the corresponding differences in chemical potentials of A and B atoms, across the interfacial region, by a symmetric matrix R.

5. The structure of the matrix R guarantees that the total free energy associated with the interface

fluxes will decrease; however, individual species, A or B, can move in a direction of their own increasing chemical potential, thus giving rise to trapping in some cases.

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