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Interface transfer coefficient in second-phase-growth models

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In order to derive an atomistic expression for the transfer coefficient across an interface, we extend the Gibbs dividing-surface scheme to kinetic problems. In equilibrium thermodynamics, this scheme consists in replacing the continuous concentration profile between two coherent phases by a stepped profile with a discontinuity at the dividing surface: the Gibbsian excess free energy (interfacial energy) is the difference between the free energies associated with the true continuous profile and with the artificial stepped one. Close to equilibrium, the diffusion flux along the actual continuous concentration profile is equal to minus the gradient of the chemical potential multiplied by a mobility: the latter is a continuous function of the local equilibrium concentration, which can be evaluated in a mean-field approximation. Gibbs' dividing-surface scheme introduces a *transfer coefficient* across the (artificial) dividing interface. Equating the exact expression of the flux along the actual concentration profile to that predicted in Gibbs' scheme for the same difference in chemical potential across the system yields the expression for the transfer coefficient. In the simplest mean-field description of chemical diffusion, the transfer coefficient is found to be *negative*. The reason for that is that the mobility increases as the concentration goes to $\frac{1}{2}$, at least in the simplest case. Assuming the concentration to be uniform up to the interface underestimates the flux and must be compensated by a negative "contact resistance" between the two phases. Neglecting the transfer coefficient results in underestimating the flux: the error can be large for small samples, in particular in the case of the nucleation and growth of a phase with low diffusivity, inside a high-diffusivity matrix. The range of validity of the model is shown to coincide with that of linear diffusion theory. In this range, the transfer coefficient at the interface does not depend on the velocity of the interface.

I. INTRODUCTION

In the classical theory of second-phase growth (a precipitate in a matrix,[1] intermetallic layers between two solid solutions,[2]) it is usually claimed that solute atoms first diffuse through the matrix toward the precipitate and then cross the precipitate-matrix interface. The solute flux arriving by diffusion is equal to a mobility M multiplied by chemical potential *gradient* ($J=-M\nabla\alpha$), while the flux crossing the interface is proportional to the *difference* in chemical potential between the two phases ($J=-K\Delta\alpha$):[3] the proportionality factor K is the interfacial transfer coefficient. Under steady-state conditions, both fluxes must be equal. The flux, and as a consequence the growth rate of the second phase, is either diffusion controlled or interface-reaction controlled.

As discussed in Ref. 4, the mobility coefficient M can be given by an atomistically based expression fully compatible with a mean-field description of the equilibrium thermodynamics of the alloy. This expression was derived explicitly in the simplest approximation, the kinetic analog of the Bragg-Williams approximation of the equilibrium thermodynamics of the alloy.[5] To our knowledge, no such model exists for the solute transfer coefficient across the interface. It is the purpose of this work to propose such a model in the simple but inspiring case of the coherent interface in inhomogeneous binary solutions. The model rests on the kinetic analog of a technique used by Cahn and Hilliard to derive the Gibbs interfacial free energy from the thermodynamics of an inhomogeneous coherent system.[6]

In the following, we first recall the model introduced in Ref. 4 and deduce an expression for the interfacial transfer coefficient. We then make typical quantitative estimates of the latter and discuss some important consequences. Finally, we use the kinetic equations introduced in this paper to address the problem of moving interfaces.

II. THE MODEL

In their illuminating treatment of interfacial free energy in a coherent two-phase system, Cahn and Hilliard[6] first computed the free energy of the continuous equilibrium concentration profile in the two-phase field in the simplest mean-field model, the Bragg-Williams approximation. They then approximate this profile by a stepped one: the free energy of the idealized profile differs from that of the equilibrium profile by a quantity which, according to Gibbs' definition, is the interfacial excess free energy.

In Ref. 4, one of us proposed a mean-field description of diffusion fully compatible with Cahn's and Hilliard's thermodynamics of inhomogeneous systems.[6] It is assumed that diffusion proceeds by direct exchange be-

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tween neighboring atoms, and that the activation energy for the process is a saddle-point energy plus the amount of energy required to extract the pair of exchanging atoms from their environment. The latter energy is evaluated by counting the broken bounds in the simplest mean-field approximation, i.e., taking into account only the concentrations on neighboring sites, and not higher-order correlators (such as pair correlation functions, etc.). It is found that, *close to equilibrium* (i.e., when the chemical potential, as defined in Ref. 6, does not strongly depart from a constant along the concentration profile), the diffusion flux $J_{n,n+1}$ between planes n and $n+1$ is given by

$$J_{n,n+1}=-M_n(\alpha_{n+1}-\alpha_n)\ , \tag{1}$$

where α_n is the chemical potential in plane n, divided by $k_BT\,(\alpha_n=\beta\mu_n$ with $\beta=1/k_BT)$:

$$\alpha_n=-2\beta\omega[Zc_n+z(c_{n+1}+c_{n-1}-2c_n)]$$
$$+\ln(c_n/1-c_n)\ , \tag{2a}$$

and M_n the mobility at plane n:

$$M_n=M_{0n}\nu z\exp[-\beta E^0+\alpha(\varepsilon_B-\varepsilon_A)/2\omega]\ , \tag{2b}$$

$$M_{0n}=[(1-\bar{c}_n)(1-\bar{c}_{n+1})]^{\varepsilon_B/2\omega}[\bar{c}_n\bar{c}_{n+1}]^{\varepsilon_A/2\omega}\ . \tag{2c}$$

In Eqs. (2a)–(2c), Z is the total number of nearest neighbors (e.g., 12 in the fcc structure), z the number of bonds between one site in plane n and sites in plane $n+1$ (e.g., $z=3$ for diffusion in the $\langle 111\rangle$ direction in the fcc structure), c_n is the B atom concentration in plane n, $\varepsilon_i=\varepsilon_{AB}-\varepsilon_{ii}$, where ε_{ij} is the contribution of a pair of atoms of type i and j to the internal energy of the system, ω is the ordering energy: $\omega=\varepsilon_{AB}-(\varepsilon_{AA}+\varepsilon_{BB})/2$, ν is an attempt frequency, and E^0 is the saddle-point energy for the exchange of atoms.

Two points must be stressed:

(i) All terms entering the mobility M_n are given *their equilibrium value:* α is the value of the chemical potential along the equilibrium concentration profile (α=constant), and $\bar{c}_n$ is the concentration in plane n of the equilibrium concentration profile. As a consequence, Eq. (1) is a diffusion equation *linear* in the gradient of the actual chemical potential, although the mobility M_n includes concentrations at two neighboring points: indeed the concentrations entering the mobility are equilibrium concentrations, the gradient of which is not a driving force for diffusion (there is no diffusion along the equilibrium profile, despite its nonuniformity at the transition region between the two coexisting phases).

(ii) The kinetic problem involves two terms $(\varepsilon_A-\varepsilon_B)$ and $(\varepsilon_A+\varepsilon_B=2\omega)$, while equilibrium problems only involve the latter.

At equilibrium, $J_{n,n+1}=0$ for any n; this implies $\alpha_{n+1}=\alpha_n=\alpha$, which, according to Eq. (2a) is nothing but the condition of minimum free energy for the concentration profile as found by Cahn and Hilliard.[6] Figure 1(a) shows such a profile computed by solving Eq. (2a) close to the critical temperature $T_c\,(T=0.9T_c)$.

If the profile is slightly perturbed, an interdiffusion flux will develop according to Eq. (1). Provided we allow for exchange of matter at both ends of the profile, we can manage to maintain a flux along a static concentration profile very close to the unperturbed equilibrium concentration profile. Indeed Eq. (1) can be rewritten

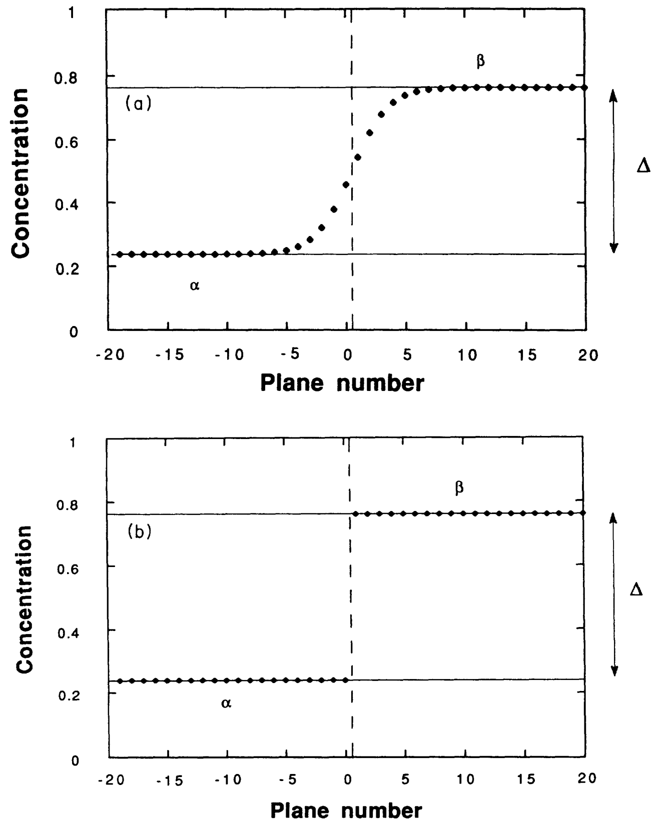

FIG. 1. Equilibrium concentration profile at $0.9T_c$ (a) and the corresponding Gibbs dividing-surface scheme (b). The concentration is the dimensionless B atomic fraction.

$$\alpha_{n+1}-\alpha_n=-J_{n,n+1}/M_n\ . \tag{3}$$

Under steady-state conditions, $J_{n,n+1}$ is independent of n (no solute accumulation) and is written J. Let the system be large enough compared to the width of the interface so that, at equilibrium, the concentrations have reached their asymptotic values at both ends of the sample. Then, for a total $2N$ planes (labeled from $-N+1$ to N), one may impose the chemical potential α_{-N} on the left end, and the steady flux J: the chemical-potential distribution $\{\alpha_n\}$ which insures the imposed steady flux is

$$\alpha_n=\alpha_{-N+1}-J\left[\sum_{k=-N+1}^{n-1}M_k^{-1}\right]\ , \tag{4}$$

and the difference in chemical potential between the two ends is

$$\sum_{-N+1}^{N-1}(\alpha_{n+1}-\alpha_n)=\alpha_{+N}-\alpha_{-N+1}=-J\left[\sum_{-N+1}^{N-1}M_n^{-1}\right]\ . \tag{5}$$

In other words, maintaining a small chemical-potential difference $\delta\alpha=\alpha_{+N}-\alpha_{-N+1}$ between the two ends of the sample generates a flux J:

$$J=-\hat{K}\delta\alpha\ , \tag{6}$$

$$\hat{K}^{-1}=\sum_{-N+1}^{N-1} M_n^{-1}\ . \tag{7a}$$

The concentration-dependent prefactor in $\hat{K}$ is then

$$\hat{K}_0^{-1}=\sum_{-N+1}^{N-1} M_{0n}^{-1}\ . \tag{7b}$$

In the following, it should be remembered that $\hat{K}$ and M_n are deduced from $\hat{K}_0$ and M_{0n} by a multiplicative factor which only depends on the temperature and the (uniform) chemical potential α. Notice that M corresponds to a conductivity, M^{-1} (and $\hat{K}^{-1}$) to a resistivity, and $\delta\alpha$ to a difference in potential in a homogeneous electrical-current problem.

We now idealize the equilibrium smooth concentration profile using the Gibbs scheme, i.e., assuming that the two contiguous phases have a uniform concentration up to a sharp dividing interface where the concentration exhibits a discontinuity [Fig. 1(b)]: the B-poor phase (planes with a negative label) has a concentration $(1-\Delta)/2$, and the B-rich phase (positive coordinates) has a concentration $(1+\Delta)/2$. Δ is the width of the two-phase field at the chosen temperature. In the Bragg-Williams approximation we use here, Δ is a solution of the implicit equation

$$\Delta=\tanh(\Delta T_c/T)\ , \tag{8}$$

where T_c is the critical temperature: $T_c/T=\beta\omega Z/2$. Notice that the interface has been arbitrarily located between planes 0 and 1. The consequence of this particular choice will be discussed later.

For the abrupt interface depicted in Fig. 1(b), it is easily found from Eq. (7b) that the overall resistivity K_0' [Eq. (6)] is given by

$$K_0'^{-1}=K_{0\alpha}^{-1}+K_{0\beta}^{-1}+4/(1-\Delta^2)\ , \tag{9a}$$

with $K_{0\alpha}^{-1}$ and $K_{0\beta}^{-1}$ given by

$$K_{0\alpha}^{-1}=4N_\alpha/[(1-\Delta)^{\varepsilon_B/2\omega}(1+\Delta)^{\varepsilon_A/2\omega}]\ , \tag{9b}$$

$$K_{0\beta}^{-1}=4N_\beta/[(1+\Delta)^{\varepsilon_B/2\omega}(1-\Delta)^{\varepsilon_A/2\omega}]\ , \tag{9c}$$

where N_α and N_β are the number of planes in the B-poor and B-rich phases, respectively. In Eq. (9a), the first term ($K_{0\alpha}^{-1}$) corresponds to the resistance of the left-hand phase, the second one ($K_{0\beta}^{-1}$) to that of the right-hand phase, and the third term to the contact resistance across the abrupt interface, as depicted in Fig. 1(b). This last term is obtained from Eq. (2c) with $n=0$, i.e., $\bar{c}_0=(1-\Delta)/2$ and $\bar{c}_1=(1+\Delta)/2$.

In the particular case where $\varepsilon_A=\varepsilon_B(\varepsilon_{AA}=\varepsilon_{BB}$ but $\varepsilon_{AB}\neq 0)$, Eqs. (9) get a very simple meaning:

$$\hat{K}'^{-1}=[\nu z\exp(-\beta E^0)]^{-1}4(N_\alpha+N_\beta-1)/(1-\Delta^2)\ , \tag{10}$$

and the flux is given by

$$J=[\nu z\exp(-\beta E^0)][(1-\Delta^2)/4][\delta\alpha/(N_\alpha+N_\beta-1)]\ . \tag{11}$$

The above flux is the flux one would find across a single phase, $N_\alpha+N_\beta$ planes thick, with a chemical-potential gradient $\delta\alpha/(N_\alpha+N_\beta-1)$, and an average concentration $(1+\Delta)/2$ [or equivalently $(1-\Delta)/2$]. Obviously, $\hat{K}'^{-1}$ is not a good estimate of the total resistance of the sample.

The value of $\hat{K}_0$ for the actual concentration profile [Fig. 1(a)] is given by

$$\hat{K}_0^{-1}=\sum_{-N+1}^{N-1}\{[(1-\bar{c}_n)(1-\bar{c}_{n+1})]^{\varepsilon_B/2\omega}\times[\bar{c}_n\bar{c}_{n+1}]^{\varepsilon_A/2\omega}\}^{-1}\ . \tag{12}$$

As a consequence, the value which must be attributed to the contact resistance K_{0i}^{-1} in Gibbs' scheme [Fig. 1(b)] if we want the *same flux* in both schemes [Figs. 1(a) and 1(b)] is such that

$$K_{0i}^{-1}=\hat{K}_0^{-1}-[K_{0\alpha}^{-1}+K_{0\beta}^{-1}]\ , \tag{13a}$$

$$K_{0i}^{-1}=\hat{K}_0^{-1}-[K_0'^{-1}-4/(1-\Delta^2)]\ . \tag{13b}$$

Equation (13a) together with Eqs. (9b) and (9c) yield the value of the transfer coefficient K_{0i} across the coherent interface, at every temperature, for the kinetic model we introduce in Ref. 4: this model is the kinetic counterpart of the regular-solution model in equilibrium thermodynamics.

Before turning to quantitative estimates in a specific diffusion problem, we notice the following relations which are obvious from the electrical analog of the diffusion problem. The flux across the two-phase sample in the Gibbs scheme is given by

$$J=-(K_\alpha^{-1}+K_\beta^{-1}+K_i^{-1})^{-1}\delta\alpha\ . \tag{14}$$

The mobility prefactors in the left-hand and right-hand phases are respectively

$$M_{0\alpha}=\tfrac{1}{4}[(1-\Delta)^{\varepsilon_B/2\omega}(1+\Delta)^{\varepsilon_A/2\omega}]\ , \tag{15a}$$

$$M_{0\beta}=\tfrac{1}{4}[(1+\Delta)^{\varepsilon_B/2\omega}(1-\Delta)^{\varepsilon_A/2\omega}]\ . \tag{15b}$$

The chemical-potential drops across the left-hand and the right-hand phases and across the interface are, respectively,

$$\delta\alpha_\alpha=\delta\alpha\times\hat{K}/K_\alpha,\quad \delta\alpha_\beta=\delta\alpha\times\hat{K}/K_\beta,\quad \delta\alpha_i=\delta\alpha\times\hat{K}/K_i\ . \tag{16}$$

The above expressions will be used later in this work.

III. QUANTITATIVE ESTIMATES

As an example, we study the diffusion across a one-dimensional bcc coherent two-phase alloy in the [100] direction. The prefactor of the interfacial transfer coefficient K_{0i} is given by Eq. (13a); it can be computed knowing $\hat{K}_0$ for the actual equilibrium concentration profile [Eq. (12)]. The equilibrium concentration profile is a function of the reduced temperature only, while $\hat{K}_0$ is a function of both the reduced temperature and the ratio $\varepsilon_A/\varepsilon_B=r$.

For computing $\hat{K}_0$ one must perform the summation of the right-hand side of Eq. (12) along the equilibrium concentration profile, linking phase α to phase β [Fig. (1)]. Provided the total number of lattice planes $(2N)$ is large enough, the concentration starts on the left end with a value $c_\alpha=(1-\Delta)/2$ equal to the solubility limit of B in the α phase, stays very close to this value up to the interfacial region, then increases smoothly up to a value close to $c_\beta=(1+\Delta)/2$, the solubility limit of B in the β phase; c_β is reached at the right end of the sample. The transition region extends over a thickness of $\mathcal{T}$ planes: $\mathcal{T}\simeq\Delta/(c_1-c_0)$, since (c_1-c_0) is the maximum value of the concentration gradient at the interface. The interface is one plane thick at 0 K and diverges with an exponent $-\frac{1}{2}$ at the critical temperature:[6] $\mathcal{T}\propto(1-T/T_c)^{-1/2}$.

Far from the interfacial region, the concentration is almost constant, so that the prefactor of the mobility can be written as

$$M_0=[(\bar{c}^{1-\rho}(1-\bar{c})^{\rho}] , \tag{17}$$

with $\bar{c}=\bar{c}_\alpha$ or $\bar{c}_\beta$, respectively, on the left or on the right side, and

$$\rho=1/(1+r)=\varepsilon_B/2\omega . \tag{18}$$

The variation of M_0 in a homogeneous phase as a function of the concentration $\bar{c}$ is shown in Fig. 2 for three distinct values of $\varepsilon_A/\varepsilon_B$ $(r=3,1,-5)$. It is easily shown (see the Appendix) that M_0 is maximum in the phase which is richer in the component with less cohesion. As an example, for $r>1$, the maximum in M_0 occurs in the B-rich phase: $\omega>0$ and $r>1$ imply $\varepsilon_{AA}<\varepsilon_{BB}<0$, i.e., pure B is less stable than pure A (the less negative the energy per bond, the less stable the constituent).

Along the equilibrium concentration profile linking phase α to phase β [Fig. (1)], the mobility prefactor is a two-point function [Eq. (2c)] which significantly differs from Eq. (17) only in the transition region between phases α and β. Summing the right-hand side of Eq. (12) and applying Eq. (13a) yields the transfer coefficient across the Gibbs dividing surface K_{0i}. This depends *a priori* on the choice we make for the location of Gibbs dividing surface. For the sake of simplicity, we chose the dividing surface with zero excess concentration, i.e., between planes 0 and 1 in Fig. 1 [at this interface, $(c_n+c_{n+1})/2=\frac{1}{2}$]. In view of the strong temperature dependence of K_{0i}, it is useful to scale it to the transfer coefficient across an abrupt interface, $(1-\Delta^2)/4$, times the thickness of the interface $\mathcal{T}$. Typical results are shown in Fig. 3.

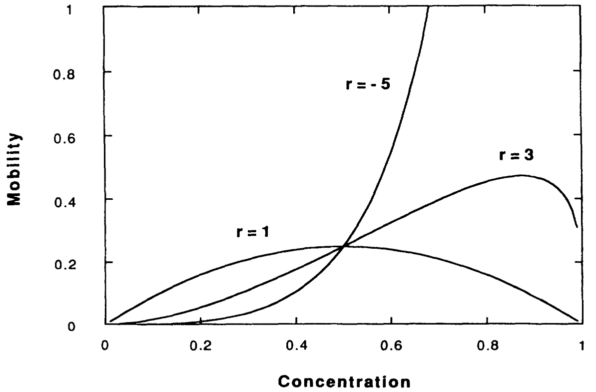

FIG. 2. Dimensionless mobility prefactor in homogeneous phase [Eq. (17)] as a function of the (dimensionless) concentration for three distinct values of $r=\varepsilon_A/\varepsilon_B$. For $r=-5$, M_0 goes to infinity as c reaches 1.

The most striking feature is that the transfer coefficient is found to be *negative* in all cases. Its absolute value increases with T/T_c and with ρ, when $\rho<\frac{1}{2}$. The case $\rho>\frac{1}{2}$ is symmetrical since changing ρ into $(1-\rho)$ is equivalent to changing c into $(1-c)$, as seen in Eq. (17). For a given value of ρ, K_{0i} goes asymptotically to infinity as T/T_c approaches 1. This is consistent with the analytical approximation $K_{0i}\propto(1-T/T_c)^{-1/2}\propto\mathcal{T}$, obtained by linearization of the concentration profile around the interface.

The fact that K_{0i} is negative does not violate the second principle of thermodynamics: indeed, K_{0i}^{-1} is a contact resistivity introduced as a correcting term in an approximation of the actual concentration profile across the two-phase system. That this correction must be nega-

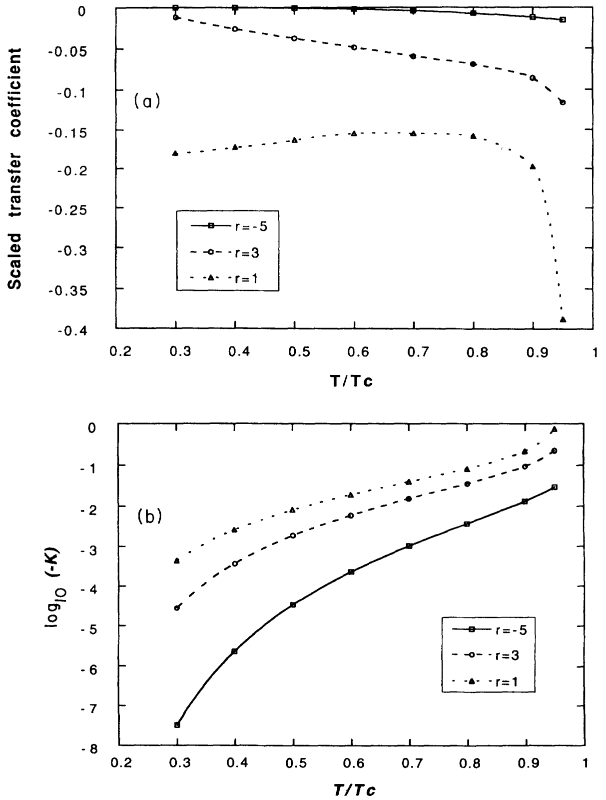

FIG. 3. (a) Dimensionless scaled interface transfer coefficient $K_{0i}\times4/[(1-\Delta^2)\mathcal{T}]$ as a function of the reduced temperature for three values of r, in linear scale. (b) Decimal logarithm of K_{0i}.

tive can be easily understood in the particular case where $\varepsilon_A=\varepsilon_B$. As seen in Fig. 2, the mobility is, in this case, a maximum at $c=\frac{1}{2}$: the mobility increases toward the interface. The region near the interface thus shows a lower resistivity than the homogeneous phases. Gibbs' scheme therefore underestimates the mobility close to the dividing surface. This error must be compensated by a negative contact resistance. This conclusion depends neither on the particular lattice nor on the particular plane orientation, as long as nearest-neighbor atoms are located in contiguous planes. In fact, lattice and plane geometrical characteristics then reduce to the parameter z alone, as a multiplying factor, in the mobility function [cf. Eq. (3a)], thus not modifying the fact that the mobility increases toward the interface.

IV. CONSEQUENCES

In the metallurgical literature dealing with precipitate coarsening and layered-compound growth, the transfer coefficient across the interface is usually neglected (the diffusion-limited case). This amounts to neglecting K_{0i}^{-1} in the expression $K_{0\alpha}^{-1}+K_{0\beta}^{-1}+K_{0i}^{-1}$ when computing the total resistance of the real system. Under a given chemical-potential difference between the two ends of the sample, the real system experiences a larger flux than the idealized one. The relative error in the flux so computed, $\delta J/J$, is

$$\delta J/J=K_{0i}^{-1}/(K_{0\alpha}^{-1}+K_{0\beta}^{-1}) \ , \tag{19}$$

where δJ is the difference between the true J and the approximated J; $\delta J/J$ is a function of T/T_c, of $\varepsilon_A/\varepsilon_B$, and of the geometry of the sample:

$$\delta J/J=\frac{1}{2N}\frac{K_{0i}^{-1}}{(N_\alpha/2N)M_{0\alpha}^{-1}+(N_\beta/2N)M_{0\beta}^{-1}} \ . \tag{20}$$

$\delta J/J$ is inversely proportional to the total number of planes $2N$ and depends on the proportions of α and β phases.

In the case where the two phases are in equal proportion, we found that for a total of 100 planes, $\delta J/J$ varies from -2% to -5% for various T/T_c and $\varepsilon_A/\varepsilon_B$ (see Table I). In a nucleation problem, where a thin phase is interfaced with a thicker one, if the mobility in the thick phase is much larger than in the thinner one, $\delta J/J$ is likely to be large. For example, with $N_\alpha=10$, $N_\beta=90$, $T/T_c=0.4$, and $\varepsilon_A/\varepsilon_B=-5$, we find $\delta J/J=-20\%$. As a conclusion, neglecting the contribution of the transfer coefficient results in underestimating the flux, leading to an error of 5%, 20%, or more, depending on the particular geometry of the sample.

TABLE I. Relative error in the flux $\delta J/J$ (%) when the interface resistance is neglected, at three typical reduced temperatures and for three distinct values of the factor $r=\varepsilon_A/\varepsilon_B$ [Eq. (20)]. The computation was performed with 100 planes ($N_\alpha=N_\beta=50$).

r	$T/T_c=0.4$	$T/T_c=0.7$	$T/T_c=0.9$
1	2.8	2	0.8
3	1.9	2.9	1.6
-5	3.8	4.4	4.6

As a further remark, we notice that the chemical potential on each plane, in the presence of a constant flux, can be calculated from Eq. (4), since the mobility along the actual profile is known. The concentration profile for an imposed $\delta\alpha$ can thus be deduced using Eq. (2a). Similarly, one would like to draw the concentration profile corresponding to Gibbs' scheme. As the mobilities are constant in each phase, the potential profile is linear and readily deduced from Eqs. (16). The transfer coefficient introduces a discontinuity at the interface, positive or negative according to the sign of K_{0i}. For small departure from equilibrium, the concentration profile deduced from Eq. (2a) will generally be linear and reach at the interface a value different from the solubility limit in the phase. In the alloy model studied here, the chemical potential $\alpha(c)$ is an increasing function of c. As K_{0i} is negative, the concentrations at the interface are pulled into the interior of the miscibility gap, leading to a scheme at variance with what is usually assumed (Fig. 4).

Until now, we have written the flux across the interface in terms of the chemical-potential difference ($J_i=-K_i\delta\alpha_i$): it is more common to write it as a function of concentration departure from equilibrium. Near equilibrium, the chemical potential in a homogeneous system is given by

$$\alpha(c_\varphi)=\alpha+(c_\varphi-\bar{c}_\varphi)(d\alpha/dc)_{\bar{c}_\varphi} \ , \tag{21}$$

where φ means the α or the β phase and the overbar indicates a value at equilibrium. The drop of the chemical potential at the interface is then

$$\begin{aligned}\delta\alpha_i&=\alpha(c_\beta)-\alpha(c_\alpha)\\&=(c_\beta-\bar{c}_\beta)(d\alpha/dc)_{\bar{c}_\beta}-(c_\alpha-\bar{c}_\alpha)(d\alpha/dc)_{\bar{c}_\alpha} \ ,\end{aligned} \tag{22}$$

and the flux is

$$J=k_\alpha(c_\alpha-\bar{c}_\alpha)-k_\beta(c_\beta-\bar{c}_\beta) \ , \tag{23a}$$

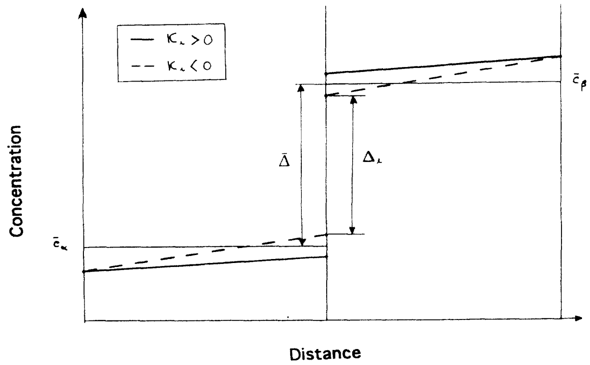

FIG. 4. Typical concentration profiles expected in the dividing-surface scheme, under a steady flux. Notice the effect of the sign of the interfacial transfer coefficient.

with

$$k_\varphi = K_i (d\alpha/dc)_{\bar{c}_\varphi} \ . \tag{23b}$$

In the Bragg-Williams approximation used here, for a homogeneous phase

$$\alpha(c) = -\frac{4T_c}{T}c + \ln\frac{c}{1-c} \ , \tag{24}$$

so that $(d\alpha/dc)_{\bar{c}_\alpha} = (d\alpha/dc)_{\bar{c}_\beta} > 0$. As a consequence, k_α and k_β are equal and both negative:

$$k_\alpha = k_\beta = k = K_i \left[-\frac{4T_c}{T} + \frac{1}{\bar{c}_\alpha} + \frac{1}{\bar{c}_\beta} \right] \ . \tag{25}$$

From Eqs. (23) and (24), the flux across the interface is

$$J = -k[\Delta_i - \bar{\Delta}] \ , \tag{26}$$

where Δ_i is the value of the concentration difference at the interface and $\bar{\Delta}$ is its equilibrium value [Eq. (8)].

Equation (23a) is identical to that used for example, by Gösele and Tu.[2] The above discussion proves that, in the model discussed here, the two coefficients k_α and k_β are equal and negative. Notice that complicating factors may arise at incoherent interfaces.[7] An atomistic model of the transfer coefficient at such interfaces remains to be established.

V. NUMERICAL ASSESSMENT OF THE MODEL

The results presented so far all rest on Eqs. (1) and (2). As shown in Ref. 4, these equations are valid close to equilibrium only (i.e., at constant chemical potential along the concentration profile): indeed, Eqs. (1), (2b), and (2c) result from a first-order expansion in the inhomogeneity in chemical potential of the general expression of the flux from plane n to $n+1$:

$$J_{n,n+1} = p_{n+1,n} - q_{n,n+1} \ , \tag{27}$$

where $p_{n+1,n}$ $(q_{n,n+1})$ is the number of exchanges per unit time of B atoms in plane $n+1$ (n) with A atoms in plane n $(n+1)$. The detailed expressions for p and q as functions of the actual local concentrations and of the energy parameters $\varepsilon_i = \varepsilon_{AB} - \varepsilon_{ii}$ $(i = A$ or $B)$ are given by Eqs. (6)–(8) in Ref. 4. The purpose of this section is to assess the validity of Eqs. (1) and (2) in two cases: that of the stationary-interface problem discussed above, and that of a moving interface, more appropriate to precipitate growth. The latter problem was treated in a continuum model by Langer and Sekerka:[8] their model can thus be compared to the present one, which rests on a well-defined mean-field treatment of an atomistic model.

A. Stationary interface

For the sake of simplicity, we restrict ourselves to the case where $\varepsilon_A = \varepsilon_B$, i.e., where the two phases are symmetrical from the kinetic point of view. We choose a sample with $N = 40$ planes, with average concentration $\frac{1}{2}$, at $0.8T_c$: the equilibrium concentration profile is similar to that of Fig. 1. We then impose at both ends fixed B atom concentrations which depart respectively by $-\delta c/2$ and $+\delta c/2$ from the equilibrium concentrations $\bar{c}_\alpha$ and $\bar{c}_\beta$. A flux of B atoms results, from phase β to phase α; because of the symmetry of the problem, no movement of the concentration profile with respect to the sample is generated. A similar procedure was used in Ref. 9 for a different diffusion model. The flux is computed from Eq. (27), and compared to the value predicted by Eqs. (1)–(7), which again should hold only in the limit of small chemical-potential gradients across the sample, $\delta\alpha/N \ll 1$. The result is shown in Fig. 5. As can be seen, the linear diffusion equation [Eq. (1)] well describes the flux up to $\delta\alpha \simeq 0.04$, i.e., to a gradient of the chemical potential of $\delta\alpha/N \simeq 0.001$ units per plane. Beyond this limit, the linear theory slightly overestimates the flux, typically by 15% for $\delta\alpha/N \simeq 0.01$.

In the linear regime, the chemical potential increases almost linearly from the left to the right [Fig. 6(a)] with a slight decrease of slope in the interfacial region where the mobility is larger. It is then easily checked that Eq. (16) correctly predicts $\delta\alpha_i$, the value of the jump in chemical potential at the dividing interface: $\delta\alpha_i$ can be measured graphically on Fig. 6(a). We find for the conditions studied here

$$\delta\alpha_i/\delta\alpha = \delta c_i/\delta c = \hat{K}/K_i \simeq -4\% \ , \tag{28}$$

where $\delta c_i = \Delta_i - \bar{\Delta}$; the value of δc_i also is correctly predicted by Eq. (26). Notice that the jump of chemical potential across the dividing interface in the case studied here is about 1.6 times larger than the change of chemical potential per interplanar distance $(\delta\alpha/N)$ and has the opposite sign. Beyond the linear regime [Fig. 6(b)] the above conclusions do not hold anymore: the chemical potential profile is curved in each phase even far from the interface, and the graphical determination of $\delta\alpha_i$ becomes unreliable. As a conclusion, the dividing-surface scheme we propose is fully consistent with the linear regime of diffusion, but is restricted to this regime.

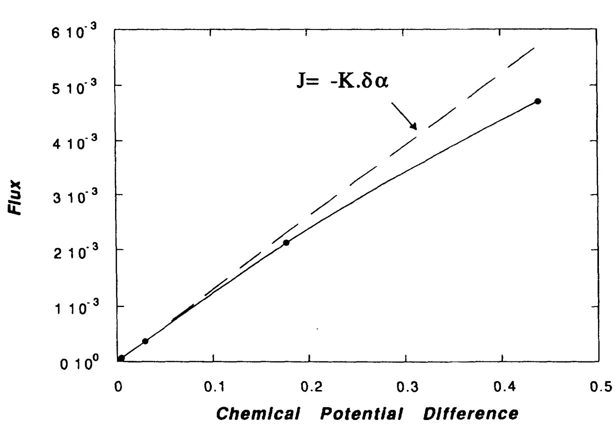

FIG. 5. Flux vs the overall reduced-chemical-potential difference across the sample (the sample is 40 planes thick). Notice that the linear diffusion theory fails for too large a driving force. The flux is in M_n/M_{0n} [Eq. (2b)] units.

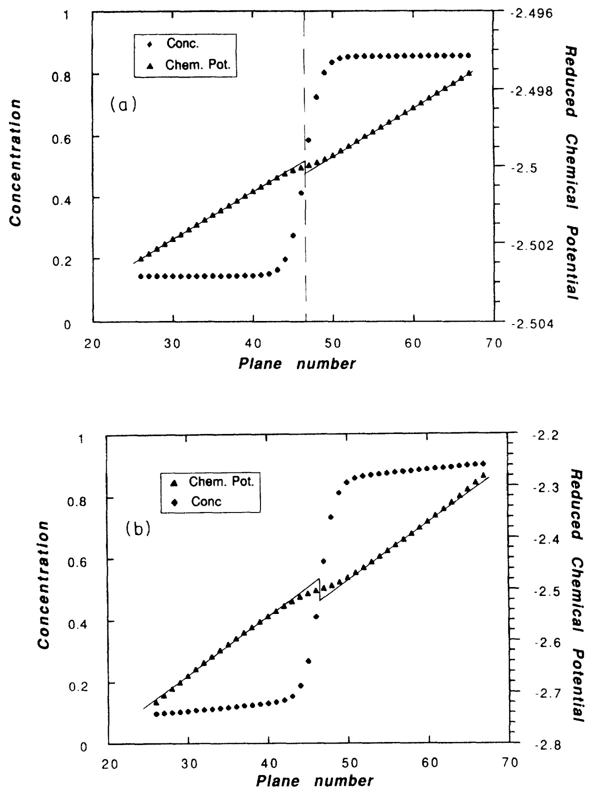

FIG. 6. Concentration and reduced chemical potential along a two-phase coherent stationary system in the presence of a diffusion flux at $0.8T_c$. For a small driving force (a) the chemical potential varies linearly with distance and exhibits a small negative inflexion in the interfacial region, resulting in a negative sign for the interfacial transfer coefficient; for a larger driving force (b) the linearity is lost.

B. Moving interface

For triggering a migration of the interface it suffices to fix the right-hand side of the sample at concentration c slightly larger than $\bar{c}_\beta$, the equilibrium concentration in the β phase, and to impose zero flux at the left-hand side of the α phase. Solving the continuity equation deduced from Eq. (27),

$$\partial c_n/\partial t = -(J_{n,n+1} - J_{n-1,n}) , \tag{29}$$

with the boundary conditions just described, yields the time evolution of the concentration profile. After a transient, the chemical potential becomes uniform in phase α, while it decreases linearly in phase β from the imposed value at the right-hand side down to its value in the α phase. A typical example is shown in Fig. 7, obtained at $0.8T_c$ with $\delta c = 7.9 \times 10^{-4}$ at the right end of the β phase. The flux through the β phase is uniform and the interface has reached a steady velocity $(2.9 \times 10^{-3}$ planes per time unit).

The dividing-surface scheme we introduced before can be extended to the present situation by arbitrarily attaching the interface to the plane with concentration $\frac{1}{2}$. Extrapolating the chemical-potential profile down to the dividing surface, we find, as in the stationary case, that the chemical potential in the β phase at the interface with the α phase is *below* its equilibrium value (cf. Fig. 7): the transfer coefficient at the moving interface is *negative*. The transfer coefficient can be measured from its definition, $K_i = -J_i/\delta\alpha_i$, or computed by applying the procedure used in this work [Eq. (13a)] to the β phase only. Both methods give the same result within numerical uncertainty, which proves that the transfer coefficient does not depend on the interface velocity *in the range of validity of linear diffusion theory.*

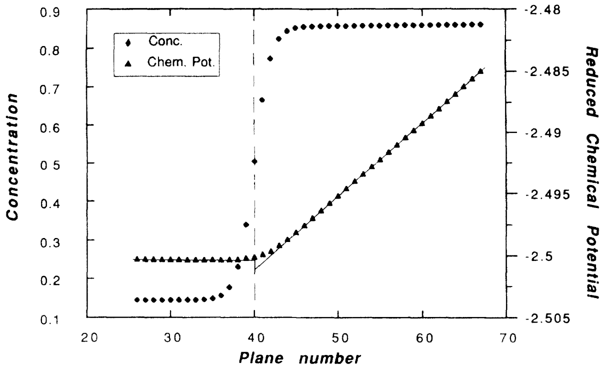

FIG. 7. Concentration and reduced chemical potential along a two-phase coherent system with a moving interface (to the left) under quasi-steady-state conditions. The flux is constant in the right-hand (β) phase and zero in the left one (α). Notice that the chemical potential in the β phase extrapolates to a value at the interface which is lower than the equilibrium value in the α phase.

This last result is at variance with what is predicted by Langer and Sekerka.[8] Notice that the mobility in Ref. 8 is given an arbitrary value, while in the present treatment the value used is fully consistent with the model used to describe the thermodynamics of the system.

VI. CONCLUSION

We have proposed an extension to nonequilibrium problems of the dividing-surface scheme introduced by Gibbs for equilibrium problems. In equilibrium thermodynamics, the Gibbs scheme consists in representing the smooth concentration profile between two phases in coherent equilibrium by a step function, i.e., by two homogeneous phases in contact along a steep interface: an excess free energy results.

Close to equilibrium, the interdiffusion flux across a two-phase coherent system is given by minus the gradient of the chemical potential multiplied by a mobility. The mobility is a continuous function of the local equilibrium concentration, the expression for which has been established for the simplest diffusion mechanism (direct exchange) in the simplest mean-field approximation in Ref. 4. Gibbs' dividing-surface scheme introduces a *transfer coefficient* across the interface: the flux across the interface is indeed proportional to the *difference* between the chemical potentials in the two phases.

Comparing the exact expression for the flux along the actual concentration profile to that predicted in Gibbs' scheme yields the expression for the transfer coefficient. The latter is found to be *negative*. The reason for that is that the mobility increases as the concentration goes to $\frac{1}{2}$, at least in the simplest case. Assuming the concentration uniform up to the interface underestimates the flux and must be compensated by a negative contact resistance between the two phases.

As a consequence, in Gibbs' scheme close to equilibrium the concentrations on each side of the interface lie inside the miscibility gap. Neglecting the transfer coefficient results in underestimating the flux: the error can be large for small samples, in particular in the case of the nucleation and growth of a phase with low diffusivity inside a high-diffusivity matrix.

Numerical study of the model shows that its range of validity coincides with that of linear diffusion theory. In this range, the transfer coefficient at the interface does not depend on the velocity of the interface.

This model may be extended to more realistic diffusion models and higher-order mean-field approximations.[10] For the time being, calculations are in progress to extend this study to cases of compound formation during interdiffusion.

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APPENDIX

In a homogeneous phase, the mobility is a function of the concentration [Eq. (17)]: We prove here that M_0 is maximum for a concentration such that the majority element is that with the weakest cohesion, i.e., the cohesive energy ($\propto \varepsilon_{ii} < 0$) with the smallest absolute value. It should be remembered that we treat here the case without mixing, i.e., $\omega = (\varepsilon_A + \varepsilon_B)/2 > 0$, which implies $\varepsilon_B(1+r) > 0$ (since $r = \varepsilon_A/\varepsilon_B$), and the $\bar{c}$ is the concentration of B atoms.

The sign of the derivative of M_0 with respect to $\bar{c}$ is given by the sign of $(1-\bar{c}-\rho)$. Three cases are to be considered.

(1) $\rho < 0$. M_0 is an increasing function of $\bar{c}$ on the segment [0,1]: it is a *maximum in pure B*. The condition $\rho < 0$ implies $r < -1$, i.e., $(1+r) < 0$, and $\varepsilon_B < 0$ since $\varepsilon_B(1+r) > 0$. Since $r < 0$ and $\varepsilon_B < 0$, one has $\varepsilon_A > 0$ and $\varepsilon_B < \varepsilon_A$ which implies $\varepsilon_{AA} < \varepsilon_{BB}$ and $|\varepsilon_{BB}| < |\varepsilon_{AA}|$, and B is the element with the weakest cohesion.

(2) $0 < \rho < 1$ (i.e., $r > 0$). M_0 goes through a maximum at $\bar{c}^* = 1-\rho = r/(1+r)$, i.e., $\bar{c}^* > (<) \frac{1}{2}$ if $r > (<) 1$. Since $r > 0$, one has $\varepsilon_A > 0$ and $\varepsilon_B > 0$, so that the maximum is in a B-rich phase ($\bar{c}^* > \frac{1}{2}$) if $r > 1$, i.e., $\varepsilon_A > \varepsilon_B$ and $\varepsilon_{AA} < \varepsilon_{BB}$, i.e., if B is the element with the weakest cohesion. Conversely, the maximum is in an A-rich phase ($\bar{c}^* < \frac{1}{2}$) if $r < 1$, i.e., if A is the element with the weakest cohesion.

(3) $1 < \rho$ (i.e., $-1 < r < 0$. M_0 is a decreasing function of $\bar{c}$ on the segment [0,1]: it is a *maximum in pure A*. The condition $1 < \rho$ implies $-1 < r < 0$, i.e., $0 < (1+r) < 1$, i.e., so that $\varepsilon_B > 0$ and $\varepsilon_A < 0$. As a consequence, $\varepsilon_{AA} > \varepsilon_{BB}$ and A is the element with the weakest cohesion.

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