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Atomic mobility in Cahn's diffusion model

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We propose a simple stochastic model for one-dimensional interdiffusion in a binary *A*-*B* solid solution. By an appropriate choice of the activation energy for the interchange of *A* and *B* atoms among neighboring planes, we prove the model drives the system to the correct steady states with statistical weights identical to those evaluated by the simplest mean-field thermodynamics. Based on this model an expression is obtained for the interdiffusion flux: The conditions under which the latter reduces to a linear-response-theory type are discussed, and the microscopic expression for mobility coefficient is elucidated. It is found to be a function of the local equilibrium composition and composition inhomogeneity.

I. INTRODUCTION

Almost thirty years ago, Hillert[1] and Cahn[2] introduced a model for interdiffusion in which the contribution of the concentration inhomogeneity to the chemical potential is taken into account. Indeed, as shown by Cahn and Hilliard,[3] the extrema of the free energy of a binary mixture (local equilibrium condition) are reached when a generalized chemical potential is uniform: The latter is a function of the local concentration and to the first order in inhomogeneity, of the local curvature of the concentration field. Any reliable kinetic model must be such that in a closed system, the interdiffusion flux J will be zero when the above chemical potential α is uniform. The simplest form is

$$J = -M\nabla\alpha \ , \tag{1}$$

where M is a mobility.[1,2] Of course, in the limit of vanishing inhomogeneity ($\alpha \rightarrow$classical chemical potential), one must recover the classical expression of the interdiffusion flux. This requirement prompted Cahn and others[4,5] to choose Darken's[6] expression for the mobility. Notice that Hillert[1] pointed out he "was not able to justify [his] choice of the form of the mobility by applying the absolute rate theory."

In this paper, we treat in full detail a simple one-dimensional model where the cohesive energy and the activation barrier for interatomic exchanges are assumed to be sums of pair interaction energies. We demonstrate the complete compatibility of our kinetic model with a simple Bragg Williams description of the thermodynamics of the system: Indeed, a stochastic version of our kinetic model yields a steady state probability of a concentration profile, in a closed system, identical to that evaluated from the thermodynamics. Based on this kinetic model, an expression for the interdiffusion flux is deduced which can be identified to Eq. (1) in the case of weak chemical potential gradients. It is found that M contains an inhomogeneity term much in the same way as α. The implications of this finding are discussed.

II. THE MODEL: STATICS AND DETERMINISTIC KINETICS

We consider N lattice planes normal to the X axis (Fig. 1), each lattice plane comprising Ω atomic sites. Each site (e.g., in plane n) has z_0 nearest neighbors in plane n, z in plane $(n+1)$, and z in plane $(n-1)$ [e.g., in an fcc structure, planes would be (111) and $z_0=6, z=3$)]. The coordinence is $Z=2z+z_0$. Two atomic species A and B are shared by the $N\times\Omega$ lattice sites. For our present purpose, a configuration of the system is defined by the set $\{B_1;\ldots B_n;\ldots B_N\}$ of the numbers of B atoms in each plane $1,\ldots N$ or equivalently by the concentrations $c_n=B_n/\Omega$, or the concentration profile $c(x)$ with $x=(n-1)a$, where a is the interplanar distance in the X direction.

The set $\{B_n\}$ may be represented by a vector $\mathbf{B}$ with components B_n in an N-dimension space. For each configuration so defined an internal energy $E(\mathbf{B})$ may be

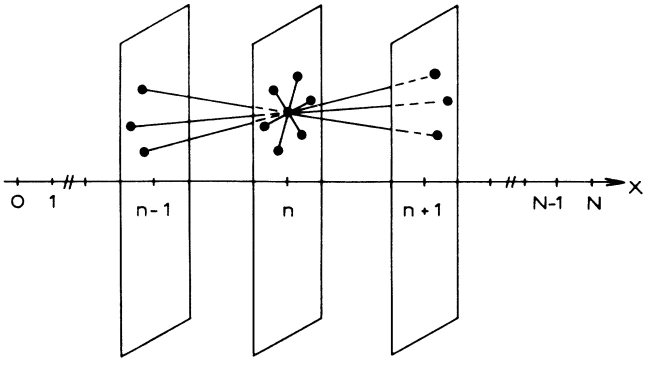

FIG. 1. Links between neighboring planes: One atom in plane n has z_0 $(=6)$ nearest neighbors in plane n, and z $(=3)$ such neighbors in planes $n+1$ and $n-1$. The coordinence is $Z=z_0+2z$ $(=12)$. Each plane contains Ω lattice sites; the numbers of B atoms in plane $n-1$, n, and $n+1$ are, respectively, B_{n-1}, B_n, and B_{n+1}.

computed. The probability for the configuration $\mathbf{B}$ to occur at equilibrium is

$$P(\mathbf{B})=\mathcal{Z}^{-1}W(\mathbf{B})\exp[-\beta E(\mathbf{B})]\ , \tag{1a}$$

with $\beta=1/kT$, and $\mathcal{Z}$ the normalization constant (partition function)

$$\mathcal{Z}=\sum_{\mathbf{B}}\exp[-\beta E(\mathbf{B})]\ , \tag{1b}$$

where the summation is performed over all the possible arrangements of the B and A atoms that keep the overall composition constant.

Equation (1a) may be rewritten

$$P(\mathbf{B})=\mathcal{Z}^{-1}\exp[-\beta\mathcal{F}(\mathbf{B})]\ , \tag{1c}$$

with

$$\mathcal{F}(\mathbf{B})=E(\mathbf{B})-TS(\mathbf{B})\ , \tag{1d}$$

$$S(\mathbf{B})=k_B\ln W(\mathbf{B})\ . \tag{1e}$$

$\mathcal{F}(\mathbf{B})$ is the Helmoltz free energy function, parametrized by $\mathbf{B}$ or by the profile $c(x):\mathcal{F}\{c(x)\}$.

A. The free energy function

Much in the same way as in Ref. 5, we assume the contributions of AA, AB, and BB pairs to the cohesive energy are, respectively, ϵ_{AA}, ϵ_{AB}, and ϵ_{BB}, and the ordering energy ω is defined as

$$\omega=\left[\epsilon_{AB}-\frac{\epsilon_{AA}+\epsilon_{BB}}{2}\right]\ .$$

To the degree of sophistication of the description of the configuration, all we know is that each atom in plane n has z_0c_n [respectively, $z_0(1-c_n)$] B (respectively, A) neighbors in plane, $n,zc_{n\pm1}$ [respectively, $z(1-c_{n\pm1})$] B (respectively, A) neighbors in planes $n\pm1$. Simple algebra yields the following expression for the internal energy of a configuration $\mathbf{B}$:

$$E(\mathbf{B})=\Omega\left[Z\omega\sum_{1}^{N}c_n(1-c_n)\right.$$
$$-2z\omega\sum_{2}^{N-2}c_n(c_{n+1}+c_{n-1}-2c_n)$$
$$\left.+\mathcal{S}+\mathcal{C}\right]\ , \tag{2a}$$

where $\mathcal{S}$ is a surface term depending on c_1,c_2,c_{N-1},c_N and $\mathcal{C}$ a constant. For a given configuration ($\mathbf{B}$ given), there are $\Omega!/B_n!(\Omega-B_n)!$ isoenergetic arrangements of the B_n B atoms among the Ω sites in each plane n. A configurational entropy $S(\mathbf{B})$ results:

$$S(\mathbf{B})=-\Omega k\sum_{1}^{N}[c_n\ln c_n+(1-c_n)\ln(1-c_n)]\ , \tag{2b}$$

and the following Helmotz free energy function may be introduced

$$\mathcal{F}(\mathbf{B})=E(\mathbf{B})-TS(\mathbf{B})\ . \tag{2c}$$

$\mathcal{F}$ is an extensive quantity in the sense that it is proportional to Ω, the normal section of the system. The free energy per unit normal section ($\Omega=1$) can be written, $f(\mathbf{B})=\mathcal{F}(\mathbf{B})/\Omega$, with

$$f(\mathbf{B})=Z\omega\sum_{1}^{N}c_n(1-c_n)$$
$$-2z\omega\sum_{2}^{N-2}c_n(c_{n+1}+c_{n-1}-2c_n)$$
$$+kT\sum_{1}^{N}[c_n\ln c_n+(1-c_n)\ln(1-c_n)]+\mathcal{S}+\mathcal{C}\ . \tag{2d}$$

The first and third terms in the right-hand side (RHS) are nothing but the regular solution model. The second term in the RHS is due to the inhomogeneity of the alloy. Simple algebra shows it can be rewritten as well as a gradient energy contribution:

$$\sum_{1}^{N-1}(c_{n+1}-c_n)^2\ . \tag{2e}$$

The probability for the profile $\mathbf{B}$ to show up at equilibrium is therefore

$$P(\mathbf{B})=\mathcal{Z}^{-1}\exp[-\beta\mathcal{F}(\mathbf{B})]\ . \tag{3a}$$

Since $\mathcal{F}$ scales with Ω [cf. Eqs. (1a)–(1c)], the larger Ω, the more peaked $P(\mathbf{B})$ will be on that profile $\mathbf{B}$ which gives $f(\mathbf{B})$ its *absolute minimum* value. In the thermodynamic limit, $\Omega\rightarrow\infty$, the only configuration with finite probability is $\mathbf{B}_{\text{eq}}$ such that

$$\mathcal{F}(\mathbf{B}_{\text{eq}})=-kT\ln\mathcal{Z}\ . \tag{3b}$$

For finite values of Ω, however, $P(\mathbf{B})$ exhibits local maxima for the local minima of $f(\mathbf{B})$, which define locally stable configurations.

We now discuss the extrema of the above free energy. Since we deal here with closed systems, i.e., systems which contain a fixed number of A and B atoms on a fixed number of lattice sites ($N\Omega$) the extrema to be found are those of $f(\mathbf{B})+\lambda NC$ where C is the average concentration in B atoms in the system:

$$NC=\sum_{1}^{N}c_n\ . \tag{4}$$

λ is the Lagrange parameter introduced by the constraint of having C fixed. The extrema of the above expression are found by setting its variation with respect to an arbitrary change in $\mathbf{B}$ (i.e., a set of δc_n preserving $C=$constant) equal to zero. After some algebra, it is found that this condition yields for $2<n<N-1$

$$-\frac{2\omega}{kT}[Zc_n+z(c_{n+1}+c_{n-1}-2c_n)]+\ln\frac{c_n}{1-c_n}=\alpha\ , \tag{5a}$$

or calling α_n the left-hand side (LHS) of Eq. (5a)

$$\alpha_n=\alpha\ , \tag{5b}$$

and slightly different conditions for $n=1$ and N.

The (local) equilibrium concentration profiles, $\mathbf{B}_{\text{extr}}$ (with components Ωc_n) are given as solutions of the difference equations (5) (see Ref. 7 for an enlightening discussion thereof). Equation (5) defines a function of c (the left-hand side) which, at equilibrium, is uniform, independent of position. This function of c may be called the *chemical potential* by analogy to standard thermodynamics: indeed, the standard expression for the chemical potential $\{-(2\omega/kT)Zc_n+\ln[c_n/(1-c_n)]$ in kT units$\}$ is recovered if we omit in Eq. (5) the inhomogeneity contribution.

B. Deterministic kinetics

Let us introduce the frequency $\Gamma_{n\to n+1}$ with which one B atom in plane (n) exchanges with one A atom in plane $(n+1)$, $\Gamma_{n\to n-1}$ the frequency at which one B atom in plane n exchanges with one A atom in plane $(n-1)$. The change in B concentration in plane n is given by

$$\frac{dc_n}{dt}=J_{n-1\to n}-J_{n\to n+1}\ , \tag{6a}$$

where $J_{n\to n+1}$ is the net flux of B atoms from plane n to $n+1$ per lattice site:

$$J_{n\to n+1}=z[c_n(1-c_{n+1})\Gamma_{n\to n+1}-c_{n+1}(1-c_n)\Gamma_{n+1\to n}]\ . \tag{6b}$$

Indeed, c_n is the probability that a site in plane n is occupied by a B atom and $z(1-c_{n+1})$ the probability it is linked to one site in plane $n+1$ occupied by an A atom. Under steady state, $dc_n/dt=0$; since we are in a closed system (no exchange of atoms with the exterior), the latter condition implies $J_{n\to n+1}=0$ whatever n.

From Eq. (6b), the steady-state concentration profiles fullfil the condition

$$\frac{c_n(1-c_{n+1})}{c_{n+1}(1-c_n)}=\frac{\Gamma_{n+1\to n}}{\Gamma_{n\to n+1}}\ , \tag{7a}$$

and we want this condition to coincide with Eq. (5). Let us choose $\Gamma_{n\to n+1}$ as

$$\Gamma_{n\to n+1}=\nu\exp(-\beta E_{n\to n+1})\ , \tag{7b}$$

with $E_{n\to n+1}$ the activation barrier for an exchange between B in plane (n) and A in plane $(n+1)$. Equation (7a) together with (7b) can be rewritten, after taking the log:

$$-E_{n\to n+1}+kT\ln\frac{c_n}{1-c_n}=-E_{n+1\to n}+kT\ln\frac{c_{n+1}}{1-c_{n+1}}\ . \tag{7c}$$

There are many choices of $E_{i\to j}$ which fulfill Eq. (7c). We use the following model: $E_{i\to j}$ is the energy required to extract one B atom from plane i, one A atom from plane j, and to insert the A and B atoms into a saddle point position with a fixed energy E^0.[8] Simple but lengthy algebra yields

$$\begin{aligned}E_{n\to n+1}={}&E^0+(\epsilon_{AB}-\epsilon_{BB})(zc_{n-1}+zc_{n+1}+z_0c_n)\\&+(\epsilon_{AA}-\epsilon_{AB})(zc_n+zc_{n+2}+z_0c_{n+1})\ ,\end{aligned} \tag{8a}$$

$$\begin{aligned}E_{n+1\to n}={}&E^0+(\epsilon_{AB}-\epsilon_{BB})(zc_n+zc_{n+2}+z_0c_{n+1})\\&+(\epsilon_{AA}-\epsilon_{AB})(zc_{n-1}+zc_{n+1}+z_0c_n)\ .\end{aligned} \tag{8b}$$

Introducing Eqs. (8) into (7c) reveals that the steady-state condition [Eq. (7c)] is identical to the condition of equilibrium [Eqs. (5a) and (5b), $\alpha_n=\alpha$]. In other words, the configurations $\mathbf{B}_{\text{ss}}$ which are a steady-state solution of the kinetic model [Eq. (8)] are the configurations $\mathbf{B}_{\text{eq}}$ which make $f(\mathbf{B})$ an extremum. The model, however, does not reproduce the property (3a). For that reason, we introduce a stochastic version of the deterministic model.

III. STOCHASTIC DESCRIPTION OF THE KINETICS

As just seen, the model (6a), with the definitions (7b), and (8), guarantees that $\mathbf{B}_{\text{ss}}=\mathbf{B}_{\text{eq}}$ where $\mathbf{B}_{\text{ss}}$ and $\mathbf{B}_{\text{eq}}$ are, respectively, a steady state and an equilibrium configuration. Let us now assess the respective probability of two steady states $\mathbf{B}_{\text{ss}}^{(1)}$ and $\mathbf{B}_{\text{ss}}^{(2)}$. We define $P(\mathbf{B},t)$ the probability for one system to have the configuration $\mathbf{B}$ at time t: If we prepare a large number of samples with the configuration $\mathbf{B}^{(0)}$ at time $t=0$, a fraction $P(\mathbf{B},t)$ of it will get the configuration $\mathbf{B}$ at time t. The time evolution of $P(\mathbf{B},t)$ is governed by the master equation

$$\frac{dP(\mathbf{B},t)}{dt}=\sum_{\{\mathbf{B}'\}}[-P(\mathbf{B},t)W_{\mathbf{B}\to\mathbf{B}'}+P(\mathbf{B}',t)W_{\mathbf{B}'\to\mathbf{B}}]\ , \tag{9}$$

where $\{\mathbf{B}'\}$ represents the set of configurations which may be reached from the configuration $\mathbf{B}$ by one atomic interchange, and $W_{\mathbf{B}\to\mathbf{B}'}$, the probability that the transition from the configurations $\mathbf{B}$ to $\mathbf{B}'$ occurs per unit time. Since atomic exchanges take place between neighboring planes only, each configuration $\mathbf{B}$ is linked to $2(N-1)$ configurations $\mathbf{B}'$, such that either

$$B_n'^{(1)}=B_n+1 \quad\text{and}\quad B'_{n+1}=B_{n+1}-1$$

or

$$B_n'^{(2)}=B_n-1 \quad\text{and}\quad B'_{n+1}=B_{n+1}+1\ ,$$

and $B'_m=B_m$ for all $m\neq n$ and $m\neq n+1$.

As an example, the probability that, per unit time, a transition occurs between $\mathbf{B}$ and $\mathbf{B}'^{(n,1)}$ defined by $B'_m=B_m$ except for $B'_n=B_n+1$ and $B'_{n+1}=B_{n+1}-1$ is

$$W_{\mathbf{B}\to\mathbf{B}'^{(n,1)}}=\Omega\frac{B_n}{\Omega}\frac{\Omega-B_{n+1}}{\Omega}\Gamma_{n\to n+1}\ , \tag{10}$$

with Γ given by Eqs. (7b) and (8) evaluated in the configuration $\mathbf{B}$. Ω factorizes in the RHS of Eq. (10) since W is larger the more numerous the atoms in each plane.

Under steady-state conditions, $dP/dt=0$, detailed balance implies that in Eq. (9),

$$P_{\text{ss}}(\mathbf{B})W_{\mathbf{B}\to\mathbf{B}'}=P_{\text{ss}}(\mathbf{B}')W_{\mathbf{B}'\to\mathbf{B}}\ . \tag{11}$$

Let us choose one of the configurations as a reference state $\mathbf{B}^0$, and define a path $\{B_n^i\}$ by which the steady state of interest $\mathbf{B}$ may be deduced from $\mathbf{B}^0$. Recursive use of Eq. (11) along this path $\{\mathbf{B}^i\}$ yields

$$\frac{P(\mathbf{B})}{P(\mathbf{B}^0)}=\prod_{\{i\}}\frac{W_{\mathbf{B}'\to\mathbf{B}}}{W_{\mathbf{B}\to\mathbf{B}'}}\ , \tag{12}$$

where the subscript "steady state" has been omitted on P. $\prod_{\{i\}}$ is the product along the path.

Taking advantage of the expression of W [Eqs. (10), (7b), and (8)], detailed careful examination of the RHS of Eq. (12) yields

$$\frac{P(\mathbf{B})}{P(\mathbf{B}^0)}=\exp(-\beta\{E(\mathbf{B})-E(\mathbf{B}^0) -T[S(\mathbf{B})-S(\mathbf{B}^0)]\}) \tag{13}$$

or

$$P_{\mathrm{ss}}(\mathbf{B})\propto \exp[-\beta\Omega f(\mathbf{B})]\ . \tag{14}$$

As a summary, the stochastic model just discussed has been built in such a way that the probability of a steady-state concentration profile $\mathbf{B}$ is identical to the probability of that profile as estimated from the thermodynamical model. We may therefore *trust the expression of the interdiffusion flux* which appears in the model [Eq. (6b)] since it drives the system to the correct configurations with the correct weight.

IV. INTERDIFFUSION FLUX

The expression of the flux of B atoms from plane n to $n+1$ (and of A atoms in the opposite direction) as given by Eq. (6b) may be rewritten as

$$J_{n\to n+1}=p-q\ , \tag{15a}$$

with

$$p=zc_n(1-c_{n+1})\Gamma_{n\to n+1}\ ;\qquad q=zc_{n+1}(1-c_n)\Gamma_{n+1\to n}\ , \tag{15b}$$

or following Polkowicz's identity:

$$J_{n\to n+1}=\sqrt{pq}\,(\sqrt{p/q}-\sqrt{q/p}\,)\ . \tag{15c}$$

From Eqs. (5a), (5b), and (15b),

$$\sqrt{p/q}=\exp\left[-\frac{\alpha_{n+1}-\alpha_n}{2}\right]\ , \tag{16}$$

where α_n is the chemical potential (in kT units) defined in Eqs. (5). If the system is *close to equilibrium*, α_n is almost uniform, so that $(\alpha_{n+1}-\alpha_n)\ll 1$ and Eq. (15c) may be expanded as

$$J_{n\to n+1}\cong -M(\alpha_{n+1}-\alpha_n)\ , \tag{17a}$$

with

$$M=\sqrt{pq}\ , \tag{17b}$$

$$M=z\nu[c_n(1-c_n)c_{n+1}(1-c_{n+1})]^{1/2}\times\exp\left[-\beta\frac{E_{n\to n+1}+E_{n+1\to n}}{2}\right]\ . \tag{17c}$$

Simple algebra shows that the activation energy of M is

$$E^0+(\epsilon_{AA}-\epsilon_{BB})\left[Z\frac{c_n+c_{n+1}}{2}+z\frac{c_n''+c_{n+1}''}{2}\right]\ , \tag{17d}$$

where c_n'' is the curvature of the concentration profile at the plane n ($c_n''=c_{n+1}+c_{n-1}-2c_n$).

As a summary, the flux may indeed be written as a mobility times a chemical potential difference between neighboring planes; but if the chemical potential contains a non-negligible contribution of the concentration inhomogeneity, such will also be the case for the mobility. To our knowledge this contribution has been omitted up to the present time.

V. DISCUSSION AND CONCLUSION

As just discussed, Eq. (1) only holds in the limit of small chemical potential gradients ($\alpha_{n+1}-\alpha_n\ll 1$), i.e., close to equilibrium ($\alpha_{n+1}=\alpha_n=\alpha$). The question remains as to how does the mobility M [Eqs. (17b) and (17c)] write in this limit.

Let us introduce a smallness parameter η which measures the departure from equilibrium:

$$\alpha_n=\alpha(1+\eta a_n)\ , \tag{18a}$$

$$c_n=\bar{c}_n(1+\eta b_n)\ , \tag{18b}$$

where a_n and b_n describe the form of the actual chemical potential and concentration profile as compared to the profile at equilibrium ($\alpha,\bar{c}_n$). It is easily shown that $\alpha_{n+1}-\alpha_n$ is of order one in η while M contains a zeroth-order term:

$$\alpha_{n+1}-\alpha_n=\eta\alpha(a_{n+1}-a_n)\ , \tag{19a}$$

$$M\cong\hat{M}+\eta M'\ . \tag{19b}$$

As a consequence, to first order in η, the flux J can be written

$$J\cong\hat{M}\eta\alpha(a_{n+1}-a_n)\ , \tag{20}$$

i.e., the mobility which is consistent with Eq. (1) is $\hat{M}$. Taking advantage of Eqs. (5), (8), and (17c), it is readily found that

$$\hat{M}=M_0\exp\left[-\beta E_0+\alpha\frac{\epsilon_B-\epsilon_A}{\omega}\right]\ , \tag{21a}$$

with $\epsilon_i=\epsilon_{AB}-\epsilon_{ii}$ ($i=A$ or B) and

$$M_0=\nu z[(1-\bar{c}_n)(1-\bar{c}_{n+1})]^{\epsilon_B/2\omega}(\bar{c}_n\bar{c}_{n+1})^{\epsilon_A/2\omega}\ . \tag{21b}$$

From Eq. (21b), we learn that the mobility is indeed a local function, but not a point function, and that it has to be evaluated along the equilibrium profile in the vicinity of which diffusion is being studied. M_0 in Eq. (21b) is unchanged by the permutation $n \leftrightarrow n+1$. In a continuous model, M_0 should therefore be a function of the local value of the concentration $c(x)$ and of the curvature of the concentration profile $\partial^2 c/\partial x^2$, or/and of the square of the concentration gradient.

Obviously, when used to describe the early stages of spinodal decomposition starting from a uniform solution, the mobility is *uniform* and can be written

$$\hat{M} = vz\bar{c}(1-\bar{c})\exp\{-\beta[E_0 + Zc(\epsilon_B - \epsilon_A)\} \ . \tag{22}$$

Another simplifying situation obtains when $\epsilon_A = \epsilon_B$, i.e., $\epsilon_{AA} = \epsilon_{BB}$. $\hat{M}$ reduces to

$$\hat{M} = vz[\bar{c}_n(1-\bar{c}_n)\bar{c}_{n+1}(1-\bar{c}_{n+1})]^{1/2}\exp(-\beta E_0) \ , \tag{23}$$

where $\bar{c}_n$ is the equilibrium profile in the vicinity of which diffusion is being studied. Notice the prefactor in Eq. (23) is the geometrical mean of $\bar{c}_n(1-\bar{c}_{n+1})$ and $\bar{c}_{n+1}(1-\bar{c}_n)$ rather than the arithmetical mean as chosen arbitrarily by Hillert.[1]

Finally we may argue that in the course of the coherent decomposition of a solid solution the concentration profile will never be too far away from a (local) equilibrium profile so that the mobility $\hat{M}$ [Eq. (21a)] may be evaluated using the actual value of c_n, c_{n+1} and the average value of the chemical potential $\alpha \cong \langle \alpha_n \rangle$. Such a conclusion deserves a careful numerical check which is in progress at the present time.

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[8] According to this model, at each atomic exchange, the system "knows" which state it is leaving but "ignores" the state it is moving to, beyond the saddle point.