

Nonparabolic nanoscale shift of phase boundaries in binary systems with restricted solubility

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Computer simulations were used to study the interplay of the diffusion asymmetry (composition dependence of diffusion coefficient) and the phase-separation tendency (chemical effect) in the kinetics of the interface shift during dissolution in a binary system with restricted solubility. We have found that—on nanoscale, taking into account only the diffusion asymmetry—the shift of the chemically sharp interface is not proportional to the square root of the time as would be expected from Fick’s laws but to t^{k_c} , where $0.25 < k_c < 1$ (deviations from the parabolic law). In ideal systems $0.5 \leq k_c \leq 1$, but with increasing mixing energy (V) the interface shift returns to the parabolic law ($k_c \approx 0.5$), and at very large V values k_c can be even less than 0.5. This effect is a real “nanoeffect,” because after dissolving a certain number of layers (long time or macroscopic limit), the interface shift returns to the parabolic behavior. It is also illustrated that these phenomena can be observed experimentally as well.

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In the past years, several papers were published about the interface motion during thin-film dissolution into a semi-infinite substrate.^{1–4} In Refs. 1–3 the atoms of the deposit (thin film) and those of the substrate had limited mutual solubility and the interface was sharp on nanoscale due to chemical reasons (phase separation). In Ref. 4 the solubility was not limited at all (ideal system) but, surprisingly at first glance, the interface remained sharp provided that the diffusion asymmetry was large (the diffusion was faster by several orders of magnitude in the substrate than in the deposit).

In phase separating systems it was obtained from computer simulations that the interface displacement was proportional to the square root of the time, whereas in ideal systems a violation of the parabolic law was observed (from atomistic simulations on a discrete lattice and also from experiments in Ni-Cu system). In both cases only extremities were investigated, since in phase-separating systems the authors neglected the composition dependence of the diffusivity (diffusion asymmetry) and in the second case only ideal system was studied.

It is important to note that while the square-root kinetics is obvious from the traditional Fick’s equations, the linear behavior cannot be explained by them, i.e., it is a good example for the deviation from the classical laws on nanoscale (see also Ref. 4).

In this paper, we investigate the influence of the interplay of the diffusion asymmetry and chemical effect (phase-separation tendency) on the kinetics of the interface shift. We demonstrate by computer simulations how these parameters could influence the kinetics of the interface motion.

The model used in our calculations is based on Martin’s deterministic kinetic equations,^{4,5} where time derivatives of atomic fractions of A atoms in the i th atomic layer perpendicular to the x axis can be given by

$$\frac{dC_i}{dt} = -z_v [C_i(1 - C_{i-1})\Gamma_{i,i-1} - (1 - C_i)C_{i-1}\Gamma_{i-1,i} + C_i(1 - C_{i+1})\Gamma_{i,i+1} - (1 - C_i)C_{i+1}\Gamma_{i+1,i}], \quad (1)$$

In this exchange model $\Gamma_{i,i+1}$ is the probability per unit time (jump frequency) that an A atom in layer i exchanges its position with a B atom in the layer $i + 1$ and z_v is the vertical coordination number. C_i denotes the atomic fraction of A atoms on plane i . It is plausible to assume that the jump frequencies have an Arrhenius-type temperature dependence

$$\Gamma_{i,i+1} = \nu \exp\left(-\frac{E_{i,i+1}}{kT}\right), \quad (2)$$

where ν denotes the attempt frequency, k denotes the Boltzmann constant, T is the absolute temperature, and $E_{i,i+1}$ is the activation barrier, which must be chosen to fulfil the condition of detailed balance under steady state ($dC_i/dt = 0$),

$$\frac{C_i(1 - C_{i+1})}{C_{i+1}(1 - C_i)} = \frac{\Gamma_{i+1,i}}{\Gamma_{i,i+1}}. \quad (3)$$

There are many choices of $E_{i,i+1}$ which fulfil Eq. (3).⁵ For instance, the following choice:⁶

$$E_{i,i+1} = E^0 - [z_v(C_i + C_{i+2}) + z_l C_{i+1}](V_{AB} - V_{BB}) + [z_v(C_{i-1} + C_{i+1}) + z_l C_i](V_{AB} - V_{AA}) - Z(V_{AB} + V_{BB}) \quad (4)$$

satisfies it (for $E_{i+1,i}$ a similar expression can be written), where V_{ij} are the nearest-neighbor pair interaction energies of ij atomic pairs, z_l is the lateral coordination number, and $Z = z_l + 2z_v$. E^0 , the saddle point energy, is independent of composition. It is easy to show that $E_{i,i+1}$ and $E_{i+1,i}$ energies can also be expressed in the following form:⁷

$$E_{i,i+1} = \hat{E}^0 - \alpha_i + \varepsilon_i, \quad (5)$$

$$E_{i+1,i} = \hat{E}^0 - \alpha_i - \varepsilon_i, \quad (6)$$

where \hat{E}^0 contains E^0 and all the concentration independent additional terms. Furthermore, α_i and ε_i are proportional to

$V_{AA} - V_{BB}$ and to the solid solution parameter, $V = V_{AB} - (V_{AA} + V_{BB})/2$, respectively,

$$\alpha_i = [z_v(C_{i-1} + C_{i+1} + C_i + C_{i+2}) + z_l(C_i + C_{i+1})] \frac{V_{AA} - V_{BB}}{2} \quad (7)$$

and

$$\varepsilon_i = [z_v(C_{i-1} + C_{i+1} - C_i - C_{i+2}) + z_l(C_i - C_{i+1})] V. \quad (8)$$

Since \hat{E}^0 is constant for a given system, and ε_i as well as α_i depend only on V and on $(V_{AA} - V_{BB})$, respectively, the only term which describes the phase-separation tendency is ε_i . Furthermore, in homogeneous systems ($C_i = C = \text{const} \forall i$) ε_i is obviously equal to zero, and α_i depends on the value of C . Consequently, α_i is responsible for the composition dependence of the jump frequency or the diffusion coefficient (see also Refs. 7 and 8) in a homogeneous alloy. For the sake of simplicity, in what follows $Z(V_{AA} - V_{BB})/kT$ will be denoted by m , which gives the “strength” of the composition dependence of the diffusion coefficient [or $m' = m \log_{10} e$ is the difference in orders of magnitude between the diffusion coefficients in pure A and B materials (Refs. 8)]. It is worth mentioning that in the frame of the model used in simulations of Refs. 1–3 for phase-separating systems $\hat{E}^0 - \alpha_i$ was always composition independent, i.e., $m = 0$ was assumed.

To investigate the interface shift, we have solved Eq. (1) numerically for an fcc structure. The input parameters were z_l , z_v , V , m' , T , and the initial composition distribution. For the description of the interface shift, we started from the following initial condition: on the left- and right-hand sides of the interface all the atomic planes were occupied only by A atoms ($C_i = 1$ for all i to left) as well as by B atoms ($C_i = 0$ for all i to right), respectively.

In order to avoid “finite effects,” a continuous boundary condition was applied, i.e., when the composition of the atomic planes at the either ends of the sample were changed by $\Delta C = 0.1 C_{sol}$ (C_{sol} is the solubility limit), ten pure A or B atomic planes were added to the sample. Therefore, if, e.g., there were 30 A and 30 B atomic planes initially ($C_1 = \dots = C_{30} = 1$, $C_{31} = \dots = C_{60} = 0$) and, e.g., the composition of the 60th plane changed from 0 to $0.1 C_{sol}$, ten pure B atomic planes were added to the end of sample ($C_{60} = 0.1 C_{sol}$, $C_{61} = \dots = C_{70} = 0$). Note that if the above condition was changed by decreasing ΔC the solution of Eq. (1) practically was not influenced but, due to the rapid “growth” of the sample, the calculations were significantly slowed down.

The position of the interface was determined by the plane with the composition 0.5 (it can obviously lie between two atomic planes). After determining this position (p), its logarithm versus the logarithm of the time ($\log p \propto \log t$) was plotted. Fitting a straight line to the data, its slope gave the power of the function describing the shift of the interface (it will be called *kinetic exponent* and will be denoted by k_c). Obviously for parabolic interface shift $k_c = 0.5$.

Since we wanted to demonstrate the effects of the composition dependence of diffusion coefficients as well as the

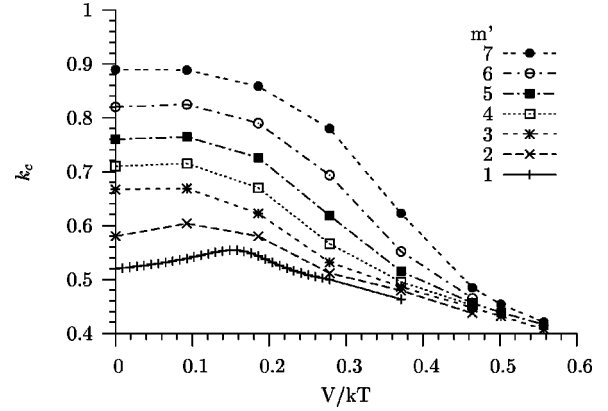


FIG. 1. Kinetic exponent vs V/kT for different m' values. For small m' values there is a small maximum on the curves. Increasing m' at a fixed V/kT , k_c always increases, leading to a deviation from the parabolic law.

phase-separation tendency on the kinetics of the interface shift, the parameters m' and V (or V/kT) were changed during the calculations. (In one case—in order to show the influence of the orientation—we also changed the values of z_l and z_v).

In the first case the direction of diffusion was (111), i.e., $z_l = 6$ and $z_v = 3$. The parameters m' and V/kT were varied from 1 to 7 and from 0 to 0.46 (or V from 0 to 0.05 eV at $T = 1250$ K), respectively. Figure 1 shows the initial values of the kinetic exponent, k_c (obtained by fitting to the interval corresponding to dissolution of the first five planes), versus V/kT for different m' values. It can be seen that k_c is almost constant and, as is expected, is very close to 0.5 for small m' (the discussion of the small deviations from the “pure” parabolic growth will be given below). At the same time, the deviation from the square-root kinetics increases with increasing m' for a fixed value of V/kT .

For the illustration of the interface shift Fig. 2 shows the position (and the shape) of the interface at different times for $m' = 1, V/kT = 0.28$ and $m' = 7, V/kT = 0$, respectively. It can be seen that in the first case the profiles are situated equidistantly with a square-root time scale, whereas in the second case—using the same time scale—the distances between the curves increase with time, indicating the deviation from the parabolic law (in this case the value of k_c was 0.88).

The deviation from the parabolic law is a real “nanoeffect,” because after dissolving a certain number of layers (long time or macroscopic limit), the interface shift returns to the parabolic behavior independently of the input parameters (see Fig. 3).

For the investigation of the influence of orientation we also carried out calculations for $z_l = 4$ and $z_v = 4$. Since the main tendencies were the same as those obtained for the previous orientation (only the value of k_c was changed slightly), these results will not be shown in the discussions.

In order to understand the character of the curves in Fig. 1, first one should consider the well-known Cahn-Hilliard form of the Fick’s second equation^{7,9} (for composition dependent D)

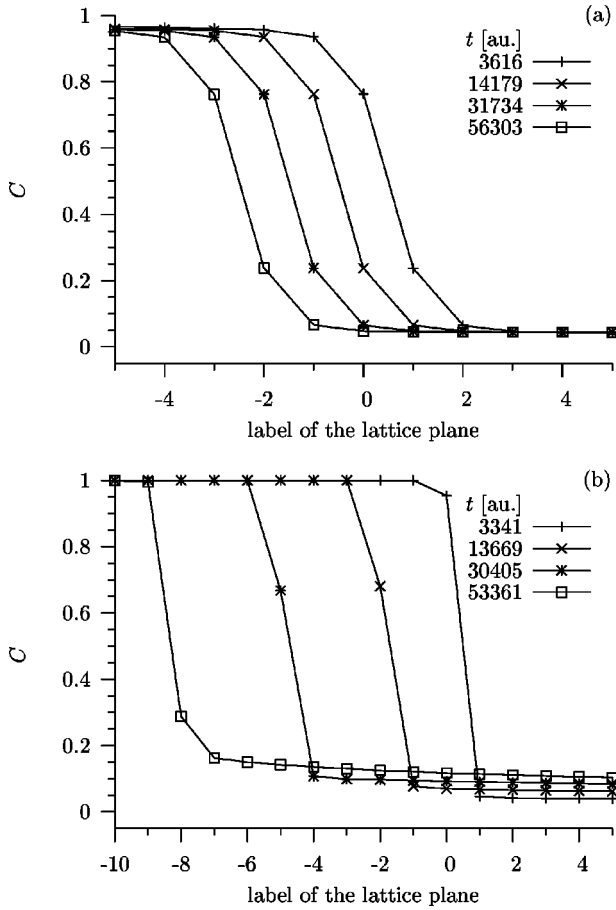


FIG. 2. Position of the interface at different times for (a) $m' = 1$, $V/kT = 0.28$ and (b) $m' = 7$, $V/kT = 0$. It can be seen that, using a square-root time scale, in (a) the profiles are situated equidistantly, whereas in (b) there is a deviation from the parabolic law. (Note that only some atomic layers around the interface are shown in the figure.)

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[\frac{D}{\Omega} \left(\frac{\partial C}{\partial x} - \frac{2\kappa}{f_0''} \frac{\partial^3 C}{\partial x^3} \right) \right], \quad (9)$$

where Ω is the atomic volume. D is the diffusion coefficient related to the jump frequency by the relation $D = z_v d^2 \Gamma_i \Theta$ (here d is the interplanar space in direction of diffusion and Θ is the thermodynamic factor),⁷ κ is the gradient energy coefficient, f_0'' is the second derivative (by composition) of the free energy. Furthermore,⁹

$$\frac{\kappa}{f_0''} = \frac{z_v d^2 V}{-2ZV + \frac{kT}{C(1-C)}} = \frac{z_v d^2 V/kT}{-2ZV/kT + \frac{1}{C(1-C)}}. \quad (10)$$

In Eq. (9) the input parameters, in principle, can be concentration dependent. Note that Eq. (9) can be obtained from the discrete equations if $\varepsilon_i/kT \ll 1$, and if the diffusion length is longer than $(10-100)d$ (see Refs. 7 and 8).

If the second term in Eq. (9) is negligible, this expression is just the traditional Fick's second equation, from which—

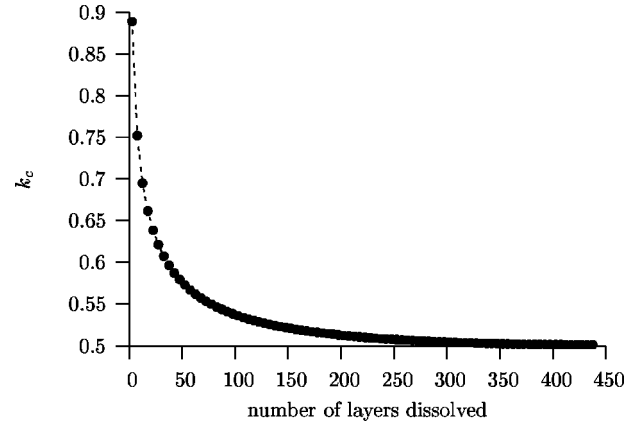


FIG. 3. Change of k_c during dissolution ($m' = 7$, $V/kT = 0.09$). The more the number of layers dissolved, the closer the value of k_c is to 0.5.

the boundary conditions allow the application of the Boltzmann transformation (e.g., if the “finite effects” are negligible) with $\lambda = x/t^{1/2}$ —it is clear that the shift of a plane with constant concentration should be proportional to the square root of the time ($k_c = 0.5$) even for composition dependent D .

On the other hand, if the first term is negligible in Eq. (9), the transformation can be done with $\lambda = x/t^{1/4}$. Therefore, in this case k_c should be equal to 1/4. Thus k_c can be less than 1/2 for high V/kT as can be seen in Fig. 1.

As was already mentioned above, the curves in Fig. 1 are not monotonic (especially for small m'), they have a maximum. The reason of this character is that κ/f_0'' changes its sign at a certain value of V/kT . In our case this change takes place at $V/kT = 0.16$ and the maximum of the curve for $m' = 1$ is just here. Note that for higher m' the maximum is less pronounced and shifted to the lower values of V/kT . This behavior cannot be explained by considerations based on the continuum equations alone, but can be obtained from an atomistic approach (valid on nanoscale as well) only. Indeed—according to Eq. (9) and Eq. (10)—the maximum should be situated at the same V/kT value for strongly concentration dependent input parameters as for $m' = 0$, i.e., the position of the maximum should be independent of m' .

As we have seen above, already the effect of the V/kT parameter on the maximum of the k_c curves cannot be fully accounted for from a continuum description. This is even more valid for the general effect of m' on the kinetic exponent. Indeed, as can be seen in Fig. 1 for $V/kT = 0$, the kinetic exponent increases with increasing m' . This means that the continuum and discrete atomic equations do not give the same results at the length/time scale (nanoscale) investigated (see also Refs. 4 and 8).

Since our equations are deterministic, they do not account for the possible fluctuations (stochastic behavior), which could be especially important on nanoscale. On the basis of our previous results on the linear shift of sharp interface in ideal binary systems¹⁰—where these effects have also been investigated by Monte Carlo simulations and it has been

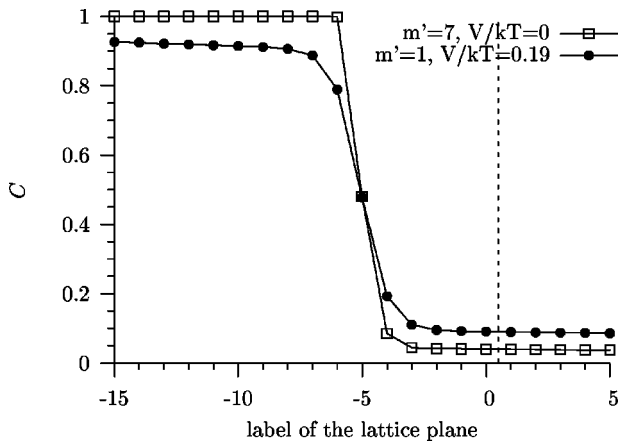


FIG. 4. Sharpness of the interface for two different cases. The dashed line shows the initial position of the interface.

shown that they do not influence the kinetics of the shift—we expect that these conclusions apply for this case as well.

For the further analysis of the character of the curves, it is worth studying the influence of m' and V/kT as well on the abruptness of the interface. It is known from previous works^{4,10} that in completely miscible systems ($V/kT=0$) the originally sharp interface can remain sharp⁴ or the originally wide interface can become sharper^{10,11} if the parameter m' is large enough. A similar statement is valid for the parameter V/kT for $m'=0$: larger V/kT results in sharper interface. Regarding the combined effect of V/kT and m' , we find that if m' is large enough the interface could be even sharper than for a relatively strong phase-separation tendency (see Fig. 4).

Since for sharper interface the curvature of the composition profile (proportional to the third derivative) is higher, the effect of the gradient energy corrections [see, e.g., the second term in Eq. (9)] is also more important. This is why for larger m' the “compensation role” of this term is stronger as well. This means, e.g., for $m'=3$ the kinetic exponent changes by 0.22 in the range 0–0.46 of V/kT ; whereas for $m'=7$ this change is equal to 0.41.

According to the discussions above, Fig. 1 and Fig. 2 reflect an interplay of two effects: (i) the change of k_c due to the gradient energy effects scaled by V [and included, e.g., in the continuum equation (9) as well] and (ii) the change of k_c due to the diffusion asymmetry measured by m' [and can only be obtained from the discrete atomic equations (1)]. This latter nanoeffect—as was shown in Ref. 4 and can be seen from Fig. 3—should diminish for long diffusion distances/times.

For the illustration of the importance of the above statements, it is worth considering typical values for V and m' . For example, at those temperatures, where the diffusion coefficient is large enough to produce nanoscale diffusion already after several hours, m' can be between 4 (in Cu-Ni or Si-Ge systems at about 700 K) and 7.3 (for Mo-V system at about 1050 K).¹⁰ On the other hand, the value of V can lie typically between 0 and 0.05 eV. For example, at 750 K: for Cu-Ag system $m' \cong 1.5$, $V/kT=0.49$,¹ for Cu-Fe system $m' \cong 6$, $V/kT=0.55$,² for Ni-Ag system $m' \cong 5$, $V/kT=0.82$ (Ref. 3), and for Ni-Au system $m' \cong 6$, $V/kT=0.36$. Thus one can conclude that there exist binary systems in which the deviation from the parabolic law can be observed experimentally as well on nanoscale.

We have shown from computer simulations that the shift of a chemically sharp interface (in a phase-separation binary AB system) can deviate from the parabolic law on nanoscale. The deviation depends on the strength of the composition dependence of the diffusion coefficient (parameter m') and the phase-separation tendency (parameter V/kT). For small values of V/kT with increasing m' the kinetic exponent k_c can even approach 1. On the other hand, increasing V/kT decreases this deviation and, e.g., for small m' values $k_c < 0.5$ can also be obtained for $V/kT > 0.4$. It is illustrated that the above deviations can be experimentally observed in certain binary systems at nanoscale.

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