

Parabolic vs Linear Interface Shift on the Nanoscale

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It was shown very recently that diffusion nonlinearity, caused by the strong composition dependence of diffusion coefficients, can lead to surprising effects on the nanoscale: a nonparabolic shift of interfaces (both in ideal and phase separating systems) and sharpening of an initially diffuse interface in ideal systems. Some of these can not be interpreted even qualitatively from Fick's classic equations. For instance, the nonparabolic shift of an interface at the very beginning is a consequence of the violation of Fick's first equation on the nanoscale, and the transition from this to the classic parabolic behavior depends on the strength of the nonlinearity and the value of the solid solution parameter V (proportional to the heat of mixing). Experimental and theoretical efforts to explore the above phenomena are summarized in this paper.

1. Introduction

Diffusion in nanostructures presents challenging features even if the role of structural defects (dislocations, phase or grain boundaries) can be neglected. This can be the case for diffusion in amorphous materials or in epitaxial, highly ideal thin films or multilayers, where diffusion along short circuits can be ignored, and "only" fundamental difficulties, related to nanoscale effects, arise. For example, the continuum approach cannot be automatically applied,^[1,2] and there is also a gradient energy correction to the driving force for diffusion. This correction becomes important if large changes in the concentration take place along distances comparable with the atomic jump distance, a , and results in an additional term in the atomic flux proportional to the third derivative of the concentration. It was shown recently by our group^[1-15] that these effects can lead to unusual phenomena, especially if there is a strong nonlinearity in the problem, i.e., if the diffusion coefficient has strong concentration dependence.

2. Basic Equations

To have a general expression for the atomic fluxes, valid also on the nanoscale, one has to choose a proper microscopic model. Let us start from a set of deterministic kinetic equations,^[1,2,4,5,16] obtained from Martin's model,^[17] in which the effect of the driving forces can be generally described by the ε_i/kT parameter present in the expression of atomic fluxes between the i th and $(i+1)$ th atomic layers, perpendicular to the x -axis;

$$\begin{aligned} J_{i,i+1} &= z_v[\Gamma_{i,i+1}c_i(1-c_{i+1}) - \Gamma_{i+1,i}c_{i+1}(1-c_i)] \\ &= z_v\Gamma_i\{c_i(1-c_{i+1})\exp(-\varepsilon_i/kT) - c_{i+1}(1-c_i)\exp(\varepsilon_i/kT)\} \end{aligned} \quad (\text{Eq 1})$$

In this exchange model $\Gamma_{i,i+1}$ is the probability per unit time that an A atom in layer i exchanges its position with a B atom in the layer $i+1$. z_v is the vertical coordination number, and c_i denotes the atomic fraction of A atoms on plane i . It is usually assumed^[1,2,4,5,16] that the jump frequencies have Arrhenius-type temperature dependence:

$$\begin{aligned} \Gamma_{i,i+1} &= \mu_o \exp[-E_{i,i+1}/kT] = \Gamma_i \exp[(-\varepsilon_i)/kT] \\ \Gamma_{i+1,i} &= \mu_o \exp[-E_{i+1,i}/kT] = \Gamma_i \exp[(\varepsilon_i)/kT] \end{aligned} \quad (\text{Eq 2})$$

with

$$\Gamma_i = \mu_o \exp[-(E^o - \alpha_i)/kT] = \Gamma_o \exp[\alpha_i/kT] \quad (\text{Eq 3})$$

where μ_o denotes the attempt frequency, k is the Boltzmann constant, T is the absolute temperature, and $E_{i,i+1} = E^o - \alpha_i + \varepsilon_i$ and $E_{i+1,i} = E^o - \alpha_i - \varepsilon_i$ are the activation barriers (E^o is a composition-independent constant including saddle point energy as well), which must be chosen to fulfill the condition of detailed balance under steady state ($J_{i,i+1} = J_{i+1,i} = \partial c_i / \partial t = 0$). There are many choices of $E_{i,i+1}$, which fulfill this condition.^[17] For instance, the following choices:

$$\alpha_i = [z_v(c_{i-1} + c_{i+1} + c_i + c_{i+2}) + z_l(c_i + c_{i+1})](V_{AA} - V_{BB})/2 \quad (\text{Eq 4})$$

$$\varepsilon_i = [z_v(c_{i-1} + c_{i+1} - c_i - c_{i+2}) + z_l(c_i - c_{i+1})]V \quad (\text{Eq 5})$$

satisfy it,^[1,2] where $V_{ij} (<0)$ are the nearest neighbor pair interaction energies of ij atomic pairs, z_l is the lateral coordination number, $z = 2z_v + z_l$, and $V = V_{AB} - (V_{AA} + V_{BB})/2$ is the solid-solution parameter proportional to the heat of mixing. For phase separating systems $V > 0$. The parameter $M = mkT/2Z$ determines the strength of the composition dependence of the transition rates^[6] in a homogeneous alloy. It can be estimated, e.g., from the nearest neighbor pair interaction energies of ij atomic pairs, V_{ij} , as

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$M = (V_{AA} - V_{BB})/2$, or it can be deduced from the composition dependence of the diffusion coefficients^[8]: $D(c) = D(0)\exp(mc)$. For example, m is about 10 for the copper-nickel system and about 16 for the molybdenum-vanadium system. Previous work^[5,10,11] has found that a parameter m' can be defined as $m' = m \log_{10} e$, and this parameter describes the composition dependence of the diffusion coefficient. For the copper-nickel system with an m of 10, m' is about 4.5, which indicates a variation of the diffusion coefficient across the composition range to be about 7 orders of magnitude.

From the rearrangement of Eq 1:

$$j = aJ_{i,i+1}/\Omega \\ = (D/a\Omega)\{2c_i c_{i+1} \sinh(\varepsilon_i/kT) - c_{i+1} \exp(\varepsilon_i/kT) + c_i \exp(-\varepsilon_i/kT)\} \quad (\text{Eq 6})$$

can be obtained,^[7] where the notation $D = z_v a^2 \Gamma_i$ for the diffusion coefficient has been introduced and Ω is the atomic volume.

It should be noted that according to Eq 4, in general (i.e., in an inhomogeneous system) $\alpha_i = M[c + (a/2)\partial^2 c/\partial x^2]$ in Γ_i or D . According to this, the diffusion coefficient is not only an (exponential) function of the composition, but depends on the second (or even on the fourth or higher) derivative as well; this can be important for a large composition discontinuity (i.e., at the very beginning of the diffusional intermixing).

It is important to emphasize that relation Eq 6 (or Eq 1) is the general form of the expression of atomic fluxes and is valid also on the nanoscale. From this one can get the well-known Fick first equation by making a Taylor series expansion of the composition up to the first order and for negligible driving forces ($\varepsilon_i \cong 0$)^[1,2,4]:

$$j = -(D/\Omega) \text{grad } c \quad (\text{Eq 7})$$

Furthermore it can be shown that for $\varepsilon_i/kT \ll 1$, using the relation $[-c_{i-1} - 3c_{i+1} + 3c_i + c_{i+2}] = a^3 \partial^3 c/\partial x^3$ obtained from the Taylor expansion of composition up to the third order and neglecting the second derivatives of composition in writing $2c(1-c) \cong [c_i(1-c_{i+1}) + c_{i+1}(1-c_i)]$, Eq 6 leads to the classic Cahn-Hilliard type equation.^[1,2,4]

3. Results of Simulations and Experiments

3.1 Homogenization Starts with the Shift of the Interface

It was obtained from simulations in Ref 8 that in molybdenum/vanadium multilayers, because of the strong concentration dependence of $D_{Mo} = D_V = D$ the interface between the molybdenum and vanadium remains sharp with width of the order of atomic dimensions and shifts as a whole as long as the component with small D has not been consumed (Fig. 1). It can also be seen that the diffusion is very asymmetrical: there is a fast dissolution and diffusion of molybdenum into vanadium, but there is no diffusion of vanadium into molybdenum. This behavior, as illustrated in Fig. 2, was indeed observed in amorphous silicon/germanium system by the Auger depth profiling tech-

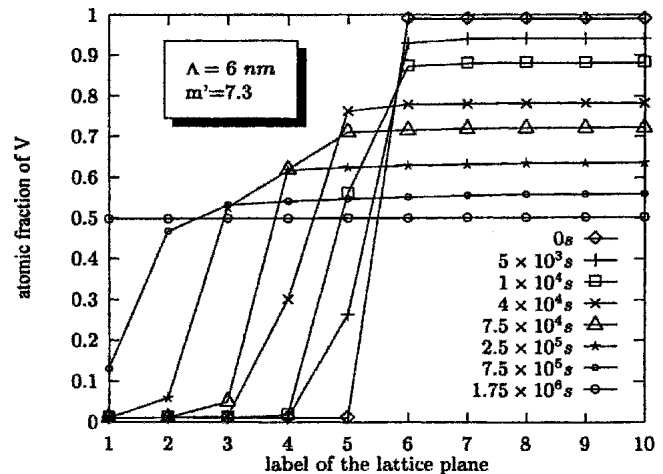


Fig. 1 Concentration distributions at different times in the molybdenum/vanadium system ($m' = 7.3$)^[8] at $T = 1053$ K and for $A = 6$ nm

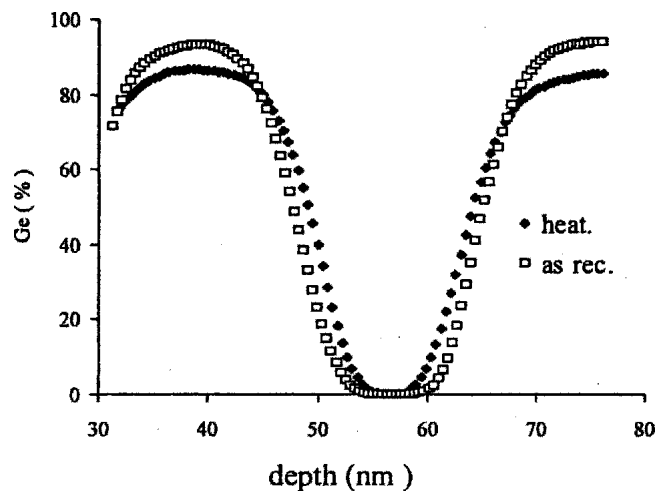


Fig. 2 Auger depth profiles for the as-received and annealed (680 K for 100 h) amorphous silicon/germanium multiplayer.^[9] The silicon content increases in germanium, and the silicon layer shrinks.

nique^[9] (in both systems $V \cong 0$). This phenomenon is surprising at first sight because, from a naïve view of the first Fick relation, one would expect flattening of the originally sharp interface. However, as it was illustrated in Ref 9, this behavior qualitatively follows implicitly from Fick's law if the strong composition dependence of D is taken into account (see also below). On the other hand, this classic relation cannot predict the correct kinetics of the interface shift, and only the simulations based on the atomistic approach gave results in accordance with the experiments.

3.2 Nonparabolic Shift of Sharp Interface in Ideal Systems

The nonlinearity (strong composition dependence of D) can lead to even more interesting results if we have dissolution of a thin film into a substrate.^[5] Figure 3 shows the

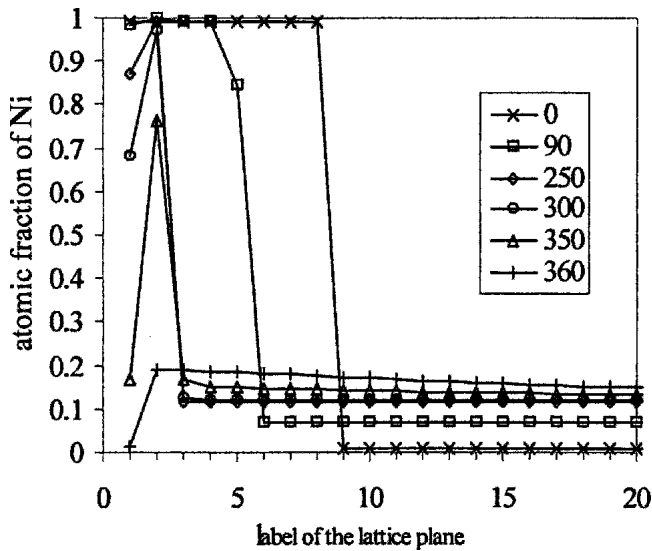


Fig. 3 Concentration profiles for nickel dissolution into 51 layers of copper-111 (of which only 12 are shown here) for different times (given in special units; Ref 5)

results of simulations carried out for nickel dissolution into copper (again the system is ideal, i.e., $V = 0$). It can be seen that the dissolution starts at the interfacial layer, and until this is consumed, the next layer remains complete. Thus the interface shifts step by step.

The layer-by-layer dissolution takes place until the moving “interface” reaches the nickel layer just before the last. Then, because of the driving force for surface segregation, the intermixing will be continued by the saturation of copper in the top layer, and the change in the second layer will be retarded according to the segregation isotherm. The layer-by-layer dissolution, if the substrate is semiinfinite and the diffusion coefficient depends strongly on the concentration,^[5] results in a periodic behavior as a function of time: each plane practically dissolves subsequently reproducing the same process. Therefore, the average value of v should be constant, independent of time, and the interface shifts linearly with time, which is in contrast to the parabolic law ($v \propto t^{-1/2}$), would be expected from a continuum model. Of course, after the dissolution of more and more layers one will have a transition to the parabolic dissolution. Obviously, this transition will depend on the value of m' .^[5] Figure 4(a) shows the position of the interface vs time, obtained from simulation for a semiinfinite copper-111 substrate with 100 atomic layers of nickel. Because of the periodicity, mentioned above, the curve has periodic oscillations around the fitted straight line, but the slope of the straight line is $1 \pm 8 \times 10^{-4}$, i.e., the average shift is linear. It was also shown by simulations that already for 1000 atomic layers and at longer times the dissolution obeys the parabolic law.^[2,5]

The above simulation result was confirmed^[5] by measuring the kinetics of the Auger signals of nickel and copper from the top of the eight-monolayer nickel. Figure 4(b) shows the final results for the average time evolution of the nickel thickness vs time for 679 K. It can be seen that n is a linear function of time up to the second layer.

The layered deterministic model properly takes care of the discreteness of the lattice, but the effect of fluctuations is not included. A more realistic description can be achieved with a detailed Monte-Carlo (MC) study. We have found from MC simulations,^[2,4] similar to the deterministic model, that the interface motion is proportional to time, in contrast to the square root dependence, expected from the continuum diffusion model. However, in contrast to the deterministic model, in the MC simulation the fluctuations led to a small broadening of the interface, and this results in a smearing out of the oscillations of the interface velocity. The interface preserves its shape, and in this way a nearly steady configuration is maintained during the dissolution and shift.

3.3 Nonparabolic Interface Shift in Phase Separating System

We have seen that the interface remained sharp on nanoscale and shifted linearly provided that the diffusion asymmetry was large (the diffusion was faster by several orders of magnitude in the substrate than in the deposit) in ideal systems. In phase separating systems, where the interface is sharp for chemical reasons (phase separation), previous computer simulations^[18-20] showed that the interface displacement was proportional to the square root of the time. However, in these simulations the composition dependence of the diffusivity (diffusion asymmetry) was neglected. Thus it was very plausible 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. In Ref 10 we have demonstrated by computer simulations (in fcc structure for 111 plane; $z_1 = 6$ and $z_v = 3$) how these parameters could influence the kinetics of the interface motion.

The position of the interface was fixed to the plane with the composition 0.5 (it can obviously lie between two atomic planes as well). After determining this position, the position logarithm vs the logarithm of time was plotted. Fitting a straight line to the data (which implies power law behavior: $y \propto t^{k_c}$), its slope gave the power of the function describing the shift of the interface coordinate (the slope is called the *kinetic exponent* and denoted by k_c). Obviously for a parabolic interface shift $k_c = 0.5$. Because we wanted to demonstrate the effects of the composition dependence of diffusion coefficients as well as the phase separation tendency on the kinetics of the interface shift, the parameters m' and V (or V/kT) were changed during the calculations.

Figure 5(a) shows the initial values of the kinetic exponent, k_c (obtained by fitting to the interval corresponding to the dissolution of the first five atomic planes) vs V/kT for different m' values. It can be seen that k_c is almost constant and, as was expected, k_c is very close to 0.5 for small m' (weak composition dependence of the diffusion coefficients). At the same time, the deviation from the square root kinetics increases with increasing m' for a fixed value of V/kT . The deviation from the parabolic law is again a real “nano-effect,” because after dissolving a certain number of

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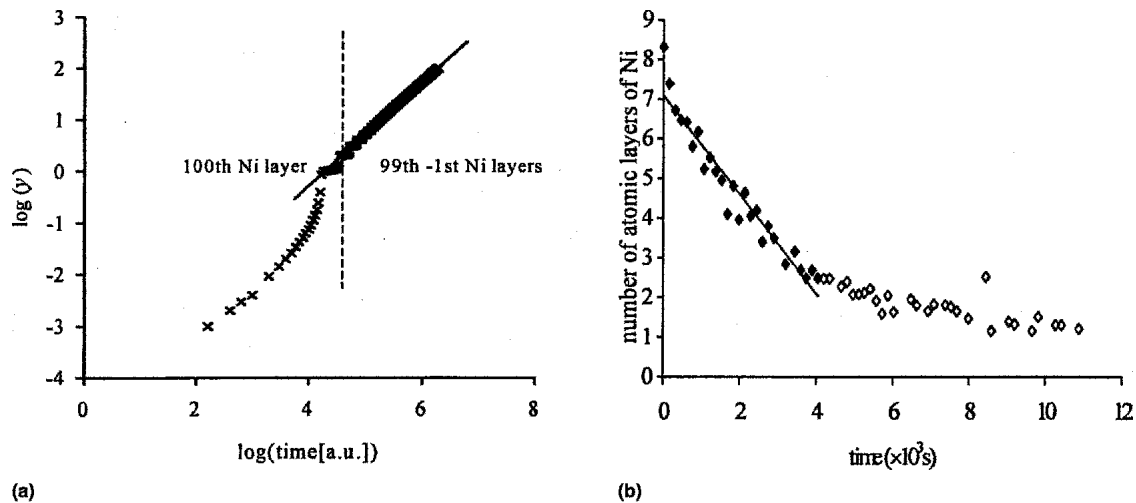


Fig. 4 (a) Position of the interface vs time for the dissolution of the 100 nickel layer into copper-111 substrate (see also the text). (b) Change of the nickel thickness at 679 K^[5]

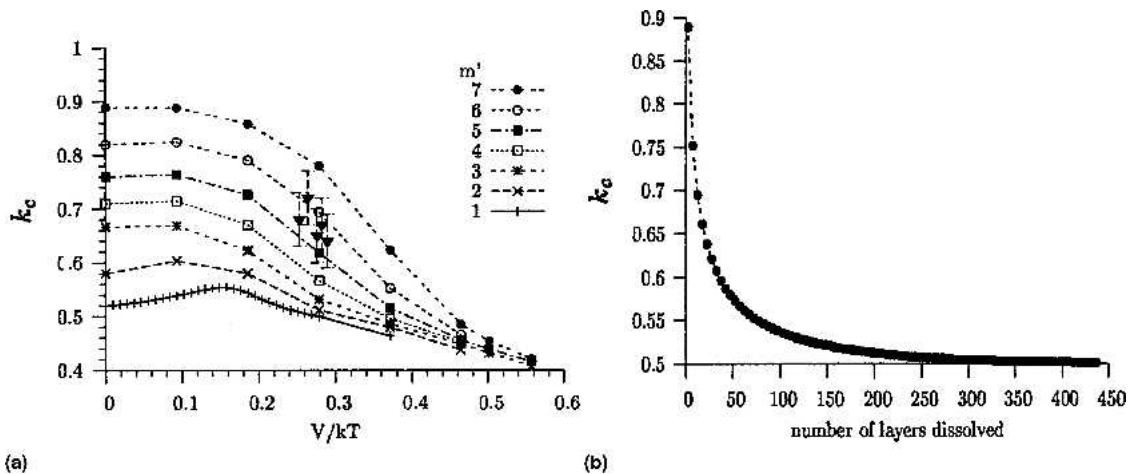


Fig. 5 (a) Calculated and experimental initial values of the kinetic exponent vs V/kT for different m' values (Ref 10 and 11, respectively). (b) Change of k_c during dissolution ($m' = 7$, $V/kT = 0.09$). The more layers that are dissolved, the closer the value of k_c to 0.5.

layers (long time or macroscopic limit), the interface shift returns to the parabolic behavior independently of the input parameters (Fig. 5b).

We have shown recently from ultraviolet photoelectron spectroscopy and x-ray photoelectron spectroscopy measurements^[11] that during the dissolution of a 3 nm thick nickel layer into single crystalline gold substrate, that the dissolution kinetics indeed deviates from the parabolic behavior, and the k_c values obtained were in very good agreement with those estimated from the m' and V/kT values (see Fig. 5a where points with error bars show the experimental results).

3.4 Sharpening of an Initially Diffuse Interface in Ideal Binary Systems

Another interesting feature obtained again by the same type of model calculations and also by MC technique (Ref

12) is that an initially wide A/B interface can become sharp on nanoscale even in an ideal system. Although such a process is obvious in an alloy with large miscibility gap (the metastable solid solution in the smeared interface region decomposes, and a sharp interface is formed), it is surprising at first sight in systems with complete mutual solubility because according to the macroscopic Fick's first law the direction of the atomic flux is always opposite to the direction of the concentration gradient. Indeed, for composition-independent D , the concentration profile will gradually decay, and only a flattening of the (sharp or broadened) interface, produced experimentally, is generally expected. However, there is already a plausible interpretation for the interface sharpening, if the composition dependence of D is also taken into account, from the continuum Fick's first law. If the concentration gradient is constant along the interface, the interface D is only D on which the absolute value of the atomic flux depends. Therefore the flux distribution follows

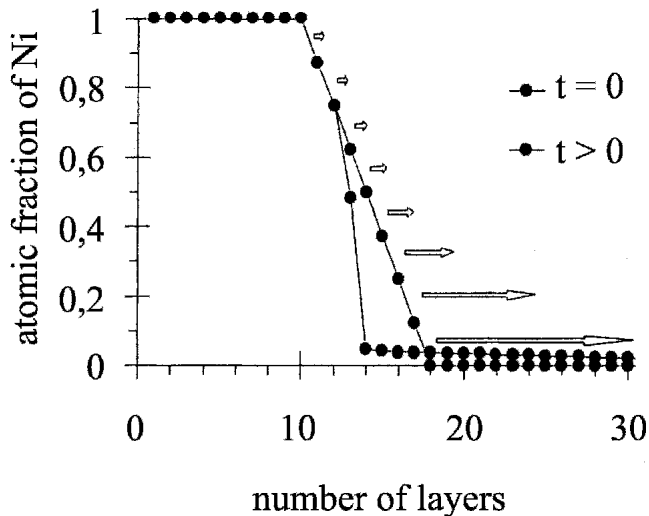


Fig. 6 Flux distribution and sharpening of an initially linear composition profile if the diffusion coefficient has strong composition dependence

the $D = D(c)$ function, and thus even the continuum flux equation is capable of describing some sharpening (Fig. 6).

Obviously at longer annealing times, as expected from general thermodynamics, homogenization should take place. Indeed, this is the case for the multilayer sample; although at the beginning, the process decreases the gradient by filling up of the copper layer with nickel (and not by flattening of the interface), the final state is the completely intermixed homogeneous alloy. For the case of semiinfinite geometry the first part of the intermixing (the initial sharpening and linear shift of the interface) will be extended to times under which the deposited film will be consumed. Of course for thick films, before reaching this stage, the kinetics of the dissolution will gradually change from linear to parabolic (as we have seen before), and this transition time will be determined by the “strength” of the concentration dependence of the diffusion coefficient, m' . For $m' = 0$ the “normal” intermixing with the formation of a symmetrical diffusion profile will take place, whereas with increasing m' the diffusion profile will be more and more asymmetrical, and finally the above discussed effects can be observed on nanoscale.

It is important to note that m' is inversely proportional to the temperature (see the text after Eq 5), and thus with decreasing temperature it is easy to reach those values for which the above nonlinear effects can be observed.

Using the synchrotron facility in Berlin (Bessy), we could show experimentally the interface sharpening in molybdenum/vanadium multilayer^[14] by high-angle x-ray diffraction measurements. The idea is that the high-angle satellites bring information about the sharpness of the interfaces (which were produced artificially diffuse), and during a special heat treatment at gradually increasing temperatures the change of the interface thickness can be determined. As is shown in Fig. 7 the interfaces became sharper.

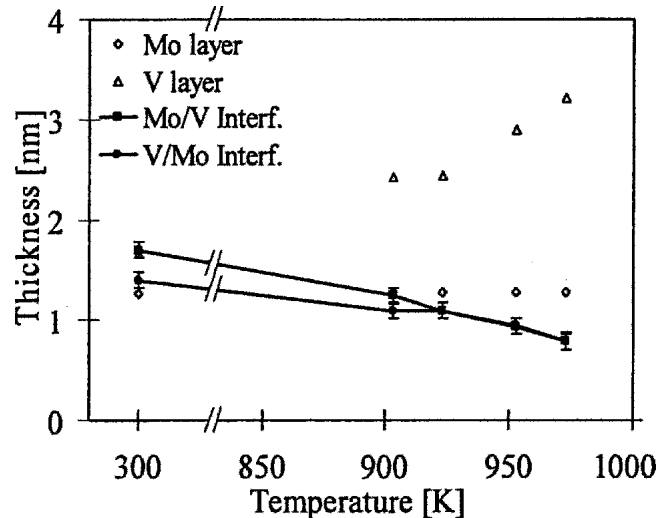


Fig. 7 Change of the thickness of the molybdenum/vanadium layers and the decrease of chemical sharpness the molybdenum/vanadium and vanadium/molybdenum interfaces^[14]

3.5 What Is the Characteristic Distance of the Transition from the Nonclassic (Nonparabolic) to the Classic (Parabolic) Behavior?

As we have seen above for ideal^[5] and phase separating systems^[10,11] the m' parameter (describing the composition dependence of the diffusion coefficient) and the solid-solution parameter (proportional to the heat of mixing), V , control the above transition. It was shown in Ref 15 that such a characteristic thickness of the diffusion zone, X_c , can be determined. At X_c the atomic flux in the faster B -rich β phase J_β ($D_\beta \gg D_\alpha$, where D_β and D_α denote the intrinsic diffusion coefficients in the β and the A -rich α phase, respectively) and the atomic flux across the α/β interface, J_I , are equal to each other. For $X < X_c$ the J_β flux will be larger than J_I , which in fact determines the diffusion permeability of the interface.^[15]

$$J_I = z_v \Gamma_i \Delta c \quad (\text{Eq 8})$$

Here $\Delta c = c_i - c_{i+1} = \langle c \rangle - c_\beta$. $\langle c \rangle$ denotes the time-averaged value of the composition just in the interface, c_i during a layer-by-layer dissolution mode: each atomic plane dissolves subsequently, the dissolution of the next plane began only after the complete dissolution of the previous one, reproducing the same process.^[5] Furthermore, c_β denotes the breaking point in the composition profile (for large V values it corresponds to the solubility limit),^[15] as is illustrated in Fig. 8. The idea of the derivation of a relation for X_c was simple: at very short times (small thicknesses of the diffusion zone) the finite permeability of the interface, determined by Eq 8, will control the process (and, e.g., assuming constant J_I , Stefan's law leads to a constant velocity for the interface shift, i.e., the shift of the interface is linear), whereas for longer times, because the composition gradient gradually decays, J_β will become less than J_I , and the diffusion will control the further thickening of the

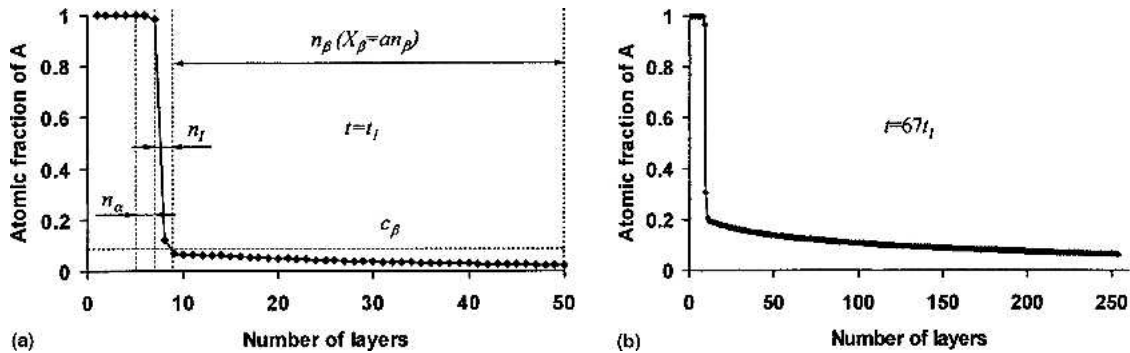


Fig. 8 Calculated composition profiles at $V/kT = 0.09 \cong 0$ (nearly ideal system) and $m = -16.11$ for two different running times (a) $t = t_1$ and (b) $t = 67t_1$. It can be seen that because of the large diffusion asymmetry (lml is large), the upper part of the interface remains sharp and shifts. The composition of the kink of the profile (denoted by c_β in the text) increases slightly with time. The division of the composition profile into three regions is illustrated in (a), and the composition of the plane belonging to the interface is denoted by c_i in the text.^[15]

diffusion zone. Thus for J_β the classic expression $J_\beta = -(D/\Omega)\text{grad } c \cong D_\beta c_\beta / X_\beta$ was used with $D_\beta = z_v a^2 \Gamma_o \exp(mc_\beta/2)$.

It has been shown (Ref 15) in that for a very asymmetric diffusion profile (which is the case here because of the strong composition dependence of D ; see also Fig. 8) $X_c \cong X_\beta$ and:

$$X_\beta/a = \{c_\beta/\Delta c\} \exp[(m/2)(c_\beta - \{z_v/Z + (z_1 + z_v) \langle c \rangle + c_\beta\}/Z)] \exp(\varepsilon_i/kT) \quad (\text{Eq 9})$$

Positive values of V (or ε_i) led to a decrease of X_c compared with the values obtained for the same m with $V = 0$.

Thus in Beke and Erdélyi^[15] a natural resolution for a long-standing paradox in diffusion has been offered. We have shown that the growth rate of the diffusion zone (reaction layer) should not go to infinity with decreasing time (as $1/\sqrt{t}$), just because the diffusion permeability of the interface (being sharp either because of the presence of a miscibility gap, because of the large diffusion asymmetry, or because there is an abrupt jump of the composition in the diffusion couple at the beginning) is finite. It was found that X_c , depending on the phase separation tendency and the diffusion asymmetry (measured by the strength of the composition dependence of the diffusion coefficients), lies between $0.05a$ and $450a$, illustrating that these effects are measurable on nanoscale.

3.6 On the Atomistic Meaning of the Interface Transfer Coefficient, K

To illustrate the importance of this question let us cite the last sentences of H. Schmalzried from the epilogue of his book,^[21] “We must remain aware, however, that the kinetic coefficients are ad hoc parameters, unless they can be derived from atomistic theory. . . . However, if the definition is correct and unique, one day we will have the unambiguous answer to the problem.”

We have seen above that J_1 has the form of Eq 8, following the phenomenological definition of $K_1 = K(c_e - c)$

(c and c_e denote the current and the equilibrium composition at the interface, respectively) and taking $c_e = \langle c \rangle$ and $c \cong c_\beta$. It was shown in Ref 15 that $K \cong z_v \Gamma_i$, i.e.,

$$K \cong v z_v \exp(-Q_K/kT) \quad (\text{Eq 10})$$

with $Q_K = E_o + z_1 V + m/2$. In fact, K is proportional to the jump frequency from the A-rich phase to the B-rich one. This is different from the jump frequency in the B-rich phase (where the jump frequencies are larger at the same temperature) just because these frequencies depend on the composition.

If there is an abrupt interface present at the very beginning of the intermixing, then the interface transfer controls the flux only until the gradients will be large enough to establish the diffusion flux J_β larger than J_1 . In fact the magnitude of the finite value of $J_1 \cong K$ gives the permeability of the interface and it is determined by the m and V/kT parameters. It is important to emphasize that this interpretation is forced by the demand that one would like to express the fluxes by the classic $J \sim -\text{grad } p$ form. In fact, the validity of Fick’s first equation gradually breaks down with decreasing diffusion distances, and, as we have seen above, the “improved” forms of the continuum expressions of the atomic fluxes higher order derivatives of the composition should appear. These should lead to a “slowing down” of the flux, and this can be taken into account by the treatment presented in Ref 15. Thus the $1/\sqrt{t}$ dependence of the rate of the shift will be violated on the nanoscale just because the classic continuum description fails and for strongly composition dependent jump frequencies (for large lml values) even a linear shift can be experimentally observed. Our results illustrate that the shift of the interface can be different from the parabolic behavior just because the permeability of the interface is finite, and this can already lead to measurable effects in the interface kinetics on the nanoscale. Thus, effects of other factors (like sluggish structural rearrangements in noncoherent interfaces, slow reaction) in making the atomic transfer more restrained should be additionally considered, but then an extra activation barrier

should be included into the atomistic model description, which was not the case in Ref 15.

4. Conclusions

It can be concluded that Fick's first law is less and less valid on the nanoscale (as the diffusion distance becomes more and more comparable with the atomic spacing). This can lead to surprising, measurable effects (interface sharpening, nonparabolic shift of interfaces) if the composition dependence of the diffusion coefficient is strong. The analysis of these effects leads to an atomic interpretation of the interface transfer coefficient K . K measures the interface permeability, which is always finite, and this offers a plausible resolution of the well-known diffusion paradox predicting a $1/\sqrt{t}$ dependence of the rate of the interface shift. Although it is almost exclusively accepted in the literature that linear growth kinetics is the result of interface reaction control, our results suggest that the linear or nonparabolic growth of a reaction layer on the nanoscale cannot be automatically interpreted by an interface reaction.

Acknowledgments

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