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PARABOLIC VERSUS LINEAR INTERFACE SHIFT ON THE NANOSCALE

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Abstract

It has been shown very recently that the diffusion non-linearity, due to the strong composition dependence of the diffusion coefficients, can lead to surprising effects on nanoscale: i) non parabolic shift of interfaces (both in ideal and phase separating systems), ii) sharpening of an initially diffuse interface in ideal systems. Some of these can not be interpreted even qualitatively from Fick's classical equations. For instance the non-parabolic shift of an interface at the very beginning is a consequence of the violation of the classical Fick's I. equation on the nanoscale and the transition from this to the classical parabolic behaviour depends on the strength of the non-linearity 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.

Keywords: Diffusion; Nano materials; Non-parabolic kinetics; Interface shift; Interface sharpening

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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, raise. For example the continuum approach can not 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 *a,* and results in an additional term in the atomic flux, proportional to the third derivative of the concentration. It was shown recently in our group [1-15], that these effects can lead to unusual phenomena especially if there is a strong non-linearity in the problem i.e. if the diffusion coefficient has a strong concentration dependence.

2 Basic equations

In order to have a general expression for the atomic fluxes, valid also on the nanaoscale, 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 the 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 the x-axis;

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

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 Arhennius-type temperature dependence:

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

with

$$\Gamma_i=\nu_o\exp[-(E^o-\alpha_i)/kT]=\Gamma_o\exp[\alpha_i/kT], \tag{3}$$

where ν_o denotes the attempt frequency, k the Boltzmann constant, T 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 fulfil this condition [17]. For instance the following choices

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

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

satisfy it [1,2], where $V_{ij}(<0)$ are the nearest neighbour pair interaction energies of *ij* atomic pairs, z_l is the lateral coordination number 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 neighbour pair interaction energies of *ij* atomic pairs, V_{ij}, as $M=(V_{AA}-V_{BB})/2$, or can be deduced from the composition dependence of the diffusion coefficients [8]: *D(c)=D(0)*exp(*mc*). For example *m* is about 10 as well as 16 in the Ni-Cu and Mo-V systems respectively, which corresponds to m'=mloge=4.5 as well as 7 orders of magnitude change in the whole composition range.

From the rearrangement of (1):

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

can be obtained [7], where the notation $D=z_va^2\Gamma_i$ for the diffusion coefficient has been introduced.

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

It is important to emphasize that relation (6) (or (1)) is the general form of the expression of atomic flues, valid also on the nanoscale. From this one can get the well-known Fick I 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]:

$$j=-(D/\Omega)\mathrm{grad}c. \tag{7}$$

Furthermore it can be shown that for $\varepsilon_i/kT<<1$ – and using the relation $[-c_{i-1}-3c_{i+1}+3c_i+c_{i+2}]=a^3\partial^3c/\partial x^3$, obtained from the Taylor expansion of composition *up to the third order* and neglect already the second derivatives of composition in writing $2c(1-c)\cong[c_i(1-c_{i+1})+c_{i+1}(1-c_i)]$ – (6) leads to the classical 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 [8] that in Mo/V multilayers, due to the strong concentration dependence of $D_{Mo}=D_V=D$ the interface between the Mo and V remains atomic sharp and shifts as a whole until 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

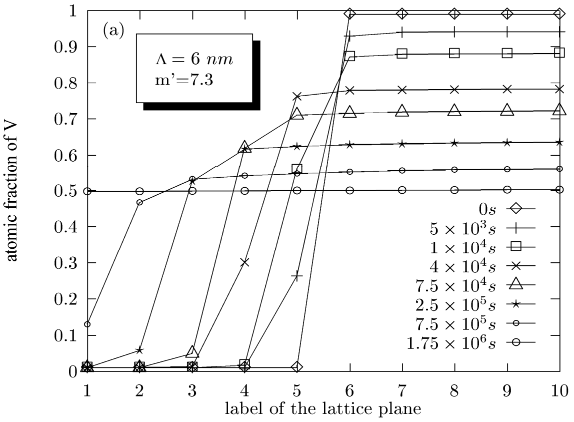

Figure 1: Concentration distributions at different times in Mo-V system (*m'* = 7.3) [8] at.

dissolution and diffusion of Mo into V, but there is no diffusion in Mo. This behaviour, as it is illustrated in Fig. 2, was indeed observed in amorphous Si/Ge system by Auger-depth profiling technique [9] (in both systems $V \cong 0$.). *This phenomena is surprising at first sight because form a naïve view of the Fick I relation one would expect flattening of the originally sharp interface.* However, as it was illustrated in [9], *this behaviour qualitatively follows already from this law as well if the strong composition dependence of D is taken into account (see also below). On the other hand this classical relation cannot predict a correct kinetics of the interface shift* and only the simulations based on the atomistic approach gave results in accordance with the experiments.

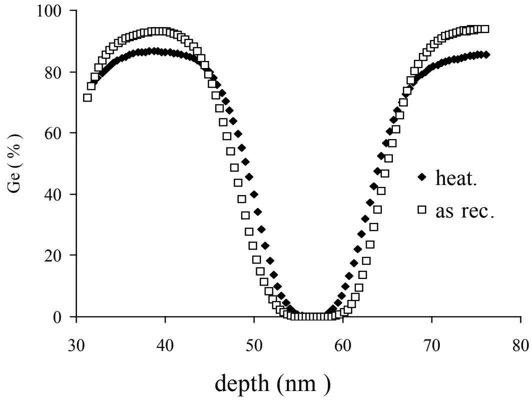

Figure 2: Auger depth profiles for the as-received and annealed (at 680 K for 100 h) amorphous Si/Ge multiplayer [9]. The Si content increases in Ge and the Si layer shrinks.

3.2. Non-parabolic shift of sharp interface in ideal systems

The non-linearity (strong composition dependence of D) can lead to even more interesting results if we have dissolution of a thin film into a substrate [5]. Fig. 3. shows the results of simulations carried out for Ni dissolution into Cu (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 not consumed, the next layer remains complete. Thus the interface shifts step by step. This layer-by-layer dissolution takes place until the moving "interface" reaches the Ni layer just before the last. Then, due to the driving force for surface segregation, the intermixing will be continued by the saturation of Cu 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 semi-infinite and the diffusion coefficient depends strongly on the concentration [5] – results in a

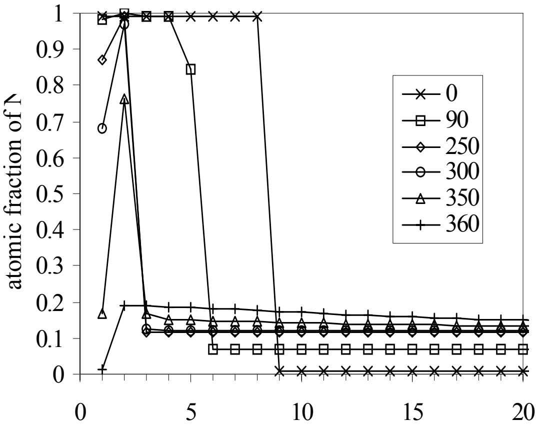

Figure 3: Concentration profiles for Ni dissolution into 51 layers of Cu(111) (of which only 12 is shown here) for different times (given in special units [5]).

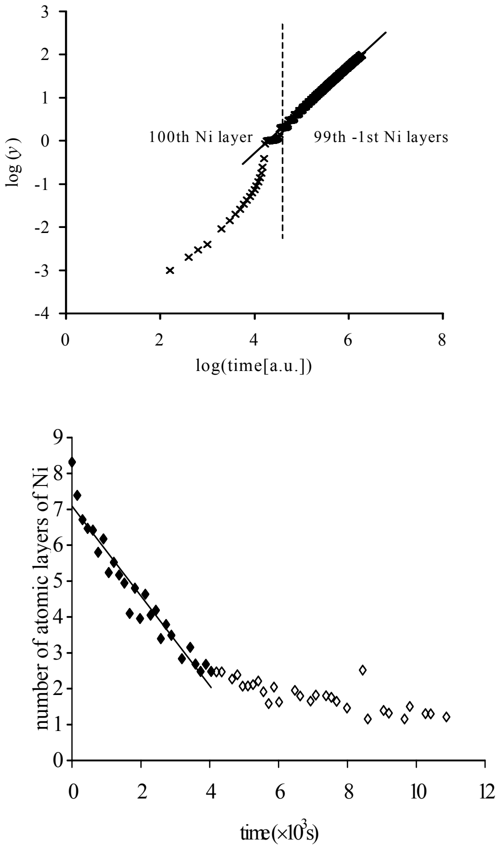

Figure 4:.a): Position of the interface versus time for the dissolution of 100 Ni layer into Cu(111) substrate (see also the text). b): Change of the Ni thickness at 679 K [5].

periodic behaviour 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]. Fig. 4a. shows the position of the interface versus time, obtained from simulation for a semi-infinite Cu(111) substrate with 100 atomic layers of Ni. Due to the periodicity, mentioned above, the curve has periodic oscillations around the straight line fitted, but the slope of the straight line is $1 \pm 8 \times 10^{-4}$, i.e. the average shift is indeed linear. It was also shown by simulations that already for 1000 atomic layers and at longer times the dissolution is indeed obeys the parabolic law [2,5].

The above simulation result was confirmed [5] by measuring the kinetics of the Auger signals of Ni and Cu from the top of the 8 monolayer Ni. Fig. 4b. shows the final results for the average time evolution of the Ni thickness versus time for 679 K. It can be seen that *n* is indeed 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 study. Indeed we have found from MC simulations [2,4], - similarly 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. Non-parabolic interface shift in phase separating system as well

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 due to chemical reasons (phase separation) - it was obtained from previous computer simulations [18-20] 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 [10] we have demonstrated by computer simulations (in fcc structure for 111 plane; z_l=6 and z_v=3) how these parameters could influence the kinetics of the interface motion.

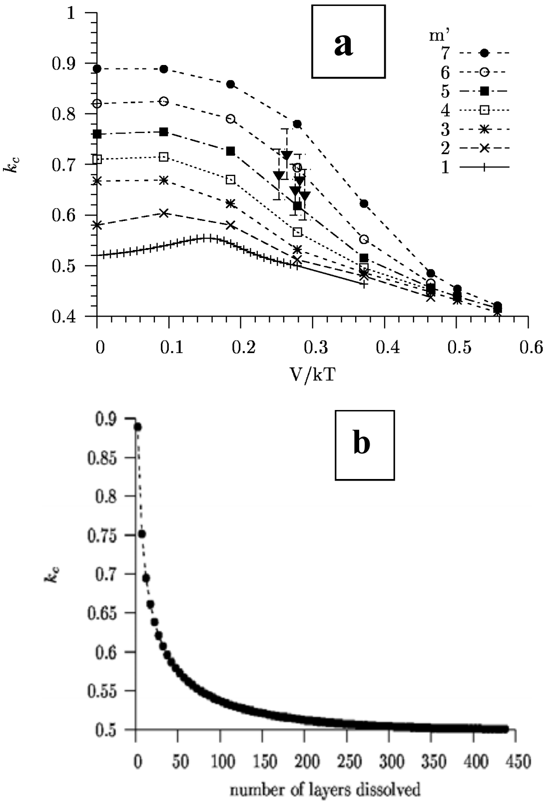

Figure 5: a): Calculated and the experimental initial values of the kinetic exponent versus *V/kT* for different m' values [10], and [11], respectively. b): Change of k_c during dissolution (*m'*=7, *V/kT*=0.09). The more layers are dissolved the closer the value of k_c to 0.5 is.

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, its logarithm versus the logarithm of the time was plotted. Fitting a straight line to the data (which implies power law behaviour: $y \propto t^{k_c}$), its slope gave the power of the function describing the shift of the interface (it is called *kinetic exponent* and 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 phase separation tendency on the kinetics of the interface shift, the parameters *m'* and *V* (or *V/kT*) were changed during the calculations.

Figure 5a 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) versus *V/kT* for different *m'* values. It can be seen that k_c is almost constant and, as it is expected, it is very close to 0.5 for small *m'* (week 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 layers (long time or macroscopic limit), the interface shift returns to the parabolic behaviour independently of the input parameters (see Fig. 5b).

We have shown recently from UPS and XPS measurements [11] that during the dissolution of a 3 nm thick Ni layer into single crystalline Au substrate, that the dissolution kinetics indeed deviates from the parabolic behaviour and the k_c values obtained were 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 Monte Carlo technique [12], is that an initially wide A/B interface can become sharp on nanoscale even in an ideal system. While 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 I 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 if D is also taken into account – from the continuum Fick I law. If the concentration gradient is constant along the interface it is only D on which the absolute value of the atomic flux depends. Therefore the 'flux distribution' follows the D=D(c) function and thus even the continuum flux equation is capable to describe some sharpening (see Fig. 6).

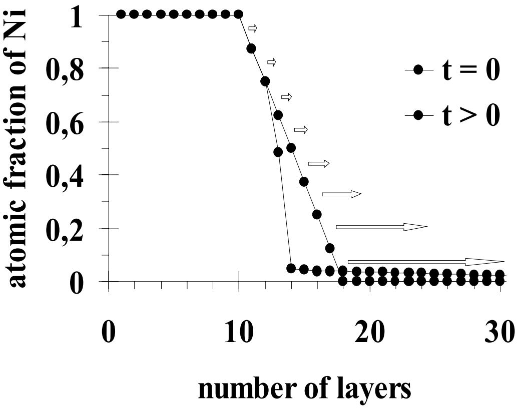

Figure 6: Flux distribution and sharpening of an initially linear composition profile if the diffusion coefficient has strong composition dependence.

Obviously at longer annealing times - as it is 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 Cu layer with Ni (and not by flattening of the interface), the final state is the completely intermixed homogeneous alloy. For the case of semi-infinite 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 consumes. 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, while 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 below eq. (5)), and thus with decreasing temperature it is easy to reach those values for which the above non-linear effects can be observed.

Using the synchrotron facility in Berlin (Bessy), we could show experimentally the interface sharpening in Mo/V 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 it is shown in Fig. 7 the interfaces indeed became sharper.

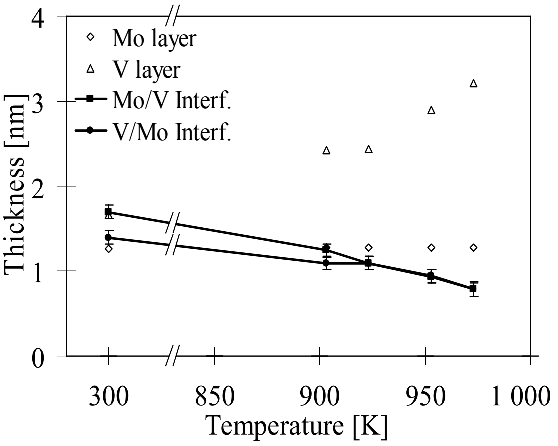

Figure 7: Change of the thicknesses of the Mo, V layers and the decrease of chemical sharpness the Mo/V and V/Mo interfaces [14].

3.5. What is the characteristic distance of the transition from the non-classical (non-parabolic) to the classical (parabolic) behaviour?

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. Indeed, it was shown in [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 ($D_\beta >> D_\alpha$, 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]:

$$J_I=z_v\Gamma_i\Delta c. \quad (8)$$

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

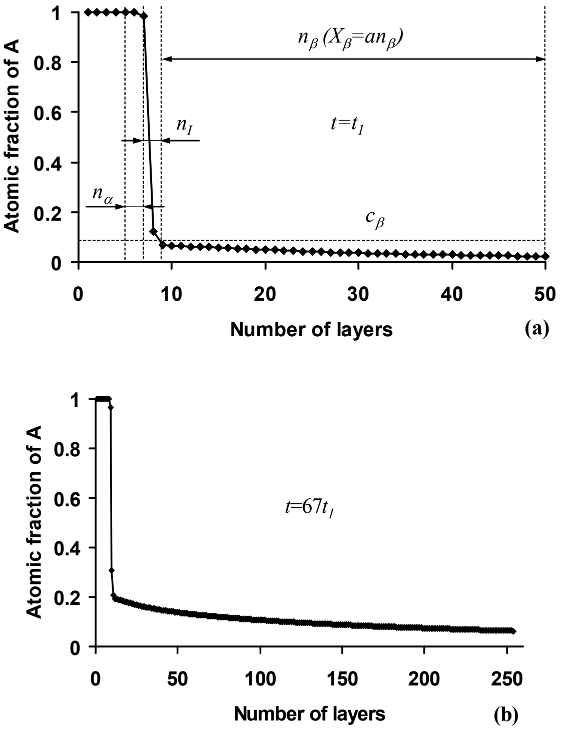

Figure 8: Calculated composition profiles at $V/kT=0{,}09\cong 0$ (nearly ideal system) and $m=-16{,}11$ for two different running times; a) $t=t_I$ and b) $t=67t_I$. It can be seen that, because of the large diffusion asymmetry ($|m|$ is large), the upper part of interface remains sharp and shifts. The composition at the kink of the profile (denoted by c_β in the text) slightly increases 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].

the complete dissolution of the pervious 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 it 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 (8), will control the process (and e.g. assuming constant J_I, the Stefan's law leads to a constant velocity for the interface shit, i.e. the shift of the interface is linear), while for longer times, because the composition gradient gradually decays, J_β will become less than J_I, and the diffusion controls the further thickening of the diffusion zone. Thus for J_β the classical expression $J_\beta=-(D/\Omega)\mathrm{grad}c \cong D_\beta c_\beta/X_\beta$ was used with $D_\beta=z_v a^2\Gamma_o \exp(mc_\beta/2)$.

Now it was obtained in [15] that for 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

$$X_\beta/a= =\{c_\beta/\Delta c\}\exp[(m/2)(c_\beta-\{z_v/Z+(z_l+z_v)(<c>+c_\beta\}/Z\})]\exp(\varepsilon_i/kT). \qquad (9)$$

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

Thus in [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, or 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 0.05*a* and 450*a*, illustrating that these effects are measurable on nanoscale.

3.6. On the atomistic meaning of the interface transfer coefficient, K.

In order 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_I has the form of (8) and following the phenomenological definition of K: $J_I=K(c_e-c)$ (c and c_e denote the current and the equilibrium composition at the interface, respectively) and taking $c_e=<c>$ and $c \cong c_\beta$, It was shown in [15] that $K \cong z_v\Gamma_i$, i.e.

$$K \cong \nu z_v \exp\left(-Q_K/kT\right), \qquad (10)$$

with $Q_K=E_o+z_lV+m/2$. 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_I. In fact the magnitude of the finite value of $J_I \cong K$ 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 classical $J\sim$ -gradρ form. In fact the validity of Fick's I equation gradually brakes down with decreasing diffusion distances and in , 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 such the treatment presented in [15]. Thus the $1/\sqrt{t}$ dependence of the rate of the shift will be violated on the nanoscale just because the classical continuum description fails and for strongly composition dependent jump frequencies (for large |m| values) even a linear shift can be experimentally observed. Our results, illustrate that the shift of the interface can be different from the parabolic behaviour 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 problems with sluggish structural rearrangements in non-coherent interfaces, slow reaction) in making the atomic transfer more restraint should be additionally considered, but then an extra activation barrier should be included into the atomistic model description, which was not the case in [15].

5 Conclusions

It can be concluded that the Fick I 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 surprising, measurable effects (interface sharpening, non parabolic shift of interfaces) if the composition dependence of the diffusion coefficient if 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 are the result of interface reaction control, our results suggest that the linear or non-parabolic growth of a reaction layer on the nanoscale, cannot be automatically interpreted by an interface reaction.*

Acknowledgments

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