diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

On the Validity of the Einstein's Relation and the Fick I Law on the Nanoscale

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Abstract

The classical Einstein's relation for the Brownian migration has a mesoscopic character and it deteriorates when e.g. diffusion in solids is considered in the nanoscale (i.e. if the diffusion distance is comparable with the atomic spacing). This behaviour is strongly related to the well-known diffusion paradox, predicting infinitely fast diffusion kinetics at short times (distances). Indeed, according to the Fick I law the gradient is infinite if there is a discontinuity in the density at the beginning (which is the case in typical interdiffusion measurements). In this paper these questions and a possible resolution of the above paradox will be discussed on the basis of results obtained in our Laboratory.

1. Introduction

The subject is very deeply related to the anniversaries, celebrated by the diffusion community this year. First the deviations from the parabolic behaviour in ideal systems (where Brownian migration of particles takes place) in fact are related to the problem of the validity of the Einstein's relation $<R^2> \sim t$; for $t \rightarrow 0$ this leads to absurd conclusion especially if one looks for the particle velocity [1]. This is, because the extrapolation of Einstein's mesoscopic description to the microscopic level can not work [1]. On the other hand, and as a consequence, the Fick I law will also be less and less valid in the nanoscale [2,3,4]. Examples of deviations from the behaviour predicted by the above mesoscopic or continuum relations in the nanoscale will be reviewed here on the basis of simulations carried out in the framework of deterministic kinetic equations based on the Martin's model [5] and experimental results obtained in our Laboratory.

2. Basic equations

Let us start from a set of deterministic kinetic equations [2,3,4,6,7], obtained from the Martin's model [5], 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;

$$J_{\mathrm{i,i+1}} = z_{\mathrm{v}}[\Gamma_{\mathrm{i,i+1}} c_{\mathrm{i}}(1-c_{\mathrm{i+1}}) - \Gamma_{\mathrm{i+1,i}}\, c_{\mathrm{i+1}}(1-c_{\mathrm{i}})] = \\ = z_v \Gamma_{\mathrm{i}}\{c_{\mathrm{i}}(1-c_{\mathrm{i+1}})\exp(-\varepsilon_i/kT) - c_{i+1}(1-c_{\mathrm{i}})\exp(\varepsilon_i/kT)\}. \tag{1}$$

In this exchange model $\Gamma_{\mathrm{i,i+1}}$ 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 [2,3,4,6,7] that the jump frequencies have Arhennius-type temperature dependence:

$$\Gamma_{\mathrm{i,i+1}} = \nu_0 \exp[-E_{i,i+1}/kT] = \Gamma_{\mathrm{i}} \exp[(-\varepsilon_{\mathrm{i}})/kT] \,, \\ \Gamma_{\mathrm{i+1,i}} = \nu_0 \exp[-E_{i+1,i}/kT] = \Gamma_{\mathrm{i}} \exp[(\varepsilon_{\mathrm{i}})/kT], \tag{2}$$

with

$$\Gamma_{\mathrm{i}} = \nu_0 \exp[-(E^o-\alpha_{\mathrm{i}})/kT] = \Gamma_0 \exp[\alpha_i/kT], \tag{3}$$

where ν_0 denotes the attempt frequency, k the Boltzmann constant, T the absolute temperature and $E_{i,\mathrm{i+1}}= E^o-\alpha_i+\varepsilon_{\mathrm{i}}$ 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 $E_{\mathrm{i,i+1}}$, which fulfil this condition [5]. For instance the following choices

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

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

satisfy it [2,3], where $V_{\mathrm{ij}}(<0)$ 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 [8] 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 and 16 in the Ni-Cu and Mo-V systems, respectively, which corresponds to m'=mloge=4-5 and 7 orders of magnitude change in the whole composition range.

In the above model, $\varepsilon_i \sim V$ and thus (5) measures the effect of the chemical driving force, $F=kT\text{grad}\{\ln\gamma\}$, where γ is the activity coefficient which can be expressed by V in the usual way ($kT\ln\gamma$ is the contribution to the chemical potential, μ, related to the deviation from ideal solution behaviour: $\ln\gamma \approx V$) [9]. Till now the effect of such driving force was only investigated on the nanoscale and only very recently some considerations were published on the effect of large stress (pressure) gradients [9, 10].

In general, in the presence of any driving force F=-grad u (u is the potential energy) the work done by the force over the distance between the atomic planes, a, is given by $2\varepsilon_i=Fa$. Indeed, the form of equations (2) corresponds to the usual energy diagram for diffusing atoms under the influence of a potential gradient $\Delta u/a$ (see e.g. Fig.1 in [11] or Fig.3.3 in [12]) and the change in the energy barrier of the jump is ε_i. In the following we will use ε_i in this, extended, sense.

From rearrangement of (1) one obtains [9]:

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

where the notation $D=z_v a^2\Gamma_i$ for the diffusion coefficient has been introduced. Now, it was also shown in [9] that the continuum form of (6), making a Taylor series expansion of the composition *up to the third order*, has the form

$$j = (z_v a\Gamma_i/\Omega)\{2\eta\sinh(\varepsilon_i/kT) - \beta[\exp(\varepsilon_i/kT) + \exp(-\varepsilon_i/kT)]\} \qquad (7)$$

where

$$\eta = c^2 - c - (1-c)(a/2)^2\partial^2 c/\partial x^2 - [(a/2)\partial c/\partial x]^2 + [\{(a/2)^2/2\}\partial^2 c/\partial x^2]^2$$

and

$$\beta = (a/2)\partial c/\partial x + [(a/2)^3/6]\partial^3 c/\partial x^3.$$

It should be noted that – according to (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. This final expression needs some comments: 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, 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 fluxs, 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* ($\varepsilon_i \cong 0$) [2,3,6]:

$$j = -(D/\Omega)\text{grad } c. \qquad (9)$$

On the other hand, for a homogeneous composition profile we have [9]

$$j = (z_v a\Gamma_i/\Omega)\{2\sinh(\varepsilon_i/kT)\}c(1-c). \qquad (10)$$

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*, neglecting 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 [2,3,6].

3. Results of simulations and experiments

3.1. Homogenization starts with the shift of the interface

It was obtained from simulations in [13] 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 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 [14] (in both systems $V\cong0.$). *This phenomenon is surprising at first sight because from a naïve view of the Fick I relation one would expect flattening of the originally sharp interface.* However, as it was illustrated in [13], *this behaviour qualitatively follows already from this law as well if the strong composition dependence of D is taken into account. On the other hand – as we will see below – 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.

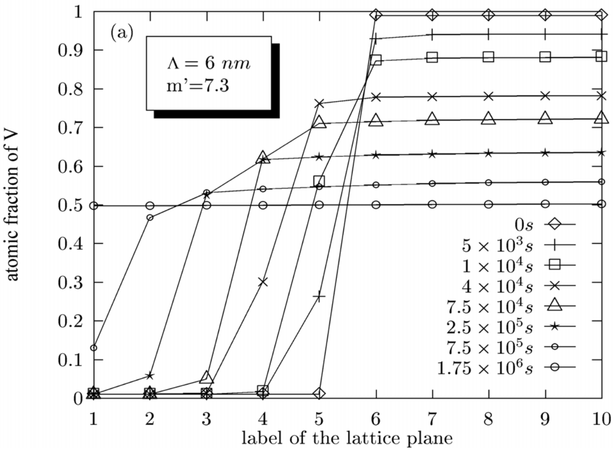

Fig.1: Concentration distributions at different times in Mo-V system (m' = 7.3) [13] at T = 1053 K and for Λ = 6 nm.

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 [7]. 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 [7] – results in a 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 ($v \propto t^{-1/2}$) to be expected from 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’ [7]. 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 $1 \pm 8\times10^{-4}$, 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 indeed obeys the parabolic law [3,7].

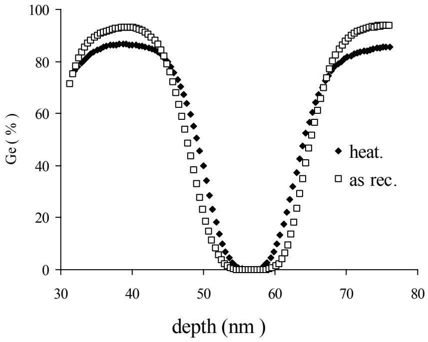

Fig. 2: Auger depth profiles for the as-received and annealed (at 680 K for 100 h) amorphous Si/Ge multiplayer [14]. The Si content increases in Ge and the Si layer shrinks.

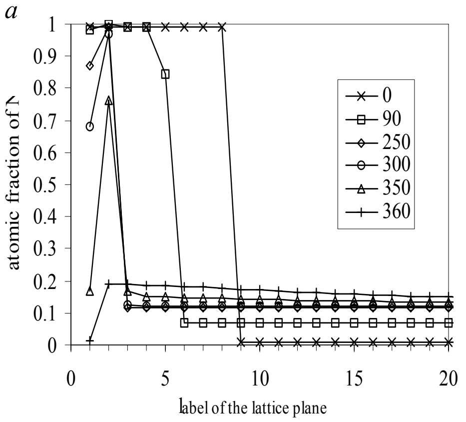

Fig.3: Concentration profiles for Ni dissolution into 51 layers of Cu(111) (of which only 20 are shown here) for different times (given in special units [7]).

Although the oscillating character of the dissolution – because of technical difficulties - could not be resolved experimentally in [7], the above simulation result was confirmed by measuring the kinetics of the Auger signals of Ni and Cu from the top of the 8 monolayers 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

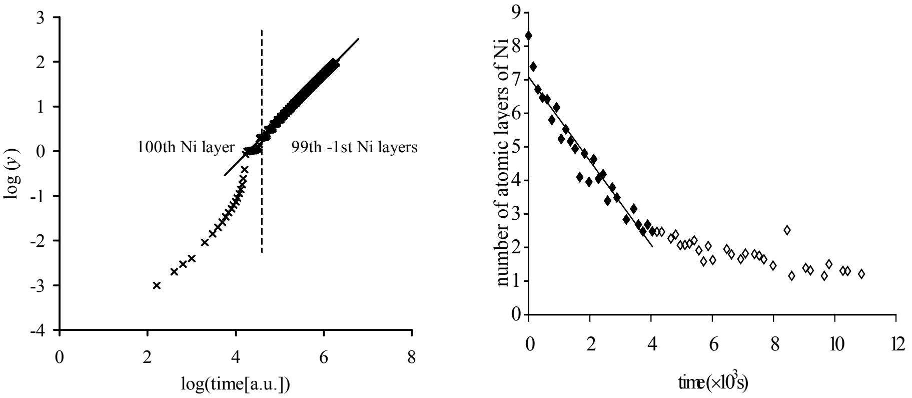

Fig.4:.a): Position of the interface versus time for the dissolution of 100 Ni layer into Cu(111) substrate (see also the text). b): Change of the Ni thickness at 679 K [7].

with a detailed Monte-Carlo study. Thus Monte-Carlo simulations were performed [3] with the same assumptions as in the layered deterministic model described above. The atomic arrangements around the moving interface (at 1000 K in Ni/Cu system [3,6]) can

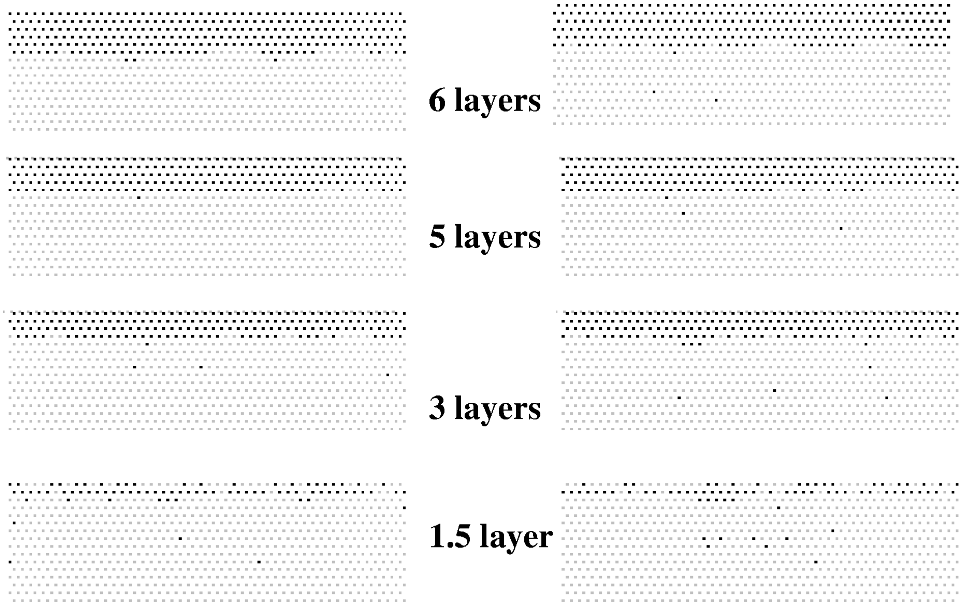

Fig.5. Cross-section of the sample at different times in two MC simulation runs [3]. The black and gray dots represent different atoms.

be seen on Fig.5. It can be seen that the width of the diffusion front extends to about two monolayers only. The top view of the dissolving interface [3,6] also revealed that the shape of the moving interface was stable.

In conclusion, after taking into account the fluctuations by MC simulation, we have found - 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

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 [15-17] 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 [18] 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.

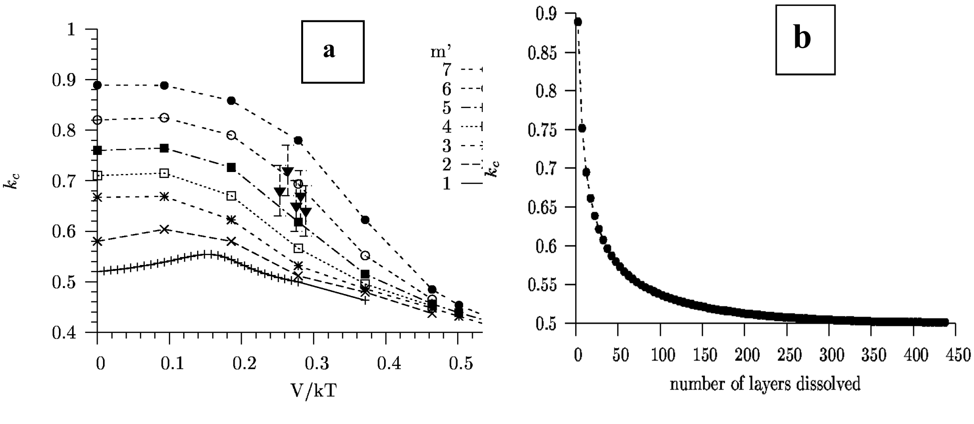

Fig. 6: a): Calculated and experimental initial values of the kinetic exponent versus V/kT for different m' values [18], and [19], respectively. b): Change of k_c during dissolution (m'=7, V/kT=0.09). The more layers are dissolved the closer is the value of k_c to 0.5.

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 6a 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' (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 layers (long time or macroscopic limit), the interface shift returns to the parabolic behaviour independently of the input parameters (see Fig. 6b).

On the basis of our previous results on the linear shift of a sharp interface in ideal binary systems, obtained by Monte Carlo simulations, it is expected that the above conclusions (drawn from the deterministic model) on the non-linear interface shift in phase separating systems remain valid including the fluctuations as well.

Thus Fig. 6 reflects an interplay of two effects: i) the change of k_c due to the gradient energy effects scaled by V/kT, ii) the change of k_c due to the diffusion asymmetry measured by m'. This latter nano-effect – similarly to the case of the shift of the interface in an ideal binary system – as it can be seen in Fig.6b, should diminish for long diffusion distances/times.

We have shown recently from UPS and XPS measurements [19] that during the dissolution of a 3 nm thick Ni layer into single crystalline Au substrate the dissolution kinetics indeed deviates from the parabolic behaviour and that the k_c values obtained were in very good agreement with those estimated from the m' and V/kT values (See Fig 6a 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 [20] 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.

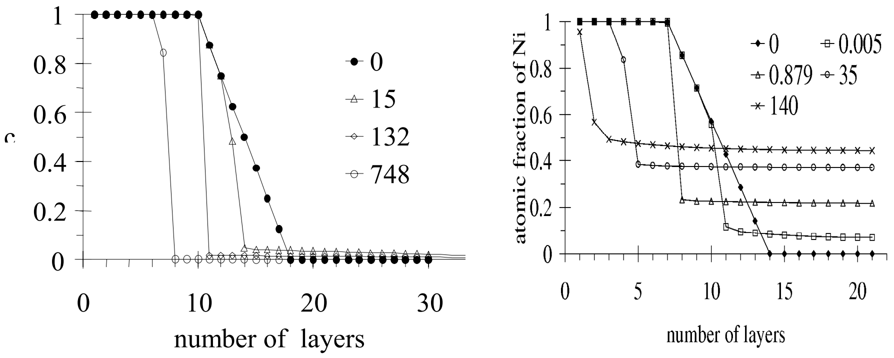

Fig.7: a): Sharpening of the initially linear concentration profile of Ni during interdiffusion with Cu [20]. b): Interface sharpening in an A/B multilayer system. (Time units shown must be multiplied by 10^6).

The problem is interesting not only from a fundamental point of view, but has technological importance as well. The Ni/Cu system for example is a model material for giant magnetoresistance (GMR), and in these systems the abruptness of the interface, and the knowledge of the possibilities for their improvement, is a key point. Furthermore, multilayers made of Mo and V (which is also an ideal binary system) are model materials for X-ray mirrors, or Si/Ge systems are basic semiconductor structures, where again the sharpness of the interfaces can be a very important requirement for many applications. It is also well known that in Si-Ge multilayers grown by MBE (molecular beam epitaxy) the Ge/Si interface, produced by the deposition of Si on Ge, is always less sharp (due to the mixing driven by the segregation of Ge during the growth) than the Si/Ge interface [21]. Thus this effect offers a way to improve the multilayers by sharpening the interface and to eliminate the asymmetry by annealing at moderate temperatures for relatively short times.

Figure 7a shows the dissolution of 10 atomic layers of A into a bulk B(111) semi-infinite substrate (fcc structure with T=1000 K, V_{AA}= -074 eV and V_{BB}= -058 eV i.e. for m'=9). It can be seen that at the beginning the initially wide interface becomes more and more sharp. After the sharpening process - as it is expected - the dissolution takes place in the same way as obtained for the shift of the initially sharp interface above: the interface remains atomic sharp and shifts step-by-step. The process clearly reflects the asymmetry of the diffusion: there is practically no diffusion in pure A and the diffusion is a very fast in pure B, leading to a gradual sharpening of the composition profile.

As it was already mentioned an initially abrupt interface can remain sharp during diffusional intermixing in multilayers as well (see Fig. 1). Therefore, it is an interesting question whether an originally wide interface can also become sharper in multilayers. The situation differs from the dissolution of a thin film into semi-infinite substrate: the most important effect is that Ni atoms can saturate the Cu layer, and this leads to the change of the diffusivity there. However, as Fig. 7b shows, the first part of the process is the interface sharpening in this case as well, after which the interface shifts step by step and just after consuming of the whole Ni layer complete homogenization takes place.

The above result gives also a plausible explanation for the apparent contradiction with the continuum Fick I law:

$$\boldsymbol{j} = - D \, \mathrm{grad}\, \rho \ , \tag{14}$$

where ρ is the density ($\rho = c/\Omega$). Since in ideal binary systems D has a positive value, for concentration-independent diffusion coefficients, this equation should lead to flattening of the interface. 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.

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 layer Cu 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 is 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, 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

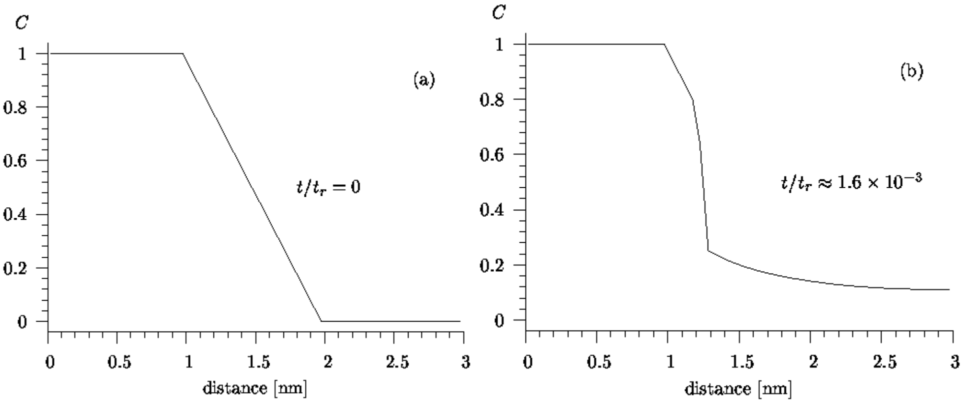

Fig. 8: Time evolution of the composition profile of Mo, at two different normalized times, when all the stress effects are ignored [22] (continuum approach).

below eq. (13)), and thus with decreasing temperature it is easy to reach those values for which the above non-linear effects can be observed. Indeed, as it can be checked from the known pair interaction energies or from the experimental *D* values, it is very general that at low temperatures m' is large enough that the sharpening of the interface is expected.

In order to take into account fluctuations (stochastic processes) we have performed computer calculations by Monte Carlo simulations as well, with the same input parameters, and they resulted in the same behaviour, i.e. the interface became sharp in this case as well. Although the above calculations were carried out for direct exchange mechanism of atoms, the conclusions are independent of the mechanism of diffusion and they are expected to be valid, e.g., for vacancy mechanism as well.

The role of stresses can be very important in processes on nanoscale. Thus the following question arises: how the stresses can influence the interface sharpening? This problem was addressed in [22].

Since, as we have seen, in principle the continuum flux equations are also capable to describe the sharpening, at least qualitatively and because the treatment of stress effects is not well developed for the discrete, atomistic kinetic approach [23], computer simulations were carried out in the framework of Stephenson's continuum model [24] for Mo-V multilayer system. Exponential composition dependent diffusion coefficients were used and it was assumed that $D_v=2D_{Mo}$. The modulation length of the multilayer was 6 nm, the initial `diffuseness' of the interface between the Mo and V layers was 1 nm. Fig. 8 shows the time evolution of the composition profile when all the stress effects are ignored, and beside the `filling-up' of V by Mo, there is indeed interface sharpening, similarly as observed above in the discrete model. The time scale is normalized; t_r is the stress relaxation time (corresponding to a simple Newtonian flow; $t_r=6\eta(1-\nu)/E$; η the viscosity, E the Young modulus and ν the Poisson ratio, respectively).

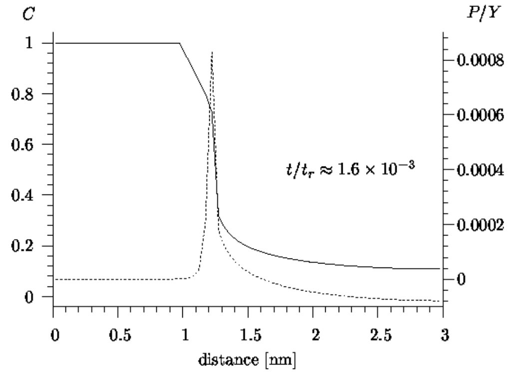

Fig.9: Time evolution of the composition profile of Mo at $t/t_r=1.6\text{x}10^{-3}$ when only the diffusional stress ($D_V/D_{Mo}=2$) is taken into account [22]. The initial state is the same as in Fig. 8. The dotted line is the normalized pressure (P/Y).

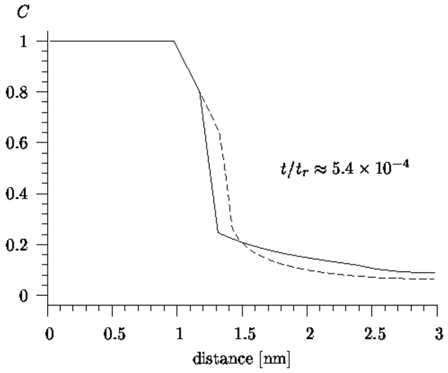

Fig.10: Demonstration of the influence of the strength of the diffusional stress: $D_V/D_{Mo}=2$ solid line, $D_V/D_{Mo}=10$ dashed line.

In Fig. 9 the sample initially is stress-free and during mixing a stress peek develops on the Mo side close to the interface and on the V side an almost homogeneous stress field (with opposite sign) appears. This is because the Mo atoms near the interface can easily dissolve into the V and diffuse there, whereas the V atoms practically cannot penetrate into the Mo (diffusion asymmetry due to the strong composition dependence of D_i).

In order to illustrate stronger stress effects, in Figure 10 the dashed line corresponds to a five times larger volume flow (the diffusion-induced stress is determined by the net volume flow caused by the differences of D_i). It can be seen that in the second case a slowing down effect is already visible, but the sharpening is still present (obviously with a slower rate). The slowing down effect is due to the presence of the pressure peak in the Mo side just at the sharp interface formed (see, e.g., Fig. 9). The pressure peak shifts with the moving interface and there is a steady state during which the height of the pressure peak is almost constant (it decreases only because of the finite size of the V layer). The presence of the stress gradient due to this peak just compensates the difference in the atomic fluxes, as it is expected from the LeChatelier-Braun principle: the diffusion-induced stresses compensate the effect generating them. This results in a slowing down of the intermixing and to the slowing down of its first stage (sharpening), but still the sharpening takes place.

Indeed, by X-ray measurements, using the synchrotron facility in Berlin (Bessy), in Mo/V multilayers we could show experimentally the interface sharpening [25]. 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. 11 the interfaces indeed became sharper.

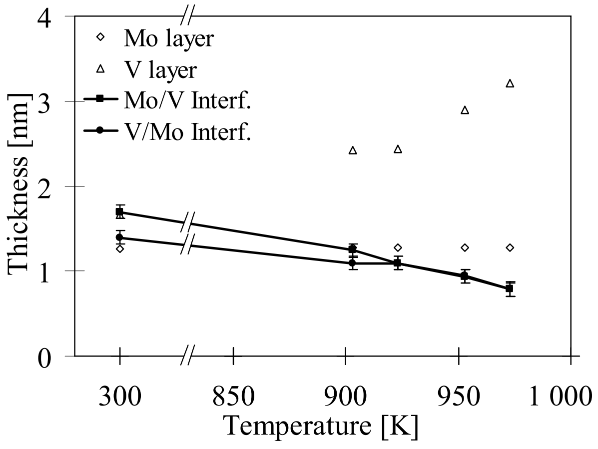

Fig.11: Change of the thicknesses of the Mo, V layers and the decrease of chemical sharpness of the Mo/V and V/Mo interfaces [25]

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 [7] and phase separating systems [10,14] 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 also shown in [26] 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_β>>D_α, 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 [26]:

$$J_I=z_v\Gamma_i\Delta c. \tag{15}$$

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 pervious one –, reproducing the same process [7]. Furthermore, c_β denotes the breaking point in the composition profile (for large V values it corresponds to the solubility limit) [26], as it is illustrated in Fig. 12. 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 (15), will control the process (and e.g. assuming constant J_I, the Stefan's law leads to a constant velocity for the interface shift, 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 $D_\beta=z_v a^2\Gamma_o\exp(mc_\beta/2)$.

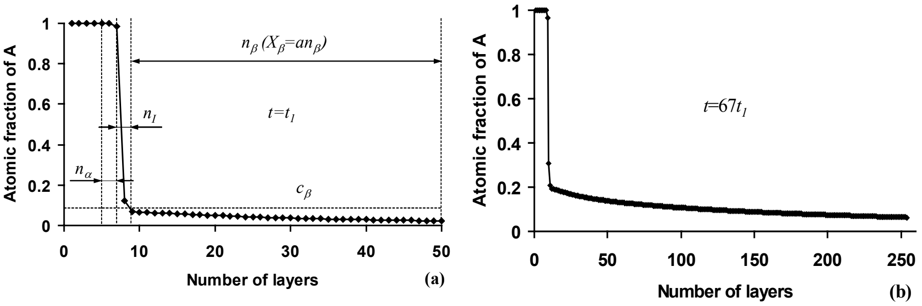

Fig.12: Calculated composition profiles at $V/kT=0{,}09\cong 0$ (nearly ideal system) and $m=-16{,}11$ for two different running times; a) $t=t_1$ and b) $t=67t_1$. It can be seen that, because of the large diffusion asymmetry ($|m|$ is large), the upper part of interface remains sharp and shifts. The 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 [26].

Now it was obtained in [26] that for a very asymmetric diffusion profile (which is the case here because of the strong composition dependence of D: see also Fig.1) $X_c\cong X_\beta$ and

$$X_\beta/a=\{c_\beta/\Delta c\}\exp[(m/2)(c_\beta-\{z_v/Z+(z_l+z_v)(\langle c\rangle+c_\beta\}/Z\})]\exp(\varepsilon_i/kT) \tag{16}$$

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. However, in that *case the values of* c_β *and* V *(*ε_i*) were coupled* via the well-know relation for the solubility limit:

$$c_\beta=(1-c_\beta)\exp[-ZV(1-2c_\beta)/kT]\cong\exp[-ZV/kT], \qquad (17)$$

and thus the decrease of c_β always compensated the role of the factor $\exp(\varepsilon_i/kT)$ in the right hand side of (8) (which is larger than 1 for positive ε_i).

Thus in [26] 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 $0.05a$ and $450a$, 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 [27]: “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 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 breakes down with decreasing diffusion distances and, as we have seen above, in 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 [26]. 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 [26].

4. Conclusions

It can be concluded that the Einstein's relation and the Fick I law are 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, 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.

5. Acknowledgments

This work has been supported by the following Hungarian grants: OTKA T-038125, F-043372, T-029162 and T-61253.

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