

# Stress effects on the kinetics of nanoscale diffusion processes

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Schmitz et al. [Acta Materialia 57 (2009) 2673] showed experimentally that stress effects significantly influence the intermixing rate but surprisingly the parabolic growth rate is preserved. The influence on the intermixing rate was interpreted as a switching between the Darken and Nernst–Planck regimes caused by the diffusion-induced stress. We analyse theoretically how the stress field shifts the system from the Darken to the Nernst–Planck regime, why stress relaxation is not observed even though expected and why the diffusion kinetics is not influenced by the developing stress field.

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During intermixing stress-free strain develops due to the net volume transport caused either by the difference in the intrinsic diffusion coefficients and/or the atomic volumes or by the abrupt change in the specific volumes if a new phase grows. As a consequence, stress develops within a certain characteristic time, leading to a steady state. The stress field may also relax within a characteristic time [1,2]. Due to terms proportional to the stress gradient in the atomic fluxes (see later Eq. (5)), the kinetics is obviously expected to differ from “pure diffusional” (Fickian or parabolic) type in the transient stages. In the steady state – when the stress field remains roughly the same – if it can be developed, the kinetics can remain Fickian, but the intermixing rates can still differ considerably from the stress-free case.

It was shown recently [3] that stress effects may have an easily measurable influence on the intermixing rate in nanostructures of spherical symmetry but surprisingly the diffusion kinetics remains parabolic in time. The influence on intermixing rate was interpreted as a switching between the Darken and Nernst–Planck regimes caused by the diffusion-induced stress.

Due to the complexity of the problem, however, until now there has been no systematic investigation into the effect of stresses on the kinetics.

In this communication we analyse theoretically – for the sake of simplicity, for a planar model geometry – how the stress field shifts the system from the Darken

to the Nernst–Planck regime. We show that the development of the Nernst–Planck regime is very fast, finished before any detectable shift of the interface, and that stress relaxation is not observed, although this would be expected since the time interval investigated was much longer than the stress relaxation time. We explain why the diffusion kinetics is not influenced by the developing stress field, even though this would be expected.

Stephenson – in a one-dimensional, isotropic  $n$  component system – derived a set of coupled differential equations for the description of the resultant stress development and stress relaxation by viscous flow, convective transport and composition evaluation [2,4]:

$$\frac{DP}{Dt} = -\frac{2E}{9(1-\nu)} \left[ \sum_{i=1}^n (\Omega_i \nabla j_i) + \frac{3}{4\eta} P \right], \quad (1)$$

$$\nabla v = -\sum_{i=1}^n (\Omega_i \nabla j_i) - \frac{3(1-2\nu)}{E} \frac{DP}{Dt}, \quad (2)$$

$$\frac{D\rho_i}{Dt} = -\nabla j_i, \quad i = 1, \dots, n \quad (3)$$

where  $D/Dt$  denotes the substantial derivative,  $v$  is the velocity field required to determine the spatial evolution of the system (Kirkendall velocity),  $P$  is the pressure,  $t$  is the time,  $E$  is Young’s modulus and  $\eta$  is the shear viscosity. Furthermore,  $\Omega_i$ ,  $\rho_i$  and  $j_i$  are the molar volume, the material density and the atomic flux of component  $i$ , respectively. The atomic fraction  $c_i$  instead of  $\rho_i$  is, however, more convenient for describing the evolution of the

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system. Using  $c_i = \rho_i / \rho$ , where  $\rho = \sum_{i=1}^n \rho_i$  is the total material density, Eq. (3) becomes

$$\frac{Dc_i}{Dt} = -\frac{1}{\rho} \nabla j_i + \frac{c_i}{\rho} \sum_{k=1}^n \nabla j_k, \quad i = 1, \dots, n \quad (4)$$

The atomic flux is given by

$$j_i = -\rho \left[ \Theta_i D_i^* \nabla c_i + D_i^* \frac{c_i \Omega_i}{RT} \nabla P \right], \quad i = 1, \dots, n \quad (5)$$

Here  $D_i^*$  is the tracer diffusion coefficient,  $R$  is the molar gas constant,  $T$  is the absolute temperature and  $\Theta_i$  is the thermodynamic factor. Note that in this paper we restrict ourselves to an ideal binary system, i.e.  $\Theta_i = 1$ .

Ignoring the stress effects, Stephenson's model is equivalent to Fick's model: ignoring the second term in Eqs. (5) and (3) is just Fick's second law. It is well known – according to Boltzmann's transformation [5,6] – that the solution of Fick's second equation results in the parabolic shift of planes with constant  $c_i$ :  $x_p^2 \propto t$  or  $x_p \propto \sqrt{t}$ . Thus Stephenson's model is suitable to investigate how the stress effects influence the diffusion kinetics, whether anomalous diffusion kinetics can be observed thanks to developing–relaxing stress fields.

Theoretically, the time evolution of the effect of diffusional stresses can be classified into four different stages [1,2,4]: (i)  $t < t_{QSS}$ , (ii)  $t_{QSS} < t < t_r$ , (iii)  $t \approx t_r$  and (iv)  $t \gg t_r$ . Here  $t_{QSS}$  is the time necessary to develop a steady-state stress distribution and  $t_r$  is the stress relaxation time of “pure” Newtonian flow determined by the second term in Eq. (1). Supposing that in a stressed sample the sum of the divergences of the atomic fluxes are negligible, Eq. (1) becomes

$$\frac{DP}{Dt} = -\frac{E}{6(1-\nu)\eta} P \quad (6)$$

and its solution is  $P = P_0 \exp \left[ -\frac{E}{6(1-\nu)\eta} t \right]$ , where  $P_0$  is the value of the pressure at the beginning of the observation of the relaxation. The relaxation time is the time necessary for the pressure (stress) to decrease to the  $e$ th part of its initial value:  $t_r = 6(1-\nu)\eta/E$ .

We solved the above system of Eqs. (1), (2), (4) and (5) numerically with input parameters corresponding to the Si/Ge binary system ( $i = A, B$  in Eqs. (1)–(5)). However, not to be restricted to one specific case, we varied the parameters across a wide range (the figures in bold correspond to the Si/Ge system [4,7–9]): Young's

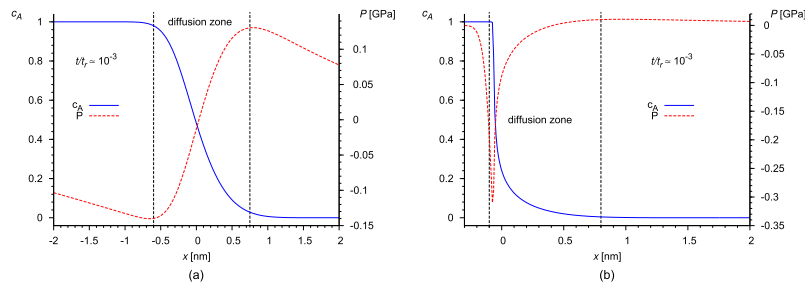
modulus was supposed to be composition-dependent  $E = c_A E_A + c_B E_B$ , where  $E_A = 18.5, \mathbf{185}$  and 1850 GPa,  $E_B = 10.3, \mathbf{103}, 1030, 16.3, \mathbf{163}$  and 1630 GPa; Poisson's ratio:  $\nu_A = \nu_B = 0.27$ ; viscosity:  $\eta_A = \eta_B = 2 \times 10^{12}, \mathbf{2 \times 10^{14}}$  and  $2 \times 10^{16}$  Pas; molar volumes:  $\Omega_A = 1.20 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ ,  $\Omega_B = 1.36 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ ;  $T = 700 \text{ K}$ . We supposed exponentially composition-dependent diffusion coefficients:  $D_i^* = D_i^0 \exp(-mc_A)$  and that  $D_A^0/D_B^0 = 1, \mathbf{2.4}$  and 10; moreover,  $m' = m \log_{10} e = 0, \mathbf{4}$  and 7 (where  $e$  is the base of natural logarithm and  $m'$  gives, in orders of magnitude, the ratios of the diffusion coefficients in the pure  $A$  and  $B$  matrixes; for instance,  $m' = 4$  means that the  $A$  atoms jumps 10,000 times faster in the  $A$  matrix than in the  $B$ ) [10].

Note that, using these parameter values,  $t_r$  falls in the range of  $(5-9) \times 10^6 \text{ s}$ .

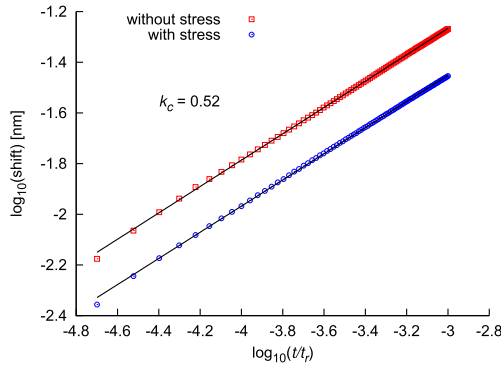
For the numerical work, all equations were transformed into the form containing only dimensionless variables and parameters:  $x' = x/l$ ;  $t' = tD/l^2$ ;  $P' = P/E$ ;  $D_i' = D_i/D$ ;  $\eta' = \eta D/E l^2$ ;  $\Omega_i' = \Omega$ ;  $\rho_i' = \rho_i \Omega$ . Here  $l$  is an arbitrary length comparable to the length-scale of the investigated problem,  $E$  is the average Young modulus,  $\Omega$  is the average atomic volume and  $D$  was chosen to be equal to  $D_A^0$ .

Figure 1a and b illustrates two typical, markedly different composition and pressure profiles calculated for stress-free initial conditions, i.e. only stresses of diffusion origin were taken into account. The results in Figure 1a were obtained by supposing a composition-independent diffusion coefficient, and accordingly the profiles evolve symmetrically, whereas in Figure 1b they are asymmetrical as a result of the strongly composition-dependent diffusion coefficient. If, for example, the diffusion is orders of magnitude faster in the  $B$  matrix than in  $A$ ,  $A$  atoms can hardly dissolve into the  $B$  matrix whereas  $B$  atoms can hardly penetrate into the  $A$  matrix. Consequently, a stress peak develops on the  $A$  side close to the interface and on the  $B$  side an almost homogeneous stress field (with opposite sign) appears. This sharp stress peak shifts with the moving interface.

In order to investigate the diffusion kinetics, the logarithm of the position of planes with constant composition ( $c_A = 0.1, 0.2, \dots, 0.9$ ) – Kirkendall planes – was plotted as a function of the logarithm of time:  $x_p \propto t^{k_c}$ , i.e.  $\log_{10} x_p \propto k_c \log_{10} t$ , where  $k_c$  is the kinetic exponent. If the kinetics is parabolic, the data points fit a straight line with a slope of 0.5. If, however, the kinetics is anomalous



**Figure 1.** Illustration of the time evolution of the composition (atomic fraction of component  $A$ ) and pressure ( $P$ ) profiles for (a) composition-independent ( $m' = 0$ ) and (b) strongly composition-dependent ( $m' = 7$ ) diffusion coefficients. Input parameters:  $m' = 0$ ,  $D_A^0/D_B^0 = 2.4$ ,  $E_A = 185 \text{ GPa}$ ,  $E_B = 103 \text{ GPa}$ ,  $\eta = 2 \times 10^{14}$ . The initial composition profile was rectangular, the sample was stress free and the interface was at 0 nm in both cases. Only the interface region is plotted.



**Figure 2.** Position of a plane with constant composition ( $c_A = 0.6$ ) as a function of time ( $x_p \propto t^{k_c}$ , i.e.  $\log_{10} x_p \propto k_c \log_{10} t$ ).  $D_A^0/D_B^0 = 10$ , and the other input parameters are the same as in Fig. 1a. As can be seen, the plane shift is around 0.1 nm but  $k_c$  is already close to 0.5. Moreover, the intercept is lower for the case when stress is considered; therefore the intermixing rate is slower.

alous, either the slope differs from 0.5 or the data points do not fit a straight line.

As an illustration, Figure 2 shows two examples, obtained by taking into account and neglecting stress. It can be seen that the data points fit a straight line with a slope of  $\approx 0.5$  very well. Not only in these cases but in all others,  $k_c$  was never smaller than 0.5 or larger than 0.55. Although the stress did not influence the value of  $k_c$  significantly, it slowed down the intermixing process (the intercept is lower).

As mentioned above, the time evolution of the effect of diffusional stresses can be classified into four different stages in symmetric systems (with  $m' = 0$ ): (i)  $t < t_{Qss}$ , (ii)  $t_{Qss} < t < t_r$ , (iii)  $t \approx t_r$  and (iv)  $t \gg t_r$ .

We observed that stage (i) is extremely short. Intermixing on the scale of a few tenths of a nanometer is enough to reach it, in agreement with the experimental observation of Schmitz et al. [3]. This means that a stress gradient in the central zone, where the composition falls, becomes quasi-stationary extremely quickly for composition-independent diffusivities ( $m' = 0$ , symmetric diffusion) as can be seen in Figure 1a. In the case of composition-dependent diffusivities ( $m' \neq 0$ , asymmetric diffusion), the stress profile also becomes quasi-stationary. In this case, however, two significant stress gradients develop at one of the borders of the diffusion zone (the left boundary in Fig. 1b). Thus, markedly different influences of the stress profiles on the atomic fluxes would be expected in stage (ii).

In stage (ii), in symmetric diffusion case, a slowing down of the intermixing is expected because the stationary stress gradient tends to diminish the volume flow itself. The larger the difference in the resultant volume flow – as measured by  $\Omega_A D_A - \Omega_B D_B$  – the more pronounced the effect. Note that stress gradients also develop outside of the diffusion zone (see Fig. 1a), but here their influences on the intermixing process are negligible.

For asymmetric diffusion, the situation is more complicated, since there are two stress gradients with opposite signs at one of the borders of the diffusion zone, as can be seen in Figure 1b. One of these stress gradients decreases and the other increases the resultant volume

flow. The computer simulations show that even in this case the stress effects slow down the intermixing process, i.e. the slowing down effect plays the dominant role.

As shown above, the stress effects have practically not affect on the value of the kinetic exponent  $k_c$ . To understand this, we must analyse the expression for the atomic currents. It is obvious that the diffusion kinetics may differ from the classical Fickian one only if the second term in Eq. (5) becomes dominant or at least comparable to the first one. For further analysis, we reformulate Eq. (5)

$$j_i = -\rho \Theta_i D_i^* \nabla c_i \left[ 1 + \frac{c_i \Omega_i}{RT \Theta_i} \frac{dP}{dc_i} \right] \quad (7)$$

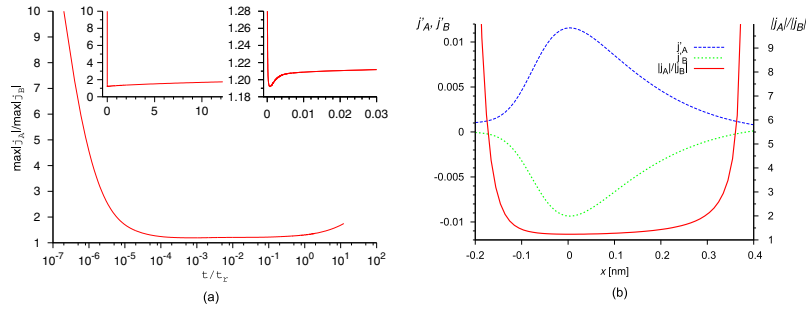
where  $dP/dc_i = \nabla P / \nabla c_i$ . Thus  $\frac{c_i \Omega_i}{RT \Theta_i} \frac{dP}{dc_i}$  has to be compared to unity to estimate the weight of the influence of the pressure gradient on the atomic flux.

Since the composition and the pressure fall in very similar length scales in the diffusion zone,  $dP/dc_i$  is practically constant. Its value can be estimated as  $c_i$  changes between 0 and 1 in the diffusion zone, and the change in pressure can be determined from the simulations. Therefore  $dc_i \approx \pm 1$ . Moreover,  $dP \approx 0.3$  GPa in Figure 1. Thus  $dP/dc_i \approx \pm 0.3$  GPa. Note that, depending on the input parameters, the absolute value of  $dP/dc_i$  falls in the range of 0.2 – 1 GPa.

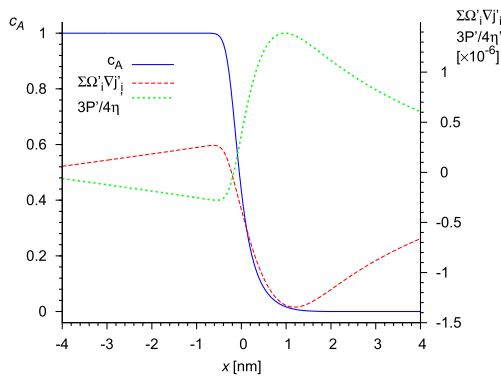
Substituting  $c_i = 0.5$  (as an average value in the diffusion zone),  $\Omega_i = 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ ,  $T = 700 \text{ K}$  and  $\Theta_i = 1$ , the absolute value of  $\frac{c_i \Omega_i}{RT \Theta_i} \frac{dP}{dc_i}$  is equal to approximately 0.17 – 0.86, and thus has an important influence on the atomic flux. This is why it slows down the intermixing. However, as the composition and the pressure fall in very similar length scales and their maxima hardly change, the  $dP/dc_i$  ratio is practically constant for a very long time, even for  $t > t_r$ . A multiplying constant in the flux, however, obviously does not change the kinetic exponent, but may result in the slowing down of the process.

Defining  $\Theta_i D_i^* \left[ 1 + \frac{c_i \Omega_i}{RT \Theta_i} \frac{dP}{dc_i} \right]$  as an effective diffusion coefficient  $D_i^{eff}$ , the expression (7) for the flux can be written in the form of  $j_i = -\rho D_i^{eff} \nabla c_i$ . This means that in our simulations one of the two atomic fluxes – that belonging to the slower diffusing ( $B$ ) atoms – is enhanced by a factor of 1.17 – 1.86, whereas the other – that belonging to the faster diffusing ( $A$ ) atoms – is diminished by a factor of 0.83 – 0.14. The respective enhancement and diminishing of the atomic fluxes practically eradicates their initial difference. This means that the system is in a Nernst–Planck regime. This can be seen at the beginning of the curve in Figure 3a, where the ratio of the atomic fluxes is plotted as a function of time. The fluxes depend, of course, on the position (see Fig. 3b); however, their ratio is practically constant in the diffusion zone. In Figure 3a, the ratio is calculated from the maximal absolute value of the fluxes, i.e.  $\max |j_A| / \max |j_B|$ . As can be seen, the ratio decreases extremely quickly from 10 to approximately 1.

In the Nernst–Planck limit  $D_A^{eff} \approx D_B^{eff} = \tilde{D}_{NP}$ , where  $\tilde{D}_{NP}$  is the interdiffusion coefficient in this limit, whereas in the Darken limit (no stress)  $D_A \approx \tilde{D}_D : \tilde{D}_D / \tilde{D}_{NP} \approx 1.2 - 7.1$  in our calculations. Note that this diminution is of the same order of magnitude as that observed



**Figure 3.** (a) Ratio of the atomic fluxes of the  $A$  and  $B$  atoms vs. the logarithm of time. The left inset shows the same curve but the time scale is linear, whereas the right inset shows the curve around its minimum. (b) Atomic fluxes (their dimensionless form:  $j'_i = j_i \Omega / D$ ) and their ratio in the diffusion zone at  $t/t_r \approx 1/5$  (see also the text). Input parameters:  $m' = 0$ ,  $D_A^0/D_B^0 = 10$ ,  $E_A = 1850$  GPa,  $E_B = 1630$  GPa,  $\eta = 2 \times 10^{12}$ .



**Figure 4.** Composition profile as well as the dimensionless form of  $\sum_i \Omega_i \nabla j_i$  and  $\frac{3}{4\eta}P$  from Eq. (1) at  $t/t_r \approx 2$ . This figure is similar at any  $t/t_r$  in the steady-state regime. For the input parameters, see Fig. 3.

in Ref. [3]. In that study  $\tilde{D}_D/\tilde{D}_{NP} \approx 2.6$ , where  $\tilde{D}_D$  and  $\tilde{D}_{NP}$  were calculated from the growth rate of the  $\Theta'$  phase in the Cu/Al/Cu as well as Al/Cu/Al triple layers.

In stages (iii) and (iv), significant stress relaxation is expected. However, surprisingly, we observe hardly any decrease in the stress levels, even though the investigated time interval was much longer than the stress relaxation time  $t_r$ . This is so because in our case  $\sum_i \Omega_i \nabla j_i$  is not negligible compared to  $\frac{3}{4\eta}P$  in Eq. (1) even in the steady-state regime, as can be seen, for example, in Figure 4. Consequently, the stress is not only relaxing but also always redeveloping, and the estimation of  $t_r$  from Eq. (6) leads to an unrealistic value.

We obtained that (i) stress effects do not have measurable effects on the kinetic coefficient of the interface shift, i.e. the parabolic growth rate is preserved independently of the developing stress field. However, the intermixing rate decreases. (ii) The stress field enhances the atomic flux of the slower component but diminishes the other. As a consequence, their initial difference is equilibrated, leading to the establishment of the Nernst–Planck regime. The development of the

Nernst–Planck regime is very fast, finishing before any detectable shift of the interface. These findings are in agreement with the results in Ref. [3]. (iii) This steady-state stage was long enough not to reach its relaxation in the limits of the time interval investigated, although it was much longer than the stress relaxation time. This is so because the composition profile is not static but changes quickly in the time scale of the stress relaxation belonging to a pure Newtonian flow and thus the stress redevelops continuously.

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