

Stress effects on the kinetics of nanoscale diffusion processes

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Abstract

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

Keywords: diffusion induced stress, diffusion kinetics, stress relaxation, Nernst-Planck regime

During intermixing stress free strain develops due to the net volume transport caused either by the difference in the intrinsic diffusion coefficients and/or atomic volumes or by the abrupt change of 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 relax also within a characteristic time. [1, 2] Due to terms proportional to the stress gradient in the atomic fluxes [see also later eq. (5)], the kinetics is obviously expected to differ from the “pure diffusional” (Fickian or parabolic) one in the transient stages. In steady state—when the stress field approximately does not change—, if it can be developed, the kinetics can remain Fickian, but the intermixing rates still can differ considerably from the stress free case.

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

Due to the complexity of the problem, however, until now there have not been systematic investigations about 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 Darken to 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 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 although it would be expected.

Stephenson—in 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: [4, 2]

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

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

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

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 η is the shear viscosity. Furthermore Ω_i , ρ_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 ρ_i is, however, more convenient for describing the evolution of the system. Using that $c_i = \rho_i/\rho$, where $\rho = \sum_{i=1}^n \rho_i$ is the total material density, eq. (3) becomes

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

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 the molar gas constant, T the absolute temperature and Θ_i the thermodynamic factor. Note that in this paper we restrict ourself 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 eq. (5), eq. (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 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 equations (1, 2, 4 and 5) numerically with input parameters corresponding to Si/Ge binary system [$i = A, B$ in eqs. (1)–(5)]. However, not to be restricted to one specific case, we varied the parameters in a wide range (the bold ones correspond to the Si/Ge[7, 4, 8, 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 2×10^{16} Pas; molar volumes: $\Omega_A = 1.20 \times 10^{-5}$ m³/mol, $\Omega_B = 1.36 \times 10^{-5}$ m³/mol; $T = 700$ K. We supposed exponentially composition dependent diffusion coefficients: $D_i^* = D_i^0 \exp(-m c_A)$ 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 $(5 - 9) \times 10^6$ 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, Ω is the average atomic volume and D was chosen to be equal to D_A^0 .

Figs. 1a and 1b illustrate 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 Fig. 1a were obtained by supposing composition independent diffusion coefficient and accordingly the profiles evolve symmetrically, whereas in Fig. 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 , practically only A atoms can dissolve into the B matrix and B atoms can hardly penetrate into the A matrix. Consequently, a stress peak develops in 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 called *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, either the slope differs from 0.5 or the data points do not fit a straight line.

As an illustration Fig. 2 shows two examples, obtained by taking into account and neglecting stress. It can be seen that the data points fit very well a straight line with a slope of ≈ 0.5 . 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 significantly the value of k_c , it *slowed down* the intermixing process (the intercept is lower).

As was mentioned in the introduction, 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 nanometer is enough to reach it. It is 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 fast for composition independent diffusivities ($m' = 0$, symmetric diffusion) as can be seen in Fig. 1a. In case of composition dependent diffusivities ($m' \neq 0$, asymmetric diffusion) the stress profile becomes also quasi-stationary, in this case, however, two significant stress gradients develop at the one of the borders of the diffusion zone (left boundary in Fig. 1b). Thus markedly different influence of the stress profiles on the atomic fluxes would be expected in stage ii).

In stage ii), in symmetric diffusion case, slowing down of the intermixing is expected because the stationary stress gradient

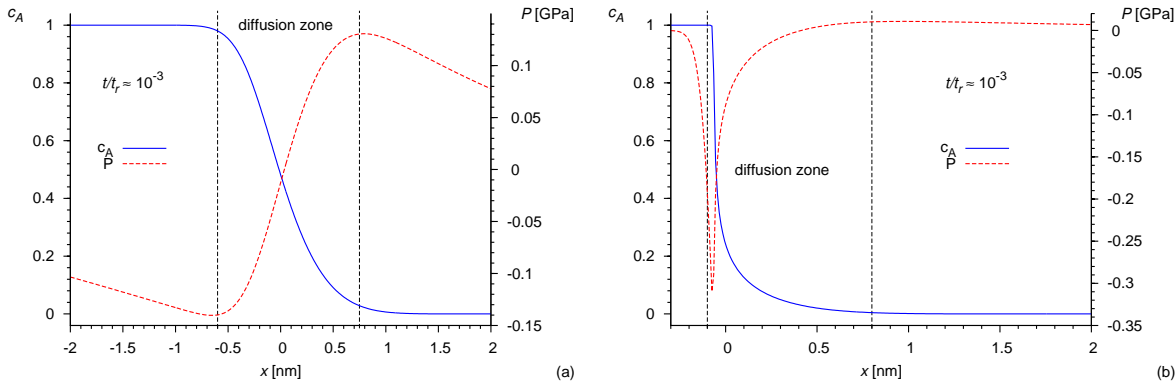


Figure 1: Illustration of the time evolution of the composition (atomic fraction of component A) and pressure (P) profiles for (a) *composition independent* ($m' = 0$) and (b) *strongly composition dependent* ($m' = 7$) diffusion coefficients. Input parameters: $m' = 0$, $D_A^0/D_B^0 = 2.4$, $E_A = 185$ GPa, $E_B = 103$ 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.

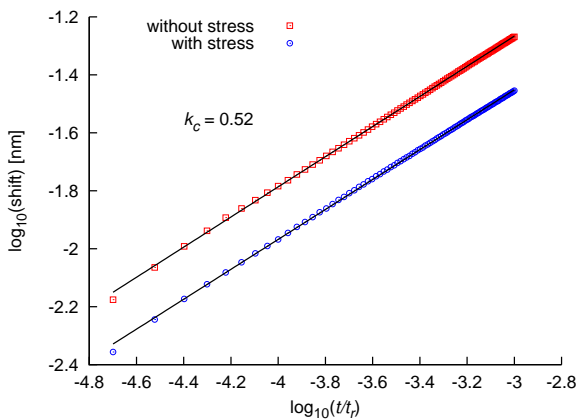


Figure 2: Position of a plane with constant composition ($c_A = 0.6$) as a function of time ($x_p \propto t^{k_c}$, i.e. $\log_{10} x_p \propto k_c \log_{10} t$). $D_A^0/D_B^0 = 10$, other input parameters are the same as in Fig. 1a. As can be seen, the plane shift is in the range of 0.1 nm but k_c is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

tends to diminish the volume flow itself. The larger the difference in the resultant volume flow—measured by $\Omega_A D_A - \Omega_B D_B$ —the more pronounced is 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, however, the conclusion is not so obvious, since there are two stress gradients with opposite signs at one of the borders of the diffusion zone as can be seen in Fig. 1b. Thus one of them decreases whereas 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 was shown above, the stress effects have practically not influence on the value of the kinetic exponent k_c . To understand it, we have to analyze 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 falls in very similar length scale 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 as well as the change in the pressure can be determined from the simulations. Therefore $dc_i \approx \pm 1$. Moreover, for instance, $dP \approx 0.3$ GPa in Fig. 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), $\Omega_i = 10^{-5}$ m³/mol, $T = 700$ 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, thus has important influence on the atomic flux. That is why it slows down the intermixing. However, as the composition and the pressure fall in very similar length scale and their maxima hardly change the dP/dc_i ratio is practically constant for 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 only 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—belonging to the slower diffusing (B) atoms—is enhanced by a factor of 1.17 – 1.86, whereas the other—belonging to the faster diffusing (A) atoms—is diminished by a factor of 0.83–0.14. The enhancement and diminishing of the atomic fluxes practically equilibrate their initial difference. This means that the system is in Nernst-Planck regime. This can be seen at the beginning of the curve in Fig. 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 Fig. 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

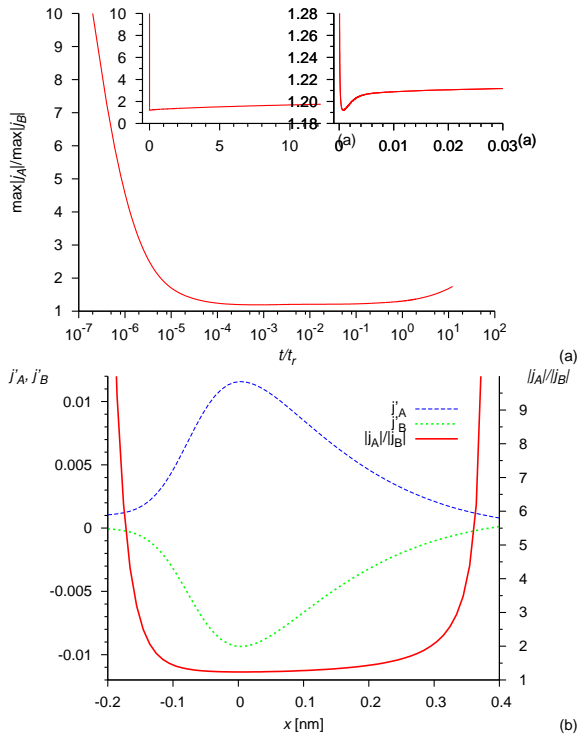


Figure 3: (a) Ratio of the atomic fluxes of the A and B atoms versus the logarithm of time. The left inset shows the same curve but the timescale is linear, whereas the right inset shows the curve around its minimum. (b) Atomic fluxes (their dimensionless form: $j'_i = j_i \Omega_i / D$) and their ratio 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, $\eta = 2 \times 10^{12}$.

decreases from 10 to approximately 1 extremely fast.

Since 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 in the same order of magnitude, which has been observed in Ref. [3]. It was obtained there that $\tilde{D}_D/\tilde{D}_{NP} \approx 2.6$, where \tilde{D}_D and \tilde{D}_{NP} were calculated from the growth rate of Θ' phase in the Cu/Al/Cu as well as Al/Cu/Al triple layers.

In stage iii) and iv), significant stress relaxation is expected. However surprisingly, we hardly observe any decrease in the stress levels although 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 as compared to $\frac{3}{4\eta} P$ in eq. (1) even in the steady state regime as can be seen for example in Fig. 4. Consequently the stress is not only relaxing but also always re-developing, and the estimation of t_r from eq. (6) leads to 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 whereas 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

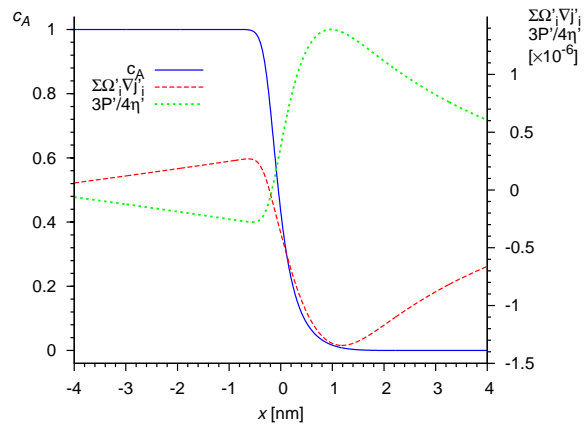


Figure 4: Composition profile as well as the dimensionless form of $\sum_i \Omega_i \nabla j_i$ and $\frac{3}{4\eta} P$ from eq. (1) at $t/t_r \approx 2$. This figure looks similar at any t/t_r in the steady state regime. For the input parameters see Fig. 3

regime is very fast, finishes before any detectable shift of the interface. These 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 fast in the timescale of the stress relaxation belonging to a pure Newtonian flow and thus the stress re-develops continuously.

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References

- [1] Beke, D.L., Szabó, I.A., Erdélyi, Z., Opposits, G.. Materials Science and Engineering A 2004;387-389:4 – 10.
- [2] Beke, D., Nemes, P., Erdélyi, Z., Szabó, I., Langer, G.. In: Mat. Res. Symp. Proc.; vol. 527. 1998, p. 99–110.
- [3] Schmitz, G., Ene, C.B., Nowak, C.. Acta Materialia 2009;57(9):2673 – 2683.
- [4] Stephenson, G.. Acta Metallurgica 1988;36(10):2663 – 2683.
- [5] Philibert, J.. Atom movements: Diffusion and mass transport in solids. Les Editions de Physique; 1991.
- [6] Mehrer, H.. Diffusion in Solids. Springer-Verlag Berlin Heidelberg; 2007.
- [7] Spaepen, F.. Journal of Magnetism and Magnetic Materials 1996;156(1-3):407 – 410.
- [8] Prokes, S.M., Spaepen, F.. Applied Physics Letters 1985;47(3):234–236.
- [9] Wortman, J.J., Evans, R.A.. Journal of Applied Physics 1965;36(1):153–156.
- [10] Erdélyi, Z., Balogh, Z., Beke, D.. Acta Materialia 2010;58(17):5639 – 5645.