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Importance of proper choice of transition rates in kinetic simulations of dynamic processes

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Proper transition rates in kinetic mean-field and Monte Carlo simulations of dynamic processes are very important to obtain realistic results. We show that by proper choice of the transition rates one can unify the advantages and eliminate the disadvantages of different models used in the literature [see, e.g., Senhaji *et al.*, Surf. Sci. **274**, 297 (1992) (kinetic tight binding Ising model), Martin, Phys. Rev. B **41**, 2279 (1990) and Cserháti *et al.*, Surf. Sci. **290**, 345 (1993)]. Furthermore, we also show that this choice cannot be considered simply as an extension of the previous ones. It contains an additional parameter controlling the ratio of the transition rates in the bulk and close to the surface $(\Gamma_{surf}/\Gamma_{bulk})$, which influences the kinetics of surface segregation. We show that some results obtained previously need reconsideration. We illustrate, e.g., how the composition dependence of the transition rates (diffusion coefficient) influences the 'surfactant formation and dissolution mode'. For example, the dissolution kinetics can deviate from the parabolic law on the nanoscale in accordance with our recent results [Erdélyi *et al.*, Phys. Rev. B **69**, 113407 (2004)]. Furthermore, we also present how the $(\Gamma_{surf}/\Gamma_{bulk})$ ratio affects the kinetic segregation isotherm.

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I. INTRODUCTION

The kinetic tight binding Ising model[1] (KTBIM) was developed in order to describe the kinetics of either segregation of B atoms in an $A(B)$ alloy or dissolution of a thin deposit of A atoms into a B substrate. For example, Delage *et al.*[2] and Roussel *et al.*[3] have studied the dissolution of a ten-atomic-layer-thick deposit into a semi-infinite substrate when the substrate atoms have a tendency to segregate onto the deposit. Using this KTBIM, Delage *et al.* calculated the dissolution of ten-atomic layers of Fe into a Cu(110) single crystal, whereas Roussel *et al.* performed the same calculations but for the Ni/Ag(100) system. It has been shown that, in spite of the relatively thick deposit, the segregation could lead to a rapid enrichment of the surface by the substrate atoms and thus to burying of the almost intact deposit. Then, in this *surfactant dissolution mode*, two simultaneous layer-by-layer dissolution processes take place and compete with each other: layer-by-layer dissolution from the top as well as from the bottom of the film. This competition continues until the whole deposit has been dissolved into the substrate.

Furthermore, Roussel *et al.* found that this behavior can be observed only above a critical temperature whereas at lower temperatures the surfactant dissolution mode changes into the simple ("classical") layer-by-layer dissolution mode (see Fig. 1 in Ref. 3). In addition the authors obtained that the displacement of the interface is proportional to $t^{1/2}$ in all cases, whereas the surface enrichment in substrate atoms is found to increase linearly with time (linear time dependence of the surfactant effect).

Kinetic mean-field and Monte Carlo simulations of dynamic processes have become very common in many branches of condensed-matter and materials physics. The proper choice of the transition rates is very important to obtain realistic results. Several papers deal with this problem under different conditions.[1,4–7]

In this article we show that in the KTBIM the composition dependence of the transition rates (diffusion coefficient) is neglected, although in real systems usually it cannot be done[8,9] The transition rates used in calculations by Cserháti *et al.*[5] (based on Martin's original pair interaction picture[4]) include it but the segregation tendency is connected to the strength of the composition dependence of the transition rates (both are calculated from the pair interaction energies). Thus we can observe a strong segregation tendency only in the case of strongly composition-dependent diffusion coefficients, which is obviously unrealistic. For example, in real Cu—Ag systems the composition dependence of the diffusivity can practically be neglected,[8] but strong surface segregation is obtained (see, e.g., Ref. 10). Thus, an inadequate choice of the transition rates can result in effects hardly observable in real systems.

It will be illustrated—by a proper choice of the activation energy terms describing the segregation tendency, the composition dependence of the diffusion coefficient, and the jump frequencies between the surface and subsurface layers—that both the surfactant dissolution mode and the parabolic dissolution kinetics can be observed only if the diffusion jump frequencies (transition rates) are independent of composition. Furthermore, we will show that the transition rates close to the surface must be underestimated in the KTBIM and that the ratio of the transition rates in the bulk and close to the surface influences the kinetics of surface segregation.

II. BASIC EQUATIONS: ADEQUATE CHOICE OF ACTIVATION ENERGIES

The KTBIM is in fact based on a one-dimensional deterministic model[4] in which atomic planes (with an area of q) perpendicular to the direction of diffusion are considered. The time dependence of the atomic fraction of layer i (C_i) is calculated as a detailed balance between incoming and outgoing fluxes:

$$\frac{dC_i}{dt} = -z_v[C_i(1-C_{i-1})\Gamma_{i,i-1} - (1-C_i)C_{i-1}\Gamma_{i-1,i} + C_i(1-C_{i+1})\Gamma_{i,i+1} - (1-C_i)C_{i+1}\Gamma_{i+1,i}], \qquad (1)$$

where $\Gamma_{i,i+1}$ is the frequency with which an A atom in plane i exchanges with a B atom in plane $i+1$, and z_v is the vertical coordination number. For the exchange frequency an Arrhenius-type temperature dependence is assumed:

$$\Gamma_{i,i+1} = \nu \exp\left(-\frac{E_{i,i+1}}{kT}\right), \qquad (2)$$

were ν denotes the attempt frequency, k is the Boltzmann constant, T is the absolute temperature, and $E_{i,i+1}$ is the activation barrier, which can be chosen in different ways (but satisfying the steady-state condition) as was shown in Ref. 4.

A. In the bulk

For instance, the following choice is adequate (note that it is almost the same as in Ref. 4):[10,11]

$$E_{i,i+1} = \hat{E}^0 - \alpha_i + \varepsilon_i \text{ and } E_{i+1,i} = \hat{E}^0 - \alpha_i - \varepsilon_i, \qquad (3)$$

where $\hat{E}^0(>0)$ is a composition-independent term (the composition-independent part of the activation energy) containing the saddle point energy, and

$$\alpha_i = [z_v(C_{i-1} + C_{i+1} + C_i + C_{i+2}) + z_l(C_i + C_{i+1})]M, \qquad (4)$$

$$\varepsilon_i = [z_v(C_{i-1} + C_{i+1} - C_i - C_{i+2}) + z_l(C_i - C_{i+1})]V. \qquad (5)$$

Here z_l is the lateral coordination number, $M=(V_{AA} - V_{BB})/2$, and $V=V_{AB}-(V_{AA}+V_{BB})/2$, where V_{XY} (>0) are the nearest-neighbor pair interaction energies between species X and Y $(X,Y=A$ or $B)$. As will be discussed below, M in α_i determines the strength of the composition dependence of the transition rates, whereas V in ε_i is the regular solid solution parameter,[10] proportional to the heat of mixing and measures the phase separating $(V>0)$ or the ordering $(V<0)$ tendency. Furthermore,

$$\Gamma_{i,i+1} = \Gamma_i \gamma_i \text{ and } \Gamma_{i+1,i} = \Gamma_i/\gamma_i \qquad (6)$$

where

$$\Gamma_i = \nu \exp\left(-\frac{\hat{E}^0 - \alpha_i}{kT}\right) \text{ and } \gamma_i = \exp\left(-\frac{\varepsilon_i}{kT}\right). \qquad (7)$$

On the other hand, in the KTBIM the following choice is used:[2,3,12]

$$E^{KTBIM}_{i,i+1} = E_i = V'[(z_l - z_v)(C_i - C_{i+1}) + z_v(C_{i+2} - C_{i-1})],$$

$$E^{KTBIM}_{i+1,i} = -E_i; \qquad (8)$$

here V' is the effective pair interaction energy between atoms.[3,2] Reformulating it as

$$E_i = -[z_v(C_{i-1} + C_{i+1} - C_i - C_{i+2}) + z_l(C_i - C_{i+1})]V', \qquad (9)$$

we can see that with $V=-V'$ (i.e., $V'>0$, ordering; $V'<0$, phase separation), $E_i=\varepsilon_i$. Furthermore, in the KTBIM $\nu = D/d^2$ is used, where D is a *composition-independent* diffusion coefficient, and d is the interplanar spacing in the direction of diffusion. Therefore

$$\Gamma^{KTBIM}_{i,i+1} = \frac{D}{d^2}\gamma_i \text{ and } \Gamma^{KTBIM}_{i+1,i} = \frac{D}{d^2}/\gamma_i. \qquad (10)$$

From these expressions, it is clear that if $V=0$ (i.e., the system is completely miscible) $\gamma_i = 1 \, \forall i$ independently of the composition distribution; therefore $\Gamma^{KTBIM}_{i,i+1} = \Gamma^{KTBIM}_{i+1,i} = D/d^2 \, \forall i$. This means that the exchange frequencies or the diffusion coefficients are the same, for instance, in an A-rich and in a B-rich sample, although it is clear from, e.g., radiotracer experiments that they are usually different (diffusion asymmetry). The same conclusion can be drawn if $V \neq 0$ but the composition distribution is homogeneous $(C_i = C = \text{const} \, \forall i)$, since $\gamma_i = 1 \, \forall i$ in this case as well. It is, however, obvious that using the exchange frequencies given by Eq. (6) this problem does not enter. As was shown in detail in Ref. 10, Γ_i is proportional to the tracer diffusion coefficient (D^*), which is in general *composition dependent*: $D^* = D_0 \exp(mC)$ where $m = 2ZM/kT$. Here we introduce the parameter $m' = m \log_{10} e$ describing the strength of the diffusion asymmetry, which gives the difference between the diffusion coefficients in pure A and B matrices in orders of magnitude. Moreover, γ_i and the thermodynamic factor for diffusion[13] (Θ) are interrelated; from γ_i, Θ can be derived.[10] The $D^*\Theta$ product is the intrinsic diffusion coefficient.[13]

Here it is worth noting that, although in many cases the M and V parameters are determined from pair interaction energies, one can use their experimental values or can calculate them from more suitable models since they are input parameters (numbers) and their values do not influence the validity of Eq. (1).

B. Near the surface

Near the surface the jump frequencies usually are considered different than in the bulk, since it is supposed that close to the surface, the number of bonds, the structure, etc. can be modified (e.g., by relaxation).

In the simplest case, we can write the "surface equations" (for $i=0$ and 1) from a breaking bond model (BBM) (see, e.g., Ref. 5). After some algebra, taking also into account that V can be enhanced at the surface[1] [e.g., $V_s = 1.5V$ for the (100) surface] the following expressions are obtained:

$$E_{0,1} = \hat{E}^0_s - \alpha_0 + \varepsilon_0 - z_v(V_s - V) + (z_l + z_v)V - z_l V_s + \Delta\sigma,$$

$$E_{1,0} = \hat{E}^0_s - \alpha_0 - \varepsilon_0 - z_v(V_s - V),$$

$$E_{1,2} = \hat{E}^0 - \alpha_1 + \varepsilon_1 - z_v(V_s - V),$$

$$E_{2,1} = \hat{E}^0 - \alpha_1 - \varepsilon_1. \qquad (11)$$

Here $\hat{E}^0_s$ is the composition-independent term near the surface and is equal to $\hat{E}^0 + z_v V_{BB}$. This means that the atomic jumps ($\Gamma_{1,0}$ and $\Gamma_{0,1}$; from here denoted by Γ_{surf}) are faster here than in the bulk (Γ_{bulk}). $\Delta\sigma = z_v(V_{AA}-V_{BB})/2$, which corresponds to the difference in surface energies (ΔH^{surf}).[10] Moreover,

$$\alpha_0 = [z_v(C_0 + C_1 + C_2) + z_l(C_0 + C_1)]M, \tag{12}$$

$$\varepsilon_0 = [(z_v - z_l)C_0 + z_v C_1]V_s - (z_l C_1 + z_v C_2)V, \tag{13}$$

$$\varepsilon_1 = [z_v(C_2 - C_1 - C_3) + z_l(C_1 - C_2)]V + z_v C_1 V_s. \tag{14}$$

Note that α_1 can be calculated from Eq. (4) with $i=1$ ($i=0$ is the surface).

This (BBM) choice includes some restrictions, namely, it contains *only* the energy gain due to the difference in the surface energies; moreover the segregation tendency and the diffusion asymmetry are linked to each other since both depend on the $V_{AA}-V_{BB}$ difference.

The second restriction does not arise in the KTBIM since the diffusion asymmetry is ignored. The first one, however, is eliminated by the following choice of the activation energy:[12]

$$E_0^{KTBIM} = V_0'(z_v - z_l)C_0 + (V' z_l - V_0' z_v)C_1 + V' z_v C_2 + [\Delta\tau - V'(z_l + z_v) + V_0' z_l]/2, \tag{15}$$

$$E_1^{KTBIM} = V'(z_v - z_l)(C_1 - C_2) + z_v(V' C_3 - V_0' C_0) + (V_0' - V')z_v/2. \tag{16}$$

Here $\Delta\tau$ is the segregation energy gain, which contains both the energy gain due to the difference in surface energies and also that due to the difference in size of the two elements (ΔH^{size}). That is, $\Delta\tau = \Delta H^{surf} + \Delta H^{size}$. Reformulating E_0^{KTBIM} and E_1^{KTBIM} similarly to E_i^{KTBIM} [see Eq. (9)],

$$E_0^{KTBIM} = -[(z_v - z_l)C_0 + z_v C_1]V_s' + (z_l C_1 + z_v C_2)V' + [\Delta\tau - V'(z_l + z_v) + V_s' z_l]/2, \tag{17}$$

$$E_1^{KTBIM} = -[z_v(C_2 - C_1 - C_3) - z_l(C_1 - C_2)]V - z_v C_1 V_s' + z_v(V_s' - V')/2. \tag{18}$$

Thus, for example, taking $\Delta\sigma = \Delta\tau$ the size effect can also be included in Eqs. (11). Additionally we can also separate the composition dependence of the diffusivity from the segregation tendency (M and $\Delta\tau$ can be considered as independent input parameters), which is more realistic (e.g., in the Cu—Ag system the segregation tendency is strong, while the diffusion asymmetry is moderate). Thus, Eqs. (11) can contain all the advantages of the KTBIM choice but retain the composition dependence, as well.

Furthermore, Eqs. (11) have another favorable feature, namely, that the $\hat{E}^0 - \hat{E}_s^0$ difference can also be adjusted (again, it has not necessarily to be equal to $z_v V_{BB}$, which would follow from the BBM). Changing this difference, we can vary the $\Gamma_{surf}/\Gamma_{bulk}$ ratio, whereas it is fixed in the KTBIM and probably not in the best way. For example, we can see if $V'=0$ (i.e., $V_s'=0$ as well), $E_0 = \Delta\tau$, and $E_i = 0$ $\forall i (\neq 0)$. This means that $\Gamma_{0,1}^{KTBIM} = (D/d^2)\exp(-\Delta\tau/2kT)$, $\Gamma_{1,0}^{KTBIM} = (D/d^2)\exp(+\Delta\tau/2kT)$, and $\Gamma_{i,i+1}^{KTBIM} = \Gamma_{i+1,i}^{KTBIM} = (D/d^2) = \Gamma_{bulk}^{KTBIM}$. If for instance $\Delta\tau > 0$, $\Gamma_{0,1}^{KTBIM} < \Gamma_{bulk}^{KTBIM} < \Gamma_{1,0}^{KTBIM}$ (see also Fig. 1), then not all the jumps are faster near the surface than in the bulk, whereas $\Gamma_{bulk} \ll \Gamma_{surface}$ is expected usually. However, already in the composition-independent case the $\hat{E}^0 - \hat{E}_s^0$ difference can ensure that atoms can jump faster in the surface region. Of course, there can be cases when an additional subsurface barrier slows down drastically the atomic movements near the surface, e.g., due to electronic field (charge) effects, etc. However, by an adequate choice of the $\hat{E}^0 - \hat{E}_s^0$ difference (it can be even negative), the requested $\Gamma_{surf}/\Gamma_{bulk}$ ratio can be adjusted.

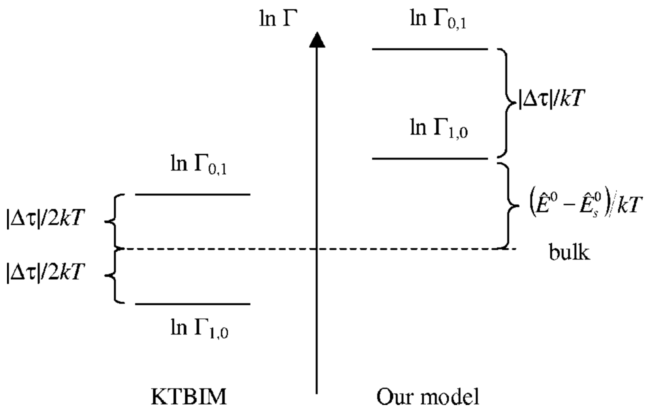

FIG. 1. Jump frequencies in the surface region as compared to the bulk jump frequencies if $\Delta\tau < 0$, $V=0$, and $M=0$.

III. CALCULATION PROCEDURE

In our kinetic mean-field (KMF) simulations the composition profiles were calculated in two steps. First the activation barrier and the exchange frequencies were calculated from Eq. (2) using Eq. (3) with Eqs. (4) and (5) in the bulk and Eq. (11) with Eqs. (12)–(14) near the surface. Then the new configuration of the composition was derived from Eqs. (1).

IV. ON THE SURFACTANT DISSOLUTION MODE

As has been seen, our equations have three advantages because they contain (i) composition-dependent diffusivity, (ii) independent parameters for segregation tendency and diffusion asymmetry, and (iii) adjustable surface and bulk jump frequency ratio ($\Gamma_{surf}/\Gamma_{bulk}$) (by the choice of $\hat{E}^0 - \hat{E}_s^0$).

A. Diffusion asymmetry

The neglect of the composition dependence of D^* has serious consequences. For instance it leads to an interface shift always proportional to the square root of the time independently of the investigated length scale. As was shown in Refs. 11 and 14 the interface shift in general is a power function of time ($\propto t^{k_c}$), and the exponent k_c can differ from 0.5 on the nanoscale.

Maybe an even more spectacular consequence is the disappearance of the surfactant dissolution mode, which is illustrated below.

Using the more general form of the exchange frequency, i.e., Eq. (6), we could reproduce the results obtained in Refs. 2 and 3 with $m'=0$, $\hat{E}^0-\hat{E}_s^0=-|\Delta\tau|/2$ (to ensure a similar $\Gamma_{surf}/\Gamma_{bulk}$ ratio as in the KTBIM; see also Fig. 1), and taking $\Delta\tau=-0.42$ eV, i.e., if the diffusion coefficient was composition independent [see Fig. 2(a)]. However, in case of composition-dependent diffusion coefficients, as can be seen in Fig. 2, the dissolution mode depends also on m'. When $m'=2$ first the "classical" dissolution mode is observed, and only after the deposit thickness reaches a certain value does the dissolution continue by the surfactant mode. This clearly means that the dissolution mode depends on the thickness of the deposit as well, as was first mentioned in Ref. 10 and later discussed in more detail in Ref. 12. If $m'=4$ we observe only the "classical" diffusion mode practically during the whole process, and the segregation of the substrate atoms can be seen only when the interface reaches the near-surface region.

Thus, generally, we can say that the existence of the surfactant dissolution mode—in addition to the thickness of the deposit, the segregation tendency $(\Delta\tau)$, the temperature (T), and the phase separation tendency (V)—depends strongly on the composition dependence of the diffusion coefficient (m') as well. It can be observed only if the composition dependence of the diffusion coefficient is negligible $(m'\approx 0)$, but the system has a strong segregation tendency and the deposit is thin. Here we must note that, regarding the diffusional data in the literature,[8] m' has quite often a value of 4 to 7 or even larger especially at low temperatures. Moreover, usually if $\Delta\tau$ is large m' is also important, since both $\Delta\tau$ and m' contain contributions from the difference of the A—A and B—B pair interaction energies $(V_{AA}-V_{BB})$.

B. The $\hat{E}^0-\hat{E}_s^0$ difference

As was also mentioned in Ref. 12, according to Laguës[15] the kinetic path should follow the one of surface local equilibrium if the flux toward the surface is much smaller than both the incoming $J_{1,0}$ and the outcoming $J_{0,1}$ surface fluxes. However, this is controlled just by the $\hat{E}^0-\hat{E}_s^0$ difference, since it determines the $\Gamma_{surf}/\Gamma_{bulk}$ ratio.

Indeed, as can be seen in Fig. 3, on changing $\hat{E}^0-\hat{E}_s^0$ the corresponding C_s vs C_2 curves are quite different (here C_2 is the atomic fraction of the substrate element in the second subsurface layer). When $\hat{E}^0-\hat{E}_s^0$ is smaller (i.e., $\Gamma_{surf}/\Gamma_{bulk}$ is larger) the agreement with equilibrium is better.

This means that the choice of the value of $\hat{E}^0-\hat{E}_s^0$ should be a very important parameter in the investigation of the *local equilibrium*.

Here we must note that numerous papers in the literature deal with the problem of local equilibrium, e.g., in the framework of the KTBIM, without considering this parameter. For instance, in the KTBIM the special choice of $\Gamma_{surf}/\Gamma_{bulk}$ results often in deviation from the local equilibrium. What is more, since this ratio is influenced by $\Delta\tau$, the deviation is larger if the segregation tendency is larger. In our model, however, it can be compensated by the adequate choice of $\hat{E}^0-\hat{E}_s^0$ if necessary.

Thus, we think that many results concerning the local equilibrium problem in the literature should be reevaluated.

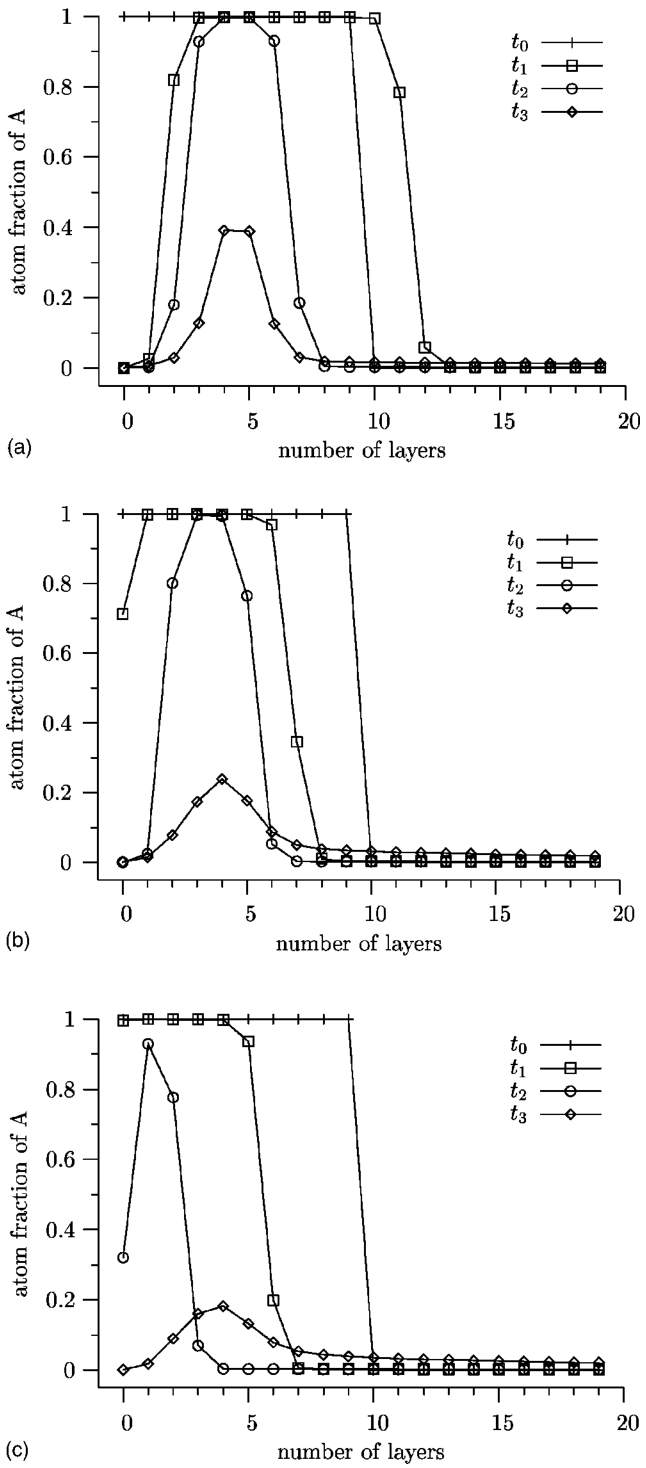

FIG. 2. Time evolution of the composition profile calculated by our KMF model. (a) $m'=0$ (surfactant mode); (b) $m'=2$ (first the "classical" dissolution mode is observed, and the dissolution continues only later by the surfactant mode); (c) $m'=4$ (only the "classical" mode).

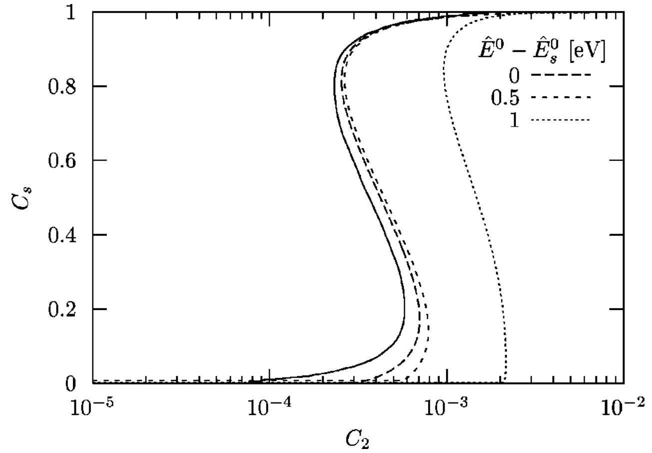

FIG. 3. C_s vs C_2 curves for different $\hat{E}^0-\hat{E}^0_s$ (i.e., $\Gamma_{surf}/\Gamma_{bulk}$). The solid line corresponds to the equilibrium curve, while the other ones are obtained from our KMF model. When $\hat{E}^0-\hat{E}^0_s$ is smaller (i.e., $\Gamma_{surf}/\Gamma_{bulk}$ is larger) the agreement with the equilibrium is better.

C. Time dependence of the surface enrichment

The $\hat{E}^0-\hat{E}^0_s$ parameter has influence on the kinetics as well.

Recently Roussel *et al.*[12] have found that the surface enrichment in the substrate element increases linearly with time instead of following the usual $\sqrt{t}$ law.

First, we also analyzed the time evolution of the surface composition of the substrate element (atomic fraction C_s) in the case of the same parameters; then we performed other calculations changing the value of $\Delta\tau$ and $\hat{E}^0-\hat{E}^0_s$.

As the dashed line in Fig. 4(a) shows C_s seems indeed to increase linearly in time; however, it curves slightly. In order to see the details better we have plotted the logarithm of C_s as a function of the logarithm of the time ($\log C_s \propto \log t$), since if C_s is indeed proportional to t (i.e., a power function $C_s \propto t^{k_c}$), the slope of this function has to be equal to 1 (i.e., $k_c=1$). What is more, we can also better see if the slope changes with time. In Fig. 4(a) the solid line represents the time evolution of k_c. As can be seen the value of k_c changes between 1 and 1.2 during the increase of C_s.

Changing the value of $\hat{E}^0-\hat{E}^0_s$ for example to 1 eV, the value of k_c varies between 1 and 7 [see Fig. 4(b)]. Therefore the C_s vs t function depends highly also on the value of $\hat{E}^0-\hat{E}^0_s$.

Similarly as in Ref. 12, we have also investigated how the value of $\Delta\tau$ influences the time dependence of the surface enrichment. We obtained that for example in the case of a value of 0.42 eV the time dependence also deviates from the linear kinetics [see Fig. 4(c)]. Thus it depends highly also on the value of $\Delta\tau$.

Roussel *et al.*[12] have given an analytical explanation for their findings. The analytical prediction of the time evolution of the surface composition can be valid only in the case of the Henry approximation, i.e., when the surface composition is proportional to the subsurface composition ($C_s=k_H C_b$, where k_H is the surface segregation coefficient and is composition independent). In the present investigated cases, however, C_s and C_b are connected by the Fowler-Guggenheim isotherm, where $C_s \propto C_b$ is not valid (see the S shape of the isotherms in Figs. 4 and 5 in Ref. 12, and also Fig. 3 in the present work). In fact, this explains the time evolution of k_c as well. Furthermore, usually deviations from the classical $\sqrt{t}$ law are expected in finite systems[13] if the diffusion zone reaches the edge of the sample (here that of the deposit). The "reflections" disturb the "usual" behavior (and the Boltzmann transformation cannot be applied). Finally, we also note that the validity of the classical continu-

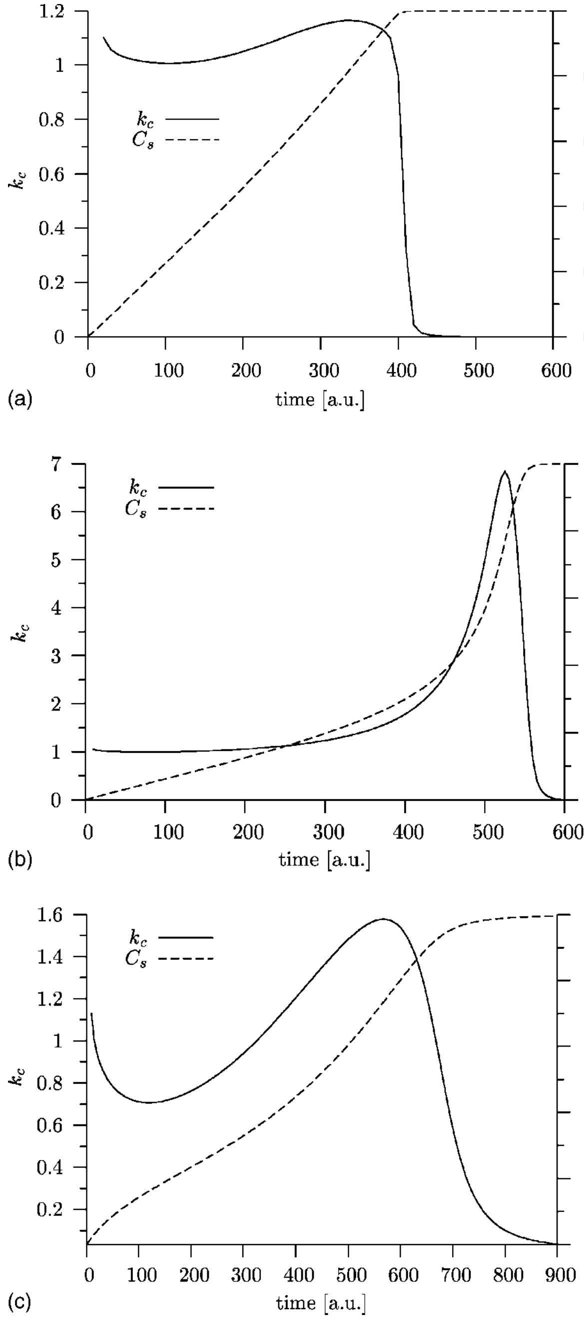

FIG. 4. Time evolution of k_c and C_s calculated by our KMF model. (a) $\Delta\tau$=0.92 eV, $\hat{E}^0-\hat{E}^0_s=0$; (b) $\Delta\tau$=0.92 eV, $\hat{E}^0-\hat{E}^0_s=1$ eV; (c) $\Delta\tau$=0.42 eV, $\hat{E}^0-\hat{E}^0_s=0$.

ous equations is restricted at atomic scales, and in particular conclusions concerning kinetics fail at short diffusion distances.[10,14,16]

V. CONCLUSIONS

We have shown that with a proper choice of the transition rates we can unify the advantages and eliminate the disadvantages of different models used in the literature. We have also shown that this choice cannot be considered simply as an extension of the previous ones. It contains an additional parameter $(\hat{E}^0-\hat{E}_s^0)$ controlling the ratio of the transition rates in the bulk and close to the surface. It has been illustrated that the $\hat{E}^0-\hat{E}_s^0$ difference influences the kinetics of surface segregation and due to this some results obtained previously in the literature need reevaluating. We have illustrated that the composition dependence of the transition rates influences the surfactant formation and dissolution mode.

Finally, we note that of course this choice of the activation energies can be used not only in deterministic kinetic models but in Monte Carlo techniques.

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