Rev.Adv.Mater.Sci. 21(2009) 6-17

# ON THE DETERMINATION OF THE EQUILIBRIUM SURFACE SEGREGATION ISOTHERMS FORM KINETIC MEASUREMENTS

**Z. Erdélyi, A. Taranovskyy and D.L. Beke**

Departement of Solid State Physics, University of Debrecen, P.O. Box 2 H-4010 Debrecen, Hungary

*Received: December 20, 2008*

**Abstract.** Thirty years ago, Lagües and Domange [1] studying dissolution and segregation kinetics, introduced the s urface local equilibrium hypothesis. This hypothesis is based on the idea that the kinetics (diffusion) is faster in the near surface region (selvedge) than in the bulk and thus it can be assumed that the atoms just below the selvedge can be in equilibrium with the atoms of the deposit. In this contribution, based on our recent work [2], using three dimensional kinetic Monte Carlo (KMC) and one dimensional kinetic mean filed (KMF) models, we show that the local equilibrium can be violated even in simple cases when complex surface phenomena (defects, relaxation, size effects, etc.) are not taken into account. Furthermore we illustrate that, even if the above hypothesis is obeyed, the determination of the surface segregation isotherms from kinetics can lead to uncertain result because of the restricted validity of Fick's first equation on the nanoscale.

## 1. INTRODUCTION

The surface segregation isotherm is in fact the relation between surface and bulk concentration of the *segregating element* at thermodynamic equilibrium at a fixed temperature $T$: $C_s^{eq} = f\left(C_b^{eq}, T\right)$. Therefore, in principle to determine the equilibrium isotherm one has to prepare large (semi-infinite) homogeneous samples with different compositions, heat treat them at a fixed temperature and measure the equilibrium surface composition of each samples. Plotting these values as the function of the corresponding bulk compositions the above relation can be constructed. Instead of this lengthy procedure Lagües and Domange [1] proposed a method by which the segregation isotherm can be readily deduced from the measured time dependence of the surface composition obtained in one sample. They introduced a model for the dissolution of a one layer thick deposit into a semi-infinite sample, according to which the dissolution process can be schematically divided into two steps. In the first step the atoms diffuse through the selvedge, the transition layer connecting the surface and the bulk (Fig. 1). The selvedge ends where the solubility and diffusion attain the bulk value. According to Lagües and Damange the thickness of the selvedge is in the range of 1-10 atomic layers. The second step is the diffusion into the bulk. They assumed that the diffusion through the selvedge is fast as compared to diffusion in the bulk and this is expected to be generally true, unless there exists a large extra potential barrier in the selvedge. Supposing that the atoms just below the selvedge remain in thermodynamic equilibrium with the deposit atoms, the $C_s(t)$ surface concentration and the $C_b(x = 0, t)$ concentration just below the selvedge remain equal to the values of the equilibrium isotherm during dissolu-

Corresponding author: Z. Erdelyi, e-mail: zerdelyi@dragon.unideb.hu

tion. This is called as *surface local equilibrium hypothesis*. To deduce the equilibrium isotherm from a single measurement needs two steps: i) measuring the time evolution of the surface concentration during the dissolution of one atomic layer thick deposit into a substrate; ii) calculating subsurface concentration from the corresponding solution of the Fick's equations (e.g. Refs. [1-3]). The local surface equilibrium hypothesis can also be formulated as the coincidence of the *equilibrium and kinetic segregation isotherms*, i.e. it fulfils if the and functions are identical.

In [2] we focused on the dissolution of one atomic layer thick deposit. In this contribution, besides summarizing the results of [2], we report further ones obtained for the dissolution of thick (10 atomic layers) deposits.

## 2.1. One dimensional kinetic mean field model (KMF)

The details of the model is described in [2] and [4]. The input parameters in the model are [4]: $V$ regular solid solution parameter, which measures the phase separating ($V$>0) or ordering ($V$<0) tendency; $\Delta\tau$ = -0.42 eV segregation energy gain; $T$=1200 K temperature; $z_v$=4, $z_l$=4 vertical and lateral coordination numbers; $\hat{E}^{'0} - \hat{E}_s^{'0}$ = -1 ev difference in saddle point energies in the volume and on the surface (determining the ratio of jump frequencies at the surface and in the bulk); $m'$ diffusion asymmetry parameter (if e.g. $m'$=4, the diffusion is 4 orders of magnitude faster in one matrix than in the other).

## 2.2. Three dimensional kinetic Monte Carlo model (KMC)

Monte Carlo simulations of the kinetic process were performed by using the residence-time algorithm [5]. For further details see [2]. In order to make the KMF and KMC results comparable, the KMC jump probabilities were chosen to be "equal" to the KMF jump frequencies and the other input parameters were the same as in case of KMF.

To deduce the isotherms, we plotted the composition profiles at different times. Furthermore, in order to compare the kinetic segregation isotherms with the equilibrium ones (see also Ref. 2), we had to plot the composition of the topmost (surface) layer as the function of the composition of the layer just below the surface region (surface selvedge). Since, however, we do not know what the thickness of the surface selvedge is, we plotted $C_s(t)$ in the function of the underlayers [$C_1(t)$, $C_2(t)$, …] and we searched

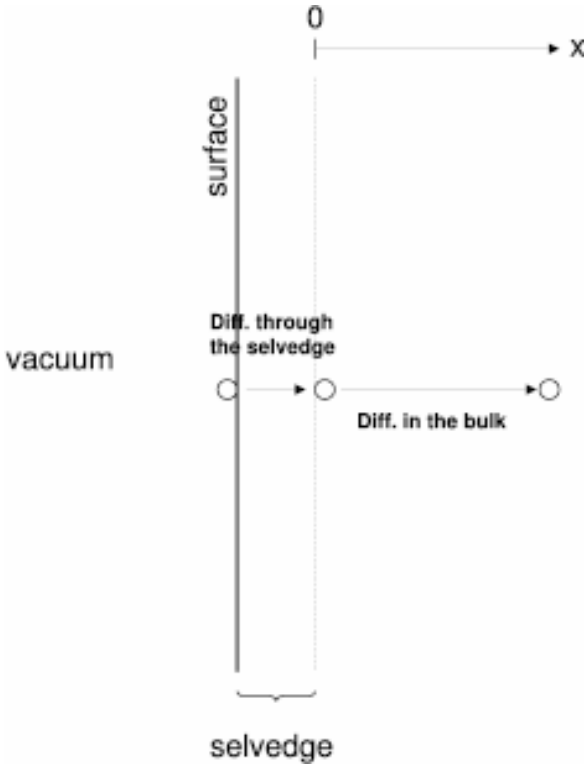


**Fig. 1.** Schematic drawing of the model of Lagües and Domange. (after Lagües and Domange [1]).

the $C_s(t)$ vs. $C_l(t)$ relation, which was the closest to the equilibrium isotherm. Hence, we could find not only the kinetic isotherm but we could also identify the thickness of surface selvedge.

## 3. RESULTS AND DISCUSSION

Regarding the energetics of a binary system, several cases could be envisaged. However, we report only the experimentally important cases: i) the substrate atoms segregate at the free surface and the diffusion is faster in the substrate; ii) the atoms of the deposit layer segregate and the diffusion is faster in the deposit; iii)-iv) correspond to cases i) and ii) but the diffusion is identical in both matrixes (no diffusion asymmetry). All these cases were studied for both ideal ($V$=0) and phase separating ($V$>0) systems. To identify the different cases, we use four character strings: the first and second characters are related to the chemical behaviour of the system ('I' and 'P' for ideal and phase separating system, respectively) and the segregation behaviour ('d' if the deposit atoms and 's' if the substrate atoms have segregation tendency, respectively). The third and fourth characters characterize the thickness of

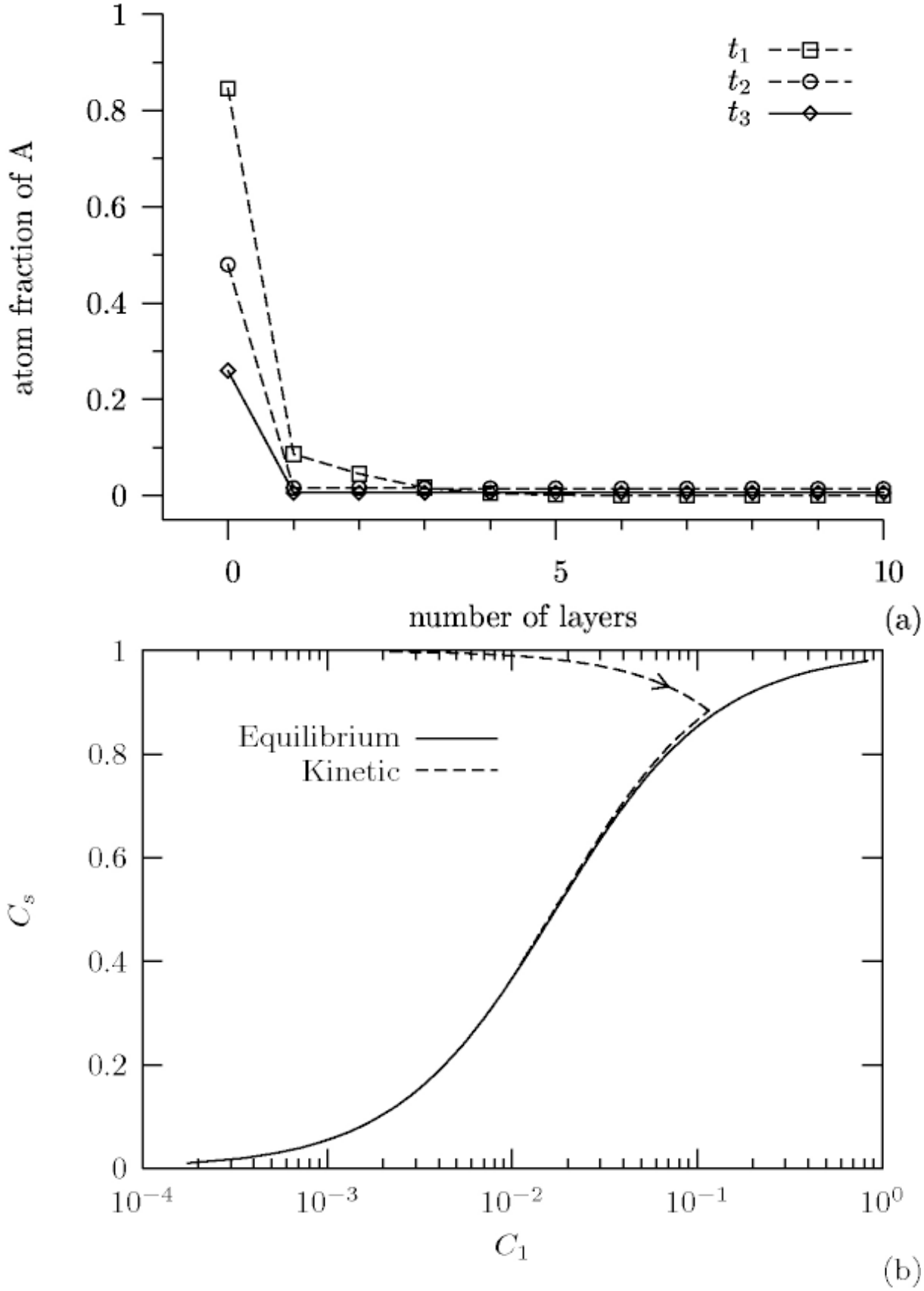


**Fig. 2.** Case Id10: (a) Time evolution of the composition profile. (b) The corresponding equilibrium and kinetic surface segregation isotherms. The arrow shows the direction of the kinetic path on the kinetic isotherm. $C_s$ and $C_1$ denote here the atomic fraction of the *A* deposit atoms on the surface and in the first underlayer, respectively. The *x*-axis is logarithmic to show better the details.

the deposit (using '1' or 't' in case of a 1 atomic layer thick or a 10 atomic layer thick deposit) and the diffusion behaviour (using 'a' if the diffusion is asymmetric and '0' if symmetric), respectively. For example the 'Id10' means that the system is ideal, the deposit atoms have segregation tendency, initially the deposit is 1 atomic layer thick and there is no diffusion asymmetry in the system.

Here we emphasize that to obtain the surface segregation isotherms we have always to plot the composition of the *segregating elements*. In the figures showing the composition profiles in the next subsections, we plot always the *composition of the deposit atoms* vs. depth to show how the deposit dissolves into the substrate.

## 3.1. Id10 and Idt0

Fig. 2 shows the time evolution of the composition profile for Id10; and the corresponding equilibrium and kinetic surface segregation isotherms, which are different at the beginning. This is due to the initial condition: at the initial state a pure *A* layer is on the surface of a pure *B* matrix and thus the surface layer is not in equilibrium with the bulk layers. However, the dissolution of *A* atoms leads to a very fast establishment of the equilibrium and from this point the equilibrium obeys during the whole process. The Idt0 case (Fig. 3) is the same as Id10 one, but initially there is a 10 atomic layer thick deposit on the top of the substrate. The corresponding kinetic and equilibrium isotherms coincide during the whole process. In these cases the surface selvedge ends at the first subsurface layer and the surface local equilibrium (SLE) is obeyed.

## 3.2. Is10

Here the initial state is the same as in case Id10, but the substrate elements segregate to the free surface (Fig. 4). Again, the $C_s(t)$ vs. $C_1(t)$curve is the closest to the equilibrium isotherm, i.e. the surface selvedge ends at the first subsurface. However, here the kinetic and equilibrium isotherms coincide only at the end of the dissolution process. The reason is that initially $C_s(t)$ and $C_1(t)$ are very far from being in equilibrium and drastic change in the composition distribution is necessary to get closer to the local equilibrium. Therefore the *the SLE is not obeyed*.

## 3.3 Ist0

The behaviour is similar to the Idt0 case. The kinetic and equilibrium isotherms coincide during the whole dissolution process. The SLE is obeyed, since the $C_s(t)$ and $C_1(t)$ are in local equilibrium already at the initial state and can continue to stay in equilibrium due to the atomic jumps much faster in the surface region than in the bulk. The selvedge is 1 atomic layer thick.

## 3.4 Id1a, Idta, Is1a, Ista

We have repeated the calculations presented above but taking into account that usually the diffusion is several orders of magnitude faster in the matrix of which atoms segregate. Regarding the diffusion literature, in real systems this difference is between 4 and 7 orders of magnitude. In our calculations we have chosen this value to 4, i.e. $m' = 4$. The time evolution of the composition profiles do not differ significantly either considering ($m' = 4$) or neglecting ($m' = 0$) the diffusion, this means that Id10 similar to Id1a and the Is10 similar to Is1a, with the same conclusions drown above.

On the other hand there are significant differences for the dissolution kinetics of thick deposits (Fig. 5). This is because in case Idta the diffusion is faster in the deposit than in the substrate and so initially the substrate atoms diffuse very fast into the deposit and distribute almost homogeneously, whereas the *A* deposit atoms can hardly diffuse into the substrate. However, with increasing *B* content in the deposit the diffusion asymmetry decreases, which leads finally to a similar time evolution of the composition profile as in case Idt0. In case Ista, the diffusion is faster in the substrate, thus only the *A* deposit atoms close to the interface can dissolve into the substrate and diffuse away very fast. This leads to an abrupt interface shift, which continues until the interface reaches the near surface region. At this point the substrate atoms start to jump out to the surface, as the system can reduce its free energy faster in this way. Despite the significant deviation between the time evolutions of the composition profiles, we have obtained that the kinetic isotherms were the same in all the four cases with no diffusion asymmetry. This is due to the fact that the diffusion asymmetry does not modify significantly the composition profile in the near surface region.

## 3.5. Pd10 and Pdt0

The case Pd10 differs form Id10 only in taking the system phase separating ($V = 0.053$ eV). The time evolution of the composition profiles in the cases Pd10 and Id10 are quite similar, significant deviation cannot be observed. However, the surface segregation isotherms are obviously very different since

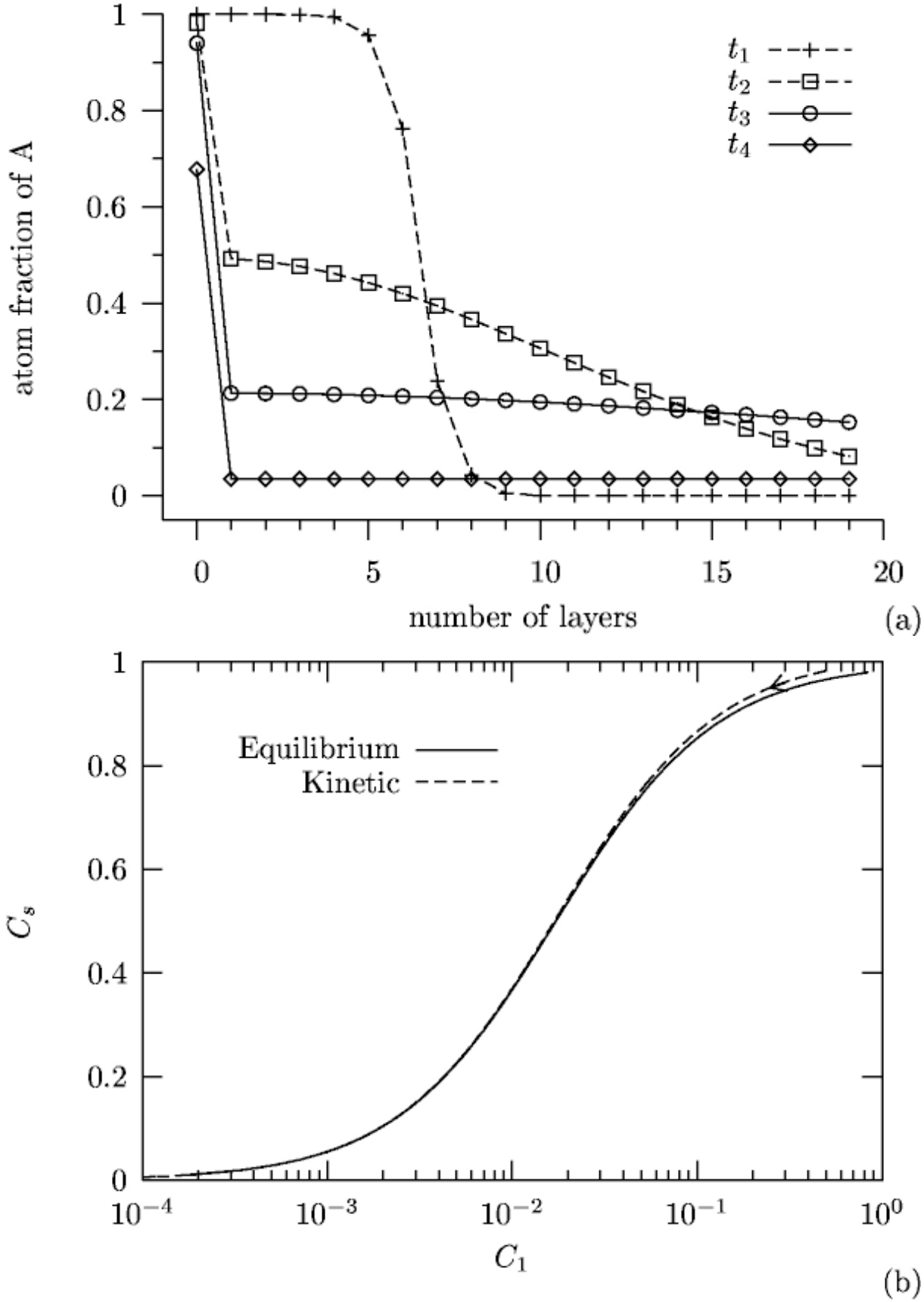


**Fig. 3.** Case Idt0: (a) Time evolution of the composition profile during the dissolution of a 10 atomic layers thick deposit into a semi infinite *B* matrix. (b) The corresponding equilibrium and kinetic surface segregation isotherms. The arrow shows the direction of the kinetic path on the kinetic isotherm.

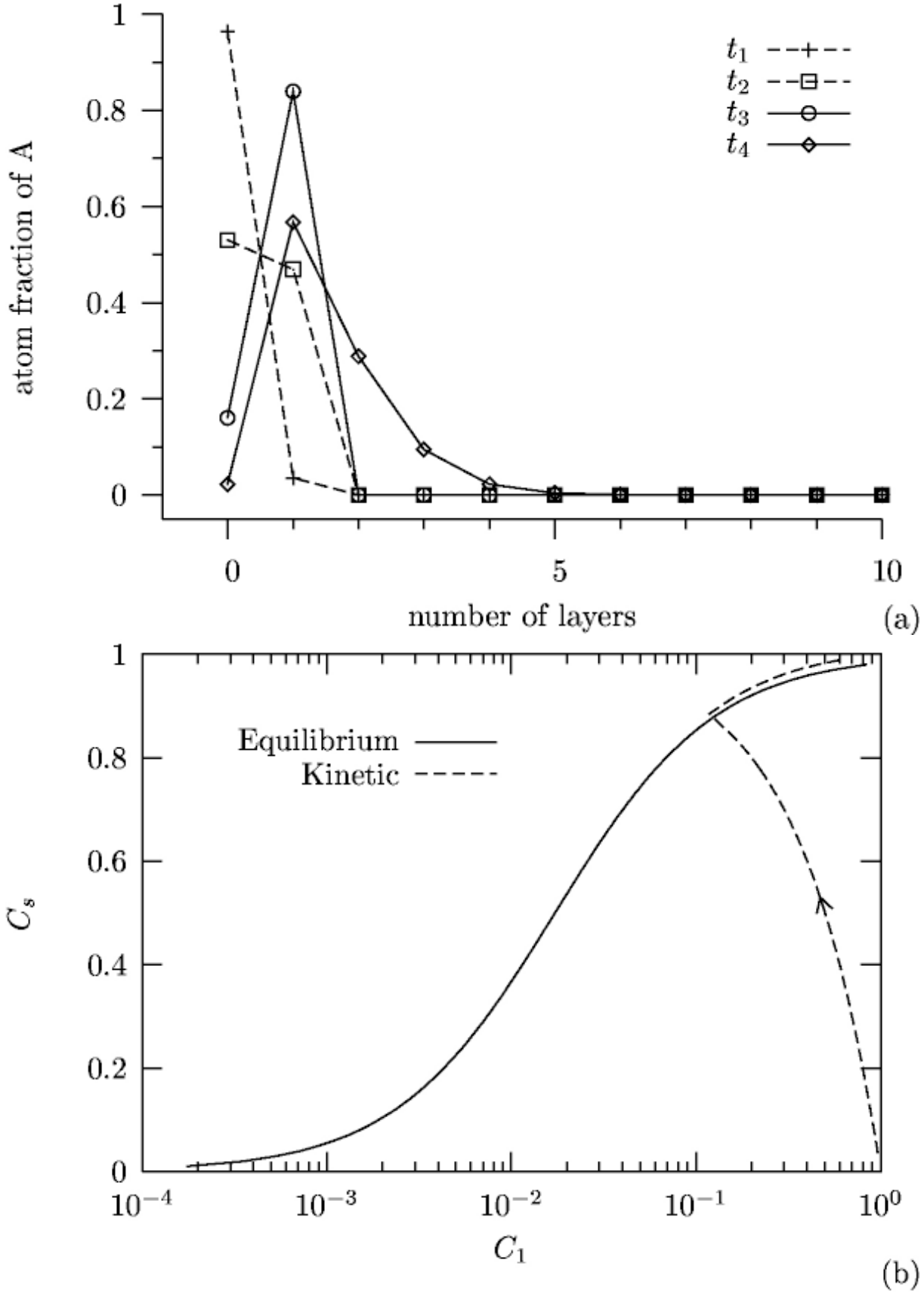


**Fig. 4.** Case Is10: (a) Time evolution of the composition profile (only the first 20 atomic layers are shown). (b) The corresponding equilibrium and kinetic surface segregation isotherms. The arrow shows the direction of the kinetic path on the kinetic isotherm. $C_s$ and $C_1$ denote here the atomic fraction of the *B* substrate atoms on the surface and in the first underlayer, respectively.

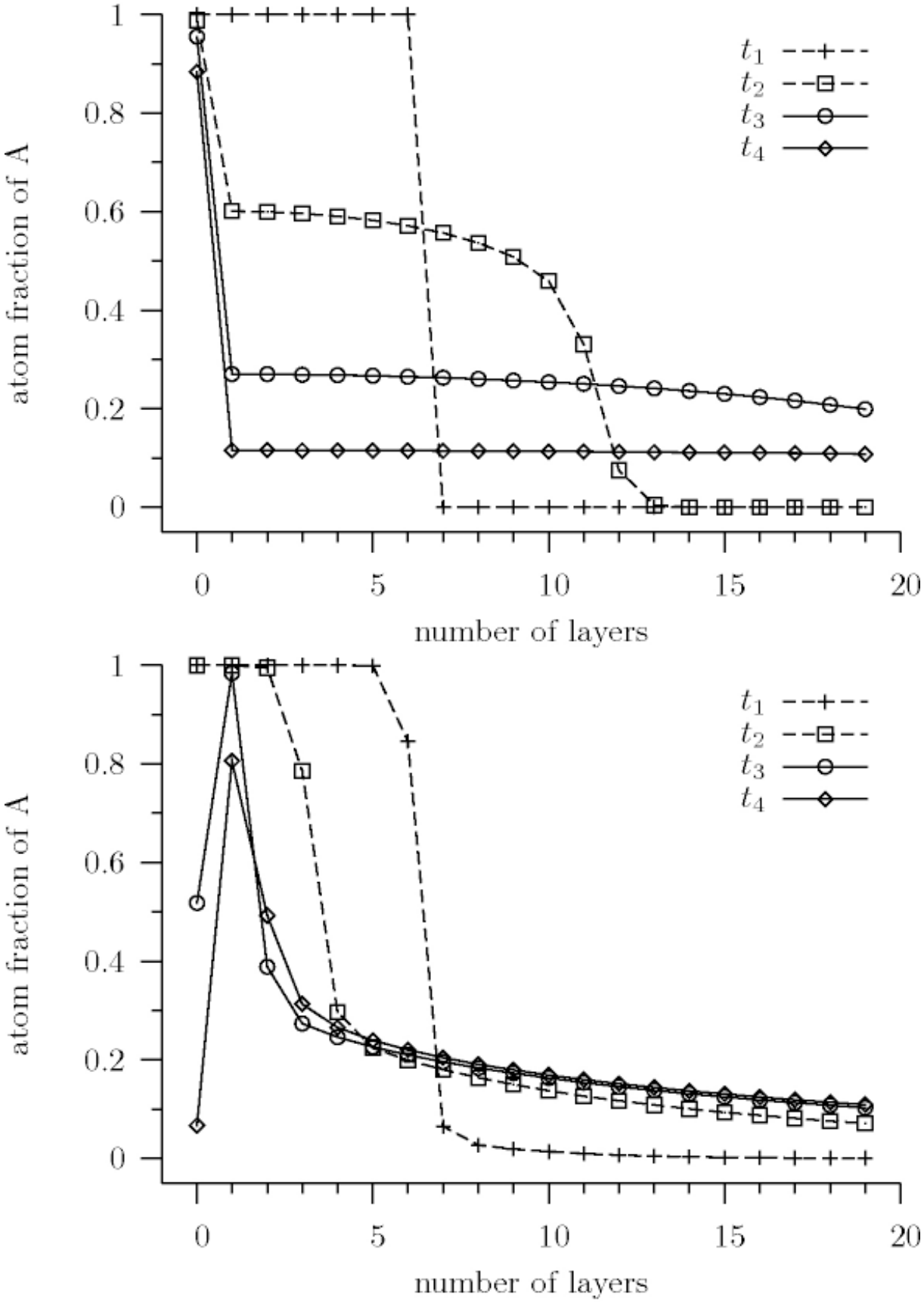


**Fig. 5.** Time evolution of the composition profile during the dissolution of a 10 atomic layers thick deposit into a semi infinite *B* matrix (only the first 20 atomic layers are shown). (a) Case Idta. The input parameters are the same as for Idt0, but *m*' = 4. (b) Case Ista. The input parameters are the same as for Ist0, but *m*' = 4.

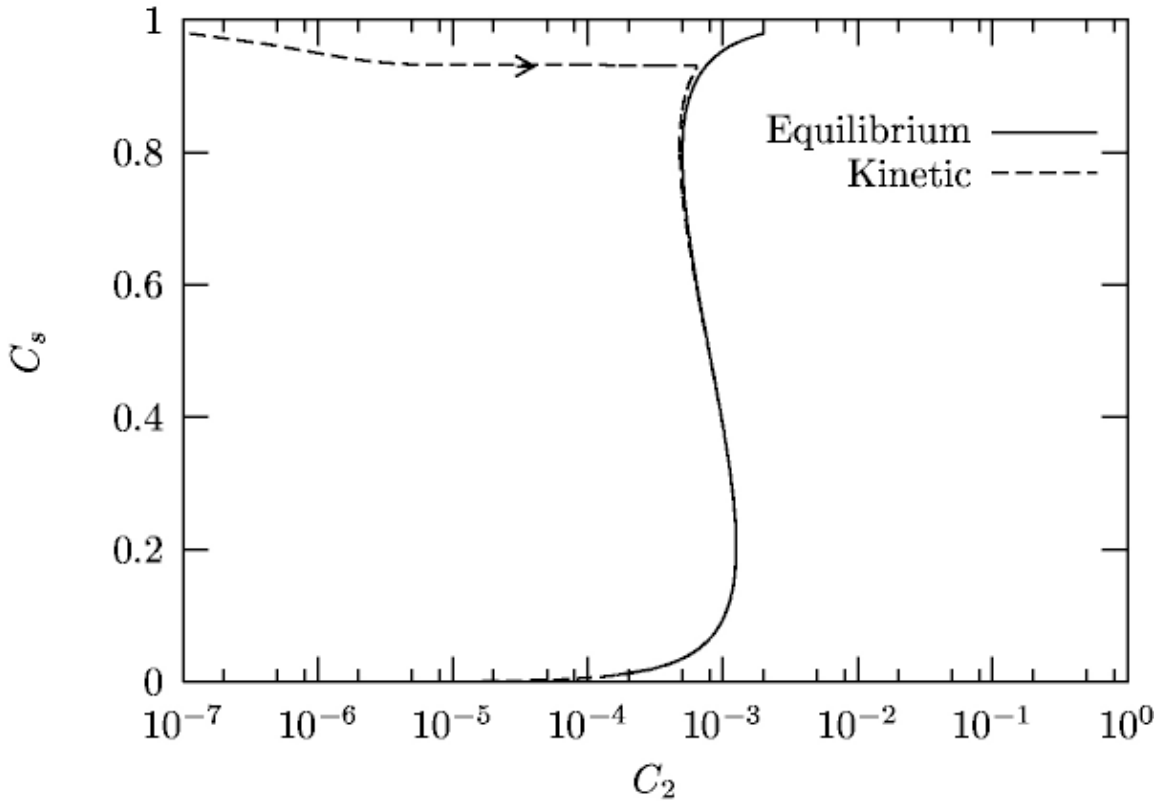


**Fig. 6.** Case Pd10: Equilibrium and kinetic surface segregation isotherms with $V$=0.053 eV. The arrow shows the direction of the kinetic path on the kinetic isotherm. $C_s$ and $C_2$ denote here the atomic fraction of the *A* deposit atoms on the surface and in the second underlayer, respectively.

in case Id1s a McLean type isotherm, whereas here a Fowler-Guggenheim isotherm is obtained. But as can be seen in Fig. 6 the kinetic and equilibrium isotherms coincide well except for the very beginning of the dissolution process. The explanation for the deviation is the same as for case Id10. We must note, however, that here not the $C_s(t)$ vs. $C_1(t)$curve is the closet to the equilibrium isotherm but the $C_s(t)$ vs. $C_2(t)$. This means that the surface selvedge ends at the *second subsurface layer*.

Using the same parameters as previously, but starting with a thick deposit (Pdt0), the interface remains abrupt and shifts towards the free surface as the phase separating tendency keeps the interface sharp. Thus the surface composition may start to decrease only when the interface reaches the subsurface layer. From this point practically we observe a very similar process as in case Pd1s. However, here at the initial state both $C_s$ and $C_b$ are equal to one, thus the kinetic segregation isotherm fits completely to the equilibrium. Thus in these cases *the surface selvedge ends at the second subsurface layer* and the SLE is obeyed.

## 3.6. Ps10

In this case the time evolution of the composition profile is very similar to that observed for case Is10. However, the kinetic and equilibrium surface segregation isotherms are very much more far from the equilibrium one (Fig. 7). The reason is that initially the surface and the second underlayer compositions [$C_s(t = 0)$ and $C_2(t = 0)$] are very far from to be in equilibrium, moreover $C_2(t = 0)$ is much larger than the critical composition at which the surface transition related to the Fowler-Guggenheim type segregation takes place. This means that the system would like to cover the surface with substrate atoms as fast as possible even if the system is out of equilibrium meantime. The total free energy decreases faster in this way. In this case the surface selvedge ends at *the second subsurface layer*.

## 3.7. Pst0

In this case in spite of the thick deposit, the segregation could lead to a rapid enrichment of the surface by the substrate atoms and thus to burying of

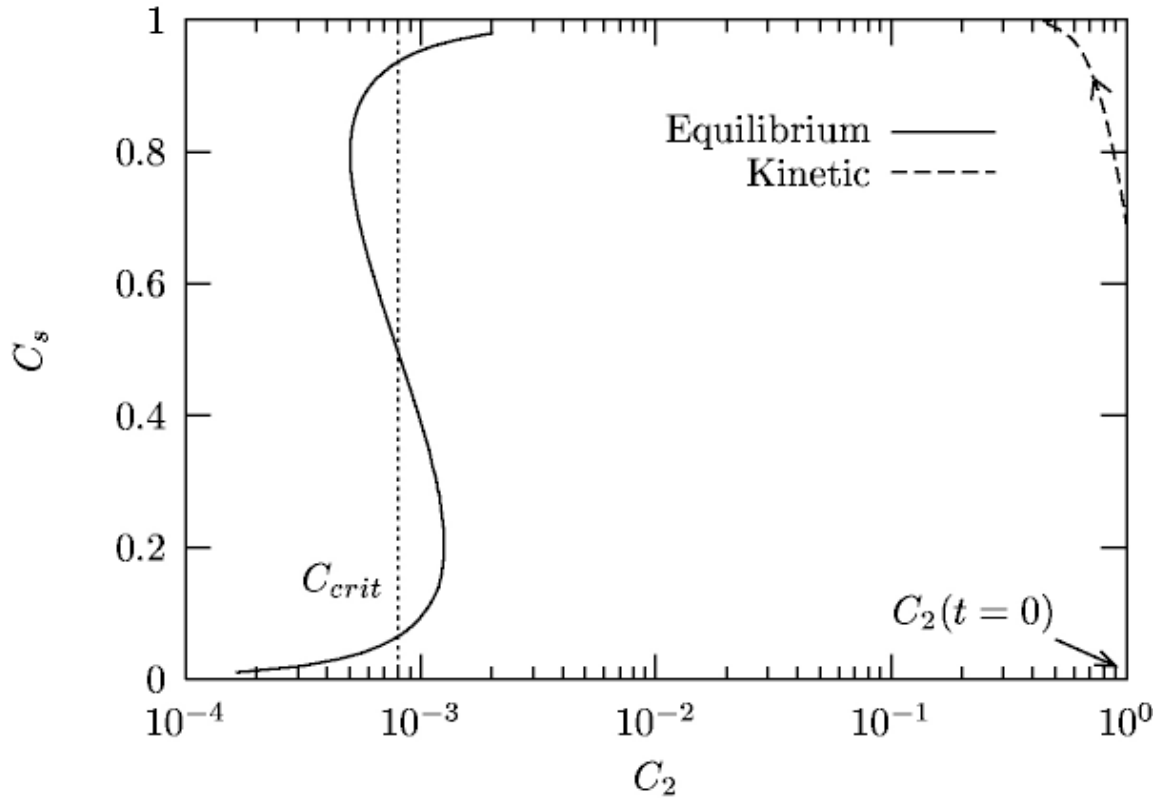


**Fig. 7.** Case Ps10: Equilibrium and kinetic surface segregation isotherms with $V$ = 0.053 eV. The arrow on the dashed line shows the direction of the kinetic path on the kinetic isotherm. $C_s$ and $C_2$ denote here the atomic fraction of the B substrate atoms on the surface and in the second underlayer, respectively. $C_{crit}$ (dotted line) is the composition above which the surface transition takes place.

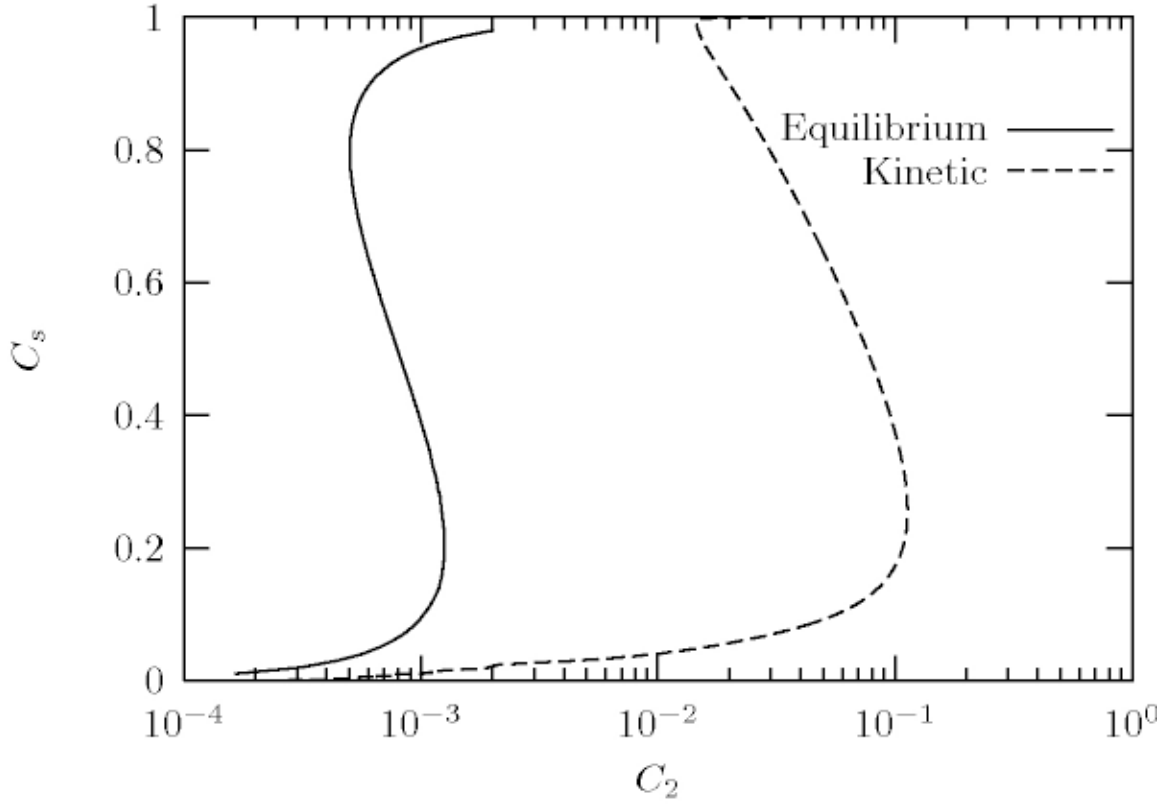


**Fig. 8.** Case Psta: Equilibrium and kinetic surface segregation isotherms. The arrow shows the direction of the kinetic path on the kinetic isotherm. $C_s$ and $C_1$ denote here the atomic fraction of the *B* substrate atoms on the surface and in the first underlayer, respectively.

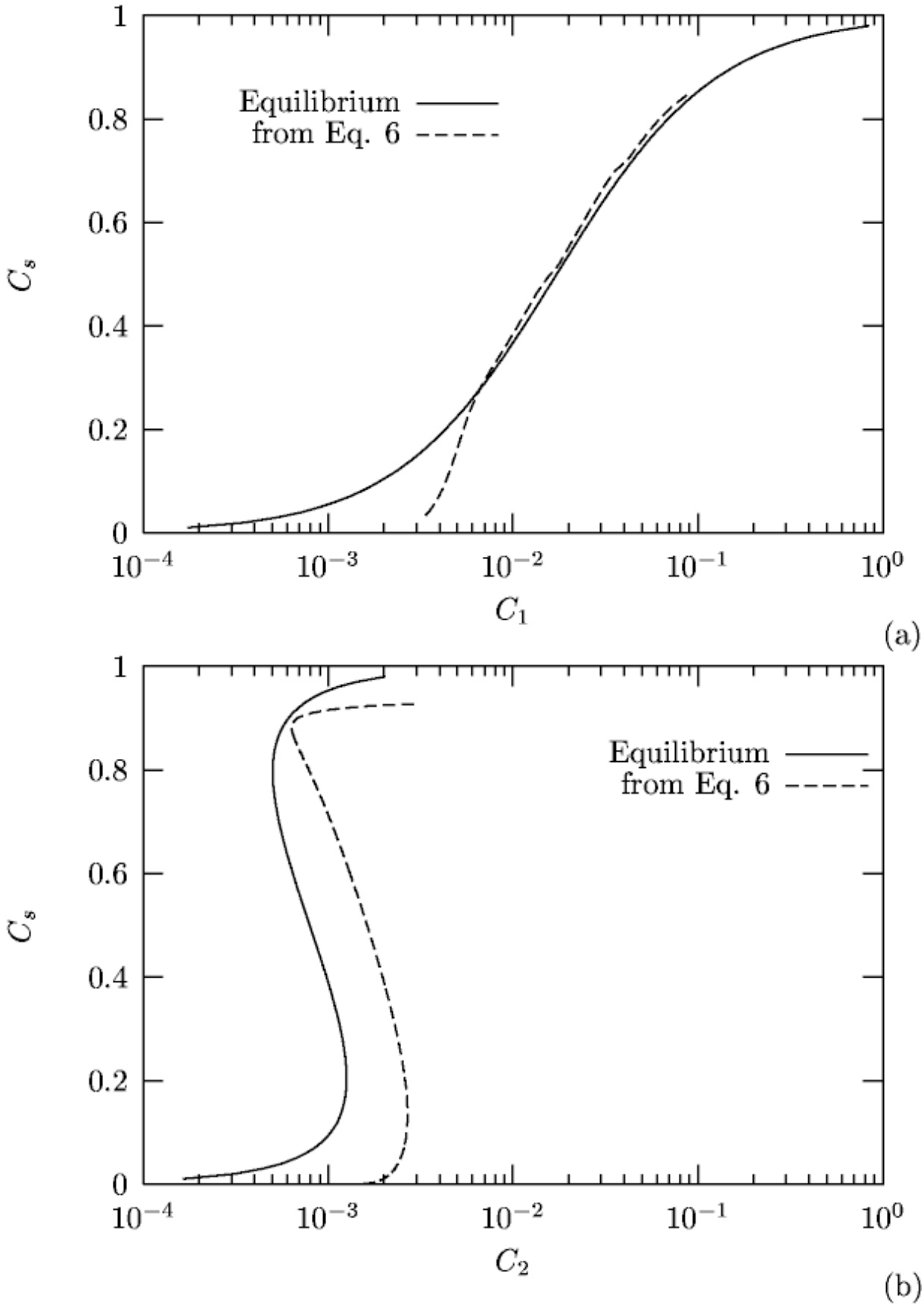


**Fig. 9.** Kinetic isotherms obtained from Eq. 1 compared to the equilibrium ones: (a) case Id10 (b) case Pd10.

**Table 1.** Summary of the results. The tables show if the SLE obeyed (*Y*) or not (*N*) and the thickness of the selvedge (1 or 2). The first and second (white) characters (black background) in the top left cells are related to the chemical and the segregation behaviour of the system. The characters in the column and line headers characterize the thickness of the deposit and the diffusion behaviour (see also the first paragraph in section 3).

| Id | 1 | t |
|---|---|---|
| 0 | *Y/1* | *Y/1* |
| a | *Y/1* | *Y/1* |

| Is | 1 | t |
|---|---|---|
| 0 | *N/1* | *Y/1* |
| a | *N/1* | *Y/1* |

| Pd | 1 | t |
|---|---|---|
| 0 | *Y/2* | *Y/2* |
| a | *Y/2* | *Y/2* |

| Ps | 1 | t |
|---|---|---|
| 0 | *N/2* | *Y/2* |
| a | *N/2* | *N/2* |

the almost intact deposit. The SLE is found to be obeyed and the selvedge ends at the second subsurface layer.

### 3.8. Pd1a, Pdta, and Ps1a

These cases are very similar to cases Pd10, Pdt0 and Ps10. The corresponding composition profiles evolve practically in the same way, only the time scale can be different. The kinetic isotherms look also just as in the Pd10, Pdt0 and Ps10 cases, therefore they fit quite well to the equilibrium isotherms for the cases Pd1a, Pdta, and deviate very significantly for the case Ps1a. Therefore the SLE is obeyed for cases Pd1a and Pdta, but *not obeyed* for Ps1a, furthermore the surface selvedge ends in all the cases at the second subsurface layers.

### 3.9. Psta

The time evolution of the composition profile is quite similar to that observed in the Ista case. Here the stepwise character is somewhat more pronounced during the process because besides the diffusion asymmetry the phase separation tendency also helps keeping it. However, whereas in the Ista case the local equilibrium hypothesis is obeyed, here the kinetic isotherm deviates from the equilibrium one, despite the fact that $C_s$ and $C_2$ start from being equilibrium. (Fig. 8) Therefore here the SLE is *not obeyed* and the selvedge ends at the second subsurface layer.

### 3.10. Comparison of KMF results to the KMC results

To be sure of the results obtained in KMF, we compared them with KMC results. The comparison showed that both the KMC composition profiles and the kinetic isotherms are quite similar to KMF ones.

### 3.11. Equilibrium surface segregation isotherms from a single kinetic measurement

In checking whether the equilibrium isotherm from a single kinetic measurement can be determined or not, we consider only the cases when the local equilibrium hypothesis is obeyed and when the deposit element segregates (usual experimental situations) [3]. To deduce the equilibrium isotherm from a single kinetic calculation, we needed two steps: i) calculation of the time evolution of the surface concentration during the dissolution of a one atomic layer thick deposit into a substrate; ii) calculating $C_b(x{=}0,t)$ subsurface concentration from the corresponding solution of the Fick's equations (e.g. [2]):

$$C_b(x,t) = C_0 + \int_0^t J_0(t-\tau)\frac{\exp\left(-x^2/4D\tau\right)}{(\pi D\tau)^{1/2}}, \qquad (1)$$

where $C_0$ is the initial concentration in the bulk; $D$ is the bulk diffusion coefficient; $t$ is the time; $J_0$ is the dissolution flux from the surface into the bulk (no desorption), which is equal to the variation of the surface concentration $C_s$, i.e. $dC_s/dt = -J_0$, and measured experimentally.

We have shown that in case Id10 the kinetic and the equilibrium isotherms coincide mainly, however in case Pd10 they differ significantly [2] (Fig. 9). We note here, that the same conclusions can be drawn for cases Id1a and Pd1a. It is, however, not evident since although the kinetic isotherms are the same for case Id10 and Id1a, as well as Pd1a and Pd10, but the time evolution of the composition profiles are different.

## 4. CONCLUSIONS

1) The isotherms, as it is expected, are McLean-type for ideal and Fowler-Guggenheim-type for phase separating systems.

2) It can be seen in Table 1 that for one atomic layer thick deposits the surface local equilibrium does not obeys if the substrate atoms segregate.
3) The thickness of the selvedge is 1 as well as 2 atomic layers thick for ideal as well as for phase separating systems, respectively.
4) For asymmetric diffusion the composition profiles evolve practically in the same way as for symmetric case, only the time scale is different.
5) We have illustrated that, even if the above hypothesis is obeyed, the determination of the surface segregation isotherms, by measuring segregation kinetics in an initially homogeneous alloy, can lead to uncertain result because of the restricted validity of Fick's first equation on the nanoscale.

## 5. SUMMARY

We have shown that even in simple cases the local equilibrium can be violated in much more cases than was expected formerly (Table 1). Thus the use of models supposing local equilibrium to evaluate and interpret (experimental) data is hazardous. Furthermore we have illustrated that, even if the above hypothesis is obeyed, the determination of the surface segregation isotherms, by measuring segregation kinetics in an initially homogeneous alloy, can lead to uncertain result because of the restricted validity of Fick's first equation on the nanoscale. At the same time we found that the selvedge is typically ends at the first or second subsurface layer if other complex phenomena such as e.g. surface structure relaxation, etc. are not included. Furthermore we have illustrated that, even if SLE is obeyed, the determination of the surface segregation isotherms, by measuring segregation kinetics in an initially homogeneous alloy, can lead to uncertain result because of the restricted validity of Fick's first equation on the nanoscale.

## ACKNOWLEDGEMENTS

This work is supported by the OTKA Board of Hungary (No. K67969, K61253 projects). One of the authors (Z. Erdélyi) of this paper is a grantee of the "Bolyac János" scholarship.

## REFERENCES

[1] M. Lagües and J.L. Domange // *Surf. Sci.* **47** (1975) 77.
[2] Z. Erdélyi, A. Taranovskyy and D.L. Beke // *Surf. Sci.* **602** (2008) 805.
[3] J. Eugéne, B. Aufray and F. Cabané // *Surf. Sci.* **241** (1991) 1.
[4] Z. Erdélyi and D.L. Beke // *Phys. Rev. B* **70** (2004) 245428.
[5] e.g.: F. Soisson, A. Barbu and G. Martin // *Acta Mater.* **44** (1996) 3789.