

KINETIC OF SURFACE SEGREGATION AND SPINODAL DECOMPOSITION  
IN THIN FILMS - GENERALIZATION OF MARTIN'S MODEL FOR  
VACANCY MECHANISM

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**Abstract**

It is shown that the generalization of the Martin's kinetic deterministic equations (with direct exchange of atoms) for vacancy mechanism is capable to describe the solid–vapour equilibrium in both pure or binary solid solution systems. The correct equilibrium values of vacancies are already well reproduced by taking only one initially empty plane at the surface, although the “solid–vapour” interface is about two atomic planes thick. For the process leading to phase separated and surface segregated states, the model gave the same kinetics in initially homogeneous, fifty–fifty spinodal systems as the direct exchange of atoms. We have shown that in weakly segregating systems, above a certain critical slab thickness,  $d_c$ , an interesting reversal takes place during the above process; first there is an increase (segregation) of B atoms at the surface, which – as a result of the coarsening of the spinodal structure – is followed by a fast decrease of the B atoms at the surface. On the other hand in slabs with  $d < d_c$  – due to a special size effect – this reversal can not take place.

## Introduction

In 1990 G. Martin [7] derived a simple, but very useful set of deterministic kinetic equations for one-dimensional interdiffusion in a binary solid solution. However, these equations are given for the exchange mechanism, i.e. they are based on the definition of the exchange probability between the two species. Generalization for a vacancy mechanism (on the basis of a more sophisticated master equation) was presented by Belashenko and Vaks [3], but this yielded unrealistic phenomenological transport coefficients, because the correlation effects were neglected. The improvement of these equations was given by Nastar et al. [8] and also a general set of kinetic equations has been derived by them.

In our paper – focusing on changes of the concentration distributions in slabs due to surface segregation and spinodal decomposition and/or phase separation – we present a generalization of the original Martin's kinetic deterministic equations for vacancy mechanism. Although correlation effects are not involved the advantage of this approach is its relative simplicity. Furthermore, as we will illustrate here, these simple equations are capable for the description of the kinetics of processes establishing equilibrium between the solid solution and its vapour phase as well.

The organization of the paper is as follows. First the generalized model is presented, then the calculation procedure is described, which is followed by the presentation of the results and their discussion, as well as by the conclusions.

## The model

As it is well known the Martin's model [7] consists of a slab of material with  $N$  lattice planes, normal to the  $y$  axis. Each atom in a plane (e.g. in the  $i$ th atomic layer) has  $z_1$  nearest neighbours in this plane as well as  $z_v$  in plane  $(i+1)$  and plane  $(i-1)$ . Thus the coordination number is  $Z = z_1 + 2z_v$ .

The change in concentration of A or B in plane  $i$  is given by

$$dc^K/dt = J_{i-1,i}^K - J_{i,i+1}^K, \quad K=A,B, \quad (1)$$

where  $J_{i,i+1}^K$  is the net flux per lattice site of K atoms from layer  $i$  to  $i+1$ . Let us now define  $J_{i,i+1}^K$  as:

$$J_{i,i+1}^K = z_v \{ c_i^K c_{i+1}^v \Gamma_{i,i+1}^K - c_{i+1}^K c_i^v \Gamma_{i+1,i}^K \}. \quad (2)$$

Here e.g.  $c_i^K$  and  $c_i^v$  are the fractions of K atoms and vacancies, respectively in the  $i$ th layer (see also [6]). Obviously

$$c_i^A + c_i^B + c_i^v = 1, \quad (3)$$

and

$$dc^v/dt = -dc^A/dt - dc^B/dt. \quad (4)$$

Furthermore in (2)  $z_v c_{i+1}^v$  is the probability to find a vacancy on a lattice site in layer  $(i+1)$ , next to the jumping atom being in layer  $i$  and  $\Gamma_{i,i+1}^K$  is the frequency with which one K atom in plane  $i$  exchanges with a vacancy in plane  $(i+1)$  (the first index denotes the plane where the jumping atom is). Under steady state

$$dc^K/dt = 0, \quad K=A,B, \quad (5)$$

which means – in a closed system – that  $J_{i,i+1}^K = 0$  whatever  $i$  [1]. Therefore

$$(c_{i,i+1}^K c_{i+1,i}^v) / (c_{i,i+1}^v c_{i+1,i}^K) = \Gamma_{i+1,i}^K / \Gamma_{i,i+1}^K, \quad K=A,B. \quad (6)$$

The atom-vacancy exchange frequencies can be given by expressions such as

$$\Gamma_{i,i+1}^K = \nu \exp(-E_{i,i+1}^K / kT), \quad K=A,B, \quad (7)$$

where  $k$  and  $T$  have their usual meaning and the pre-exponential factor (the attempt frequency)  $\nu$  is in the order of the lattice vibration frequency i.e.  $\nu \approx 10^{13} \text{ s}^{-1}$ . In principle  $E_{i,i+1}^K$  is the activation barrier for the atom-vacancy exchange. For reason of simplicity and without loss of generality we took the saddle point energy equal to zero (see also [4]) and thus  $E_{i,i+1}^K = -E_i^K$ , i.e.  $E_{i,i+1}^K$  can be taken as the negative value of the energy of K atom in the layer  $i$ . There are many choices of  $E_i^K$  which fulfil (6) [7].

It is worth to check whether (6) – with appropriate  $E_i^K$  energies – is identical to the condition of equilibrium or not. This can be done in a similar way as it was made in [7] for the direct exchange model. In order to find the free energy per number of lattice sites in one plane,  $f = u - Ts$ , first we need expressions for the internal energy,  $u$ , and the entropy,  $s$ , of a binary system with vacancies ( $f$  is related to the free energy per atom,  $f_a$ , by  $f_a = f/N$ ). Using the Ising model with only nearest neighbour interactions and the Bragg-Williams approximation the internal energy can be given as

$$u = 1/2 \sum_i (c_i^A E_i^A + c_i^B E_i^B), \quad (8)$$

where the summation should be taken from  $i=1$  to  $i=N$ . The factor  $1/2$  is to avoid the double counting of bonds, and the binding energy of a K atom in an internal plane  $i$  is:

$$E_i^K = z_v [(c_{i+1}^A + c_{i-1}^A) V_{AK} + (c_{i+1}^B + c_{i-1}^B) V_{KB}] + z_l (c_i^A V_{AK} + c_i^B V_{KB}), \quad (9)$$

where  $V_{AK}$  and  $V_{KB}$  are the nearest neighbour pair interaction energies ( $V_{AK}, V_{KB} < 0$ ). Using (3)

$$u = (1/2) \sum_K \{ z_v \sum_i c_i^K [(c_{i+1}^A + c_{i-1}^A) V_{AK} + (c_{i+1}^B + c_{i-1}^B) V_{KB}] + z_i \sum_i c_i^K (c_i^A V_{AK} + c_i^B V_{KB}) + z_v [(c_1^K c_2^A + c_{N-1}^K c_N^A) V_{AK} + (c_1^K c_2^B + c_{N-1}^K c_N^B) V_{KB}] \}. \quad (10)$$

Here  $\sum_i$  means summation from  $i=2$  to  $i=N-1$ . Furthermore the configurational entropy is given by

$$s = - \sum_i [c_i^A \ln c_i^A + (1 - c_i^A - c_i^v) \ln(1 - c_i^A - c_i^v) + c_i^v \ln c_i^v]. \quad (11)$$

Now in a closed system the number of lattice sites and the number of A and B atoms are constants, and thus for the average fractions

$$\underline{c}^A + \underline{c}^B + \underline{c}^v = 1 \quad \text{and} \quad \underline{c}^A + \underline{c}^B = \text{const.} \quad (12)$$

relations should be fulfilled (where the average fractions are given by  $N \underline{c}^\alpha = \sum_i c_i^\alpha$  with  $\alpha=A, B, v$ )

It can be seen from (3), (10), (11) and (12) that the state of the system is given by two sets of fractions  $c_1^A, \dots, c_N^A$  as well as  $c_1^v, \dots, c_N^v$ , which can be represented by vectors  $C^A$  and  $C^v$ , respectively. Thus the extrema to be found are those of  $f(C^A, C^v) + \lambda_A N \underline{c}^A + \lambda_v N \underline{c}^v$ , where  $\lambda_A$  and  $\lambda_v$  are Lagrange parameters introduced by the constraints (12). After simple, but lengthy algebra (taking the derivatives by  $c_i^A$  and  $c_i^v$ , respectively) – and using the notations  $V = V_{AB} - (V_{AA} + V_{BB})/2$  as well as  $P = V + (V_{AA} - V_{BB})/2 = V_{AB} - V_{BB}$  – it is found that for  $2 < i < N-1$

$$- (2V/kT) [Z c_i^A + z_v (c_{i+1}^A + c_{i-1}^A - 2c_i^A)] - (P/kT) [Z c_i^v + z_v (c_{i+1}^v + c_{i-1}^v - 2c_i^v)] + PZ + \ln(c_i^A / \{1 - c_i^A - c_i^v\}) = \lambda_A/kT \quad (13)$$

and

$$- (V_{BB}/kT) [Z(1 - c_i^v) - z_v (c_{i+1}^v + c_{i-1}^v - 2c_i^v)] - (P/kT) [Z c_i^A + z_v (c_{i+1}^A + c_{i-1}^A - 2c_i^A)] + \ln(c_i^v / \{1 - c_i^A - c_i^v\}) = \lambda_v/kT. \quad (14)$$

Relations for  $i=1, 2$  as well as for  $i=N-1, N$  can be also easily obtained.

Let us check now whether (6) with the choice  $E_{i,i+1}^K = -E_i^K$  (see also (9)) corresponds to the equilibrium conditions (13) and (14), or not. Since (6) should be

valid for both  $K=A$  and  $K=B$ , combining these equations the following steady state condition results;

$$(c_i^A c_{i+1}^B)/(c_i^B c_{i+1}^A) = (\Gamma_{i+1,i}^A \Gamma_{i,i+1}^B / \Gamma_{i,i+1}^A \Gamma_{i+1,i}^B). \quad (15)$$

But - taking into account (7) - this leads to

$$kT \ln(c_i^A/c_i^B) + E_i^A - E_i^B = kT \ln(c_{i+1}^A/c_{i+1}^B) + E_{i+1}^A - E_{i+1}^B. \quad (16)$$

Substituting  $E_i^K$  and  $E_{i+1}^K$  from (9) one can see that the left hand side of (16) is identical to (13) ( $\lambda_A$  is constant).

It can be also seen that, since in the bulk layers  $c_i^v \ll 1$ , i.e. the second term in (13) can be neglected, we arrive - apart from the constant  $ZP$  - at the same condition derived by Martin (eq. (5a) in [7]) for the exchange model without vacancies. On the other hand equation (14) is in fact the condition for the vacancy equilibrium. Accordingly  $\lambda_v=0$  ( $\lambda_v$ , similarly as  $\lambda_A$  for species A, can be called the vacancy chemical potential [7] and in equilibrium it should be equal to zero). Thus, neglecting the inhomogeneity terms and using that  $c_i^v \ll c_i^A$ , for an internal layer

$$kT \ln c_i^v / (1 - c_i^A) = (Z/kT)(V_{BB} + P c_i^A), \quad (17)$$

which in a pure B matrix ( $c_i^A=0$ ) - as it is expected from a model of breaking bonds - gives

$$kT \ln c_i^v = ZV_{BB}. \quad (18)$$

This result rises the problem of getting realistic vacancy concentrations. If we would take  $V_{BB}$  from the cohesive energy in the pure B, the vacancy formation energy would be very high within the Ising model and Bragg-Williams approximation. This is because (18) says that  $\Delta H_v^B = -ZV_{BB}$ . However, this "vacancy formation energy", as determined by equation (14), is fixed - similarly as the  $E_{i,i+1}^K$  migration energies in (15) and (16) - apart from an additive constant only. In fact in (14) the reference state is the vapour: we need  $ZV_{BB}$  energy to take one atom from the bulk and put it far from the solid into the vapour. (We will see later that the model is really capable to treat the solid-vapour equilibrium.) However, the vacancies are formed at the solid-vapour interface (which is the only source/sink of vacancies here) and during the process they flow into the crystal until the equilibrium is established. Thus better to choose the reference state - according to the usually accepted "rule" (see e.g. Beke, [1]) that during the formation of a vacancy from the  $Z$  bonds broken about  $Z/2$  bonds are re-established at the surface - by adding the constant  $ZV_{BB}/2$  to the left hand side of (14) i.e.

$$\Delta H_v = -ZV_{BB}/2. \quad (19)$$

But the real vacancy formation energies are still smaller than this value because in our model the relaxation energies are not involved. Thus still realistic pair interaction energies would result in much too high vacancy formation energies and so in very low and unrealistic vacancy content, making the diffusion process (and simultaneously the program) extremely slow. Therefore we decided to derive the pair interaction energies from the real vacancy formation energies, in pure A and B, according to (19).

### Calculation procedure

A numerical method can be used to solve the set of coupled differential equations (1) (with (2), (4), (7) and (9)) to obtain the time evolution of the concentrations in different planes. We have a symmetrical system with a symmetry plane in the centre, numbered by  $n$ , i.e.  $c_{n+1}^A = c_{n-1}^A$ ,  $c_{n+1}^B = c_{n-1}^B$  and obviously  $c_{n+1}^v = c_{n-1}^v$ .

Due to K atom-vacancy exchanges between layer  $i$  and layer  $i+1$ , the rate of the change of A atoms in the  $i^{\text{th}}$  layer can be given as:

$$(dc_i^K)/dt = -J_{i,i+1}^K. \quad (20)$$

Thus eq. (1) can be given as:

$$dc_i^K/dt = (dc_i^K)/dt - (dc_{i,1}^K)/dt. \quad (21)$$

The calculation procedure now is as follows. An initial atomic configuration of the layers is defined and the right-hand side of eq. (20) (for  $K=A$  and  $B$ ) is calculated for the first layer. A (small) time step  $dt$  is chosen and the corresponding changes of the concentrations of A and B atoms as well as vacancies in the first layer,  $dc_1^\alpha$  ( $\alpha=A, B, V$ ), are evaluated from the above equations after a (small) time step  $dt$ . Then obviously

$$dc_2^\alpha = -dc_1^\alpha. \quad (22)$$

Then the concentrations in the first and second layers are updated and again a time step  $dt$  is made. This procedure for the first layer is continued until the sign of the change reverses. Then subsequently the second and the third as well as the third and fourth layers are brought into quasi-equilibrium in the same way, and so forth. After the one but last and the last layers have been brought into quasi-equilibrium, the whole procedure is repeated.

With the first layer (layer 1) as a source and sink of vacancies, the system will establish a momentary quasi equilibrium of vacancy fraction in each layer and, at a much slower rate, of fractions of A and B atoms. Like in nature the vacancy diffusion is fast, whereas the atomic diffusion is slow.

The main difficulty is the right choice of the magnitude of the time steps. If the time step is chosen too short, virtually 'nothing' will happen, whereas if it is too long, atomic fractions could fall outside the [0,1] range ( $dc_i^K$  and so  $-dc_{i+1}^K$  in eq. (21) could be higher than the maximum possible change of  $c_i^K$  or  $c_{i+1}^K$ , which is e.g. equal to  $c_i^K$  or  $(1-c_i^K)$  depending on the sign of  $dc_i^K$ ). Because of the high vacancy content of the first (and later on also of the second) layer, and moreover, because of the relatively small activation energy for atoms in these layers (due to the contact with vacuum in the first layer), the atomic diffusion in these layers is very fast as compared to the bulk.

We solved the problem of choosing an efficient time step in the following way. We determined say for the layer  $i$  the minimum value of  $dc_i^\alpha$  and  $dc_{i+1}^\alpha$  ( $\alpha=A,B,v$ ) for  $dt=1$ , and then we chose  $dt$  in such a way that the relative change of this minimum value was, for example, 0.1% or 0.01%. The other quantities will then change by a smaller relative amount. Then this procedure was repeated until the variations changed sign and the time elapsed was summed during such a procedure. The maximum time elapsed between any two of the layers  $1 \dots n$  during such a run was taken as the period of time for the whole run. (If one would continue during such a whole period the process in the other layers as well, changes in the concentration would do nothing else than always alternately reverse sign during such a period, so that virtually 'nothing' would happen any further for those layers.) This trick is necessary to obtain results within feasible computer running times.

## Results and discussion

### 1. Pure bcc system

The program was run for a pure metal B with  $V_{BB} = -0.22$  eV (i.e. with a vacancy formation energy of 0.88 eV), for a slab consisting of 13 layers taking  $z_v=4$  and  $z_i=0$  as well as using one initial empty plane at the surface. The vacancy fraction in a bulk crystal is then given by eq. (18) with (19). In Table 1  $c_v$  values, obtained from the simulations, are given for the central (7<sup>th</sup> layer) at various temperatures. The results of the program after long enough running time are compared to those calculated from eqs. (18) and (19). Even for a structure consisting of as few as 13 layers, the agreement between the results of the simulations and the analytical equation for bulk material is very good. In fact the influence of the surface extends essentially to the first few planes only.

Table 1

Vacancy fraction in a pure metal B at various temperatures from eqs.(18) with (19) as compared to the vacancy fraction in the central (7<sup>th</sup>) layer obtained from the program ( $V_{BB} = -0.22$  eV)

$z_v = 4$   
 $z_a = 0$

Temperature $T$ (K)	$c_V$ program	$C_V$ eq.(18-19)
1400	$6.79 \times 10^{-4}$	$6.79 \times 10^{-4}$
1300	$3.87 \times 10^{-4}$	$3.87 \times 10^{-4}$
1200	$2.01 \times 10^{-4}$	$2.01 \times 10^{-4}$
1100	$9.34 \times 10^{-5}$	$9.30 \times 10^{-5}$
1000	$3.67 \times 10^{-5}$	$3.67 \times 10^{-5}$
900	$1.17 \times 10^{-5}$	$1.18 \times 10^{-5}$

Let us now inspect these first planes. We can get an analytical expression for the fractions in these planes again minimizing  $f$  in respect to  $c_1^B$  and  $c_2^B$  if  $c_1^A=0$ , ( $z_v=4$ ,  $z_a=0$ ). The result is:

$$c_1^B c_2^V / c_1^V c_2^B = \exp(-E_1^B/kT) / \exp(-E_2^B/kT) \quad (23)$$

Eq. (23) is nothing else than the mass-action law for the reaction (in self-explanatory notation):



It is trivial that:

$$c_1^B + c_1^V = 1 \quad (25a)$$

$$c_2^B + c_2^V = 1. \quad (25b)$$

Furthermore, in the starting configuration the first plane is completely occupied by vacancies and the second layer by atoms. Let us suppose that, during the process of vacancy-atom exchanges, the sum of atoms and vacancies in the first two planes remains the same, i.e.:

$$c_1^V + c_2^V = 1 \quad (26a)$$

$$c_1^B + c_2^B = 1. \quad (26b)$$



Moreover, let us assume that the third plane is approximately occupied by atoms only (negligible amount of vacancies as compared to the amount of A atoms in this plane):

$$E_1^B = 4c_2^B V_{BB} \quad \text{and} \quad E_2^B = 4(c_1^B + 1)V_{BB}. \quad (27)$$

Note that after some algebra an expression can be derived from the above relations for  $c_2^V$ :

$$c_2^V / (1 - c_2^V) = \exp(4c_2^V V_{BB} / kT). \quad (28)$$

This is an implicit equation that can be solved numerically. In Table 2 we compare the results obtained by eq. (28) with the vacancy fractions found from the simulations. The agreement is good in spite of the simplifying assumption by which the above equation was obtained. It means that the far majority of vacancies resides in the first two planes.

Table 2

Vacancy fractions in a pure metal A in the first and second layer at various temperatures following the program and compared with the results of eq.(28). Also the results from the program for the third layer are given ( $V_{BB} = -0.22$  eV)

Temp. $T$ (K)	$c_1^V$ program	$c_1^V$ eq.(28)	$c_2^V$ program	$c_2^V$ eq.(28)	$c_3^V$
1400	$8.02 \times 10^{-1}$	$8.05 \times 10^{-1}$	$1.93 \times 10^{-1}$	$1.95 \times 10^{-1}$	$2.74 \times 10^{-3}$
1300	$8.11 \times 10^{-1}$	$8.13 \times 10^{-1}$	$1.86 \times 10^{-1}$	$1.87 \times 10^{-1}$	$1.65 \times 10^{-3}$
1200	$8.20 \times 10^{-1}$	$8.21 \times 10^{-1}$	$1.78 \times 10^{-1}$	$1.79 \times 10^{-1}$	$9.10 \times 10^{-4}$
1100	$8.29 \times 10^{-1}$	$8.30 \times 10^{-1}$	$1.70 \times 10^{-1}$	$1.70 \times 10^{-1}$	$4.60 \times 10^{-4}$
1000	$8.38 \times 10^{-1}$	$8.39 \times 10^{-1}$	$1.61 \times 10^{-1}$	$1.61 \times 10^{-1}$	$1.91 \times 10^{-4}$
900	$8.48 \times 10^{-1}$	$8.48 \times 10^{-1}$	$1.52 \times 10^{-1}$	$1.52 \times 10^{-1}$	$6.50 \times 10^{-5}$

Physically the result indicates that a surface will not be perfect, but always will be partly empty, partly occupied by atoms, just for thermodynamic reasons (kinks, islands, terraces).

In order to check the influence of the number of terminal vacant planes, we repeated some of these calculations by using initially 3 terminal empty planes as well. According to the results this parameter does not play an important role in determining the vacancy equilibrium concentration. We also carried out runs for cases with different initial concentrations of vacancies in the slab. The final state was always the same with a "solid-vapour interface" of about two atomic planes thick i.e. the atomic fraction of vacancies changed from its equilibrium value in the solid to its equilibrium value in the vapour across two planes (Table 1, and see also later). This illustrates that the program

is capable to describe the solid-vapour equilibrium already with two or three initial empty terminal planes, moreover for establishing the vacancy equilibrium inside the sample, already one terminal plane would be enough. However, for reasons of safety, we made our further calculations for alloys by using 1, 3 or 4 initial empty terminal planes, too.

## 2. Strongly segregating bcc AB alloy

It is usual to classify the binary alloys into two groups: strongly and weakly segregating systems. From the equation of the surface segregation isotherm it is easy to show (see e.g. [5]) that there exists a certain bulk composition

$$c_h = 1/2 + (V_{AA} - V_{BB})/4V, \quad (29)$$

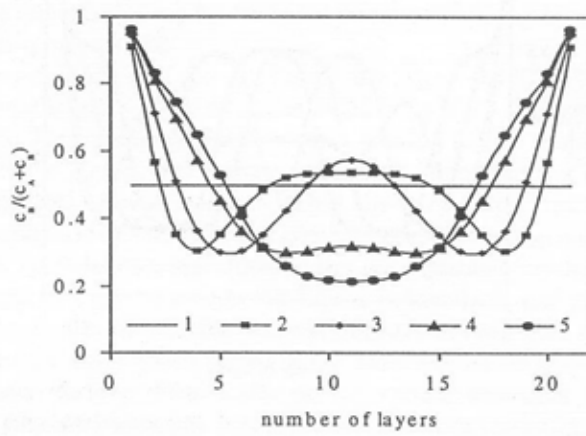
so that for bulk compositions,  $c_b$ , smaller than  $c_h$  there is a segregation and for  $c_b > c_h$  there is a desegregation. Accordingly, if  $c_b < 1$  the system is weakly segregating, while in the opposite case we speak about a strongly segregating system (because now only segregation occurs at any bulk composition:  $0 \leq c_b \leq 1$ ). Furthermore for weakly segregating systems if  $T < T_h$  (the temperature of the miscibility gap at  $c_h$ ), depending on the bulk composition either segregation or desegregation is expected.

Beke et al. [2] investigated the interplay between the surface segregation and spinodal decomposition as well as the effect of the slab thickness in a strongly segregating spinodal system with parameters  $(V_{BB} - V_{AA}) = 0.15 \text{ eV}$  and  $V = V_{AB} - (V_{AA} + V_{BB})/2 = +0.035 \text{ eV}$ , in the framework of the direct exchange model. In order to compare their results with those obtained from our present model we ran our program with the same values for (100) direction ( $z_1 = 4, z_2 = 0$ ) at 1400 K.

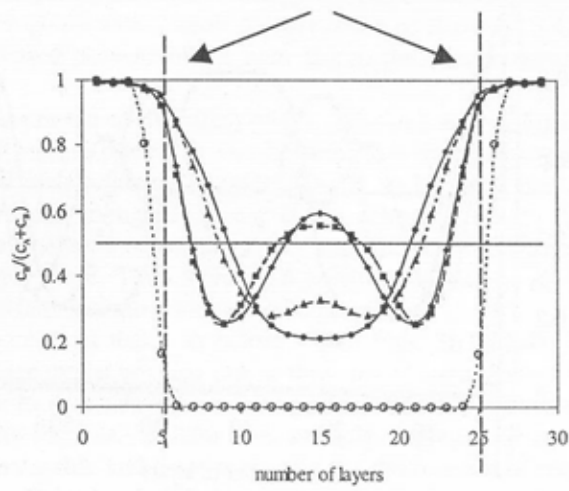
Note however, that now the absolute magnitudes of the interaction energies were  $V_{BB} = -0.22 \text{ eV}, V_{AA} = -0.37 \text{ eV}$  (which – according to (19) – correspond to the vacancy formation energies in Cu and V, respectively) and  $V_{AB} = -0.26 \text{ eV}$ .

Fig. 1 and 2 show the time evolution of the system with and without vacancies for two different slab thickness. It can be seen that the agreement is good, i.e. not only the final states are the same, but the details of the kinetics are also similar. Note that e.g. on Fig. 2b the curve corresponding to the longest time is comparable to the curve denoted by the same symbols in Fig. 2a. In fact – due to the arbitrariness of choosing the saddle point energy and  $v$  in (7) – the absolute time scales are not comparable for the two mechanisms. However, on a time scale normalised for example by the time necessary to reach the stage where the two spinodal waves meet in the centre (illustrated by full squares in Fig. 2a and 2b) the two figures would be practically identical.

It is also important to note that the number of the initial empty terminal planes did not influence the results i.e. the kinetics in both (exchange and vacancy) models are the same.



(a)  
original surfaces



(b)

Figure 1. Time evolution of composition in a BCC (100) structure without (a) [2] and with vacancies (b) (21 atomic planes and 4-4 initial empty planes on the surfaces). Increasing numbers at the curves indicate the time sequence. Dashed line with open circles denotes the vacancy distribution in the latest state

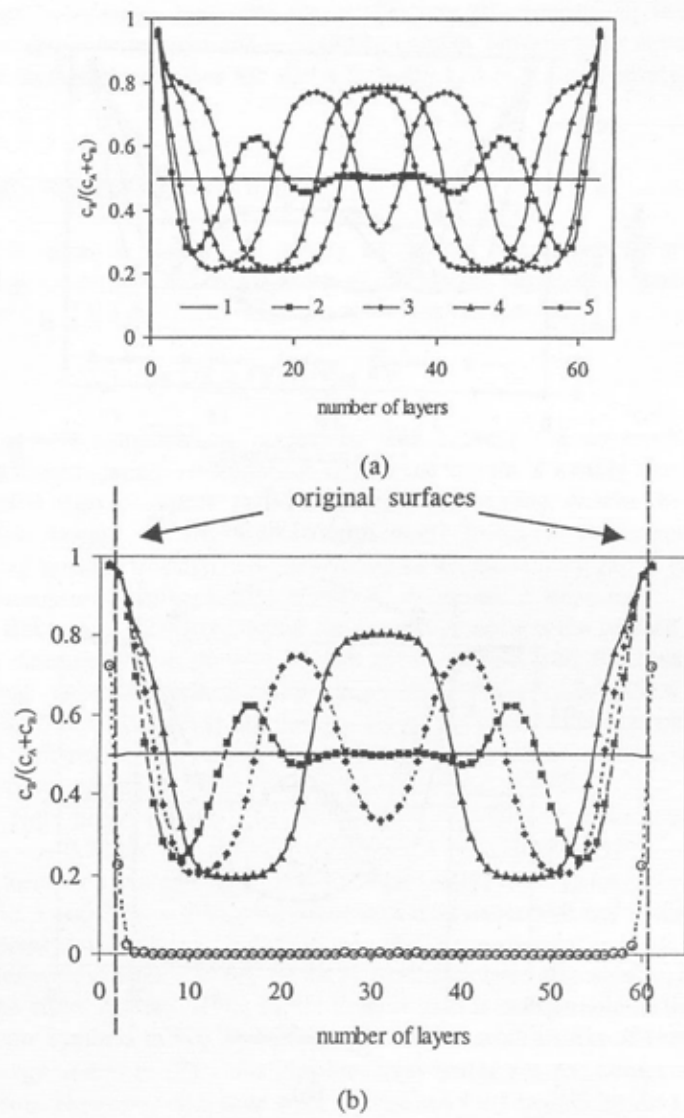


Figure 2. Time evolution of composition in a BCC (111) structure without (a) [2] and with vacancies (b) (61 atomic planes and 1-1 initial empty planes on the surfaces). Increasing numbers at the curves indicate the time sequence. Dashed line with open circles denotes the vacancy distribution in the latest state.

### 3. Weakly segregating fcc alloy

We also carried out calculations for the (111) direction ( $z_v=3$ ,  $z_l=6$ ) at 1000 K for weakly segregating system with

$$V_{BB} = -0.1555\text{eV}, V_{AA} = -0.1728\text{eV} \text{ and } V_{AB} = -0.12975\text{eV}.$$

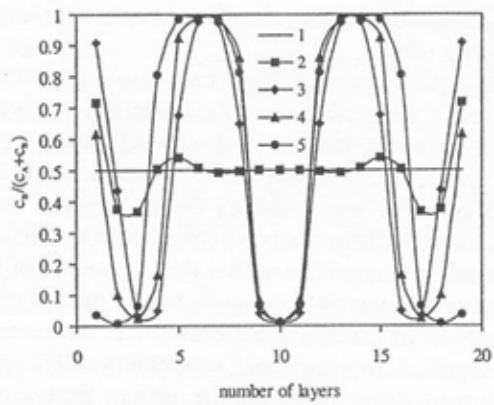
Accordingly  $c_h=0.69$  and – from a regular solution model –  $T_h=2043$  K in this model system i.e.  $T < T_h$ . Figures 3a and 3b show that, starting from a homogeneous fifty-fifty alloy with 19 atomic planes, first a segregation of B atoms starts at the surface and the segregation generated spinodal wave reaches the centre and overlaps with its symmetrical counterpart. However, there is a competition between the surface segregation of B atoms and the spinodal decomposition and/or the coarsening of the spinodal structure developed. Indeed as it can be seen in this figure, before the B-rich phase could develop at the surface the amplitude of the concentration wave in the centre reached already the concentrations of the equilibrium phases and a relatively stable spinodally decomposed structure has been formed there. Later on the system decreases its free energy by eliminating the first interfaces just below the free surfaces (coarsening of the structure) and as a result the surface structure makes a sudden “reversal”. This means that a morphology A/B...B/A develops with a small segregation of B atoms on the surfaces of the A-rich phase. Although the surface energy of such a configuration should be larger than that of a B-rich phase with a small desegregation of B atoms, the overall energy of the system is decreased because of the gain due to the disappearance of two internal interfaces.

For the illustration of the effect of the slab thickness,  $d$ , Figs. 4a and 4b show the situation for 7 atomic planes. It can be seen that the system arrives at a B/A/B morphology with B rich segregated layers. This is so because, due to the small slab thickness, there are not enough B atoms in the centre to supply the growth of the spinodal wave up to the level of the miscibility gap, and thus the formation of the B-rich phase is not possible there. Thus there exist a critical thickness,  $d_c$ , below which the “reversal” of the surface structure does not take place.

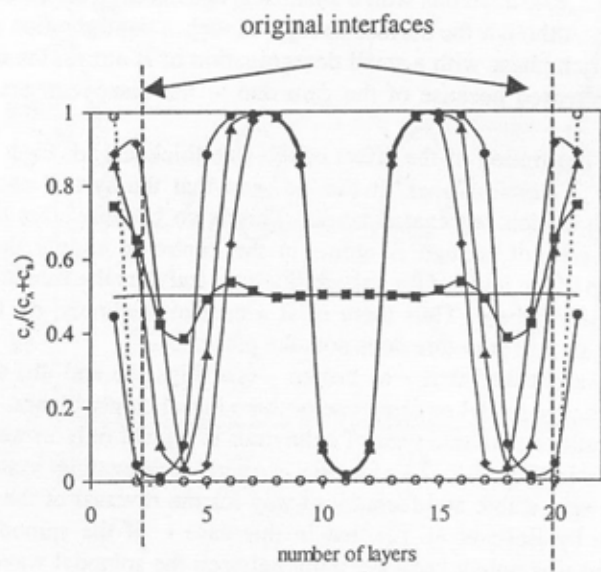
Again we checked that – as before – (see Figs. 3b and 4b) the result are the same for the exchange model or using one or three initial empty planes.

It is worth to note this type of behaviour is typical only in weakly segregating systems. Indeed in Fig. 2a, 2b, for the strongly segregating system, the surface configuration is very stable and there is no way for the reversal of the configuration. It was also shown by Beke et al. [2] that in this case – if the spinodal wave became “stronger” – there was only a breaking point between the spinodal wave and the surface profile developed at the very early stage of the process.

The observed reversal thus is an inherent property of the weakly segregating system, and the characteristic time evolution of the surface concentration (first there is an increase and then there is a fast decrease of the B atoms at the surface, as well as the existence of a critical slab thickness,  $d_c$ , below which this is not observed anymore) seems to be observable experimentally in thin film samples.



(a)



(b)

Figure 3. Time evolution of composition in a FCC (111) structure without (a) and with vacancies (b) (19 atomic planes and 1 initial empty plane on the surfaces). Increasing numbers at the curves indicate the time sequence. Dashed line with open circles denotes the vacancy distribution in the latest state.

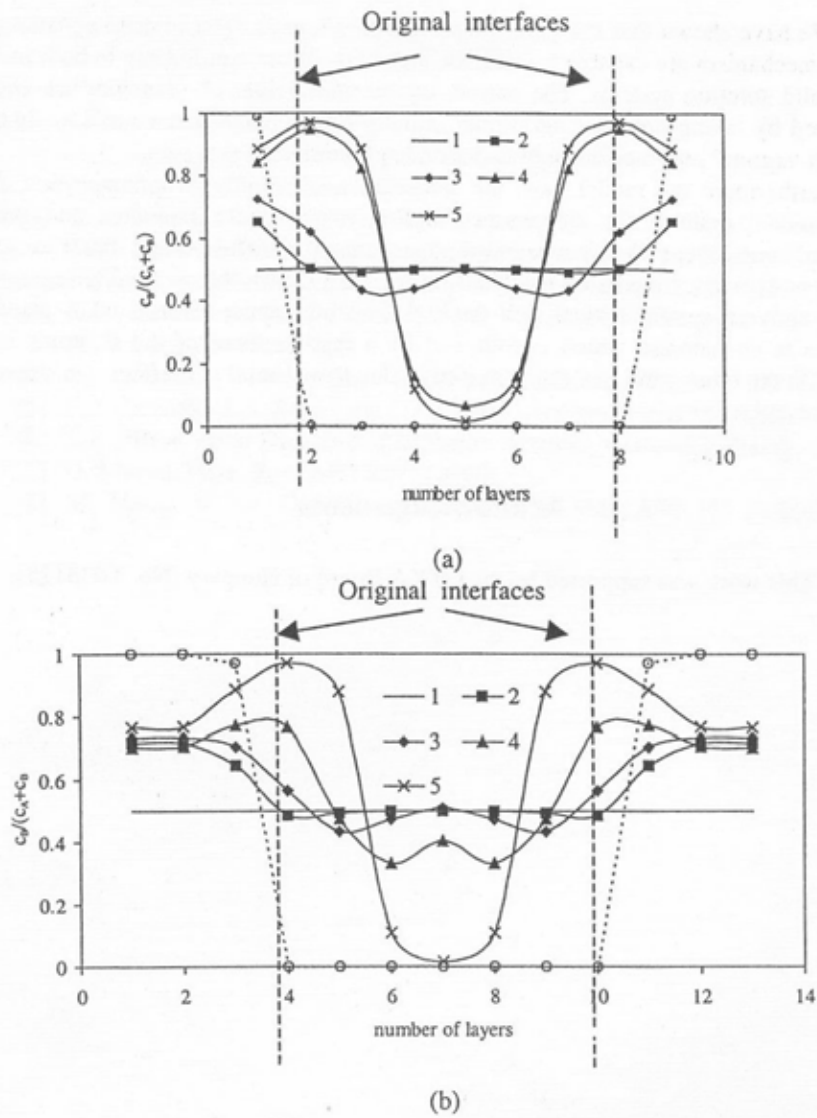


Figure 4. Time evolution of composition in a FCC (111) structure of 9 atomic planes with vacancies: (a) 1 initial empty planes on the surfaces; (b) 3 initial empty planes at the surfaces. Increasing numbers at the curves indicate the time sequence. Dashed line with open circles denotes the vacancy distribution in the latest state.

## Conclusions

We have shown that the generalized Martin's kinetic deterministic equations for vacancy mechanism are capable to describe the solid-vapour equilibrium in both pure or binary solid solution systems. The correct equilibrium values of vacancies are already reproduced by taking only one additional initially empty plane at the surface, although the "solid-vapour" interface is about two atomic planes thick.

Furthermore the model gave the same kinetics in initially homogeneous, fifty-fifty spinodal systems for the process leading to the phase separated and surface segregated state independently whether the mechanism of diffusion is a direct exchange of atoms or a vacancy mediated mechanism. We have shown that in weakly segregating systems, above a certain critical slab thickness, an interesting reversal takes place i.e. first there is an increase which is followed by a fast decrease of the B atoms at the surface. On the other hand in slabs with  $d < d_c$  – due to a special size effect – this reversal can not take place.

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