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Segregation in thin films of binary alloys $A_x\ B_{1-x}$

Ana María Llois and Claudio R. Mirasso
Departamento de Física, Comisión Nacional de Energía Atómica,
avenida del Libertador 8250, 1429 Buenos Aires, Argentina
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The concentration profiles in thin fcc metal slabs of two segregating components have been calculated within the mean-field approximation. Special attention has been placed on the contribution of the mixing energy. Interesting differences with the kind of profile that appears in semi-infinite systems (surfaces) are found. We also study an open linear chain and have obtained similar results to those of Arroyo and Joud using Monte Carlo simulation.

I. INTRODUCTION

The problem of surface segregation in substitutional alloys of transition metals has been studied both theoretically[1–4] as well as experimentally[5–8] in recent years. Given an average bulk composition, it is known that the concentration near the surface is usually different from the bulk one. Most of the theoretical studies have tried to predict surface segregation and segregation profiles assuming that after three or four layers below the surface the system has attained its bulk values.[1,2]

In the last decade the construction of new superlayered materials, which have interesting mechanical and electronic properties,[9,10] has been a wide field of investigation. In this sense, it is of interest to know which are the effects of the boundaries in the segregation profile of a thin slab, depending on the number of layers it contains.

In this work, we investigate the segregation characteristics of thin films of binary alloys (A_xB_{1-x}) within the mean-field approximation (MFA). We consider that this approach to the study of segregation in multilayered systems is a good starting point, even if the transition temperatures obtained using MFA are usually larger than those obtained by techniques which take into account correlations. We study the system behavior as a function of the total number of layers of the slab, temperature, and average concentration.

The concentration profile is usually related to the mixing energy because a monotonous profile is obtained when the alloy tends to segregate and an oscillating one when it tends to order in the bulk. There are two other factors which may influence segregation: differences in size and surface energies of the constitutents of the alloys.[4] In this first approach we mainly consider the effect of the mixing energy.

For the calculation we consider only nearest-neighbor interactions, supposing that the energy of the system can be written as the sum of the interaction energy between pairs (Ising model). We treat mainly the case of segregating alloys of fcc structure.

In Sec. II we describe the formalism used. We obtain a set of coupled nonlinear equations through whose resolution the layer concentrations are obtained.

In Sec. III we show the concentration profiles obtained for the slab and compare them with those obtained for the semi-infinite system using MFA (Ref. 2) and Monte Carlo simulation.[3] The behavior found for the slab is different from the one observed in the semi-infinite case, in the sense that the concentration profiles depend on the number of layers considered. This differences are due to the fact that we are studying thin films of a few number of layers. Interesting features also appear when one changes other parameters, such as average concentrations, mixing energy versus surface energy differences and temperature. For a linear chain of 20 atoms we obtain results very close to those of a Monte Carlo simulation.[3] When using the same set of parameters as Arroyo and Joud the behavior of the system is similar to the semi-infinite case, in the sense that after three layers the concentration remains constant. However, we show that when the temperature is lowered or the interaction parameters are changed, the concentration of the internal layers cannot be set equal to the third or fourth one, this behavior being qualitatively the same as observed for the slab.

II. FORMALISM

We consider a solid slab of a binary alloy A_xB_{1-x} in vacuum, described by an Ising Hamiltonian with nearest-neighbor interactions only, which is appropriate for a fcc lattice of transition metals. We shall closely follow the notation of Treglia *et al.*,[2]

$$H = \tfrac{1}{2}\sum_{n,m}\sum_{i,j}\varepsilon_{nm}^{ij}P_n^iP_m^j\ . \tag{1}$$

ε_{nm}^{ij} is the interaction energy of an atom of type i at site n and an atom of type j at site m $(i,j = A,B)$. P_n^i is the occupation number equal to 1 (0) if site n is (is not) occupied by an atom of type i. For a binary alloy $P_n^A + P_n^B = 1$, so that (1) can be rewritten in terms of $P_n = P_n^A$:

$$H = H_0 + \sum_{n} P_n \sum_{(m \neq n)} (\tau_{nm} - V_{nm}) + \sum_{n,m} P_n P_m V_{nm} \ , \tag{2}$$

where $H_0 = \frac{1}{2} \sum_{n,m} \epsilon_{nm}^{BB}$, $V_{nm} = \frac{1}{2}(\epsilon_{nm}^{BB} + \epsilon_{nm}^{AA} - 2\epsilon_{nm}^{AB})$, and $\tau_{nm} = \frac{1}{2}(\epsilon_{nm}^{AA} - \epsilon_{nm}^{BB})$.

Here, V_{nm} is the mixing energy and we assume that it has the same value in the surface as in the interior of the slab, so that $V_{nm} = V$. The same holds for τ_{nm}, so that $\tau_{nm} = \tau$. $V > 0$ indicates the tendency of the alloy to order in a bulk, whereas $V < 0$ indicates tendency to segregation. In general we shall assume that $\epsilon_{nm}^{AA} = \epsilon_{nm}^{BB}$, so that the surface energies are the same.

H can be written in terms of the coordination number Z of each site as

$$H = H_0 + (\tau - V) \sum_{n} P_n Z_n + V \sum_{(n \neq m)} P_n P_m \ . \tag{3}$$

In the MFA the average $\langle P_n P_m \rangle$ factorizes into $\langle P_n \rangle \langle P_m \rangle$. Setting $\langle P_n \rangle \equiv c_n$, c_n being the concentration of A-type atoms, then $\langle P_n P_m \rangle = c_n c_m$.

As we have two surfaces and a finite number of layers, the concentration is going to differ from layer to layer, so that we define c_p ($p = 1, 2, ..., M$, where M = number of layers of the slab) as the pth layer concentration. Averaging H over all configurations we obtain

$$\begin{aligned} \langle H \rangle = H_0 + (\tau - V) N \sum_{p=1}^{M} c_p (Z_p + Z_p^{+} + Z_p^{2+} \\ + Z_p^{-} + Z_p^{2-}) \\ + NV \sum_{p} c_p (Z_p c_p + Z_p^{+} c_{p+1} + Z_p^{-} c_{p-1} \\ + Z_p^{2+} c_{p+2} + Z_p^{2-} c_{p-2}) \ . \end{aligned} \tag{4}$$

Z_p, Z_p^{+}, Z_p^{2+}, Z_p^{-}, and Z_p^{2-} are the coordination numbers (number of nearest-neighbors) of site n, which belongs to layer p, in the same layer and in the first and second ones above and below, respectively. N is the number of atoms per layer. For a fcc (111) plane $Z_p = 6, Z_p^{+} = Z_p^{-} = 3$, $Z_p^{2+} = Z_p^{2-} = 0$, and for the (110) $Z_p = 2, Z_p^{+} = Z_p^{-} = 4$, $Z_p^{2+} = Z_p^{2-} = 1$.

Averaging the entropy within the same approximation one obtains for the Gibbs free energy

$$\begin{aligned} G = \langle H \rangle + NkT \sum_{p=1}^{M} [c_p \ln c_p + (1 - c_p) \ln (1 - c_p)] \\ -N \sum_{p=1}^{M} c_p \mu \ . \end{aligned} \tag{5}$$

One of the constraints of the system has already been used, $c_A + c_B = 1$, and for the other one, which takes into account the conservation of mass ($\sum_{p=1}^{M} c_p = M c_A$) only one Lagrange multiplier $\lambda = \mu$ (chemical potential) is needed to minimize G.

The minimization of G ($\partial G / \partial c_i = 0$, $\forall i$) leads to a set of coupled non-linear equations of the general form

$$\begin{aligned} \frac{\partial G}{\partial c_i} = & (\tau - V)(Z_i + Z_i^{+} + Z_i^{2+} + Z_i^{-} + Z_i^{2-}) \\ & + V(2 c_i Z_i + c_{i+1} Z_i^{+} + c_{i-1} Z_i^{-} + c_{i+2} Z_i^{2+} + c_{i-2} Z_i^{2-} + c_{i-1} Z_{i-1}^{+} + c_{i+1} Z_{i+1}^{-} + c_{i+2} Z_{i+2}^{2-} + c_{i-2} Z_{i-2}^{2+}) \\ & + kT \ln \left(\frac{c_i}{1 - c_i} \right) - \mu = 0 \ , \quad \text{for} \quad i = 1, 2, ..., M \ , \end{aligned} \tag{6}$$

and the additional one concerning the conservation of mass. We have then a system of $M + 1$ nonlinear equations to be solved for the concentrations and the chemical potential.

III. NUMERICAL RESULTS

We have solved the set of Eqs. (6) for M going from 3 to 24 using Harwell routines which solve nonlinear systems by means of the Newton-Raphson method. For increasing M the number of possible solutions of Eqs. (6) also increases, so that one has to select the one having the lowest free energy.

In the case $V > 0$ we obtain results similar to those for semi-infinite systems,[1] so that we are going to concentrate our attention to the case $V < 0$ (segregating one). As mentioned in the introduction, in what follows we mainly consider the mixing energy effect ($\tau = 0$).

In the semi-infinite case the layer concentration tends after few layers to the bulk value independently of the temperature considered. For the slab, at low temperatures and $V < 0$, the atoms of type A (minority ones, $0 < c_A < 0.5$), mostly segregate towards one of the surfaces while the B-type atoms segregate towards the other one. That is, there exists an interphase interface of the type A-rich on one side and B-rich on the other, inside the slab, whose location depends on the relative concentrations.

The system also presents two other transition regions, one at each surface of the slab. They lead to a variation of the concentration there. These two transition regions are due to the lower coordination of the surfaces with respect to the bulk, being that the internal energy there is lower than in inner layers. It is then easier for the thermal agitation to disorder the surface sites than the bulk ones, so that the former have a greater tendency to reach the average concentration.

The presence of the two different types of interfaces gives rise to an interesting feature of the system, which is that for each c_A, as T increases, there is a minimum number of layers after which there appears a "modulation" in the concentration profile. By "modulation" we mean the fact that the maximum A and B concentrations do not lie in the outermost layers of the slab but in internal ones. This results from the overlap of the different interfaces mentioned above.

With increasing number of layers and average concentrations, for a given value of T, the maxima in the concentration profile shift inwards.

In our calculations we mainly chose $V = -0.1$ eV, which is a reasonable intermediate value according to Miedema's tables.[11] These values of the parameters are in the miscibility gap for the interactions.

In Figs. 1(a) and 1(b) we show for 10 layers and $|kT/V| = 3.69$ (which corresponds to $T \sim 4000\,^{\circ}\mathrm{C}$) the profile for different average concentrations for the (111) and (110) fcc planes, respectively. In the (111) case, for $c_A = 0.1$ and 0.2 the number of layers is not enough to have more concentration of A atoms in the second layer than on the first one. For $c_A = 0.3$ and 0.4 the maximum concentration of A-type atoms is on the second layer and for 0.5 on the third one. In the (110) case for $c_A = 0.1$ and 0.2 we have qualitatively the same situation as for the (111) case. For $c_A = 0.3$ the maximum is on the first layer, but its concentration is very close to the concentration on the second one. For $c_A = 0.4$ the maximum is on the second layer and for 0.5 it is on the third one.

Comparing the results obtained for the (111) and (110) planes, one sees that the second one tends to thermalize more rapidly than the first one. This is due to the fact that in the (110) case the coordination with the adjacent planes is larger than in the (111) case and also that there exists a nearest neighbor link between the ith and the $i+2$th plane, which favors the homogenization.

For M layers at low temperatures there appear $I = \lfloor Mc_A \rfloor$ layers (where $\lfloor x \rfloor$ indicates the largest integer part no greater than x) on one side of the slab with A concentration approaching 1 and the $(I+1)$th layer having $c_{I+1} = Mc_A - I$. In the case of the fcc (111) surface, for each average concentration, the modulation appears when $I \geq 2$ and $c_3 > 0.5$. For the fcc (110) surface, the modulation appears also for $I > 2$ but c_3 must be larger due to the greater tendency to homogenization already mentioned.

For each concentration, and number of layers of the slab, there exists a second-order transition for which, at a certain $T = T_S$, the interphase interface disappears and the concentration profile becames symmetric with respect to the center of the slab. In Fig. 2 we show T_S as a function of the number of layers for $c_A = 0.2$, 0.4, and 0.5. Let us remark that the surface effects do not disappear at T_S, being that segregation exists towards

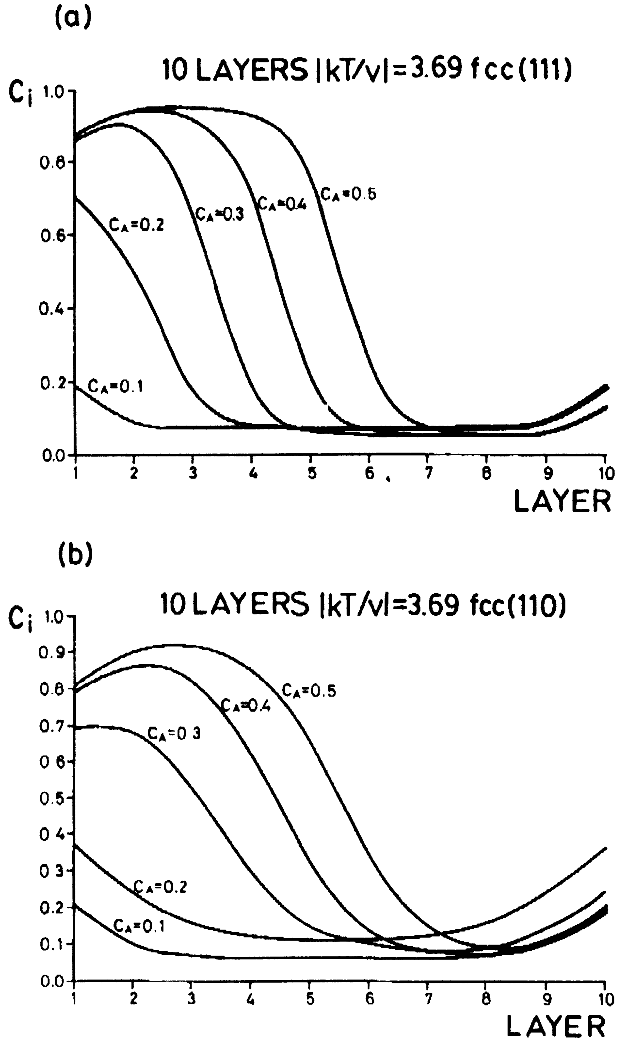

FIG. 1. Concentration profile for a slab of 10 layers, $V = -0.1$ eV, $\tau = 0$, and $|kT/V| = 3.69$ for different average concentrations of A-type atoms. (a) (111) surface plane, (b) (110) surface plane.

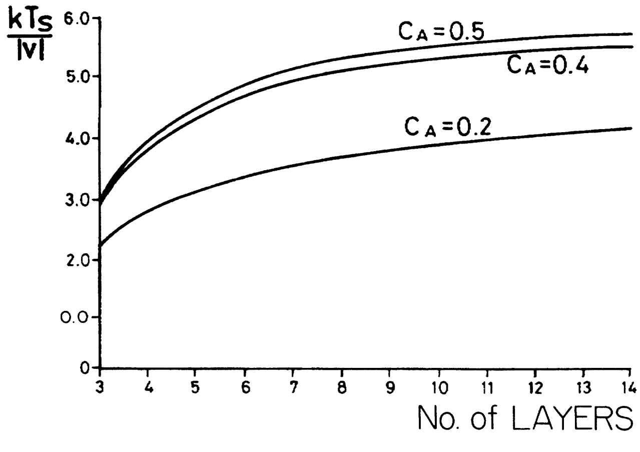

FIG. 2. Symmetrization temperature, T_S, as a function of the number of layers for a (111) fcc slab for $c_A = 0.2$, 0.4, and 0.5.

the surfaces of the minority component of the system. Above T_S the concentration profile is symmetric, there is no modulation (the interphase interface has disappeared) and the profile becomes similar to the one obtained in the semi-infinite case, in the sense that, after a few layers, c_i is close to the average concentration.

The case $c_A = 0.5$ and $\tau = 0$ is a special one in the sense that $c_i = 0.5$ for all i is one of the possible solutions of system (6) for all T. Below T_S this solution is not the one with the lowest free energy, remaining as the only one above it. This is due to the fact that A- and B-type atoms in this case are equivalent and that consequently there is an absence of surface segregation.

In Figs. 3(a) and 3(b) we show, as an example, the profiles for the case of 20 layers and $c_A = 0.4$ and 0.5, respectively. The temperature is taken as a parameter. In both cases it can be seen that for the lower temperatures there are I layers with the concentrations of A-type atoms close to 1. The remaining ones have A concentrations close to 0. As T increases the profile shows a clear modulated aspect. It can also be seen that the system tends to symmetrize.

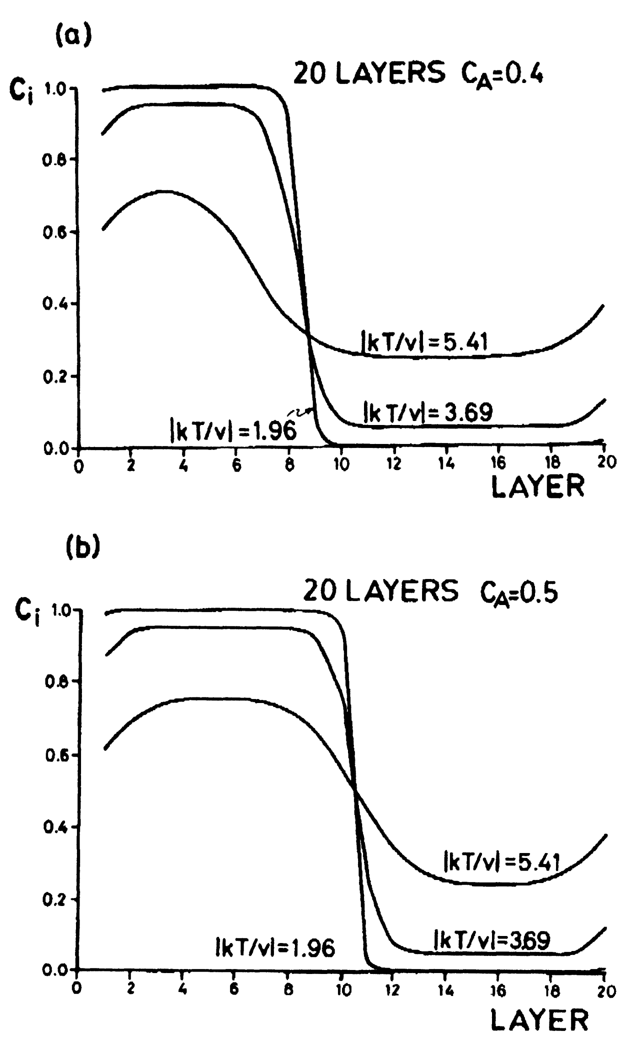

FIG. 3. Concentration profile for a slab of 20 layers, fcc (111) plane, for different values of $|kT/V|$. (a) average A concentration $c_A = 0.4$, (b) $c_A = 0.5$.

In Fig. 4 we show for $|kT/V| = 3.69$, 4.55, and 5.41 (corresponding to $T = 4000$, 5000, and 6000 °C) the concentration profiles for a system with 10 layers. It can be seen that the maximum A-concentration in this case is in a more external layer than for the 20-layer system.

In the semi-infinite case, c_1, c_2, and c_3 have a nonmonotonous behavior as a function of c_A compared to the monotonous one for very small V or very high temperatures, as is shown in Figs. 4 and 5 of Ref. 2. We have investigated this nonmonotonous behavior in the case of a slab. In the A-rich side the A concentration of each layer, as a function of c_A, is monotonous independently of the thickness of the slab, as is shown for the surface layer of the A-rich side (c_1) of an eight-layers slab in Fig. 5(a). In the B-rich side, the A-concentration of the layers is nonmonotonous as can be seen in Fig. 5(b) for c_8. This behavior is due to the concentration dependence of the values of the transition temperature T_S for a given number of layers (see Fig. 2). For instance, for the surface layer on the B-rich side, the A concentration increases above the average one until T_S is reached. Above this temperature it begins to decrease towards homogenization.

In order to compare our MFA results with those obtained in Ref. 3, using Monte Carlo simulation, we studied a 20-atom one-dimensional system for $c_A = 0.5$, $\tau = 0.2$ eV, $V = 0$, -0.1 and 0.1 eV, and $T = 1730$ °C. These are the same parameter values used by Arroyo and Joud. In Figs. 6(a)–6(c) we show the results obtained, which are extremely close to those of Fig. 3 of Ref. 3. However, the behavior of the system is more complicated, because one has the possibility of varying the three parameters T, τ, and V. In this sense, we observed for this one dimensional case that as T is lowered for $V = -0.1$ eV and $\tau = 0.2$ eV, the step effect present in the 3D case

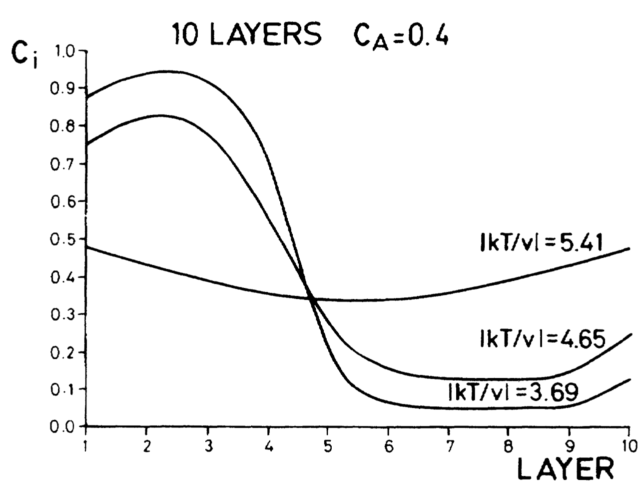

FIG. 4. Same as Fig. 3(a) but for 10 layers.

also appears. If τ is lowered (in this case to $\tau = 0.05$ eV), at lower temperatures, we also obtain the "modulation" effect as it is shown in Fig. 6(d) for $T = 600\,^\circ$C. In this case the maximum is on the fourth layer. There is, then, a compromise between the values of τ and V for the appearence of the modulation. This compromise also exists in the 3D case. This means that the two different systems (1D and slab) have qualitatively the same behavior.

The results obtained for the slab are interesting in the context of superlattices, because they lead us to think that, depending on the number of layers sandwiched, it is possible to introduce extra modulations. We want to remark that the results obtained for a slab in vacuum are also valid for the case in which the slab is surrounded by a material C, with potential interaction $V_{AC} \sim V_{BC} << V_{AB}$.

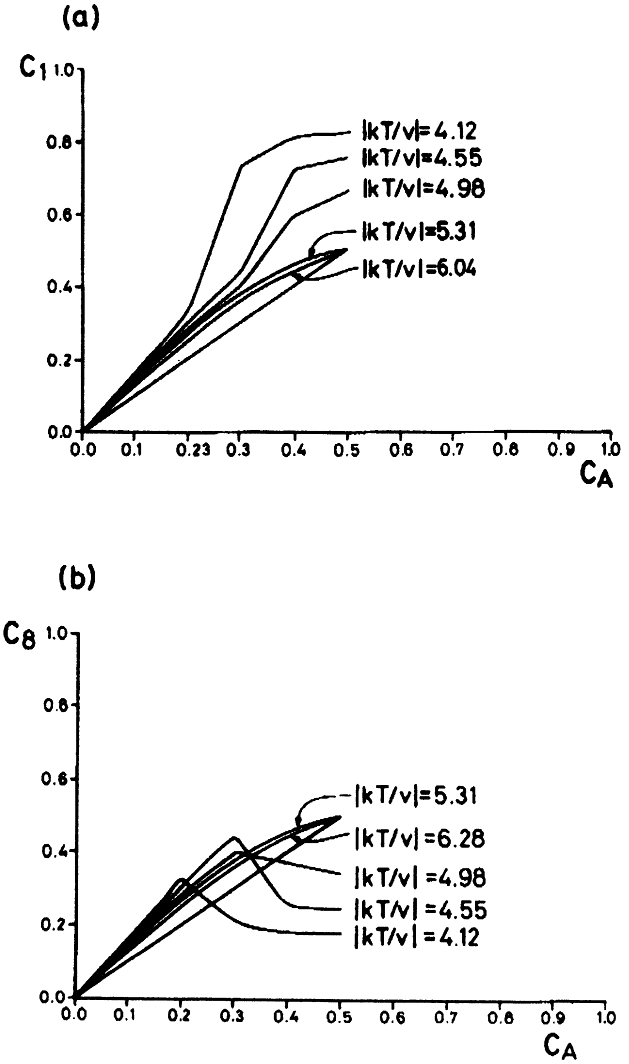

FIG. 5. Variation of the surface A concentrations in the A- and B-rich sides [(a) and (b), respectively] of an eight-layers slab, as a function of the average concentration (c_A) for a (111) fcc slab at different temperatures.

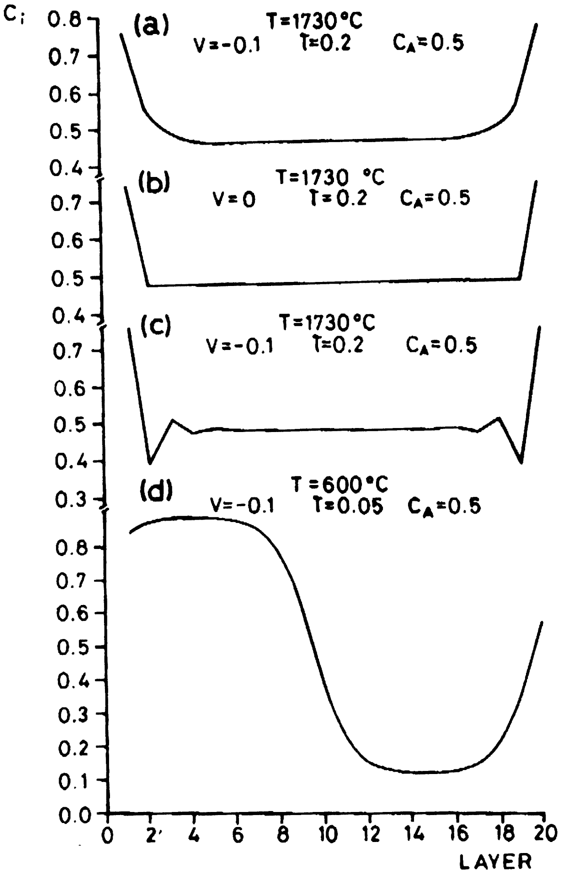

FIG. 6. Concentration profile for a linear chain of 20 atoms and $c_A = 0.5$: (a) $V = -0.1$ eV, $\tau = 0.2$ eV, and $T = 1730\,^\circ$C, (b) $V = 0$, $\tau = 0.2$ eV, and $T = 1730\,^\circ$C, (c) $V = 0.1$ eV, $\tau = 0.2$ eV, and $T = 1730\,^\circ$C, and (d) $V = -0.1$ eV, $\tau = 0.05$ eV, and $T = 600\,^\circ$C.

IV. SUMMARY AND CONCLUSIONS

We have calculated the segregation profiles of thin slabs of binary alloys, within the MFA, concentrating on the case of segregating alloys. We have mainly taken into account the contribution of the mixing energy.

At low temperatures the behavior of the system is different from the one corresponding to a semi-infinite medium (segregating surface). Above the symmetrization temperature, T_S, which depends on the concentration and thickness of the slab, the concentration after a few layers tends to the average one, similar to what happens in the semi-infinite case.

For each average concentration there is a minimum number of layers for which there appears a "modulation" in the concentration profile, due to the simultaneous presence of two kinds of interfaces. These features also appear when one takes into account differences in the surface energies of the constituents of the alloys. The amount of segregation for a given temperature depends on the plane considered. We have also calculated the segregation profiles for an open linear chain (A_xB_{1-x}) within the MFA and compared them with those obtained using Monte Carlo by Arroyo and Joud.[3] Our results are very close to those of Ref. 3, showing that the MFA is a good approximation in this case. We show that the "modulated" behavior also appears in the linear chain.

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