

## SEGREGATION IN THIN FILMS: THE EFFECT OF MASS BALANCE AND BONDING TO THE SUPPORT

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(Received March 22, 1984; accepted April 27, 1984)

The effect of mass balance on segregation in thin films is studied by minimizing the free energy of the film with respect to the composition of each layer for a fixed overall mole fraction. It is shown that the Bragg–Williams and quasi-chemical approximations give almost identical results. The effect of a difference in bond strength of the two components with the support is shown to lead to large variations in the composition of the outer film surface, even for thick (more than about 30 layers) films.

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### 1. INTRODUCTION

The surface composition of alloy crystals, thin layers or catalysts is of prime importance in determining their chemical and physical properties for processes occurring at the surface. A large number of theoretical papers deal with the problem of the surface composition of alloys in relation to their bulk composition. Several models have been proposed and discussed that account for a difference in composition of the first layer<sup>1–7</sup>, a more extended concentration profile<sup>8</sup> or the existence of strain in the lattice<sup>9–13</sup>. In all these approaches, however, a fixed bulk composition is assumed to be reached eventually in the interior of the crystal, which governs, via the equality of the chemical potential of all components, the (near-) surface composition.

In the case of thin films, invariably deposited onto some substrate, the existence of a bulk is not obvious. Also the effect of different bond strengths of the film's constituents to the substrate requires examination with regard to the composition of the "vacuum" side of the film. Furthermore, as is well known, some alloys exhibit a miscibility gap below a certain critical temperature  $T_c$ , which precludes the assignment of every possible fixed bulk value for its chemical composition. Some results of mass depletion on surface segregation have been published<sup>8</sup> and a sample calculation for a thin film has been presented<sup>14,15</sup>.

In this paper we wish to examine the composition of a film of variable thickness, each layer having a uniform composition, by minimizing the free energy of the total system. No bulk is assumed in the calculations. We shall also consider the effect of binding to a substrate on the composition of the exposed side of the film. Most of the

calculations will be performed in the Bragg-Williams or mean field approximation<sup>16-18</sup>, with neglect of strain effects. Thus we consider a film made up of two types of atoms A and B, of equal atomic radius. The pairwise nearest-neighbour bond energies  $H_{AA}$  and  $H_{BB}$  for the pure components are taken from data on the heats of sublimation, and the quantity  $H_{AB}$ , the bond energy of an A-B pair, is considered a parameter. All bond energies are taken to be negative.

## 2. THEORY

The simplest approximation for the description of the composition of binary alloys is the mean field or Bragg-Williams approximation<sup>6,16-18</sup>. This theory assumes only nearest-neighbour interactions between A-A, B-B and A-B atom pairs. It computes the mixing energy for a random distribution of A in B and takes the entropy of mixing as ideal. Surface effects are only considered to arise from missing bonds (broken bond model). If the first layer of the slab contains  $N$  atoms and consists of  $N_A^{(1)}$  atoms A and  $N_B^{(1)}$  atoms B, with mole fractions  $x_1 = N_A^{(1)}/N$  and  $(1 - x_1) = N_B^{(1)}/N$ , its energy (or enthalpy) is given by

$$\begin{aligned} E_1 = & \frac{l}{2} N_A^{(1)} H_{AA} x_1 + \frac{l}{2} N_B^{(1)} H_{BB} (1 - x_1) + \frac{l}{2} N_A^{(1)} H_{AB} (1 - x_1) + \\ & + \frac{l}{2} N_B^{(1)} H_{AB} x_1 + m N_A^{(1)} H_{AA} x_2 + m N_B^{(1)} H_{BB} (1 - x_2) + \\ & + m N_A^{(1)} H_{AB} (1 - x_2) + m N_B^{(1)} H_{AB} x_2 \end{aligned} \quad (1)$$

Here  $H_{ij}$  is the bond energy of a nearest-neighbour  $i$ - $j$  pair,  $l$  is the lateral (in-plane) number of nearest neighbours ( $l = 6$  for a (111) plane of an f.c.c. lattice),  $m$  is the number of nearest neighbours in the next plane ( $m = 3$  for a (111) plane of an f.c.c. lattice) and  $x_i$  is the mole fraction of A in layer  $i$ . The entropy of the first layer is simply given by

$$S_1 = -Nk\{x_1 \ln x_1 + (1 - x_1) \ln(1 - x_1)\} \quad (2)$$

Introducing the regular solution parameter  $\Omega$

$$\Omega = H_{AB} - \frac{1}{2}(H_{AA} + H_{BB}) \quad (3)$$

and summing over the total number  $n$  of layers in the slab we obtain the free energy of the system:

$$\begin{aligned} G = N \sum_{i=1}^n \left[ l \left\{ \frac{1}{2} x_i H_{AA} + \frac{1}{2} (1 - x_i) H_{BB} + x_i (1 - x_i) \Omega \right\} + \right. \\ \left. + m \left\{ \frac{1}{2} (x_i + x_{i+1}) H_{AA} + \left( 1 - \frac{1}{2} x_i - \frac{1}{2} x_{i+1} \right) H_{BB} + \right. \right. \\ \left. \left. + (x_i + x_{i+1} - 2x_i x_{i+1}) \Omega \right\} (1 - \delta_{i,n}) + kT \{ x_i \ln x_i + (1 - x_i) \ln(1 - x_i) \} \right] \quad (4) \end{aligned}$$

The Kronecker delta  $\delta_{i,n}$  ( $= 1$  if  $i = n$  and zero otherwise) prevents the counting of the interaction energy of the last layer ( $n$ ) with the non-existent layer  $n + 1$ . If an

average mole fraction  $\bar{x}$  is defined as

$$\bar{x} = \sum_{i=1}^n \frac{N_A^{(i)}}{nN} \quad (5)$$

which is an experimentally fixed quantity, mass balance requires that

$$\sum_{i=1}^n x_i = n\bar{x} \quad (6)$$

so that only  $n-1$  of the  $x_i$  in eqn. (4) are independent. For a free film of course the symmetry condition  $x_i = x_{n+1-i}$  holds, which facilitates numerical calculations. The effect of the film substrate (or an adsorbed layer of other material) may be incorporated by adding to eqn. (4) a term of the form

$$G^* = N\{x_n H_{AS} + (1 - x_n) H_{BS}\} \quad (7)$$

where  $H_{AS}$  and  $H_{BS}$  are the products of the number of bonds with the substrate and their strengths for atoms A and B respectively.

Inspection of eqns. (4) and (7) shows that the minimum in  $G$  or  $G + G^*$  which is obtained for a particular set of  $x_i$  depends only on  $H_{AA} - H_{BB}$  and  $H_{AS} - H_{BS}$  and not on their absolute magnitudes. The whole problem is now reduced to finding the minimum value of a given function which is obtained after eliminating one  $x_i$  from eqn. (6) and inserting this expression in eqn. (4).

A better, but more involved, model for the description of the composition of binary alloys is the quasi-chemical approximation<sup>6,16-18</sup>. In this case the mixing enthalpy and entropy are both taken as a function of  $\Omega$ , the regular solution parameter. The free energy of a slab consisting of  $n$  layers with mole fraction  $x_i$  is now given by the rather formidable expression (see Appendix A for a sketch of the derivation):

$$\begin{aligned} G = N \sum_{i=1}^n & \left( \frac{l}{2} x_i H_{AA} + \frac{l}{2} (1 - x_i) H_{BB} + kT \left\{ x_i \ln x_i + (1 - x_i) \ln(1 - x_i) \right\} + \right. \\ & + kT \left[ \frac{l}{2} x_i \ln \left\{ \frac{B_i - 1 + 2x_i}{x_i(1 + B_i)} \right\} + \frac{l}{2} (1 - x_i) \ln \left\{ \frac{B_i + 1 - 2x_i}{(1 - x_i)(1 + B_i)} \right\} \right] \Bigg) + \\ & + N \sum_{i=1}^{n-1} \left( \frac{m}{2} (x_i + x_{i+1}) H_{AA} + \frac{m}{2} (2 - x_i - x_{i+1}) H_{BB} + \right. \\ & + kT \left[ \frac{m}{2} (x_i + x_{i+1}) \ln \left\{ \frac{2(C_i - 1 + x_i + x_{i+1})}{(C_i + 1)(x_i + x_{i+1})} \right\} + \right. \\ & \left. \left. + \frac{m}{2} (2 - x_i - x_{i+1}) \ln \left\{ \frac{2(C_i + 1 - x_i - x_{i+1})}{(C_i + 1)(x_i + x_{i+1})} \right\} \right] \right) \end{aligned} \quad (8)$$

where

$$B_i = \left[ 1 - 4x_i(1 - x_i)\{1 - \exp(2\beta\Omega)\} \right]^{1/2} \quad (9)$$

$$C_i = \left[ 1 - (x_i + x_{i+1})(2 - x_i - x_{i+1})\{1 - \exp(2\beta\Omega)\} \right]^{1/2} \quad (10)$$

$$\beta = 1/kT \quad (11)$$

In this expression we notice again the intralayer contributions (proportional to  $l$  and summed over  $i = 1$  to  $n$ ) and the interlayer terms (proportional to  $m$  and summed only to  $n-1$ ). The separation in energy and entropy terms is not obvious in eqn. (8).

For a homogeneous system ( $x_i = \bar{x}$  for all  $i$  and  $n \rightarrow \infty$ ) both eqn. (4) and eqn. (8) reduce to the standard expressions for bulk alloys<sup>6,16-18</sup>.

Since we are interested in the effect of surfaces on phase separations we remind the reader that the critical mixing temperature in the Bragg-Williams approximation is given by<sup>16-18</sup>

$$T_c^{\text{BW}} = \frac{\Omega}{2k}(l+2m) \quad (12)$$

and in the quasi-chemical approximation by<sup>16-18</sup>

$$T_c^{\text{QC}} = \frac{\Omega}{k} \left\{ \ln \left( \frac{l+2m}{l+2m-2} \right) \right\}^{-1} \quad (13)$$

For f.c.c. metals with  $l+2m = 12$  the differences are small, only 9%.

Two obvious shortcomings of eqns. (4) and (8) should be mentioned at this point. Firstly, no surface relaxation effects or changes in lattice constant with composition are included<sup>5,8</sup>. Secondly, since only interactions between nearest-neighbour atoms and nearest-neighbour layers are considered, the equations are limited for f.c.c. crystals to (111) and (100) planes. The (110) planes contain one nearest-neighbour in the next-nearest-neighbour plane and thus cannot be described by our equations or similar versions.

### 3. RESULTS AND DISCUSSION

The effect of the two distinct calculations of the concentration profile, namely using the Bragg-Williams or the quasi-chemical approximation, is shown in Fig. 1 for slabs of 4, 8 and 16 layers with (111) orientation. The parameters used in the computation,  $H_{\text{AA}} = -13.5 \text{ kcal mol}^{-1}$ ,  $H_{\text{BB}} = -17.0 \text{ kcal mol}^{-1}$  and  $\Omega = 236 \text{ cal mol}^{-1}$ , are roughly appropriate to the Cu-Ni system. The full curves are the results of the quasi-chemical approximation, the crosses are obtained from the Bragg-Williams approach. The differences are seen to be minimal in all cases. Another aspect of Fig. 1 is the redistribution of the fixed amount of component A

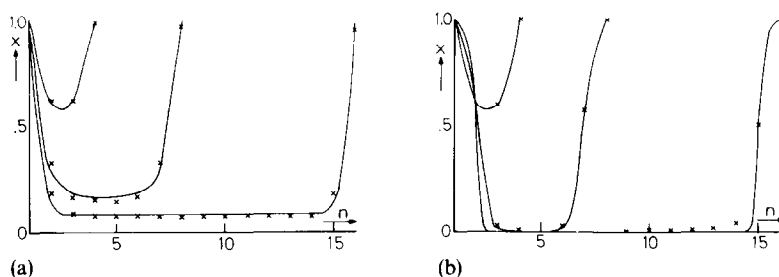


Fig. 1. Computed concentration profiles for films of 4, 8 and 16 layers in the quasi-chemical (—) and Bragg-Williams (x) approximations for temperatures of (a) 800 K and (b) 300 K ( $H_{\text{AA}} = -13.5 \text{ kcal mol}^{-1}$ ;  $H_{\text{BB}} = -17.0 \text{ kcal mol}^{-1}$ ;  $\Omega = 236 \text{ cal mol}^{-1}$ ). The total amount of component A is kept fixed at  $n\bar{x} = 3.2$  in all curves.

when the slab thickness is increased (all curves were computed with  $n\bar{x} = 3.2$ ). At 300 K, well below the bulk critical temperature of 654 K (quasi-chemical approximation) or 715 K (Bragg-Williams approximation), the segregation of component A to the outsides of the slab is maximal and the bulk composition is almost pure B, except for the four-layer system, where the mass balance imposes a "bulk" composition of 60% A. In this case an increase in temperature to 800 K does not lead to a change in composition. For thicker slabs, a slight decrease in the A content of the first layer and a larger concomitant increase in the bulk A content is evident when the temperature is increased.

In Fig. 2 the effect of an increasing number of layers at a fixed average mole fraction is shown for the same parameters as used in Fig. 1. Segregation is again seen to be extreme, especially for 300 K. A true constant bulk level is only reached for a slab of eight or more layers and the concentration gradient may extend for up to six layers. Similar observations apply to Fig. 3, where only the value of  $\Omega$  has been decreased (to 126 cal mol<sup>-1</sup>) and the critical temperature is thus lower (382 K). At 300 K, near this critical temperature, the distance over which the concentration gradient exists is appreciable. When  $\Omega$  is taken to be zero, only the outer layers of the slab are enriched in agreement with the Gibbs adsorption equation<sup>3,19</sup>. Incidentally, this case provides a check on the accuracy of the computer program used in the minimization procedure. As  $\Omega$  moves to negative values, which implies a tendency for like components to aggregate (see eqn. (3)), we observe oscillations in the composition profile as shown in Fig. 4. The oscillations are sizeable for thin slabs but disappear at higher temperatures. Similar effects have been reported by Williams

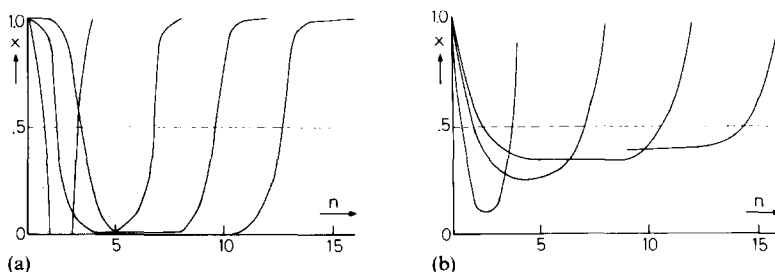


Fig. 2. Computed concentration profiles for films of 4, 8, 12 and 16 layers in the Bragg-Williams approximation at temperatures of (a) 300 K and (b) 900 K ( $H_{AA} = -13.5$  kcal mol<sup>-1</sup>;  $H_{BB} = -17.0$  kcal mol<sup>-1</sup>;  $\Omega = 236$  cal mol<sup>-1</sup>). The average mole fraction of component A is kept fixed at 0.5 (---) in all the curves. For clarity only the right-hand side of the 16-layer film is shown.

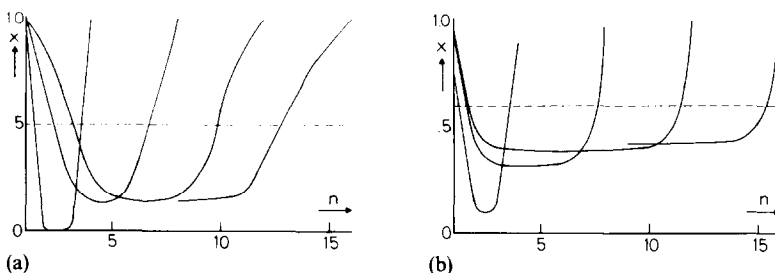


Fig. 3. As for Fig. 2 except that  $\Omega = 126$  cal mol<sup>-1</sup>: (a) 300 K; (b) 800 K.

and Nason<sup>8</sup> for a bulk system with four independent surface layers. Oscillations in the composition profile have also been reported in analogous work on liquid systems<sup>20-22</sup>.

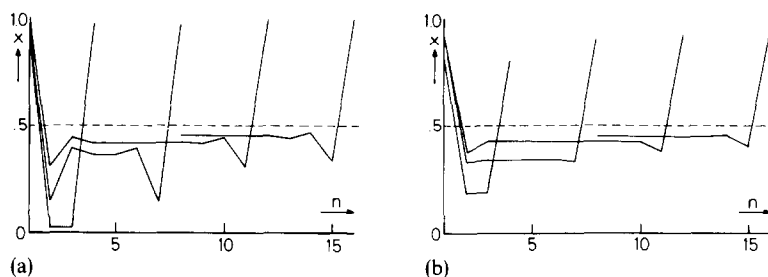


Fig. 4. As for Fig. 2 except that  $\Omega = -126 \text{ cal mol}^{-1}$ : (a) 300 K; (b) 800 K.

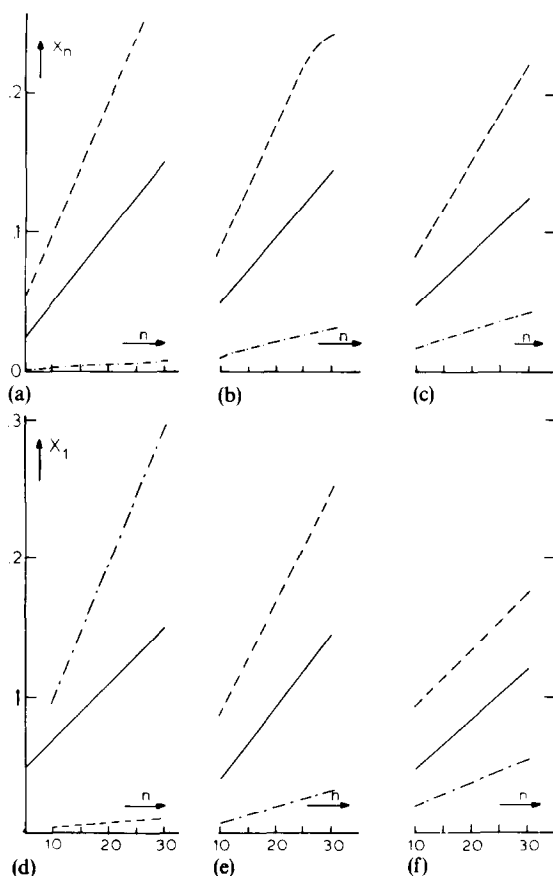


Fig. 5. (a)–(c) Composition  $x_n$  of the layer next to the substrate and (d)–(f) composition  $x_1$  of the outer film layer for different temperatures ((a), (d) 300 K; (b), (e) 500 K; (c), (f) 700 K) and different bond strengths of A and B to the substrate as functions of the number  $n$  of layers in the film: —,  $H_{AS} = H_{BS} = 0 \text{ kcal mol}^{-1}$ ; ---,  $H_{AS} = -2 \text{ kcal mol}^{-1}$ ;  $H_{BS} = 0 \text{ kcal mol}^{-1}$ ; — · —,  $H_{AS} = 0 \text{ kcal mol}^{-1}$ ,  $H_{BS} = -2 \text{ kcal mol}^{-1}$ . The overall mole fraction of A is kept fixed at 0.01 for all curves.

Thus far we have considered only free films and the solutions obtained are perfectly symmetrical around the film centre. In practice, however, films are deposited onto some substrate, which may form a stronger bond with either of the components. If, as in our previous examples, segregation is almost complete, the composition of the outer layers of the film will be given by  $x_1 = x_n = n\bar{x}/2$ , provided that this is allowed by mass balance (*i.e.*  $x_1$  must be less than unity). The full curves in Fig. 5 show the calculated composition of the outer layer for a fixed average mole fraction  $\bar{x}$  of 0.01 as a function of the number of layers. As expected, a perfect linear relation holds. If  $\bar{x}$  is taken to be 0.1 this value saturates at  $x_1 = 1$  for  $n \geq 20$  and  $T = 300$  K as illustrated in Fig. 6. At higher temperatures segregation is not complete and only a gradual levelling off is seen. In the same figures we have plotted the effect of the substrate, by allowing for differences of  $\pm 2$  kcal mol<sup>-1</sup> in the A-substrate and B-substrate bond strengths. Figures 6(a)–6(c) show the composition  $x_n$  of the layer next to the support, Figs. 6(d)–6(f) the composition of the outer exposed layer of the film. As expected, when A-substrate bonds are favoured ( $H_{AS} - H_{BS} = -2$  kcal mol<sup>-1</sup>) the layer next to the substrate is more enriched in A than is this layer in the free film (broken curves in Figs. 5(d)–5(f) and 6(d)–6(f)). In fact, an almost quantitative transfer of A from the free side of the film to the layer next to the support has taken place for  $\bar{x} = 0.01$  even for films as thick as 30 layers. The results show no tendency to level off for a still larger number. A similar trend is found when bonding of component B to the substrate is energetically more favourable (see the chain curves in Figs. 5 and 6). We can thus conclude from these examples that the effect of the substrate bonding can be quite strong even for thick films. The effect is most pronounced for low values of  $\bar{x}$ , such that even complete segregation of one component leaves the outer layers with  $x_1 = x_n < 1$ , or at elevated temperatures where the same situation prevails.

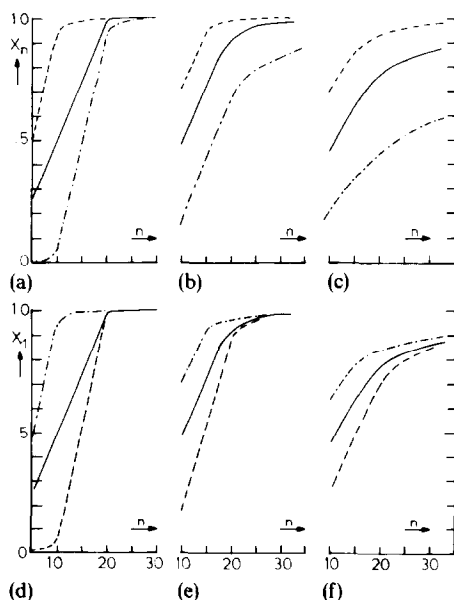


Fig. 6. As for Fig. 5 except that the overall mole fraction of A is now 0.1.

An approximate expression for the mole fraction  $\delta$  of material transferred from the outer layer to the layer next to the support is derived in Appendix B. The result is

$$\delta = \frac{H_{AS} - H_{BS}}{4l\Omega - 2kT/x(1-x)} \quad (14)$$

where  $x$  is the original mole fraction of A, present when  $H_{AS} = H_{BS}$ .

In summarizing the present work we conclude that for segregation calculations in thin films the Bragg–Williams or the quasi-chemical approximation give almost identical results. For strongly segregated systems the concentration profile is quite extended and the outer layer composition is not very dependent on temperature. The effect of a small difference in bond strength with the support between the two components has an appreciable influence on the outer layer composition, even for thick films and even above the critical mixing temperature.

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#### APPENDIX A

A statistical mechanical derivation of eqn. (8) along the lines given by Hill<sup>1</sup> proceeds as follows. The total energy of the system is given by

$$E = \sum_{i=1}^n N_{AA}^{(ii)} H_{AA} + N_{BB}^{(ii)} H_{BB} + N_{AB}^{(ii)} H_{AB} + \sum_{i=1}^{n-1} N_{AA}^{(ii+1)} H_{AA} + N_{BB}^{(ii+1)} H_{BB} + N_{AB}^{(ii+1)} H_{AB} \quad (A1)$$



where  $N_{AA}^{(ii)}$  is the number of A-A pairs in layer  $i$ ,  $N_{AA}^{(ii+1)}$  the number of A-A pairs between layers  $i$  and  $i+1$  and the other quantities have an analogous definition. The following conservation relations hold always:

$$\begin{aligned} lN_A^{(i)} &= 2N_{AA}^{(ii)} + N_{AB}^{(ii)} \\ lN_B^{(i)} &= 2N_{BB}^{(ii)} + N_{AB}^{(ii)} \\ m(N_A^{(i)} + N_A^{(i+1)}) &= 2N_{AA}^{(ii+1)} + N_{AB}^{(ii+1)} \\ m(N_B^{(i)} + N_B^{(i+1)}) &= 2N_{BB}^{(ii+1)} + N_{AB}^{(ii+1)} \\ N_A^{(i)} + N_B^{(i)} &= N \end{aligned} \quad (A2)$$

Thus only two independent quantities remain in eqn. (A1). These may be taken to be  $N_{AB}^{(ii)}$  and  $N_{AB}^{(ii+1)}$ . The canonical partition function of the system is

$$Q = \sum \sum g(N_A^{(i)}, N_B^{(i)}, N_{AB}^{(ii)}, N_{AB}^{(ii+1)}) \exp(-\beta E) \quad (A3)$$

where  $g$  is the number of ways of distributing  $N_A^{(i)}$  A atoms and  $N_B^{(i)}$  B atoms in layer  $i$  in such a way that there are exactly  $N_{AB}^{(ii)}$  A-B pairs in layer  $i$  and  $N_{AB}^{(ii+1)}$  A-B pairs between layers  $i$  and  $i+1$ . The double summation is over all values of  $N_{AB}^{(ii)}$  and  $N_{AB}^{(ii+1)}$ . The approximate value of the double sum is found by the application of the maximum term method, with respect to both  $N_{AB}^{(ii)}$  and  $N_{AB}^{(ii+1)}$ . This gives after some algebra along the lines in ref. A1

$$N_{AB}^{(ii)} = 2l \frac{N_A^{(i)}(1-x_i)}{1+B_i} \quad (A4)$$

$$B_i = [1 - 4x_i(1-x_i)\{1 - \exp(2\beta\Omega)\}]^{1/2} \quad (A5)$$

$$N_{AB}^{(ii+1)} = m \frac{(N_A^{(i)} + N_A^{(i+1)})(2-x_i-x_{i+1})}{1+C_i} \quad (A6)$$

$$C_i = [1 - (x_i + x_{i+1})(2-x_i-x_{i+1})\{1 - \exp(2\beta\Omega)\}]^{1/2} \quad (A7)$$

From the standard relation  $A = -kT \ln Q$  the Helmholtz free energy  $A$  of the system is obtained, which, after substitution of eqns. (A4)–(A7) is given in eqn. (8). For condensed systems the difference between  $A$  and  $G$  is immaterial.

### Reference for Appendix A

A1 T. L. Hill, *Introduction to Statistical Thermodynamics*, Addison-Wesley, London, 1960.

## APPENDIX B

The approximate effect of the substrate on the composition of the two outer layers of the film can be derived as follows. Originally both layers have a mole fraction  $x$ . If the composition of the intermediate layers remains unaltered, the change in enthalpy when a mole fraction  $\delta$  is transferred between the two layers is

$$\Delta H = -4\delta^2\Omega \frac{l}{2} + \delta(H_{AS} - H_{BS}) \quad (B1)$$

where  $l$  is the number of neighbours in the plane parallel to the surface and  $H_{AS}$  and

$H_{BS}$  are the strengths of the A–substrate and B–substrate bonds multiplied by their number. To second order in  $\delta$  the change in entropy is

$$\Delta S = -k\delta^2 \frac{1}{x(1-x)} \quad (\text{B2})$$

Minimizing  $\Delta G$  for this process with respect to  $\delta$  we obtain

$$\delta = \frac{H_{AS} - H_{BS}}{4l\Omega - 2kT/x(1-x)} \quad (\text{B3})$$