

Theory of surface effects in binary alloys. III. Stepped surfaces

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A theory of surface effects at stepped surfaces in binary ordering alloys is presented. The model is based on pairwise interactions between nearest neighbors and includes long- and short-range-order effects. An example of the [120] stepped surface with $\bar{1}10$ monoatomic steps and terraces on the [110] plane of a body-centered-cubic alloy is presented. Results for the concentration at all the different sites on the stepped surface as well as for the short-range order parameters as functions of temperature are presented.

I. INTRODUCTION

The composition and degree of order in an alloy near the spatial boundaries are important in many physical, chemical, and metallurgical phenomena (magnetic properties,^{1,2} catalytic activity,^{3,4} etc.) as shown by a large number of experiments performed in the last years. In particular, it has been established that the catalytic activity and selectivity of alloy surfaces can change drastically when the alloy composition⁶ is changed and that in general the chemical composition as well as the degree of chemical order are different compared to the bulk values.^{5,6} Furthermore, it has been observed, for a long time, that the properties of stepped transition-metal surfaces are very different as compared with those of plain surfaces, mainly with respect to their catalytic activity.^{7,8} More detailed studies on the catalytic properties of this kind of surface have been published^{9,10} recently. It is found that in some cases the two kind of surfaces behave in a completely different way. An example¹¹ is the absorption of H₂ on Pt. Therefore, the study of surface segregation, as well as the study of the order-disorder transformation in the neighborhood of the boundaries, is important for understanding the surface properties of alloys.

Recently, a theory for segregation at flat surfaces of ordering¹² and segregating¹³ alloys applicable over the whole range of temperatures has been proposed, hereafter referred to as I and II, respectively, and it has been applied to study the FeCo system.¹⁴ In this paper we extend that theory to study surface effects

at stepped bcc ordering alloys. An application to the FeCo system has been reported recently.¹⁵

The binary alloy A_xB_{1-x} is described by a superposition of short-range (nearest-neighbor-only) pairwise interactions. These are defined by three parameters U_{AA} , U_{BB} , and U_{AB} which give the various pair energies. The free energy is then calculated by adding the energies of all the bonds in the system and by using for the entropy Kikuchi's formula in the pair approximation.¹⁶

In Sec. II we present the theory and calculation for the bulk and for the stepped surface. The surface consists of terraces with (110) orientation and monoatomic steps of $\bar{1}10$ orientation of a body-centered-cubic alloy. The results are discussed in Sec. III. Details of the method are presented in the Appendix.

II. CALCULATIONS AND RESULTS

A. Surface properties

As discussed in I, to describe order-disorder transformations in a bcc crystal, we subdivide the original lattice into two equivalent lattices α and β . In the equiatomic concentration alloys $A_{0.5}B_{0.5}$, at $T=0$ all α sites are occupied by A atoms and β sites by B atoms. At the order-disorder temperature T_c the long order vanishes and the short-range order remains finite and goes to zero only as $T \rightarrow \infty$. Details of the calculation for the bulk order parameters can be found in I.

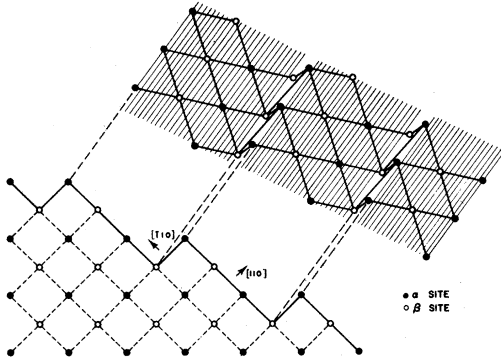


FIG. 1. Geometry assumed for the stepped surface for a bcc lattice. The full circles denote the α sites and the open ones the β sites. The terraces and the monoatomic steps are in $[110]$ and the $[\bar{1}10]$ directions, respectively. The sites on the edges of the steps lie in the $[120]$ direction.

The geometry assumed for the surface is shown in Fig. 1. This surface consists of terraces with $[110]$ orientation and monoatomic steps of $[\bar{1}10]$ orientation. The atoms on the edges of the steps lie on a $[120]$ plane.

In the $[120]$ direction each plane contains only one type of sites (α or β), and the nearest neighbors are four in the adjacent planes ($Z_1=2$) and four in the third-neighbor planes ($Z_3=2$) (Fig. 2). We have then two site probabilities per plane n , $p_l^\nu(n)$ ($l=A,B$, $\nu=\alpha,\beta$) which are equal to the concentra-

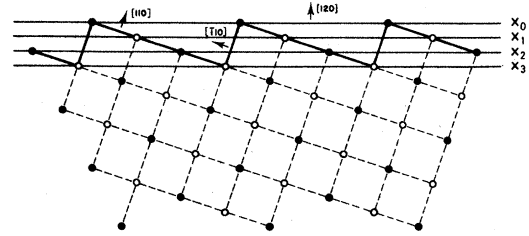


FIG. 2. Schematic representation of the bcc lattice with a stepped surface (thick line) projected on a plane. The full circles denote the α sites and the open ones the β sites. The flat lines represent the various planes as considered in the present calculation.

tion in that plane. In the complete ordered situation, planes with $x=1$ (α -type planes) and $x=0$ (β -type planes) alternate. In addition to the layer concentrations x_n ; there are four interlayer pair probabilities $p_{IJ}(n,m)$ between the n th and $(n+1)$ th planes and between the n th and $(n+3)$ th planes. The probabilities $p_{IJ}(n,m)$ can be written as functions of interlayer short-range order parameters $\sigma_{n,m}$ and the concentrations x_n and x_m as shown in Ref. 14. At the stepped surfaces, we have four different sites, whose number of nearest-neighbor atoms are 4, 6, 6, and 8 as one goes from the edge ($n=0$) to the interior of the step ($n=3$).

In the layered structure, the internal energy U can be written

$$U = \mathfrak{N}W \sum_{n=0}^{\infty} \{ Z_1 [x_{n,n+1}^2 + x_{n,n+1}(1-x_{n,n+1})\sigma_{n,n+1} + x_{n,n+1}(\Delta-1)] + Z_3 [x_{n,n+3}^2 + x_{n,n+3}(1-x_{n,n+3})\sigma_{n,n+3} + x_{n,n+3}(\Delta-1)] \} , \quad (2.1)$$

where

$$W = U_{AA} + U_{BB} - 2U_{AB} , \quad (2.2)$$

$$\Delta = (U_{AA} - U_{BB})/W , \quad (2.3)$$

$$x_{n,m} = \frac{1}{2}(x_n + x_m) , \quad (2.4)$$

and $\sigma_{n,m}$ is defined by

$$\sigma_{n,m} = 1 - \frac{p_{AB}(n,m) + p_{BA}(n,m)}{2x_{n,m}(1-x_{n,m})} . \quad (2.5)$$

Here \mathfrak{N} is the number of atoms per layer. The entropy is given by

$$S = \mathfrak{N}k \sum_{n=0}^{\infty} \left(\sum_l (Z_n - 1)L_l(n) - \sum_{l,j} [Z_1 L_{l,j}(n,n+1) + Z_3 L_{l,j}(n,n+3)] \right) . \quad (2.6)$$

In this equation Z_n is the total number of nearest neighbors of an atom on the n th layer and $L_l(n)$ and

$L_{I,I}(n,m)$ are defined by

$$L_I(n) = p_I(n) \ln p_I(n) \quad (2.7)$$

and

$$L_{I,J}(n,m) = p_{IJ}(n,m) \ln p_{IJ}(n,m) \quad (2.8)$$

The equilibrium values for the concentrations x_n and the short-range order parameter $\sigma_{n,m}$ are determined by minimizing the free energy $F = U - TS$ with respect to all these. The condition of chemical equilibrium imposes the constraints

$$\frac{\partial F}{\partial x_n} (\text{all other } x_n \text{ constant}) = \frac{\partial F}{\partial x_{\text{bulk}}} \quad (2.9)$$

B. Results at $T = 0$

As mentioned above, in the [120] direction, each plane contains only one type of site (α or β). In principle the surface layer $n = 0$ could be of type α or β . However, one would expect that the surface would be of the type $\alpha(\beta)$ if the element $A(B)$ is the one that segregates. Then, if $\Delta > 0$ all even planes ($n = 0, 2, 4, \dots$) would be of α type and all

odd planes ($n = 1, 2, \dots$) would be of β type.

At $T = 0$, and for $\Delta > 0$ all α planes would be occupied by A atoms including the planes $n = 0$ and 2. It can be shown that all β planes would be occupied by B atoms ($x_n = 0$) only if $\Delta < \Delta_0$, where

$$\Delta_0 \equiv \frac{Z - Z_3}{Z_3} \quad (2.10)$$

i.e., there is no difference between the bulk and the surface. But if $\Delta > \Delta_0$ the configuration that minimizes the free energy and fulfills Eq. (2.9) is that with $x_1 = 1.0$; $x_3 = x_5 = \dots = 0$, i.e., the three top layers would be enriched with element A ($x_0 = x_1 = x_2 = 1$). This is shown in Fig. 3. A similar analysis can be carried out for $\Delta < 0$.

C. Results at finite T

The details of the minimization of the free energy at finite temperatures are given in the Appendix. The resultant transcendental equations are solved numerically. In this calculation we have taken eight layers different from the bulk. The results for the temperature dependence of the surface concentrations and short-range order parameters for $\Delta = 1.0$ and 5.0 are shown in Figs. 4–5. We show in these figures the bulk behavior for comparison. The concentration profiles for different temperatures and $\Delta = 2.3$ and 5.0 are presented in Fig. 6. Values of $\Delta = 2.3$ correspond approximately to the FeCo system. Some results for this case are reported in Ref. 15.

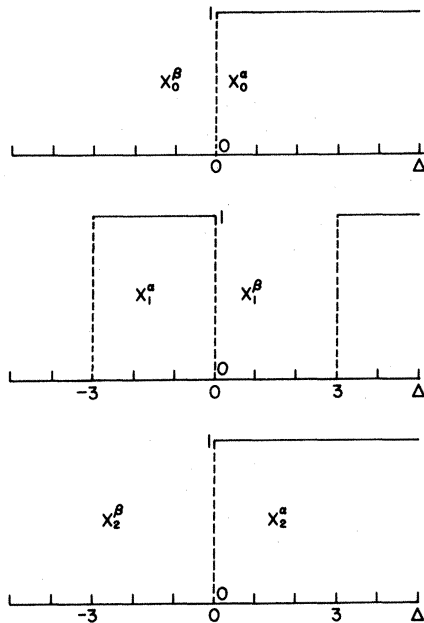


FIG. 3. Concentration of the first three layers x_0 , x_1 , and x_2 as a function of Δ [see Eq. (2.3)]. For $\Delta > 0$ (< 0) the 0th layer is of type $\alpha(\beta)$. The discontinuities take place at $\pm\Delta_0$, where $\Delta_0 \equiv (Z - Z_3)/Z_3$, Z is the number of nearest neighbors and Z_3 is the number of nearest neighbors to atoms in planes n and $n + 3$. For the bcc materials and planes in the [120] direction $\Delta_0 = 3$.

III. DISCUSSION

The theory presented here was based on the pair approximation for the energy. This is an extension of the theory outlined in I, to study the effect of steps on the surface properties. It was applied to a bcc lattice with a surface consisting of $[1\bar{1}0]$ monoatomic steps and terraces on the [110] plane.

We calculated the concentration at all different sites of the step as well as four layers deeper into the bulk. At $T = 0$, we find that there are two possible situations for $\Delta > 0$ (a similar analysis can be carried out for $\Delta < 0$). (i) For $0 < \Delta < \Delta_0$, layers with concentrations $x_n = 1$ and $x_{n+1} = 0$ ($n = 0, 2, 4, \dots$) alternate, i.e., there is no difference between bulk and surface. (ii) For $\Delta > \Delta_0$, the configuration that minimizes the free energy is $x_0 = x_1 = x_2 = 1$, $x_{n+1} = 0$, $x_n = 1$ ($n = 2, 4, \dots$) i.e., all the three top surface planes contain A atoms. In case (i), the chemical order dominates and it is preserved up to the surface. On the other hand, in case (ii) segregation governs the low-temperature behavior and destroys the spatial order.

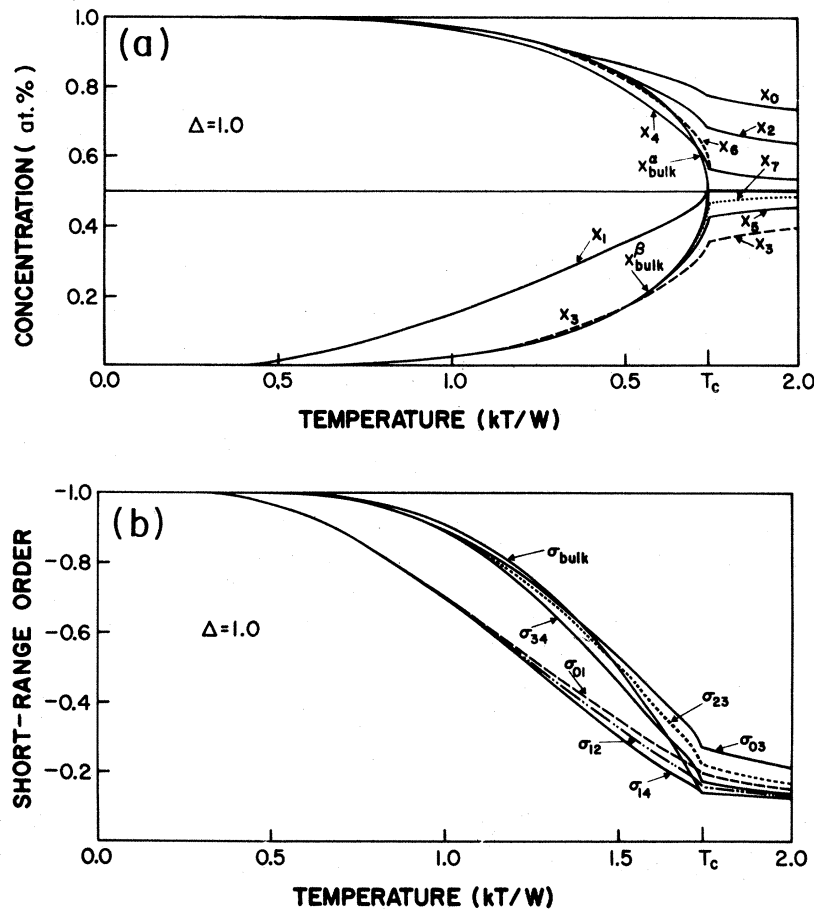


FIG. 4. (a) Temperature dependence in various layers for $\Delta = 1.0$. (b) Temperature dependence of the short-range order parameters between various layers. The bulk results are also shown for comparison.

The results for the short-range order parameters and the surface concentrations are shown in Figs. 4–6. Here, we have restricted ourselves to $\Delta > 0$, with no loss of generality. In all these cases, the plane $n = 0$ is of α type. We show also the bulk results for comparison. The values for x_{bulk}^{α} and x_{bulk}^{β} in the bulk are obtained from

$$\frac{\partial F}{\partial x_{\text{bulk}}^{\alpha}} = \frac{\partial F}{\partial x_{\text{bulk}}^{\beta}} \quad (3.1)$$

At temperatures $T > T_c$ (order-disorder transition temperature), $x^{\alpha} = x^{\beta} = 0.5$. In the pair approximation T_c is given by¹²

$$kT_c = W [2 \ln \{ Z / (Z - 2) \}]^{-1} \quad (3.2)$$

In Fig. 4 we show the results for $\Delta = 1.0$. The low-temperature behavior for the eight planes near

the surface is very similar to the bulk one. As one goes to higher temperatures, the concentrations in the first three layers begin to deviate from the bulk values. The concentration x_0 is always larger than x_{bulk}^{α} and the difference increases as $T \rightarrow T_c$, taking its maximum value at $T = T_c$. More interesting is the behavior of x_1 . The difference between x_1 and x_{bulk}^{β} starts at lower temperatures than that corresponding to the other layers. In the order phase ($T < T_c$) this layer is much richer in element A than the equivalent β layers in the bulk. The temperature dependence of x_2 is similar to that of x_0 but with weaker segregation, and $x_3, x_5, x_6,$ and x_7 show only small deviations from the bulk behavior. The concentration x_4 , however, differs to a greater extent. This effect is produced by the first-layer behavior since the first and fourth layers are connected. In Fig. 4(b) we show the results for the temperature dependence of

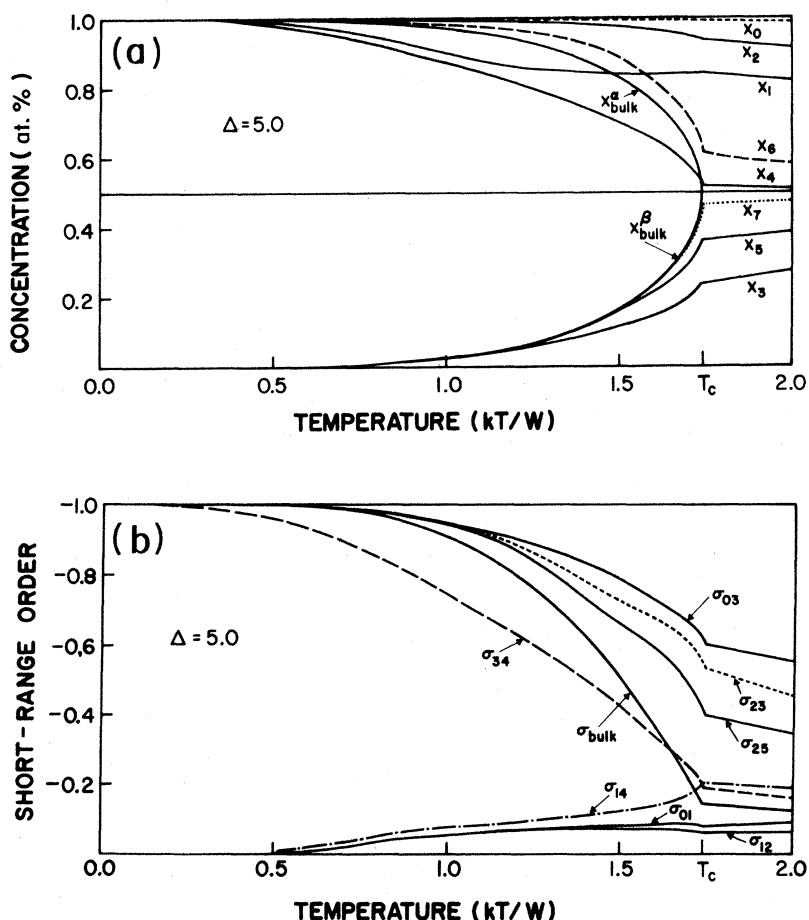


FIG. 5. (a) Temperature dependence of the concentration in various layers. (b) Temperature dependence of the short-range order parameters between various layers for $\Delta = 5$. The bulk results are also shown for comparison.

the short-range order parameters. All the σ 's associated with the first plane, σ_{01} , σ_{12} , and σ_{14} , differ the most from σ_{bulk} for $T < T_c$. On the other hand for $T > T_c$, σ_{03} and σ_{23} are the ones that deviate clearly from σ_{bulk} . This shows clearly the interplay of short-range-order effects and segregation.

In Fig. 5 we show results for $\Delta = 5$. This case corresponds to $\Delta > \Delta_0$. In this situation the concentration x_0 is practically equal to 1.0 and $x_1 \gg x_{bulk}^b$ over the whole range of temperatures plotted. The behavior of x_1 is now completely different to x_{bulk}^b . The concentration in the second plane is very similar to that in the 0th plane but with $x_2 < x_0$. All the three top layers contain mainly A atoms. However, the fourth layer, which corresponds to sites that have the full coordination number and are located in the lower part of the step, is the one with more B atoms in the system for all temperatures. This is again

driven by short-range-order effects. The concentration in all other planes have similar behavior to the one shown in Fig. 4 but the difference $x_n - x_{bulk}^{\alpha(\beta)}$ is larger.

The results for the short-range order parameters are shown in Fig. 5(b). It is illustrated here, how the $\sigma_{n,m}$ might differ completely from σ_{bulk} . In this case all σ 's associated with the first plane vanish as $T \rightarrow 0$ due to the fact that $x_1 \rightarrow 1$, instead of $x_1 \rightarrow 0$. It is worth noticing that the short-range order might be very high even at $T \approx T_c$ as in the case of σ_{03} , σ_{23} , and σ_{25} .

In Fig. 6 the concentration profiles for the first eight layers and for $\Delta = 2.3$ and 5.0 are shown. The step region corresponds to the dashed area. Sites in planes 0, 1, 2, and 3 have coordination numbers $Z = 4, 6, 6,$ and 8 correspondingly. The two curves in each diagram correspond to $kT/W = 1.0$ and 2.0,

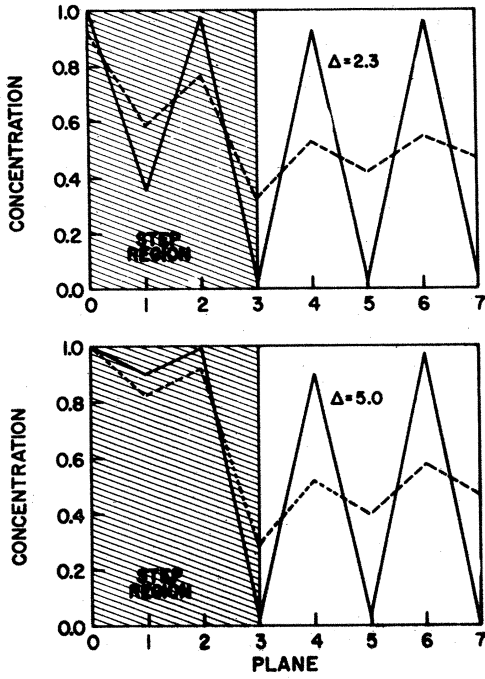


FIG. 6. Concentration profile for the first eight planes for $\Delta = 2.3$ and 5 and for two different temperatures, the full and the dashed lines correspond to $kT/W = 1.0$ and 2.0, respectively. The dashed area corresponds to the step region.

i.e., below and above than $kT_c/W = 1.738$. We see that in general the results for the step region are very different as compared with those deep into the bulk. In particular, the concentration in the first plane can get very different values as a function of tempera-

ture. This might be very important to phenomena like catalysis where special configurations of atoms are supposed to be favorable for some reactions.

Our theory, as presented here, is the first attempt to study the properties of stepped surfaces of binary alloys. Our results reflect that there may be a large variation of concentration at the different sites of the stepped surface. As a consequence, this may have a strong effect on chemisorption and other catalytic properties of the alloy surface.

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APPENDIX

Minimization of the free energy F [see Eqs. (2.1) and (2.6)] with respect to the σ_{nm} parameters yields

$$\frac{W}{kT} = \ln \frac{p_{AB}(n,m)p_{BA}(n,m)}{p_{AA}(n,m)p_{BB}(n,m)}, \quad m = n+1, n+3, \quad (A1)$$

where $p_{IJ}(n,m)$ are the pair probabilities of finding an I atom in the n th plane and a J atom in the m plane. These probabilities can be written in terms of the layer concentrations x_n and the short-range order parameters as shown in Ref. 14.

The chemical equilibrium condition, as applied to the 0th and first plane, in the case that the 0th plane is of type α , Eq. (2.9) yields the equations

$$W(Z_1 + Z_3)(\Delta - 1) = 2kT \left[(Z - 1) \ln \frac{x_{\text{bulk}}^\alpha}{y_{\text{bulk}}^\alpha} - (Z_1 + Z_3 - 1) \ln \frac{x_0}{y_0} - Z \ln \frac{p_{AB}^{\alpha\beta}}{p_{BB}^{\alpha\beta}} + Z_1 \ln \frac{p_{AB}^{\alpha\beta}(0,1)}{p_{BB}^{\alpha\beta}(0,1)} + Z_3 \ln \frac{p_{AB}^{\alpha\beta}(0,3)}{p_{BB}^{\alpha\beta}(0,3)} \right], \quad (A2)$$

$$Z_3 W(\Delta - 1) = 2kT \left[(Z - 1) \ln \frac{x_{\text{bulk}}^\beta}{y_{\text{bulk}}^\beta} - (2Z_1 + Z_3 - 1) \ln \frac{x_1}{y_1} - Z \ln \frac{p_{AB}^{\alpha\beta}}{p_{BB}^{\alpha\beta}} + Z_1 \left[\ln \frac{p_{BA}^{\alpha\beta}(0,1)}{p_{BB}^{\alpha\beta}(0,1)} + \ln \frac{p_{BA}^{\alpha\beta}(2,1)}{p_{BB}^{\alpha\beta}(2,1)} \right] + Z_3 \ln \frac{p_{BA}^{\alpha\beta}(4,1)}{p_{BB}^{\alpha\beta}(4,1)} \right]. \quad (A3)$$

Similar equations can be written for the n planes ($n = 2, 3, 4, \dots$).

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