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A Theory of Surface Enrichment in Ordered Alloys

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A very simple theory has been developed to explain experimental data on surface enrichment in Pt_3Sn. The computed surface enrichment is in accord with experimental findings. The theory predicts that in the Pt_3Sn system enrichment occurs by interchange of atoms of the element with the lower heat of sublimation from the layer just below the surface with atoms of the other element in the surface. Arguments are presented why an experiment performed on Au–Cu alloys should be capable of verifying an assumption basic to the theory.

I. Introduction

In the past few years evidence has been obtained indicating that the surface composition of a binary alloy can differ from its bulk composition; this holds for both disordered solid-solution alloys such as Ag–Pd (*1*) and ordered alloys such as Pt_3Sn (*2*). The enrichment with one alloy partner is believed to be essential to the typical catalytic properties of alloy surfaces.

The few data available seem to support the rule that the surface becomes enriched in the component having the lower sublimation energy. The theory outlined here contains this as an essential result. The basic assumption underlying it is that strain or other size effects can be ignored. Also presented are some arguments which illustrate why an experiment performed on Au_3Cu or Cu_3Au alloys should be capable of showing whether our theory is valid or whether the strain effects mentioned should be taken into account as well.

The experimental evidence of surface enrichment in Pt_3Sn stems partly from Auger spectroscopy. As this technique scans not only the atoms of the surface layer but also those at a few lower-lying levels, it may give some idea of how the composition varies over these layers. This is of interest, because surface titration gives qualitatively the same results as Auger spectroscopy (*3*), but quantitatively it yields much higher values of surface enrichment.

The very simple theory presented here assumes only nearest-neighbour interactions, an approximation commonly used in order–disorder theories of alloys (*4*). The approximations made are rather crude, but we hope that this theory may at least qualitatively explain the experimentally found behaviour.

II. Basic Features of the Theory

If E_{11} and E_{22} are the nearest-neighbour bond energies of components 1 and 2 in their pure metals, and E_{12} is the bond energy between the two components in the alloy, then we can define an important parameter for a binary alloy, viz.,

$$\alpha = E_{12} - \frac{1}{2}(E_{11} + E_{22}). \qquad (1)$$

The E's are negative quantities, so if $\alpha < 0$, alloy formation is an exothermic process and there is a critical temperature T_c below which the alloy is ordered and above which it is disordered. In the Pt_3Sn

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alloy $\alpha < 0$, T_c can be roughly estimated by means of the Bragg-Williams approximation (4):

$$kT_c = 2X_A X_B W, \tag{2}$$

with

$$W = -z\alpha, \tag{3}$$

where X_A and X_B are the concentrations of elements A and B, respectively, and z is the number of nearest neighbours. If $\alpha > 0$ the heat of formation is positive. Now there is a critical temperature below which demixing occurs and above which the alloy forms a solid solution. An example of such an alloy is Cu–Ni. Surface enrichment in this type of system has already been dealt with extensively by Sachtler *et al.* (5).

Surface enrichment takes place if a lowering of surface free energy is involved, according to the rule of Gibbs (6). The phenomena described here are most easily explained by means of a one-dimensional chain with equal concentrations of the elements. The statements are verified for the three-dimensional system in a later section.

If the one-dimensional system is ordered, i.e., for $T < T_c$, one finds surface enrichment by component 2 to occur if:

$$\frac{1}{2}(E_{11} - E_{22}) < \alpha \tag{4}$$

Formula (4) shows that surface enrichment occurs in the component with the lower heat of sublimation. This effect can, however, be counterbalanced if α is highly negative. Formula (4) applies if one inverts two neighbouring atoms at the end of the chain. If non-neighbouring atoms are interchanged, the energy is increased by -2α. Therefore the former process is favoured. At $T > T_c$, that is if disordering takes place, both processes become energetically favourable. Surface enrichment now always takes place in the component with the lower heat of sublimation. Upon neglecting the entropy of demixing, which should be small if the system is disordered, inversion is favoured over interchange of non-nearest-neighbours by the Boltzmann equilibrium constant $4e^{-2\alpha/kT}$. This is the very factor that governs short-range order in the quasi-chemical approximation if long-range order has disappeared (7). Its effect should be appreciable if $T \sim T_c$.

The consideration presented supposes that T_c is finite for a one-dimensional system. If the system were truly one-dimensional T_c would equal zero. However, as there are more than two neighbouring atoms in three dimensions, we can assume T_c to be finite.

III. Crystal Structure of Pt_3Sn

Pt_3Sn has the $AuCu_3$ L12 structure (8), with $a = 4.01$ Å. At the corners of the unit cell (see Fig. 1) tin atoms are situated, with platinum atoms at the centre of each face. The shortest Pt–Sn distance is 2.81 Å. There are important differences between the planes. The (111) plane is the most densely packed; it contains three platinum atoms for every tin atom, and hence has a composition identical with that of the bulk. Each atom has nine nearest neighbours. In the (100) plane, however, there are equal numbers of the two types of atom and each has eight nearest neighbours. In the (200) plane there are only platinum atoms, each with eight nearest neighbours. We shall consider only surface enrichment of the (111) and (100) planes. Whereas in most surfaces atoms of incomplete coordination are encountered not only

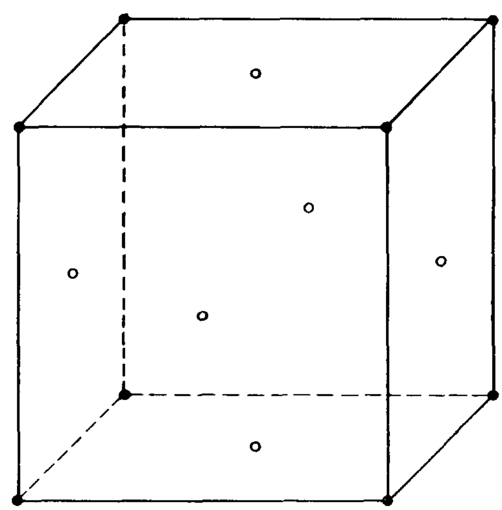

Fig. 1. The unit cell of Pt_3Sn, a cube with $a = 4.01$ Å. (●) Sn atoms; (○) Pt atoms.

in the surface plane, (111) and (100) are the only faces for which all atoms below the plane are fully coordinated.

We shall assume that only nearest-neighbour interactions are important and that they are additive. We neglect all changes in distance at the surface and assume that strain and other size effects are insignificant. The parameters $\epsilon_{11} = E_{\mathrm{Pt-Pt}}$, $\epsilon_{22} = E_{\mathrm{Sn-Sn}}$, and $\epsilon_{12} = E_{\mathrm{Sn-Pt}}$ can be derived from the pure metals and from the heat of formation of Pt_3Sn, respectively. Platinum has a f.c.c. structure; a is 3.92 Å and the shortest Pt–Pt distance is 2.76 Å, less than in Pt_3Sn. The heat of sublimation of platinum is 563.2 kJ/g. at. (*9*), so a crude approximation of ϵ_{11} for Pt_3Sn is

$$\epsilon_{11} = \frac{563.2}{6}\ \mathrm{kJ/g.at.} = 93.9\ \mathrm{kJ/g.at.} \tag{5}$$

For tin the situation is more dubious. In Pt_3Sn each tin atom has twelve nearest neighbours, whereas in gray tin it has four and in white tin six. The distances, however, between the tin atoms in Sn and Pt_3Sn do not differ much. The heat of sublimation of tin is 280.0 kJ/g.at. (*9*), thus

$$\epsilon_{22} = \frac{280}{6}\ \mathrm{kJ/g.at.} = 46.7\ \mathrm{kJ/g.at.} \tag{6}$$

The heat of formation of Pt_3Sn is unknown, but that of Pd_3Sn, which has the same structure as Pt_3Sn, has been found to be -58.6 kJ/g.at. (*10*). The formation of Pd_3Sn is accompanied by a large negative entropy change (-32.9 J/g.at. degree), which is mainly due to a decrease in vibrational entropy. Employing these figures, we find:

$$\alpha = -\frac{1}{3}(58.6 - T\cdot 32.9\times 10^{-3})\ \mathrm{kJ/g.at.} \tag{7}$$

Since the free energy of formation of Pt_3Sn is not known and platinum and palladium show only some small differences, we shall use the above value for α in our calculations.

IV. The Order–Disorder Parameters

There is a rich literature in order–disorder transitions (*4, 7*) in binary alloys and from it two parameters, S and σ, appear to be very useful in describing the phenomenon. The first is the long-range order parameter S, whose value is put equal to 1 for complete order and equal to 0 for complete disorder. For Pt_3Sn this parameter becomes zero at T_c. If x denotes the chance of finding a platinum atom in a platinum position in the completely ordered system it depends on S according to

$$x = \frac{3}{4} + \frac{1}{4}S. \tag{8}$$

The second parameter, the short-range parameter σ, does not in general vanish at the critical temperature T_c. Let p_{AB} denote the correlation probability by which, in the Bragg-Williams approximation, the expression for the number of AB pairs, n_{AB}, has to be multiplied in order to give the exact expression. If $S = 0$, σ is given by

$$\sigma = 3(p_{\mathrm{AB}} - 1). \tag{9}$$

The derivation can be found in the Appendix. It is seen that σ vanishes in the Bragg-Williams approximation, because $p_{\mathrm{AB}} = 1$. The reason why σ does not vanish if S is zero is that σ denotes the probability that formation of the pair AB is favoured over that of AA or BB. Introducing:

$$K = \frac{(n_{\mathrm{AB}})^2}{(n_{\mathrm{AA}})(n_{\mathrm{BB}})}, \tag{10}$$

we have the following relation between σ and K if $S = 0$ (see Appendix):

$$[(\sigma + 3)^2 - 16\sigma]K = 4(\sigma + 3)^2. \tag{11}$$

The parameter σ has been plotted as a function of K in Fig. 2. It is immediately seen that $\sigma = 0$, if $K = 4$. This is the value of K in the Bragg-Williams approximation. In the quasi-chemical approximation

$$K = 4e^{-2\alpha/kT}. \tag{12}$$

As is illustrated by Fig. 2, if $kT \sim -2\alpha$, σ becomes 0.36, so appreciably different from zero.

We will now present the energy expressions required for computing the surface energies. There are various expressions, depending on the value of S. Whether surface enrichment is achieved by interchange

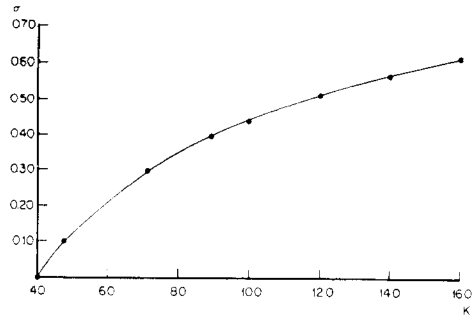

FIG. 2. σ as a function of K, if $S = 0$.

with the atoms next to the surface or with atoms from the bulk depends on the value of σ.

V. THE ENERGY EXPRESSIONS

The simplest way of evaluating the surface energy as a function of temperature is to assume that S does not change on the formation of a surface. This, of course, is not correct because the energy of the surface atoms is different from that of the bulk atoms, but it will only enhance the effects to be discussed here. The surface energies, γ, are thus:

$$\gamma(111) = \frac{3[(-4x^2 + 6x)\alpha - 3\epsilon_{12} + \epsilon_{22}]}{\sqrt{3a^2}}, \tag{13a}$$

$$\gamma(100) = \gamma(200) = \frac{4[(-4x^2 + 6x)\alpha - 3\epsilon_{12} + \epsilon_{22}]}{2a^2}, \tag{13b}$$

$$\gamma(110) = \gamma(220) = \frac{6[(-4x^2 + 6x)\alpha - 3\epsilon_{12} + \epsilon_{22}]}{2\sqrt{2a^2}}, \tag{13c}$$

The γ's show the correct dependence upon plane. The surface energy equals the surface free energy if we neglect the differences in entropy between the atoms at the surface and those in the bulk. At complete order $x = 1$, and at complete disorder $x = 3/4$, so we see that the surface energy decreases with increasing disorder. We may, therefore, expect a rapid change if $T \sim T_c$. Numerical values of the γ's derived from our choice of parameters are presented in Table 1.

If we allow for interchanges between atoms from the surface with bulk atoms, the following energies have to be added to Eq. (13) per exchange of a surface atom.

$$\Delta E_{\mathrm{Pt}\to\mathrm{Sn}}(111) = 1\tfrac{1}{2}(\epsilon_{11} - \epsilon_{22}) + (-19 + 68x - 56x^2)\alpha, \tag{14a}$$

$$\Delta E_{\mathrm{Sn}\to\mathrm{Pt}}(111) = -1\tfrac{1}{2}(\epsilon_{11} - \epsilon_{22}) + (-103 + 268x - 168x^2)\alpha, \tag{14b}$$

$$\Delta E_{\mathrm{Pt}\to\mathrm{Sn}}(200) = 2(\epsilon_{11} - \epsilon_{22}) + (-6 + 32x - 32x^2)\alpha, \tag{15a}$$

$$\Delta E_{\mathrm{Sn}\to\mathrm{Pt}}(100) = -2(\epsilon_{11} - \epsilon_{22}) + (-98 + 256x - 160x^2)\alpha, \tag{15b}$$

$\Delta E_{\mathrm{Pt}\to\mathrm{Sn}}(111)$ denotes the energy needed to replace a platinum atom at the (111) surface

TABLE 1
CALCULATED SURFACE ENERGIES (J/m², 800°K)[a]

	γ_{111}	γ_{100}	γ_{110}	$\gamma_{exp.}$[14] (M.P.)	$\gamma_{exp.}$[15] (1310°C)
Pt	3.5	4.0	4.3	1.8	2.3
Pt_3Sn ($S = 1$)	3.1	3.6	3.7		
Pt_3Sn ($S = 0$)	3.1-0.05	3.6-0.06	3.7-0.06		
$AuCu_3$	2.5	2.8	3.0		
Au_3Cu	2.3	2.6	2.8		
Au	2.2	2.5	2.8	1.2	
Cu	2.5	2.9	3.0	1.3	

[a] Parameters of the Au–Cu alloys: $\epsilon_{Au} = -63.1$ kJ/g.at., $a_{Au} = 4.07$ Å; $\epsilon_{Cu} = -56.8$ kJ/g.at., $a_{Cu} = 3.61$ Å; $\alpha_{Au_3Cu} = -1.3$ kJ/g.at., $a_{Au_3Cu} = 3.95$ Å; $\alpha_{Cu_3Au} = -2.3$ kJ/g.at., $a_{Cu_3Au} = 3.71$ Å. The values of a have been computed with the aid of Végard's rule.

by a tin atom. The other ΔE's have an analogous meaning. Expressions (14) and (15) have been evaluated by interchanging adjacent platinum and tin atoms. For interchanges other than those between next neighbours we have to add -2α to all expressions. For values of $x \neq 1$, the expressions for energy change in (200) and (100) planes have been averaged over the contribution of the complementary plane. It is seen that the energy changes decrease if x decreases.

VI. Surface-Enrichment Probabilities

The degree of surface enrichment can be derived by subtracting from the change in energy the change in entropy of mixing and by minimizing this expression *(11)*. This is basically the procedure we follow. There is, however, an essential difference between the entropy expression we use and the one found in the theory of surface tension of liquids *(11)*. This is because in our treatment the entropy of the surface is not independent of the entropy in the layer next to it. We consider surface enrichment to take place by interchange between nearest neighbours, a concept which in the case of liquids makes no sense. We have already noted that the extra energy needed to interchange non-nearest neighbours is -2α per surface atom exchanged. This is precisely the energy that governs short-range order [Eq. (12)]. So, as long as short-range order is appreciable, the interchange between non-nearest neighbours is negligible. It is within this approximation that our results are valid. As the entropy gain is much larger when interchange between non-nearest neighbour pairs becomes important our results present a lower limit if short-range order is much less than one.

If r_a and r_b are the overall relative concentrations of tin and platinum, respectively, then the entropy of mixing as a function of S for the (111) plane is

$$-kT \ln \left\{ 3^{x_a} \frac{(r_aN)!}{[(r_a - x_a)(r_a + r_bS)N]![\{r_b(r_a(1-S) + x_aS) + r_ax_a\}N]!} \times \frac{(r_bN)!}{[r_b\{(r_b + x_a) + S(r_a - x_a)\}N]![r_b(r_a - x_a)(1-S)N]!} \right\} \quad (16)$$

Here x_a is the change in the percentage composition of those atoms which have the lower concentration (prior to changing plane). The factor of 3 originates from the three possibilities of enrichment in the other plane. N is the number of surface atoms. If $S = 1$, we have the following equation for surface enrichment:

$$\frac{\frac{1}{3}x_a}{\frac{1}{4} - x_a} = e^{-\Delta E/kT}. \quad (17)$$

If $S = 0$, we find for surface enrichment probability:

$$\frac{\frac{3}{4} + x_a}{\frac{1}{4} - x_a} = 3e^{-\Delta E/kT}. \quad (18)$$

The corresponding equations for (100) and (200) planes are

$$\frac{x_a}{\frac{1}{2} - x_a} = 2e^{-\Delta E/kT} \quad \text{if } S = 1 \quad (19)$$

and Eq. (18) if $S = 0$.

VII. Results and Discussion

Table 1 lists the calculated surface energies of the (111), (100), and (110) faces of Pt, Pt_3Sn, $AuCu_3$, Au_3Cu, Au, and Cu. We find that the computed values of γ are higher than those measured. This is partly due to the fact that the measured values refer to the liquid metals. We believe that the basic reason for the discrepancy which remains is the neglect of the delocalized nature of the electrons in a metal. Preliminary results of quantum mechanical calculations *(16)* lead to values more in agreement with the experimental data for the energies involved, while the qualitative features of the model are not changed. The values for $AuCu_3$ and Au_3Cu are included because they show an interesting phenomenon.

We see that $|\epsilon_{Au}| > |\epsilon_{Cu}|$ *(9)* but find that $\gamma_{Cu} > \gamma_{AuCu_3} > \gamma_{Au_3Cu} > \gamma_{Au}$. So the surface energy in these systems is not determined by a difference in sublimation energy, but by the difference in atomic radii. The density in the surface decreases from copper to gold. If our theory is valid and if enrichment occurs in the Au_3Cu or the Cu_3Au systems, then we expect the enrichment to be in copper. However, the large difference in radii can make strain effects important and these should favour enrichment of gold atoms. So an experiment performed on this system should be capable of indicating whether or not the theory presented is valid.

The Au_3Cu and Cu_3Au systems are also of interest for a different reason. The T_c of Au_3Cu is approximately 210°C and that of Cu_3Au 390°C (*8*). Effects due to a difference in ordering of the sample should therefore be present and experimentally measurable.

Table 2 lists the numerical values of the energy involved in interchanging two atoms in the outer layers; the values are derived from formulae (14) and (15). The table clearly shows the difference in energy between an ordered ($S = 1$) and a disordered ($S = 0$) system. Substitution of these values into Eqs. (17), (18), and (19) yields the surface enrichment. The equations for x_a are

(111) plane:

$$x_a = \frac{1}{4}\frac{3e^{-\Delta E/kT}}{1 + 3e^{-\Delta E/kT}} \quad (S = 1) \quad (20a)$$

both planes:

$$x_a = \frac{3}{4}\frac{e^{-\Delta E/kT}}{1 + 3e^{-\Delta E/kT}} \quad (S = 0) \quad (20b)$$

(100–200) plane:

$$x_a = \frac{e^{-\Delta E/kT}}{1 + 2e^{-\Delta E/kT}} \quad (S = 1) \quad (20c)$$

Of course, if $\Delta E > 0$, we find an increase in concentration change of the surface with increasing temperature. Table 3 gives the values of T for which half of the atoms with lowest concentration have interchanged and $\Delta E > 0$.

Table 4 lists the values of x_a computed for the interchanges with $\Delta E < 0$. For Pt_3Sn they are computed at $T = 800°K$, and for Au_3Cu and Cu_3Au at $T = 500°K$ in order to compare our predictions with experiment. We find that the surface is enriched with the element having the lower heat of sublimation and that this enrichment is quite pronounced. In the (100) direction, there is no change in surface enrichment between the ordered and the disordered system. In both cases all the tin atoms in the layer next to the surface layer are replaced by platinum atoms. Therefore, surface enrichment is predicted to be 50% in the (200) plane in the ordered system and 25% in the (200) and (100) planes in the disordered systems. The overall enrichment along the (100) direction both in the ordered and the disordered system is therefore 25%.

In the most densely packed plane, the (111) plane, no surface enrichment occurs at very low temperature for Pt_3Sn. At 872°K, however, we find an enrichment of 12.5%, as is seen in Table 3. For a disordered crystal we have at this tempera-

TABLE 2
SURFACE-ENRICHMENT ENERGIES ($T = 800°K$)[a]

kJ/g.at.	Pt_3Sn: Pt → Sn	Pt_3Sn: Sn → Pt	Cu_3Au: Cu → Au	Cu_3Au: Au → Cu	Au_3Cu: Cu → Au	Au_3Cu: Au → Cu
$\Delta E(111)$						
$S = 1$	+8.0	+99.2	+24.4	−2.5	+14.1	−0.04
$S = 0$	−72.4	+29.6	+4.0	−10.5	+8.7	−10.0
$\Delta E(100)$						
$S = 1$	−25.2	+110.3	+25.5	−12.1	+15.2	−4.5
$S = 0$	−89.4	+46.6	+12.5	−21.7	+11.4	−12.5

[a] $\Delta E_{x\to y}$ denotes the energy needed to replace an x atom at the surface by a y atom from a layer below it.

TABLE 3
THE VALUES OF T FOR WHICH x_a IS HALF OF ITS MAXIMUM VALUE

	Pt_3Sn		Cu_3Au		Au_3Cu	
K°	Pt → Sn	Sn → Pt	Cu → Au	Au → Cu	Cu → Au	Au → Cu
T						
(111) $S = 1$	872	10,000	2,662	—	1,539	—
(111) $S = 0$	—	3,237	443	—	954	—
T						
(100) $S = 1$	—	12,055	2,785	—	1,662	—
(100) $S = 0$	—	5,096	1,370	—	1,242	—

ture an enrichment by 25%. So the behaviour of the (111) plane is different from that of the (100) and (200) planes.

In Cu_3Au and Au_3Cu there is also less enrichment in the (111) plane for both ordered and disordered systems, but the differences are smaller. In the ordered system we find 21% and 18%, respectively, and in the disordered system 25% in both cases.

VIII. CONCLUSION

On the basis of our theory we predict that in systems with a negative heat of formation surface enrichment takes place such that atoms with the higher heat of sublimation on the surface interchange with atoms with the lower heat of sublimation in the layer just below the surface. This goes for both ordered and disordered systems as long as $kT \ll |2\alpha|$.

The theory presented does not hold if $kT \geq |2\alpha|$, because then a different expression for the entropy of mixing has to be used. The pertinent theories are well documented in the literature (*11, 12*) and a recent application of them to disordered alloys is given by Ollis (*13*).

We predict that surface enrichment in the (111) plane is in general less than in the (100) plane, a result also reported by Ollis (*13*). In practice we find only a small difference for the ordered system. Surface enrichment in the ordered (111) surfaces is less than in the disordered ones. So the best check on our theory is an experiment performed on the (111) surface of a single crystal. A sharp increase in surface enrichment should then be observed at the critical temperature. In polycrystalline matter this increase will depend on the contribution of (111) planes relative to that of the other planes.

APPENDIX

The Short-Range Parameter σ

In the Bragg-Williams approximation the expressions for n_{AA}, n_{BB}, and n_{AB} are

$$n_{AA} = \frac{1}{2} zNr_A{}^2(1 - S^2), \tag{A1a}$$

TABLE 4
VALUES OF x_a FOR $E < 0$[a]

	Pt_3Sn		Cu_3Au		Au_3Cu	
	Pt → Sn	Sn → Pt	Cu → Au	Au → Cu	Cu → Au	Au → Cu
x_a						
(111) $S = 1$	—	—	—	0.21	—	0.18
(111) $S = 0$	0.25	—	—	0.25	—	0.25
x_a						
(200) $S = 1$	0.50	—	—	0.50	—	0.50
(100) $S = 0$	0.25	—	—	0.25	—	0.25

[a] The notation $x \to y$ means that an x atom at the surface is replaced by a y atom from the layer below it.

$$n_{BB} = \frac{1}{2} zN(r_B^2 - r_A^2 S^2), \qquad \text{(A1b)}$$

$$n_{AB} = \frac{1}{2} zN(2r_A r_B + 2r_A^2 S^2), \qquad \text{(A1c)}$$

where z is the number of nearest neighbours, r_A the percentage of sites A, r_B the percentage of sites B and N the total number of sites, with

$$r_A < r_B. \qquad \text{(A2)}$$

In order to make the above expressions exact we multiply the expression for n_{AA}, n_{BB}, and n_{AB} by p_{AA}, p_{BB}, and p_{AB}, respectively. The functions p describe the correlation between the probabilities of finding particles A and B next to one another. Using the relations

$$n_A = \frac{2}{z} n_{AA} + \frac{1}{2} n_{AB} \qquad \text{(A3a)}$$

and

$$n_B = \frac{2}{z} n_{BB} + \frac{1}{2} n_{AB}, \qquad \text{(A3b)}$$

we can express p_{AA} and p_{BB} in p_{AB} and find

$$n_{AA} = \frac{1}{2} zN[r_A - r_A(r_B + r_A S^2)p_{AB}], \qquad \text{(A4a)}$$

$$n_{BB} = \frac{1}{2} zN[r_B - r_A(r_B + r_A S^2)p_{AB}], \qquad \text{(A4b)}$$

$$n_{AB} = zNr_A(r_B + r_A S^2)p_{AB} \qquad \text{(A4c)}$$

These relations enable us to express the equilibrium constant K defined in Eq. (10) in p_{AB} and S:

$$K = \frac{4r_A(r_B + r_A S^2)^2 p_{AB}^2}{r_B - (r_B + r_A S^2)p_{AB} + r_A(r_B + r_A S^2)^2 p_{AB}^2}. \qquad \text{(A5)}$$

If $S = 0$, $p_{AB} = 1$, K reduces to its Bragg-Williams value of 4. If $S = 0$ Eq. (A5) reduces to

$$K = \frac{4r_A r_B p_{AB}^2}{1 - p_{AB} + r_A r_B p_{AB}^2}. \qquad \text{(A6)}$$

The short-range order parameter σ is defined as

$$\sigma = \frac{q - q(\text{random})}{q_{\max} - q(\text{random})}, \qquad \text{(A7)}$$

where q is the fraction of the pairs which are AB. Substitution of (A4c) into (A7) then gives for $S = 0$

$$\sigma = \frac{r_B}{r_A}(p_{AB} - 1). \qquad \text{(A8)}$$

Putting r_B equal to ¾ and r_A equal to ¼ we find Eq. (9) of the main text:

$$\sigma = 3(p_{AB} - 1). \qquad \text{(A9)}$$

Solving Eq. (A9) for p_{AB}, using the values of r_B and r_A, and substituting this into (A6) we obtain Eq. (11):

$$[(\sigma + 3)^2 - 16\sigma]K = 4(\sigma + 3)^2. \qquad \text{(A10)}$$

The parameter σ has been plotted as function of K in Fig. 2.

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