

Physical origin of surface segregation in binary alloys

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Mills's theory of surface effects on a magnetic system is applied to the surface segregation phenomenon in binary alloys. The effect of lattice strain energy is not considered. It is shown that there are two driving forces for the surface segregation: (1) the difference in the surface energy of the composing elements, and (2) a collective effect depending on the relative concentration only. The former force predicts that the element with lower surface energy is enriched on the surface, while the latter force predicts an enrichment of the minority element on the surface. The above results are restricted to the alloys with positive heat of mixing and at a temperature higher than the bulk critical temperature.

With recent advances in experimental surface-science techniques, there is a growing interest in the study of the surface composition of binary alloys. Experimental evidence has shown that, in general, the surface composition of a binary alloy is different from its bulk composition. A theoretical understanding of this *surface segregation* phenomenon is not only of academic interest, but is also important in many technological applications such as catalysis, corrosion, thin-film properties, etc.

Physically it is easy to understand that because the surface atoms experience a different environment than the bulk atoms, a uniform concentration of the composing elements throughout the alloy¹ will be, in general, not a state of lowest total free energy of the system. If an exchange of a bulk atom of one type with a surface atom of the other type will lower the total free energy of the system, then the former type of atoms will be enriched on the surface. Most theories use the heat of vaporization²⁻⁹ or the surface energy⁹⁻¹² of the pure solid of the composing elements to calculate the *free energy of segregation*. According to these theories, the element with a lower heat of vaporization or surface energy will be enriched on the surface.

In this paper we want to look at the origin of surface segregation more closely. We will not discuss the effect due to the difference of atomic sizes, which will produce a lattice strain energy^{13,6-8,11} in the alloy. We also limit ourself at the temperatures higher than the bulk critical temperature, so that the alloy is completely random.

We have two points to make. Firstly, previous theories do not tell us whether the use of the heat-of-vaporization data is better than the surface-energy data or the other way around. A recent calculation of Kumar⁹ has shown that the use of the surface-energy data gives a much better agreement with the experimental results than the use of the heat-of-vaporization data. But no explanation was given. We want to give a theoretical explanation that the surface energy is indeed the relevant "force" in the surface segregation phenomenon rather than the heat of vaporization. Secondly, we want to point out that even when the two composing elements have equal surface energy per atom, there is still a driving force (in addition to the lat-

tice strain energy) for surface segregation if the heat of mixing J is nonzero. Although this term appears in several of the previous theories, no systematic study of this term has been given. We find that this term does not favor either type of atoms of a given alloy to segregate on the surface. It depends on the relative concentration only. The minority element will be enriched on the surface for positive J (we exclude the case for negative J). Since the surface-energy "force" is more or less a local effect, we may say that this latter driving force is a collective effect.

In pair-bond models,^{2-5,9} which use the heat-of-vaporization data, one usually keeps the total number of each type of atoms fixed, and minimizes the total free energy of the system with respect to the concentration of each layer. This is a canonical ensemble approach. However, in order to be compatible with the actual experimental situation, it is more appropriate to introduce chemical potentials rather than to keep the total number of atoms fixed, i.e., a grand canonical ensemble approach. Although these two approaches are equivalent in the thermodynamic limit, the relevant "forces" are different. It turns out that in surface segregation the relevant force is the surface energy rather than the heat of vaporization.

We consider a semi-infinite solid binary alloy composed of A and B atoms in the half space $z > 0$, with a plane surface at $z=0$. Each lattice site can be occupied by either an A atom or a B atom. We assume the total energy of the system can be written as the sum of various pair interactions (a quasichemical approach¹⁴), and we consider only nearest-neighbor interactions. If V_{AA} , V_{BB} , and V_{AB} represent A - A , B - B , and A - B pair potentials, respectively, then after introducing the chemical potentials μ_A and μ_B , the Hamiltonian of the system can be written as

$$H = \sum'_{i,j} [C_i^A C_j^A V_{AA}(i,j) + 2C_i^A C_j^B V_{AB}(i,j) + C_i^B C_j^B V_{BB}(i,j)] - \sum_i [C_i^A \mu_A(i) + C_i^B \mu_B(i)] . \quad (1)$$

Here \sum' represents the sum over nearest-neighbor sites and $C_i^A = 1$, $C_i^B = 0$ if site i is occupied by an A atom, and

vice versa. We have written the various potentials as position dependent to allow for surface relaxations.

It is well known that Eq. (1) is equivalent to a spin- $\frac{1}{2}$ Ising model with an applied magnetic field. By introducing the spin variable S_i ($S_i = +1$ or -1) and the change of variables $C_i^A = (1 + S_i)/2$, $C_i^B = (1 - S_i)/2$, Eq. (1) can be written as

$$H = - \sum'_{i,j} J_{ij} S_i S_j - \sum_i \Delta\mu'_i S_i + H_0, \quad (2)$$

with

$$J_{ij} = \frac{1}{4} [2V_{AB}(i,j) - V_{AA}(i,j) - V_{BB}(i,j)], \quad (3)$$

$$\Delta\mu'_i = \frac{1}{2} \left[\mu_A(i) - \mu_B(i) - \sum_j [V_{AA}(i,j) - V_{BB}(i,j)] \right],$$

and H_0 represents the S -independent part of the Hamiltonian. Mills's¹⁵ has used Eq. (2) to study the effect of a surface on a magnetic system. We apply Mills's theory to the surface segregation problem, and this was first done by Binder *et al.*¹⁶ It is essentially a mean-field theory, and we have

$$\langle S_i \rangle = \tanh \left[\sum_j J_{ij} \langle S_j \rangle + \Delta\mu'_i / kT \right], \quad (4)$$

where $\langle \rangle$ represents the thermal average, k is Boltzmann's constant, and T the absolute temperature.

Because of the presence of the surface, $\langle S_i \rangle$ will in general depend on the position of site i . But since the translational symmetry parallel to the surface is still preserved,¹ we expect $\langle S_i \rangle$ to be a function of the distance between site i and the surface only. If we describe the alloy in terms of lattice layers parallel to the surface and label them by index n ($n=1,2,\dots$), then we can write $\langle S_i \rangle = m_n$, if site i is on the n th layer ($n=1$ represents the surface layer). We make the following assumptions:

(1) The heat of mixing $J_{ij} = J$, independent of i and j , if either i or j (or both) is not on the surface layer.

(2) $J_{ij} = J_s$, if both i and j are on the surface layer, due to surface relaxation.

(3) $\Delta\mu'_i = \Delta\mu'$, independent of i , if i is not on the surface layer.

(4) $\Delta\mu'_i = \Delta\mu'_s$ if i is on the surface layer.

With these assumptions, Eq. (4) becomes¹⁶

$$m_n = \tanh \left[\frac{Z_s J}{kT} m_n + \frac{Z_v J}{kT} (m_{n+1} + m_{n-1}) + \frac{\Delta\mu'}{kT} \right], \quad n \geq 2$$

$$m_1 = \tanh \left[\frac{Z_s J_s}{kT} m_1 + \frac{Z_v J}{kT} m_2 + \frac{\Delta\mu'_s}{kT} \right], \quad (5)$$

where Z_s is the number of nearest neighbors within each layer, and Z_v is the number of nearest neighbors between n th and $(n+1)$ th layers. Thus $Z = Z_s + 2Z_v$ is the total number of nearest neighbors. We then follow Mills's¹⁵ to assume that m_n varies so slowly over a distance of interlayer spacing such that we can write

$$m_{n+1} = m(z_n) + dm/dz + \frac{1}{2} d^2m/dz^2, \quad (6)$$

with lengths in units of interlayer spacing.

For $J > 0$ and at a temperature higher than critical tem-

perature T_c ($kT_c = ZJ$), the arguments of the hyperbolic tangent are small compared with one. We can then expand Eq. (5) up to third order to obtain a differential equation for m with a boundary condition^{15,16}:

$$m \left[1 - \frac{ZJ}{kT} \right] + \frac{1}{3} \left[\frac{ZJ}{kT} \right]^3 m^3 - \frac{Z_v J}{kT} \frac{d^2 m}{dz^2} = \frac{\Delta\mu'}{kT}, \quad (7)$$

and

$$\frac{Z_v J}{kT} \frac{dm}{dz} = \frac{\Delta\mu' - \Delta\mu'_s}{kT} - \left[\frac{\Delta\mu'}{kT} - m \left[1 - \frac{Z_v J}{kT} - \frac{Z_s J_s}{kT} \right] \right], \quad z=0. \quad (8)$$

Equation (7) relates $\Delta\mu'$ with the bulk concentration $m_b(z = \infty)$, and the boundary condition (8) determines how the concentration varies from the surface layer to the inner layers. We have regrouped the right-hand side of Eq. (8) in the above form for convenience of discussion. It is clear that if $dm/dz = 0$ at the surface, then we will get a uniform concentration throughout the system and there will be no surface segregation. Therefore we may say that the two terms at the right-hand side of Eq. (8) represent some kind of "driving force" for the surface segregation phenomenon. We discuss them in the following:

(a) The first term is proportional to $\Delta\mu' - \Delta\mu'_s$ and its physical meaning can be obtained from Eq. (3). We have

$$\Delta\mu' - \Delta\mu'_s = \Delta\mu'_A - \Delta\mu'_B, \quad (9)$$

with

$$2\Delta\mu'_A = \left[\frac{1}{2} (Z_s V_{AA}^s + Z_v V_{AA}) - \mu_A^s \right] - \left(\frac{1}{2} Z V_{AA} - \mu_A \right), \quad (10)$$

and a similar equation for B atoms. We see that the right-hand side of Eq. (10) represents the energy difference of a surface atom and a bulk atom in a pure A solid, if we assume that the differences in the chemical potentials is the same in a pure solid and in the alloy. Therefore, the right-hand side of (10) is the surface energy per atom of a pure A solid, and the same argument holds for B atoms. Thus we have

$$\Delta\mu' - \Delta\mu'_s = \frac{1}{2} (\sigma_A a_A - \sigma_B a_B), \quad (11)$$

where $\sigma_{A(B)}$ and $a_{A(B)}$ are the surface energy and surface area per atom for a pure A (B) solid, respectively.

Therefore, the driving force in the surface segregation phenomenon is the surface-energy difference of the composing elements. If we set $\mu_A = \mu_A^s$ and $\mu_B = \mu_B^s$, then the surface energy is simply proportional to the bond strength and we recover the results of previous pair-bond models^{2-5,9} where no chemical potentials have been introduced. In this case both the surface energy and the heat of vaporization are simply proportional to the bond strength, and the use of either experimental data to estimate the bond strength should be equally good. However, in general, we have $\mu_A \neq \mu_A^s$ and $\mu_B \neq \mu_B^s$, and the heat-of-vaporization data can no longer be used. One should use the surface-energy data in order to get a correct result.¹⁷

From Eqs. (8) and (11), we see that if $\sigma_A a_A < \sigma_B a_B$, then $dm/dz < 0$ at $z=0$. Therefore m is larger at the surface than in the interior. This means the element with lower surface energy segregates at the surface.

(b) Since the heat of mixing J is symmetric with respect to an interchange of A and B , the effect of the second term depends on the relative concentration m only. If we neglect the third-order term in Eq. (7), which is negligible at high temperatures, and assume no surface relaxation ($J_s = J$), then Eq. (8) can be written as (after omitting the surface-energy term)

$$\frac{Z_v J}{kT} \frac{dm}{dz} = (m_0 - m_b) \left[1 - \frac{ZJ}{kT} \right] + m_0 \frac{Z_v J}{kT}, \quad z=0 \quad (12)$$

where m_0 and m_b are the surface and bulk concentrations, respectively. For the case $m_b > 0$, we must have $m_0 < m_b$. Otherwise the right-hand side of Eq. (12) is positive and a contradiction occurs. Similarly for the case $m_b < 0$, we must have $m_0 > m_b$. In either case the *minority* element segregates at the surface. Since our theory is applicable only for ZJ/kT small compared with one, there is little effect by including the third-order term of Eq. (7) in the right-hand side of Eq. (12). This term is small and in general its magnitude is smaller than that of the last term in Eq. (12). Therefore we would expect our result holds for any concentration.

Since this term does not favor either of the composing elements, and its effect depends on the relative concentration only, we may say that this is a statistical (or collective) effect. Although the surface-energy term may be dominant, this term should not be neglected.

Finally we remark that the above analysis cannot be applied to the case of negative J . When $J > 0$, Eq. (7) predicts m as a monotonic function of z , and the above analysis follows. But for $J < 0$, Eq. (7) predicts an (damped) oscillatory m , and no simple conclusions can be drawn from the boundary condition (8), although some experimental evidences¹⁸ have shown that the element with lower surface energy segregates in the surface, as in the case $J > 0$. The oscillatory behavior of m near the surface is consistent with a recent calculation by Kumar.⁹

The atomic size difference can be neglected if the associated lattice strain energy is negligible in comparison with the surface-energy difference of the pure solids of the composing elements. Thus from Ref. 7, we have

$$\left| \frac{6\pi\bar{r}(r_A - r_B)^2}{(1 + \bar{\alpha})\bar{\chi}} (2x_b - 1) \right| \ll |\sigma_A a_A - \sigma_B a_B|, \quad (13)$$

where

$$\bar{\alpha} = (1 + \bar{v})r_A / 2(1 - 2\bar{v})r_B, \quad (14)$$

for the lattice strain energy to be negligible. In (13) and (14) x_b is the bulk concentration of minority element A ; \bar{r} is the mean of the atomic radii r_A and r_B in the solid; \bar{v} and $\bar{\chi}$ are, respectively, the averaged Poisson ratio and the compressibility. Our theory should work well if the inequality (13) is satisfied for an alloy composed of A and B atoms.

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¹We are interested in the high-temperature region only, where no ordering in the bulk phase exists.

²F. L. Williams and D. Nason, *Surf. Sci.* **45**, 377 (1974).

³R. A. van Santen and W. M. H. Sachtler, *J. Catal.* **33**, 202 (1974).

⁴D. Kumar, A. Mookerjee, and V. Kumar, *J. Phys. F* **6**, 725 (1976).

⁵J. L. Moran-Lopez and K. H. Bennemann, *Phys. Rev. B* **15**, 4769 (1977).

⁶F. F. Abraham, N. H. Tsai, and G. M. Pound, *Surf. Sci.* **83**, 406 (1979).

⁷V. Kumar, *Surf. Sci.* **84**, L231 (1979).

⁸F. F. Abraham and C. R. Brundle, *J. Vac. Sci. Technol.* **18**, 506 (1981).

⁹V. Kumar, *Phys. Rev. B* **23**, 3756 (1981).

¹⁰P. Wynblatt and R. C. Ku, *Surf. Sci.* **65**, 511 (1977).

¹¹A. R. Miedema, *Z. Metallkd.* **69**, 455 (1978).

¹²J. C. Hamilton, *Phys. Rev. Lett.* **42**, 989 (1979).

¹³D. McLean, *Grain Boundaries in Metals* (Oxford University Press, London, 1957).

¹⁴R. A. Swalin, *Thermodynamics of Solids* (Wiley, New York, 1972).

¹⁵D. L. Mills, *Phys. Rev. B* **3**, 3887 (1971).

¹⁶K. Binder, D. Stauffer, and V. Wildpaner, *Acta Metallurg.* **23**, 1191 (1975).

¹⁷The situation is rather like a p - n junction, where the two sides have unequal chemical potentials. In order to maintain a constant effective chemical potential throughout the entire system, a potential difference develops across the junction. The same type of potential difference exists between the surface and the bulk regions that contributes to the surface energy.

¹⁸G. C. Nelson, *Surf. Sci.* **59**, 310 (1977); M. J. Kelley, D. G. Swartzfager, and V. S. Sundaram, *J. Vac. Sci. Technol.* **16**, 664 (1979).