PHYSICAL REVIEW B VOLUME 17, NUMBER 1 1 JANUARY 1978

Landau-Ginzburg theory of order-disorder transition in semi-infinite systems

Alba Theumann* and K. H. Bennemann
Institute for Theoretical Physics, Freie Universität Berlin, 1000 Berlin 33, West Germany

(Received 1 July 1977)

The parameters of the Landau-Ginzburg functional for atomic order-disorder transitions are calculated from a microscopic Ising-like Hamiltonian. It is shown that the surface force λ^{-1} and the transition depend crucially on segregation at the surface. It is shown that the surface may order before ordering in the bulk occurs.

I. INTRODUCTION

Surface effects on the order-disorder transition in A_3B type of alloys have been studied recently[1] by means of Bragg-Williams theory. One finds that the bulk and the surface will both order at temperatures $T < T_c$, where T_c is a common critical temperature, but the order parameter is reduced at the surface due to segregation. These results are in fair agreement with experimental data for Cu_3Au.[2] However, the following problem has not been studied: The critical temperature of the order-disorder transition depends on the concentration x of one of the components as $T_c \propto x(1-x)$. Thus one would expect that if segregation occurs,[3] such that $x_s \neq x_b$, there should be two different critical temperatures for bulk and surface. As a consequence the surface may order while the bulk is still completely disordered.

The purpose of this paper is to investigate this point in the context of the Landau-Ginzburg theory for order-disorder transitions in the presence of a surface. We obtain that the order at the surface may be reduced or enhanced due to segregation. In the last case, there exists a characteristic temperature $T_s > T_b$ such that for $T_b < T_s$ the surface is ordered while the bulk remains disordered. We call T_b the bulk-transition temperature.

The order-disorder transition can be studied by means of an Ising-like model Hamiltonian.[3,4] Starting from this microscopic formulation we derive in Sec. II a Landau-Ginzburg expression for the free-energy functional. We consider here a simple model that can describe an order-disorder transition in A_xB_{1-x} alloys including surface segregation. We assume a lattice that can be decomposed in two equal interpenetrating sublattices and the interactions are taken only between nearest neighbors. As a consequence of these two assumptions we obtain only a second-order transition and not a first-order transition as it is the case in A_3B alloys.[1,2]

In Sec. III, we derive the Landau-Ginzburg (LG) equations for the order parameter. The main difference between our problem and the case of magnetic systems[5] is that we have additional constraints due to the requirement of a fixed number of atoms of either kind. Once these contraints are introduced in the theory, the LG equations are the same as those obtained in magnetic[5,8] systems, but the parameters are concentration dependent. We find that the surface force λ^{-1} depends not only on the interactions at the surface, but also on the ratio between the bulk and surface concentrations. The solution of the LG equations in semi-infinite magnetic systems is known and discussed in great detail by Lubensky *et al.*[6] The following results are found. Calling x_b (x_s) the bulk (surface) concentration we obtain $\lambda^{-1} \lessgtr 0$, if $x_b(1-x_b) \gtrless x_s(1-x_s)\nu_s^2$, where ν_s is concentration independent and depends only on the surface interactions. For $\lambda^{-1} > 0$, bulk and surface order is at the same temperature $T = T_b$ and the order parameter is reduced at the surface. When $\lambda^{-1} < 0$, then there exists a surface critical temperature $T_s > T_b$ such that for $T_b < T < T_s$ a surface transition occurs and the order parameter vanishes exponentially away from the surface. For lower temperatures $T < T_b$ the bulk is ordered, but the order parameter remains enhanced at the surface. We recall that if the interactions are such that $\nu_s = 1$, then $\lambda^{-1} \lessgtr 0$ if $x_s(1-x_s) \gtrless x_b(1-x_b)$ and we have confirmed the initial hypothesis that originated this work.

II. LANDAU-GINZBURG PARTITION FUNCTION

The order-disorder transition in an alloy A_xB_{1-x} can be studied by writing an Ising-like partition function.[2,4] The model we consider here is an alloy with $N_A = xN$ and $N_B = (1-x)N$ atoms of type A and B, respectively, distributed on the N sites of a semi-infinite crystal with a sc lattice structure. Interactions are considered to take place only between nearest neighbors and we call $w_b^{\lambda\nu'}$ the potential energy between a neighboring pair of λ, ν^1 atoms (ν, $\lambda^1 = A$ or B) in the bulk, and $w_s^{\lambda\nu'}$ the analogous potential energy when both atoms are on the surface. For simplicity, we consider that the interaction between one atom λ on the surface and one atom ν' in the bulk is also $w_b^{\lambda\nu'}$. We denote by $\vec{R}=(\vec{r}, z)$ the position of a given lattice site, where the z axis is perpendicular to the surface and $\vec{r}$ denotes the position of sites on planes parallel to the surface. The surface is a (1 0 0) plane of the crystal and it has $z=0$. We start by considering a finite crystal with L layers parallel to the surface, with M sites per layer, then $N=ML$.

By introducing the "spin" variables

$$\sigma(\vec{R}) = \begin{cases} 1 & \text{for an atom } A\,, \\ 1 & \text{for an atom } B\,, \end{cases} \tag{2.1}$$

the potential energy between two neighboring atoms at $\vec{R}$, $\vec{R}'$ can be written

$$W_{b(s)}(\vec{R}, \vec{R}') = \tfrac{1}{2}U_{b(s)}\sigma(\vec{R})\sigma(\vec{R}') + \tfrac{1}{2}V_{b(s)} \times [\sigma(\vec{R}) + \sigma(\vec{R}')] + \tfrac{1}{2}C_{b(s)}\,, \tag{2.2}$$

where

$$U_{b(s)} = W_{b(s)}^{AA} + W_{b(s)}^{BB} - 2W_{b(s)}^{AB}\,, \quad V_{b(s)} = W_{b(s)}^{AA} - W_{b(s)}^{BB}\,,$$
$$C_{b(s)} = W_{b(s)}^{AA} + W_{b(s)}^{BB} + 2W_{b(s)}^{AB}\,.$$

The suffix b applies if both $\vec{R}$, $\vec{R}'$ or one of them refer to the bulk, while the suffix s applies if $\vec{R}$, $\vec{R}'$ are both on the surface. The total energy for a given configuration $\{\sigma\}$ of A and B atoms in the crystal can then be written

$$E(\{\sigma\}) = \sum_{\vec{R},\vec{R}'} j(\vec{R}-\vec{R}')W(\vec{R}, \vec{R}')\,, \tag{2.3}$$

with $W(\vec{R}, \vec{R}')$ given by Eq. (2.2) when $z, z' \geq 0$ and equal to zero otherwise, and

$$j(\vec{R}-\vec{R}') = 1 \quad \text{if } |\vec{R}-\vec{R}'| = a \quad (a \text{ is the lattice constant}). \tag{2.4}$$

It follows from the definition of the interactions in Eq. (2.2) that all the surface effects are contained in $W(\vec{R}, \vec{R}')$ while $j(\vec{R}-\vec{R}')$ assumes that only nearest neighbors interact and is independent of the surface, i.e., translational invariant. We obtain from Eqs. (2.3) and (2.2),

$$E(\{\sigma\}) = \tfrac{1}{2}U_b \sum_{\vec{R},\vec{R}'} j(\vec{R}-\vec{R}')\sigma(\vec{R})\sigma(\vec{R}') + 6V_b \sum_{\vec{R}} \sigma(\vec{R}) + \sum_{\vec{R}_0,\vec{R}} j(\vec{R}_0-\vec{R})[U(z)-U_b]\sigma(\vec{R}_0)\sigma(\vec{R}) - \Delta \sum_{\vec{R}_0} \sigma(\vec{R}_0)\,, \tag{2.5}$$

where we neglected the constant term. $\vec{R}_0=(\vec{r}, 0)$ is a vector on the surface and

$$\Delta = 5V_b - 4V_s\,, \tag{2.6}$$

$$U(z) = \begin{cases} \delta(z)U_s + (1-\delta(z))U_b\,, & z \geq 0\,, \\ 0 \quad \text{if } z < 0\,. \end{cases} \tag{2.7}$$

The first two terms in Eq. (2.5) are the bulk contribution to the total energy while the last two terms are surface corrections. According to Eq. (2.1), $\sum_{\vec{R}}\sigma(\vec{R}) = N_A - N_B$. This term just adds a constant to the total energy. We relax this constraint by the introduction of a chemical potential and by requiring this relation to be valid on the average.

It is convenient at this point to introduce two interpenetrating sublattices. We call $\vec{\delta}$ a vector joining any two nearest-neighbor sites and $\vec{q}$ a vector such that $\vec{q}\cdot\vec{\delta} = \pi$. Then we define α and β sublattices by the requirement

$$e^{i\vec{q}\cdot\vec{R}_\alpha} = 1\,, \quad e^{i\vec{q}\cdot\vec{R}_\beta} = 1\,. \tag{2.8}$$

The energy in Eq. (2.5) can then be written

$$E(\{\sigma\}) = -\tfrac{1}{2}U_b \sum_{\vec{R},\vec{R}'} j(\vec{R}-\vec{R}')m(\vec{R})m(\vec{R}') - \sum_{z,\vec{r}_0} \mu(z)\sigma(\vec{r}^{\,0}, z) - \sum_{\vec{R}_0,\vec{R}} j(\vec{R}_b-\vec{R})[U(z)-U_b]m(\vec{R}_0)m(\vec{R}) - \Delta\sum_{\vec{R}_0}\sigma(\vec{R}_0)\,, \tag{2.9}$$

where

$$m(\vec{R}) = e^{i\vec{q}\cdot\vec{R}}\sigma(\vec{R})\,. \tag{2.10}$$

The chemical potential $\mu(z)$ is determined by

$$\frac{1}{M}\left\langle \sum_{\vec{r}} \sigma(\vec{r}, z)\right\rangle = 2x - 1 \quad \text{if } z \neq 0\,. \tag{2.11}$$

We impose this condition only in the bulk, while the concentration at the surface $z=0$ is allowed to fluctuate and will be determined by the parameter Δ in Eq. (2.9). If we call $x_s[M_A(s)/M]$ the concentration of A atoms on the surface, then

$$\frac{1}{M}\left\langle \sum_{\vec{r}} \sigma(\vec{r}, 0)\right\rangle = 2x_s - 1\,. \tag{2.12}$$

The value of $\mu(0)$ is left undetermined, but in the continuous limit we will consider

$$\mu(0) = \lim_{z\to 0} \mu(z)\,.$$

From Eqs. (2.11) and (2.12) we obtain

$$\left(\frac{1}{ML}\right)\left\langle \sum_{\vec{R}} \sigma(\vec{R})\right\rangle = 2x - 1 + \frac{2}{L}(x_s - x)\,,$$

and in the limit $L\to\infty$ we obtain the correct average number of particles.

The partition function is

$$Z = \mathrm{Tr}_{\{\sigma\}} e^{-E(\{\sigma\})/T}\,, \tag{2.13}$$

where $E(\{\sigma\})$ is given in Eq. (2.9) and Eqs. (2.11), (2.12) can be written

$$\frac{1}{M}\frac{\partial \ln Z}{\partial \bar{\mu}(Z)} = 2x - 1 \quad \text{if } Z \neq 0 \quad (\bar{\mu} = \mu/T)$$

and (2.14)

$$\frac{1}{M}\frac{\partial \ln Z}{\partial \bar{\Delta}} = 2x_s - 1 \quad (\bar{\Delta} = \Delta/T).$$

From Eqs. (2.9) and (2.13), one finds that Z corresponds to the partition function for an antiferromagnetic Ising model with constraints given by Eq. (2.14). We will look for a solution in the mean-field approximation. We call

$$\rho(z) = \sum_{\vec{r}} \sigma(\vec{r}, z) = \sum_{\vec{r}_\alpha} \sigma(\vec{r}_\alpha, z) + \sum_{\vec{r}_\beta} \sigma(\vec{r}_\beta, z),$$

$$m(z) = \sum_{\vec{r}} m(\vec{r}, z) = \sum_{\vec{r}_\alpha} \sigma(\vec{r}_\alpha, z) - \sum_{\vec{r}_\beta} \sigma(\vec{r}_\beta, z), \qquad (2.15)$$

where we used Eqs. (2.8) and (2.10), then the appropriate order parameter for the order-disorder transition is

$$O(z) = (1/M)\langle m(z)\rangle. \qquad (2.16)$$

In the complete ordered state, all the $A(B)$ atoms will be sitting on α (β) sites and $O(z) = 1$, while in the case of complete disorder A and B atoms are equally distributed and $O(z) = 0$. In the context of mean-field theory we make the following approximations on the two interacting terms in Eq. (2.9):

$$\sum_{\vec{R},\vec{R}} j(\vec{R} - \vec{R}')m(\vec{R})m(\vec{R}') \approx \frac{6}{M} \sum_{z,z'} j(z - z')m(z)m(z'), \qquad (2.17a)$$

$$\sum_{\vec{R}_0,\vec{R}} j(\vec{R}_0 - \vec{R})[U(z) - U_b]m(\vec{R}_0)m(\vec{R}) \approx -m(\vec{R}_0)g_0 T, \qquad (2.17b)$$

where from Eq. (2.14),

$$j(\vec{z} - \vec{z}') = \frac{1}{6}\sum_{\vec{R}'} j(\vec{R} - \vec{R}') = \tfrac{1}{6}[4\delta(z - z') + \delta(z - z' + a) + \delta(z - z' - a)] \qquad (2.18)$$

and

$$g_0 = \frac{6}{T}\frac{1}{M}\sum_{z} j(z)(U_b - U(z))\langle m(z)\rangle. \qquad (2.19)$$

These two approximations are of different nature. In Eq. (2.17a) we decoupled the $m(\vec{R})$, $m(\vec{R}')$ on the layer but we kept the correlations between different layers, while in Eq. (2.17b) we just made a plain mean-field approximation to evaluate the surface force. We then obtain for the exponential in Eq. (2.13),

$$e^{-E(\{\sigma\})/T} \approx \exp\left(\frac{\epsilon_b}{2M}\sum_{z,z'} j(z - z')m(z)m(z')\right) \times \exp\left(\sum \bar{\mu}(z)\rho(z) + g_0 m(0) + \bar{\Delta}\varphi(0)\right), \qquad (2.20)$$

where $m(z)$, $\rho(z)$ were defined in Eq. (2.15) and

$$\epsilon_b = 6U_b/T. \qquad (2.21)$$

We further use the well-known mathematical identity

$$\exp\left(\frac{\epsilon_b}{2M}\sum_{z,z'} j(z - z')m(z)m(z')\right) = \frac{1}{N}\int \cdots \int \prod d\eta(z) \times \exp\left(-\frac{\epsilon_b M}{2}\sum_{z,z'} j^{-1}(z - z')\eta(z)\eta(z') + \epsilon_b \sum_{z} m(z)\eta(z)\right) \qquad (2.22)$$

where N is a numerical constant and $j^{-1}(z - z')$ is the inverse potential such that

$$\sum j(z - z'')j^{-1}(z'' - z') = \delta(z - z'). \qquad (2.23)$$

By using Eqs. (2.20) and (2.22) the trace over the spin variables can be performed in Eq. (2.13). We obtain then for the partition function

$$Z = \int \cdots \int \prod d\eta(z)\, e^{-MF}, \qquad (2.24)$$

$$F = \tfrac{1}{2}\left(\epsilon_b \sum_{z,z'} j^{-1}(z - z')\eta(z)\eta(z') + \sum_{z \neq 0} V_b(\eta(z)) - V_s(\eta(0))\right), \qquad (2.25)$$

$$V_b(\eta(z)) = \ln\{\cosh[\epsilon_b \eta(z') + \bar{\mu}(z)] \times \cosh[\epsilon_b \eta(z) - \bar{\mu}(z)]\}, \qquad (2.26)$$

$$V_s(\eta(0)) = \ln\{\cosh[\epsilon_b \nu_s \eta(0) + \bar{\mu}_s] \times \cosh[\epsilon_b \nu_s(0) - \bar{\mu}_s]\},$$

$$\nu_s = 1 + g_0/\epsilon_b \eta(0), \quad \bar{\mu}_s = \bar{\mu}(0) + \bar{\Delta}. \qquad (2.27)$$

We obtain from Eqs. (2.16) and (2.22) the expression for the order parameter

$$\frac{1}{M}\langle m(z)\rangle = \frac{1}{Z}\int \cdots \int \prod d\eta(z)\, e^{-MF} \times \left(-\frac{1}{\epsilon_b}\frac{\delta F}{\delta \eta(z)} + \sum_{z'} j^{-1}(z - z')\eta(z')\right). \qquad (2.28)$$

For the continuous-limit case we write Eq. (2.25),

$$\eta(z)\eta(z') \approx \eta^2(\bar{z}) - \left(\frac{d\eta}{d\bar{z}}\right)^2 \left(\frac{z-z'}{2}\right)^2, \tag{2.29}$$

where we neglected higher derivatives and $\bar{z} = \frac{1}{2}(z+z')$. We obtain then in the continuum limit the partition function as a functional integral

$$Z = \int \delta\eta(z) e^{-M(F_b+F_s)}, \tag{2.30}$$

where adding and subtracting $V_b(\eta(0))$ to the function F in Eq. (2.25) gives

$$F_b = \frac{1}{2a} \int_0^\infty dz \left[\epsilon_b \eta^2(z) + \frac{\epsilon_b a^2}{12} \left(\frac{d\eta}{dz}\right)^2 - V_b(\eta(z))\right] \tag{2.31}$$

and

$$F_s = \tfrac{1}{2}\{V_b(\eta(0)) - V_s(\eta(0))\}. \tag{2.32}$$

The constraint equations (2.14) now become

$$\frac{1}{z} \int \delta\eta(z) e^{-M(F_b+F_s)} \frac{1}{2} \frac{\delta V_b}{\delta\bar{\mu}(z)} = 2x - 1, \tag{2.33}$$

$$\frac{1}{z} \int \delta\eta(z) e^{-M(F_b+F_s)} \frac{1}{2} \frac{\delta V_s}{\delta\bar{\mu}_s} = 2x_s - 1, \tag{2.34}$$

where from Eqs. (2.32) and (2.27) one finds $\delta F_s/\delta\bar{\Delta} = -\frac{1}{2}\delta V_s/\delta\bar{\mu}_s$.

Note, the two terms in the free energy given by Eqs. (2.31) and (2.32) are not yet in the Landau-Ginzburg form, because V_b and V_s are not expanded in powers of η. We find it more convenient to perform the expansion in the differential equations and will do it in Sec. III.

III. LANDAU-GINZBURG DIFFERENTIAL EQUATIONS

In the limit $M \to \infty$ the partition function given by Eq. (2.30) may be evaluated by steepest descents and $\eta(z)$ is given by the stationary condition

$$[\delta/\delta\eta(z)](F_b + F_s) = 0. \tag{3.1}$$

The order parameter is obtained from Eqs. (2.28) and (3.1),

$$\frac{1}{M}\langle m(z)\rangle = \sum_{z'} j^{-1}(z-z')\eta(z') \approx \sum j^{-1}(z-z')\eta(z) = \eta(z), \tag{3.2}$$

where we neglected the derivatives in the expansion of $\eta(z')$ and where $\eta(z)$ is the solution of Eq. (3.1). We obtain from Eq. (3.1) and by functional differentiation[6-8] of Eqs. (2.31) and (2.32) the expression

$$\frac{a^2}{12}\frac{d^2\eta}{dz^2} - \eta(z) + \Lambda_b(\eta(z)) = 0, \tag{3.3}$$

with boundary conditions

$$\begin{gathered} \frac{a}{12}\frac{d\eta}{dz}\bigg|_{z=0} - [\Lambda_b(\eta(0)) - \Lambda_s(\eta(0))] = 0, \\ \frac{d\eta}{dz} = 0 \text{ if } z \to \infty. \end{gathered} \tag{3.4}$$

Here,

$$\Lambda_b[\eta] = \frac{1}{2\epsilon_b}\frac{\partial V_b(\eta)}{\partial\eta} = \frac{1}{2}[\tanh(\epsilon_b\eta + \bar{\mu}) + \tanh(\epsilon_b\eta - \bar{\mu})], \tag{3.5}$$

$$\Lambda_s[\eta] = \frac{1}{2\epsilon_b}\frac{\partial V_s(\eta)}{\partial\eta} = \frac{\nu_s}{2}[\tanh(\epsilon_b\nu_s\eta + \bar{\mu}_s) + \tanh(\epsilon_b\nu_s\eta - \bar{\mu}_s)], \tag{3.6}$$

which we obtained by using Eqs. (2.26) and (2.27). The constraints in Eq. (2.33) become

$$\frac{1}{2}\frac{\partial V_b}{\partial\bar{\mu}} = \frac{1}{2}[\tanh(\epsilon_b\eta + \bar{\mu}) - \tanh(\epsilon_b\eta - \bar{\mu})] = 2x - 1. \tag{3.7}$$

The concentration x_s of A atoms on the surface is determined by [Eq. (2.34)]

$$\frac{1}{2}\frac{\partial V_s}{\partial\bar{\mu}_s} = \frac{1}{2}[\tanh(\epsilon_b\nu_s\eta + \bar{\mu}_s) - \tanh(\epsilon_b\nu_s\eta - \bar{\mu}_s)] = 2x_s - 1. \tag{3.8}$$

Note, x_s is a function of the surface parameter ν_s and Δ. Here, we consider that in the continuum limit $\bar{\mu}(0) = \bar{\mu}(z=0)$ is given by Eq. (3.7). In order to express Eqs. (3.3) and (3.4) in a LG form[6-8] we first have to eliminate $\bar{\mu}(z)$ which is itself a function of $\eta(z)$ through Eq. (3.7). We obtain from Eqs. (3.5) and (3.7),

$$\Lambda_b[\eta] = \tfrac{1}{2}\tanh(2\epsilon_b\eta)[1 + \tanh(\epsilon_b\eta + \bar{\mu})\tanh(\epsilon_b\eta - \bar{\mu})] = \tfrac{1}{2}\tanh(2\epsilon_b\eta)[1 - (2x-1)^2 + \Lambda_b^2(\eta)]. \tag{3.9}$$

This gives

$$\Lambda_b[\eta] = \frac{1}{\tanh(2\epsilon_b\eta)}\{1 - [1 - 4x(1-x)\tanh^2(2\epsilon_b\eta)]^{1/2}\}, \tag{3.10}$$

where we choose the sign in front of the square root such that $\Lambda_b[\eta] \to 0$ if $\eta \to 0$. We obtained in Eq. (3.10), $\Lambda_b(\eta)$ as a function of η and the bulk concentration x_b. The expansion in powers of η gives to third order the expression

$$\Lambda_b[\eta] = 4x(1-x)\epsilon_b\eta - 4x(1-x) \times [(2x-1)^2 + \tfrac{1}{3}](\epsilon_b\eta)^3 + O(\eta^5). \tag{3.11}$$

We obtain in a similar fashion from Eqs. (2.26) and (2.8),

$$\Lambda_s(\eta(0)) = 4x_s(1-x_s)\nu_s^2\epsilon_b\eta(0) + O(\eta^3(0)) . \tag{3.12}$$

By using Eqs. (3.11) and (3.12) in Eqs. (3.3) and (3.4) we obtain the LG differential equation for the order parameter

$$\begin{gathered} \frac{d^2\eta}{dz^2} - t\eta(z) - 2q\eta^3(z) = 0 , \\ \left.\frac{d\eta}{dz}\right|_{z=0} = \lambda^{-1}\eta(0) , \quad \frac{d\eta}{dz} = 0 \ \text{ if } \ z \to \infty , \end{gathered} \tag{3.13}$$

with $q > 0$ and

$$t = \frac{12}{a^2}\frac{T - T_b}{T_b} , \quad T_b = 6U_b 4x(1-x) . \tag{3.14}$$

The surface force is given by

$$\lambda^{-1} = (12/a)\epsilon_b[4x(1-x) - 4x_s(1-x_s)\nu_s^2] . \tag{3.15}$$

The differential equation (3.13) has already been solved for magnetic systems,[5-8] and we refer the reader to Ref. 6 for a very detailed analysis of the solutions. The behavior of the order parameter η will depend on the sign of the surface force. For $\lambda^{-1} < 0$ a surface transition occurs where the ordered state is limited to the neighborhood of the surface. We will evaluate λ^{-1} in more detail. From Eqs. (3.15), (2.27), and (2.21) one finds

$$\lambda^{-1} = \frac{12}{a}\frac{T_b}{T}\left(1 - \frac{x_s(1-x_s)}{x(1-x)}[1+h]^2\right) , \tag{3.16}$$

where using the definition of g_0 in Eq. (2.19),

$$\begin{aligned} h &= \frac{T}{6U_b\eta(0)} g_0 \\ &= \frac{1}{U_b\eta(0)} \sum_z j(z)[U_b - U(z)]\eta(z) \\ &= \frac{1}{6}\left[4\left(1 - \frac{U_s}{U_b}\right) + 1\right] . \end{aligned} \tag{3.17}$$

To obtain the last equality we used Eqs. (2.17) and (2.18) for $U(z)$ and $j(z)$, and we kept only the first term in the expansion of $\eta(z)$ around $z = 0$. It follows from Eqs. (3.16) and (3.17) that the interactions give two different contributions to the surface force: (a) The "spin-spin"-like interactions $V_{b(s)}$ cause the term in the small square brackets in Eq. (3.16). This term also appears typically in magnetic systems.[5-7] In Eq. (3.17) h is just the surface force as given in Ref. (5). (b) The combinations $V_{b(s)} = W_{b(s)}^{AA} - W_{b(s)}^{BB}$ cause the dependence on the bulk and surface concentrations x_b and x_s, respectively, through Eqs. (2.11) and (2.12). These terms do not occur for magnetic systems.

In the following we analyze two special cases.

(i) $x_s = x_b$. There is *no segregation*, $x_s = x$, and we obtain from Eq. (3.16) if we keep only the linear term in h the expression

$$\lambda^{-1} = -\frac{4}{a}\frac{T_b}{T}\left[4\left(1 - \frac{U_s}{U_b}\right) + 1\right] . \tag{3.18}$$

Note λ^{-1} is just the same as the surface force in semi-infinite[5,6] magnets.

(ii) $U_s/U_b = \frac{5}{4}$, $h = 0$. In this case,

$$\lambda^{-1} = \frac{12}{a}\left(1 - \frac{x_s(1-x_s)}{x(1-x)}\right) . \tag{3.19}$$

Then for $x_s(1-x_s) > x(1-x)$ one obtains $\lambda^{-1} < 0$ and a surface transition occurs[5,7] when the surface orders before the bulk. For $x_s(1-x_s) < x(1-x)$ the bulk and surface order at the same temperature T_b, but $\eta(0) < \eta_b$.

Applying the results obtained in Refs. 5 and 6 one finds for (i) $\lambda^{-1} > 0$: (a) $\eta_b = \eta_s = 0$ if $T > T_b, t > 0$. (b) $\eta(t) = \eta_b \tanh(z/\xi_b + \varphi_1)$ if $T < T_b, t < 0$:

$$\varphi_1 = \arg\tanh(\eta_s/\eta_b) , \tag{3.20}$$

where

$$\eta_s^2 = \eta_b^2 - \frac{\lambda^{-2}}{2q}\left[\left(1 + \frac{4\lambda^2}{\xi_b^2}\right)^{1/2} - 1\right] < \eta_b^2 . \tag{3.21}$$

Here, we introduced the bulk order parameter

$$\eta_b^2 = |t|/2q$$

and correlation length (3.22)

$$\xi_b^2 = 2/|t| .$$

For (ii) $\lambda^{-1} < 0$ we find the existence of a temperature

$$T_s = T_b\left(1 + \frac{a^2}{12}\lambda^{-2}\right) > T_b \tag{3.23}$$

such that we can distinguish three temperature regions: (a) $T > T_s$ with $\eta_b = \eta_s = 0$. (b) $T_b < T < T_s, t > 0$, with

$$\begin{gathered} \eta(z) = \left(\frac{t}{q}\right)^{1/2} \sinh^{-1}(\sqrt{t}\, z + \varphi_2) , \\ \varphi_2 = \arg\sinh[(t/q)^{1/2}\eta_s^{-1}] , \end{gathered} \tag{3.24}$$

$$\eta_s^2 = (\lambda^{-2} - t)/q \approx T_s - T . \tag{3.25}$$

Clearly, for $T_b < T < T_s$ only a transition at the surface occurs (c) $T < T_b, t < 0$. For this range of temperature the bulk starts to order too, but the order parameter near the surface is enhanced. One obtains

$$\begin{gathered} \eta(z) = \eta_b \coth(z/\xi_b + \varphi_3) , \\ \varphi_3 = \arg\coth(\eta_s/\eta_b) , \end{gathered} \tag{3.26}$$

$$\eta_s^2 = \eta_b^2 + \frac{\lambda^{-2}}{2q}\left[\left(1 + 4\frac{\lambda^2}{\xi_b^2}\right)^{1/2} + 1\right] > \eta_b^2 . \tag{3.27}$$

Here, ξ_b and η_b are given by Eq. (3.22).

The range of validity of the continuous approximations is given by the requirement that the variations of $\eta(x)$ over a lattice constant must be small. From Eqs. (3.20), (3.24), and (3.26) this leads to the general condition $\xi_b \gg a$ or $|t| \ll 1/a^2$. This condition puts also a restriction on the allowed values of λ^{-1}. Indeed, if we consider $T = T_s$, the values of T_s must satisfy

$$\frac{|T_s - T_b|}{T_b} \frac{1^2}{a^2} \ll \frac{1}{a^2},$$

or, from Eq. (3.23), $\lambda^{-2} \ll 1/a^2$.

IV. CONCLUSIONS

We have studied the order-disorder transition in a semi-infinite A_xB_{1-x} alloy by means of Landau-Ginzburg theory. The main of our work was to calculate the LG parameter at a surface starting from a microscopic Ising-like Hamiltonian for an alloy which exhibits surface segregation. We have shown that the sign of the surface force depends crucially on segregation at the surface. For surface concentrations x_s such that $x_s(1-x_s) > x(1-x)$, λ^{-1} may be negative and a surface transition occurs, similar to the case in semi-infinite magnetic systems.

When this work was finished, it came to our knowledge that Binder *et al.*[9] have applied the same methods to study the mixing transition in analogous systems. If we call $m_{\mathrm{BSW}}(z)$ and $\tilde{m}_{\mathrm{BSW}}(z)$ the order parameters of Ref. 9, it is clear that we can write the correspondence $\tilde{m}_{\mathrm{BSW}}(z) = \eta(z)$, $m_{\mathrm{BSW}}(z) = \langle (1/M)\rho(z) \rangle$, from Eqs. (2.15) and (3.2).

The essential difference between both works is that we studied the order-disorder transition described by $\eta(z)$ for a given density distribution $\langle 1/M\rho(z) \rangle = 2x - 1 = \mathrm{const}$, while Binder *et al.* consider a mixing transition described by $m_{\mathrm{BSW}}(z)$ with no spontaneous order-disorder transition. In effect, $\tilde{m}_{\mathrm{BSW}}(z)$ was considered to be vanishing in the LG equation for $m_{\mathrm{BSW}}(z)$ of Ref. 9 [Eq. (7.6)], and only the linear term was kept in Eq. (7.6) for $\tilde{m}_{\mathrm{BSW}}(z)$.

ACKNOWLEDGMENTS

We would like to thank Dr. W. Theumann, Dr. J. L. Morán-López, and Dr. K. Penson for discussions; and Dr. T. Burkhardt and Dr. E. Eisenriegler for pointing out Refs. 6 and 9 to us.

---

*Present address: Institut Laue Langevin, 38042 Grenoble Cedex, France.

[1] J. L. Morán-López and K. H. Bennemann (unpublished).

[2] V. S. Sundaram, B. Farrell, R. S. Alben, and W. D. Robertson, Phys. Rev. Lett. 31, 1136 (1973).

[3] G. Kerker, J. L. Morán-López, and K. H. Bennemann, Phys. Rev. B 15, 638 (1977).

[4] R. P. Feynmann, *Statistical Mechanics* (Benjamin, New York, 1972), Chap. 5.

[5] D. L. Mills, Phys. Rev. B 3, 3887 (1971).

[6] T. C. Lubensky and Morton H. Rubin, Phys. Rev. B 12, 3885 (1975).

[7] K. Binder and P. C. Hohenberg, Phys. Rev. B 6, 3461 (1972); 9, 2194 (1974).

[8] M. I. Kaganov and A. N. Ome Lyanchuk; Zh. Eksp. Teor. Fiz. 61, 1679 (1971) [Sov. Phys.-JETP 34, 895 (1972)].

[9] K. Binder, D. Stauffer and V. Wildpaner, Acta Metall. 23, 1191 (1975).