Improved Landau-Ginzburg equation near surfaces of solids

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We study the order parameter near the surface for an Ising model. Applications to the lattice gas, alloy problem, and ferromagnetism are noted. Away from T_c our equations differ from the Landau-Ginzburg results due to an additional nonlinear, term which can substantially affect the order parameter at low T. Our method also provides for a physically meaningful set of boundary conditions.

I. INTRODUCTION

The effect of surfaces on the order parameter in magnetic systems has been studied recently, starting with the work of Mills[1] and Wolfram *et al.*[2] and followed by the extensive analysis of Binder and Hohenberg.[3] Many works have followed,[4] some based on mean-field methods (in good agreement with even the most recent experiments in this field[5]) and others on more sophisticated scaling- and/or renormalization-group concepts introduced in Ref. 3. The most important application may, however, turn out to be the study of the surface composition of lattice gases and alloys,[6] known to differ from the bulk in many important cases. As corrosion and catalysis occur at surfaces, one clearly needs to know whether the surface composition of a given material (say stainless steel) differs from the bulk and is then subject to attack from the ambient atmosphere. Such problems can be formulated using the Ising (Bragg-Williams) model of solids.

The simplest case of a lattice gas is a monatomic solid in equilibrium with a certain number of vacancies at lattice sites. Such vacancies will be more numerous near the surface, where the number of bonds is smaller than in the bulk. One relates the thermodynamic properties of a lattice gas to those of an Ising ferromagnet as follows. The pressure p and inverse density v of the atomic system are related to the free energy per spin f, the magnetization per spin m, and the applied magnetic field H of the Ising ferromagnet as

$$p=-(f+H+2J) \quad , \quad v=2/[1-m(H,T)] \quad ,$$

where J = nearest-neighbor bond.[7] This yields the equation of state of the lattice gas, once the magnetic system is solved.

The equations of state and phase diagrams of more complex systems, such as an A_xB_{1-x} alloy, or of magnetic alloys, require the solution of fairly involved pseudomagnetic systems with various sublattices.[8] One obtains the interesting properties of the metallic system from the free energy and order parameters of the equivalent magnetic system. Because the magnetic Ising model is the prototype, it is to this almost classical model that we turn to apply the new ideas in the present work.

In the literature, the spatial variation of the order parameter near the surface has been treated in a variety of ways. Some authors[9] have chosen to treat the first (or first few) layers as the "surface," and the rest as "bulk." This assumption is appropriate if we know *a priori* that the healing length is short; but in most instances, it is the depth of the surface region which is itself the object of study. For studies of this kind, the Landau-Ginzburg (LG) equations have provided the simplest generalization of the equations for the homogeneous bulk. In many papers of the current literature[1-4] the surface is characterized through an "extrapolation length" λ that enters the boundary condition, with the order parameter attaining the bulk value within a "bulk correlation length" ζ_b. Some differences distinguishing various published treatments concern the use of mean-field versus scaling-law relations or critical exponents for the parameters that enter the LG equation. Our present work does not confront that issue, although we discuss it briefly below. We now outline the main thrust of this present work.

We derive difference equations for the order parameter, starting from a molecular-field theory[10] in which nearest-neighbor correlations are retained. As the correlations depend on the number of nearest-neighbors in this theory, it seems suitable for use near a surface where this number is less than in the bulk. As long as the spatial variation in the order

parameter is slow, the difference equations can be replaced by a differential equation. This equation is similar to the LG equation, from which it differs only by the presence of an extra, nonlinear differential term. This extra term may be large at low T, but disappears near T_c. So, while it is insignificant in critical phenomena (for which the present analysis is anyhow unsuited) this extra term may be important in the alloy problem or lattice gas (for which critical phenomena play only a minor role). A second result concerns the applicable boundary conditions. Near the surface not only is the number of bonds smaller than in the bulk, but the parameters J_s, H_s, and others may differ from those in the bulk. Our method is then to retain the difference equations for the surface layers, and to replace them by the differential equation only when the parameters (and the solution) are sufficiently slowly varying. No *ad hoc* extrapolation length λ is needed. If a length parameter is needed for heuristic purposes, we find that a quantity we denote z_0 is rather more natural to use. In the case that the surface parameters are the same as in the bulk, $z_0=0$.

II. LANDAU-GINZBURG-TYPE EQUATIONS

We recapitulate some standard results, then show where our analysis brings modifications. In successive sections, we derive the differential equations and boundary conditions. At first, we state them without proof.

The simplest applicable LG equation in dimensionless form is

$$-\frac{\partial^2 m}{\partial z^2}=m(t-m^2)+H(z) \quad . \tag{1}$$

Here $m(z)$ is the order parameter, $t=1-T/T_c$, and z measures the distance to the surface. We shall set $H(z)$, the applied field, zero in all the calculations reported in this paper. In realistic cases $H(z)\neq 0$ is required, and the numerical work to solve the equations becomes much greater. It did not seem worthwhile to enter into such complications at this stage. Nor do we consider the alloy problem, for which two order parameters and two coupled equations of the type (1) would be required, for the same reasons.

The conventional boundary conditions are two. At the surface, one involves the extrapolation length

$$\frac{1}{m}\frac{\partial m}{\partial z}=\lambda^{-1} \quad . \tag{2}$$

The extrapolation length is positive if the surface parameters are less conducive to magnetism than the bulk, and negative otherwise. If the surface is to "float" with the bulk, then λ is infinite. A second boundary condition is imposed at $z=\infty$, where $m(z)$ must asymptotically approach m_b, the bulk magnetization. From Eq. (1) we obtain $m_b=t^{1/2}$ in zero external field. Solving Eq. (1) for $m(z)$ in the usual way, one finds

$$m(z)=t^{1/2}\tanh[(z+z_0)(\tfrac{1}{2}t)^{1/2}] \quad . \tag{3}$$

From this we deduce the bulk correlation length to be $\zeta_b=(2/t^{1/2})$. The parameter z_0 is adjusted to satisfy the surface boundary condition (BC) (2)

$$z_0=(2t)^{-1/2}\ln[\lambda(2t)^{1/2}+(\lambda^2 2t+1)^{1/2}] \quad , \tag{4}$$

which yields the temperature dependence of z_0 if we believe λ to be independent of T. On the other hand, it may be more appropriate to take z_0 in Eq. (3) to be itself the constant characterizing the surface.

We now compare the above to the most simplified version of our new equations, which we present here without proof until Sec. III. Up to the surface, the differential equation is

$$-\frac{\partial^2 m}{\partial z^2}-Dm\left(\frac{\partial m}{\partial z}\right)^2=m(t-m^2)+H(z) \quad , \tag{5}$$

in which D is a new parameter $O(1)$, possibly temperature dependent but independent of z. Our equation satisfies all obvious symmetry requirements, and the added term is not smaller than the others in any obvious way. Nevertheless, we shall see that it disappears in the critical region $t\sim 0$. Again, this equation is subject to two boundary conditions. The asymptotic one requires $m(z)$ to approach m_b deep in the bulk; thus m_b is exactly the same as for Eq. (1), as can be verified by setting m' and m'' both zero. The surface boundary condition is determined by a difference equation, which we discuss in a later section. For the sake of definiteness, we can specify $m(0)=0$ as our boundary condition and determine z_0 from the physical requirement later.

Although highly nonlinear, Eq. (5) does not depend on z explicitly, except through a spatially modulated field $H(z)$. For constant field, this equation can be solved by finding an appropriate integrating factor. We give the procedure for zero field: multiply both sides of Eq. (5) by $(\partial m/\partial z)\exp(Dm^2)$. They are then perfect differentials, yielding

$$\int_0^{\mu} d\mu\,[d^{-2}e^{d(1-\mu^2)}-d^{-1}(1-\mu^2+d^{-1})]^{-1/2}=x \tag{6}$$

for $T\leq T_c$, i.e., $t\geq 0$. We have introduced dimensionless units

$$x=(z+z_0)t^{1/2},\quad d=Dt,$$

and

$$\mu(x)=m(x)/m(\infty)=m(x)t^{-1/2} \quad .$$

The integral in Eq. (6) must be evaluated numerically except when $d=0$, when $\mu=\tanh(x/2^{1/2})$ is obtained in agreement with Eq. (3). The nonlinear parameter d (or D) is, however, important only near the surface. Its impact can be assessed by solving Eq. (6) to leading order in the small parameter x. Thus, setting

$$\mu = C_1 x - C_3 x^3 + \cdots \ , \tag{7}$$

we evaluate the initial slope C_1 as a function of $d=Dt$. One readily finds

$$C_1 = [d^{-1}(e^d d^{-1} - 1 - d^{-1})]^{1/2} \ , \tag{8a}$$

and for the higher-order coefficient,

$$C_3 = C_1 (6d)^{-1}(e^d - 1) \ . \tag{8b}$$

At $d=0$, $C_1 = 2^{-1/2} = 0.7071$, $C_3 = 0.1179$. We expect d to lie in the range from zero to $O(1)$. At $d=1$, $C_1 = 0.8475$ (a 20% rise) and $C_3 = 0.2427$ (a 100% increase). At $d=2$, the initial slope $C_1 = 1.048$, some 50% greater than at $d=0$, and $C_3 = 0.5577$ for a fivefold increase.

The effects of the parameter D are negligible in the asymptotic region $x \gg 1$. But the extra rapid rise in magnetization in the surface region may ultimately justify certain studies, in which the first layer alone is considered to be "surface" and the rest are "bulk."[9]

From Eqs. (7) and (8) we estimate the surface magnetization

$$m_s = C_1(a + z_0)t \tag{9}$$

for $t \to 0$ ($T \to T_c$), in agreement with LG theory, Eq. (3). This linear surface magnetization [the bulk $m(\infty) = t^{1/2}$] is in good agreement with experiment, as noted by Binder and Hohenberg[3] and confirmed by the latest experiments of Celotta *et al.*[5] on the surface magnetization of nickel. We now turn to a derivation of our equations.

III. DERIVATIONS

We use molecular-field theory with nearest-neighbor correlations.[10] Each spin excepting those at the surface has four neighbors (the case of six neighbors is too complicated to exhibit here, but the results are similar), while the spins at the surface have only three. Labeling the planes $i = 1, 2, \ldots, \infty$ we have for $i \geq 2$ the general equations

$$m(i) = 2^{-3} \sum_{p=0}^{2} [1 - m(i)]^p [1 + m(i)]^{2-p} \binom{2}{p} \times \{\delta(i) \tanh\beta[J(2-2p) + H] + \tfrac{1}{2}\Delta^-(i) \tanh\beta(H - 2pJ) + \tfrac{1}{2}\Delta^+(i) \tanh\beta[(4-2p)J + H]\} \ , \tag{10}$$

where

$$\delta(i) \equiv 1 - m(i+1)m(i-1), \quad \Delta^-(i) \equiv [1 - m(i+1)][1 - m(i-1)] \ ,$$

and

$$\Delta^+(i) \equiv [1 + m(i+1)][1 + m(i-1)]; \quad m(0) \equiv 0 \ . \tag{11}$$

At the surface

$$m(1) = 2^{-3} \sum_{p=0}^{2} [1 - m(1)]^p [1 + m(1)]^{2-p} \binom{2}{p} \{\tanh\beta[J_s(2-2p) + H_s]\delta(1) + \tfrac{1}{2}\Delta^-(1) \tanh\beta[H_s + (2-2p)J_s - 2J] + \tfrac{1}{2}\Delta^+(1) \tanh\beta[(2-2p)J_s + 2J + H_s]\} \ , \tag{12}$$

where we allow for surface parameters J_s, H_s to differ from the bulk values. If $J_s = J$ and $H_s = H$, this equation has the same form as the rest provided we introduce a fictitious zeroth plane at which $m(0) = 0$ is set. Otherwise, the boundary condition is more complicated and is, in fact, given by Eq. (12) itself. For the remaining equations, there is no solution other than a numerical one to such an arduous set of nonlinear difference equations. But abandoning rigor, if we assume the solution to be reasonably smooth we can expand Eq. (11) in a Taylor series and transform these equations into more tractable differential equa-

tions. With $z = na$, we have

$$\delta(n) \approx 1 - m(z)^2 - a^2 m(z) \frac{\partial^2 m(z)}{\partial z^2} + a^2 \left[\frac{\partial m(z)}{\partial z} \right]^2 ,$$

$$\Delta^-(n) \approx [1 - m(z)]^2 - a^2 \left[\frac{\partial m(z)}{\partial z} \right]^2 - a^2 [1 - m(z)] \frac{\partial^2 m(z)}{\partial z^2} , \quad (13)$$

$$\Delta^+(n) \approx [1 + m(z)]^2 - a^2 \left[\frac{\partial m(z)}{\partial z} \right]^2 + a^2 [1 + m(z)] \frac{\partial^2 m(z)}{\partial z^2} .$$

Replacing these in the set of equations (10) and (11), we obtain a nonlinear differential equation of second order

$$m(z) = A(\beta, H, J, m(z)) + a^2 \left[\frac{\partial m}{\partial z} \right]^2 D(\beta, H, J, m(z)) + a^2 \frac{\partial^2 m}{\partial z^2} C(\beta, H, J, m(z)) , \quad (14)$$

with BC $m = m_b$ at $z = \infty$ and $m(1)$ satisfies Eq. (12) at $z = a$. The expressions A, D, C are unwieldy and we present only the solution of the differential equation, which can be obtained in a manner similar to the derivation of Eq. (6). The result

$$\tfrac{1}{2}^{1/2} a m_b \int_0^{\mu} d\mu \left[\left(\frac{\alpha - \mu^2}{\alpha - 1} \right)^{2/3} P(1, \alpha) - P(\mu^2, \alpha) \right]^{-1/2} = x , \quad (15)$$

where

$$\alpha \equiv a_1 / 3 a_3 m_b^2 ,$$

$$P(\mu^2, \alpha) \equiv 1 - \mu^2 - 3(\alpha - \mu^2) , \quad (16)$$

and

$$a_1 = \tanh 2J\beta + \tfrac{1}{2} \tanh 4J\beta ,$$

$$a_3 = \tanh 2J\beta - \tfrac{1}{2} \tanh 4J\beta ,$$

and we have set $H = 0$. The computed results are compared with some reasonable estimates in Fig. 1. Initially μ is linear in x.

Remarkably, we see the linear behavior to persist almost to the first surface layer, so that the first few terms in a power-series expansion of Eq. (15), in the manner of Eq. (7), should yield the surface properties without the need for numerical integration. This is useful to know when a model more complicated than the Ising ferromagnet is studied. The smoothness of the computed solutions also provides the necessary justification for the substitution of a differential equation for the original difference equations.

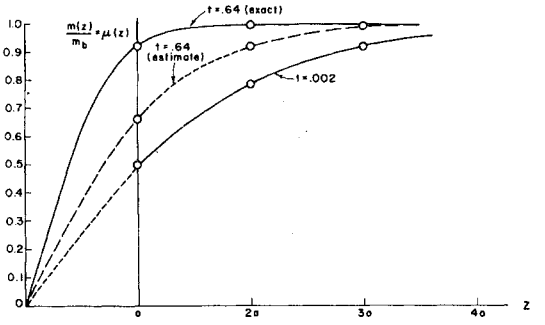

FIG. 1. Magnetization as a function of distance. We plot the numerical solution of Eq. (15) and compare it with the Landau-Ginzburg estimate: $m(z) = m_b \tanh z/\zeta_b$ (dashed line) at $t = 0.64$. The deviations are apparent. In the critical region ($t = 0.002$ is illustrated) the calculated and estimated curves agree almost exactly. In this figure, a vertical line indicates the surface at $z = a$ and circles indicate the discrete values of the magnetization $m(n)$ on the physical planes at $z = na$, $n = 1, 2, 3, \ldots$.

If we simplify Eq. (14) to the utmost, retaining only leading terms in the "small" parameters m, t, etc., we recover the modified LG equation (5). The above analysis establishes the existence of a nonlinear parameter D of $O(1)$, and also provides a strong "handle" on the surface-boundary conditions, discussed next.

IV. SURFACE-BOUNDARY CONDITION

Let us assume that the surface parameters J_s, H_s, etc., differ from the bulk only in the first surface layer. Then Eq. (14), or its simplified version Eq. (5), are to be solved down to $z = a$. As the differential equation does not contain z explicitly, its solution can be taken of the form $f(z + z_0)$. The boundary condition $m(\infty) = m_b$ is, of course, independent of any choice of z_0 and helps fix the functional form of $f(z + z_0)$. With this, we now have an expression for the surface magnetization $m(1) = f(a + z_0)$ and for the second-layer magnetization, $m(2) = f(2a + z_0)$. On the other hand, Eq. (12) provides an explicit formula relating $m(1)$ to $m(2)$. Comparison of these expressions leads to a value of z_0, hence determines

$m(z) = f(z + z_0)$ completely.

In one special case, this procedure simplifies considerably. It is when $J_s = J$, $H_s = H$, etc. In that event, Eq. (12) resembles the bulk equations, in fact becomes identical with them if one introduces a fictitious extra plane at $z = 0$ and requires $m(0)$ to vanish. Then, the boundary condition is effectively $f(z_0) = 0$. Moreover, in the absence of an external field, f is an odd function of its argument, thus $z_0 = 0$.

The reader can easily generalize the prescriptions given above, for the cases when two or more surface planes have physical parameters that differ from the bulk.

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