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# Wetting Phenomena in bcc Binary Alloys[1]

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We study the influence of the surface orientation on the wetting behavior of bcc binary alloys, using a semiinfinite lattice model equivalent to a nearest-neighbor Ising antiferromagnet in an external magnetic field. This model describes alloys that exhibit a continuous $B2$–$A2$ order–disorder transition, such as FeAl or FeCo. For *symmetry-breaking* surfaces like (100), an *effective ordering surface field* $g_1 \neq 0$ emerges. Such a field not only crucially affects the surface critical behavior at bulk criticality, but also gives rise to wetting transitions below the critical temperature $T_c$. Starting from the mean-field theory for the lattice model and making a continuum approximation, a suitable Ginzburg–Landau model is derived. Explicit results for the dependence of its parameters (e.g., of $g_1$) on the microscopic interaction constants are obtained. Utilizing these in conjunction with Landau theory, the wetting phase diagram is calculated.

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**KEY WORDS:** antiphase boundary; bcc binary alloys; Ginzburg–Landau models; surface critical behavior; wetting transitions.

## 1. INTRODUCTION

Surface critical behavior at bulk critical points can be divided into distinct universality classes [1]. For a given bulk universality class, only gross surface properties determine which surface universality class applies, such as whether or not the surface interactions exceed or are equal to a certain critical enhancement or whether a surface field $g_1$ coupling to the local order parameter exists. Recently it has been shown that the universal critical behavior at the surface of a bcc Ising antiferromagnet and of a binary alloy undergoing a continuous order–disorder bulk transition depends crucially on the orientation of the surface with respect to the crystal axes

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[2, 3]. The basic mechanism underlying this intriguing behavior is the interplay between *broken translational invariance* perpendicular to the surface and the symmetry with respect to *sublattice ordering*. For certain "symmetry-breaking" orientations an "effective" ordering surface field $g_1 \neq 0$ emerges, which depends on physical parameters like temperature and bulk composition of the alloy. That such a field exists has been pointed out in Ref. 4 in order to explain the persistence of surface order at a (100) surface above the bulk critical temperature $T_c$, detected in a Monte Carlo simulation of the $B2$–$A2$ order–disorder transition in FeAl.

The situation encountered for symmetry-breaking surfaces closely resembles the critical adsorption of fluids, where generally $g_1 \neq 0$ [5]. However, in that case the microscopic origin of $g_1$ is quite different: it is an external field reflecting, e.g., the preference of the wall for one of the two components of the binary liquid mixture. The transition that takes place in the presence of a field $g_1 \neq 0$ on approaching the bulk critical point has been called *normal* in Ref. 6. If $g_1 = 0$ (and the surface interactions are not too strongly enhanced), another transition, called *ordinary*, occurs. In accordance with the fact that $g_1$ is a relevant scaling field, the ordinary and normal transitions represent different surface universality classes.

In Refs. 2 and 3 the focus was on the behavior at $T = T_c$ and a clear identification of the normal transition, which may also be regarded as a critical point wetting phenomenon [7]. However, since $g_1$ *generally stays nonzero* away from $T_c$ for symmetry-breaking surfaces, a variety of wetting phenomena may occur for $T < T_c$. Below we determine the wetting phase diagram for a (100) surface within the mean-field approximation, utilizing the continuum model derived in Ref. 3. Our work complements previous studies on wetting in fcc Ising antiferromagnets or binary alloys [8] as well as on interface roughening at an antiphase boundary in the [100] direction in bcc binary alloys [9].

The organization of the paper is as follows. In the next section (Section 2) we define our model, explain the difference between symmetry-breaking and symmetry-preserving surfaces, and then briefly discuss the discrete mean-field equations. In Section 3 we introduce the Ginzburg–Landau model for the (100) surface derived in Ref. 3. This is then used in Section 4 to determine the wetting phase diagram.

## 2. LATTICE MODEL

### 2.1. Definition

To model the continuous $B2$–$A2$ order–disorder transition in the binary ($AB$) alloys FeAl or FeCo, we consider a bcc Ising antiferromagnet with nearest-neighbor (NN) interactions of strength $J<0$. The spin variable $\sigma_i$ takes the values $+1$ or $-1$, depending on whether lattice site $i$ is occupied by an $A$ or a $B$ atom. Within the grand-canonical ensemble, the Ising Hamiltonian reads

$$\mathscr{H} = -J \sum_{\langle i,j\rangle} \sigma_i \sigma_j - H \sum_i \sigma_i - H_1 \sum_{i \in \text{surf}} \sigma_i \tag{1}$$

where $\sum_{\langle i,j\rangle}$ runs over all NN bonds. The bulk field $H$ serves to adjust the composition of the alloy and represents the chemical potential difference between $A$ and $B$ atoms. A nonzero surface field $H_1$ occurs generally in binary alloys, giving rise to surface segregation effects. One has $H_1>0$ ($H_1<0$) if $A$ ($B$) atoms tend to segregate at the surface. It is important not to confuse $H_1$ with an "ordering" field, which would couple directly to the local order parameter. Only if $H_1$ distinguishes one of the two sublattices at the surface, as is the case for symmetry-breaking surface orientations, will $H_1$ contribute to an "effective" ordering field $g_1$. But, even then, $H_1 \neq 0$ is not a necessary condition for $g_1 \neq 0$ (cf. Section 3).

The average concentration (or occupation probability) $c_i$ of $A$ atoms on lattice site $i$ can be written in terms of the mean magnetization $m_i \equiv \langle \sigma_i \rangle$ of spin $\sigma_i$ as $c_i = \frac{1}{2}(1+m_i)$. In the ordered ($B2$) phase, the bcc lattice splits into two interpenetrating sc sublattices $\alpha$ and $\beta$ with bulk magnetization densities $m_\alpha \neq m_\beta$. They are preferentially occupied by $A$ and $B$ atoms, respectively (Fig. 1). The disordered ($A2$) structure is characterized by $m_\alpha = m_\beta \equiv m_{\text{dis}}$. The bulk order parameter is defined by

$$\phi_b \equiv \tfrac{1}{2}(m_\alpha - m_\beta) \tag{2}$$

### 2.2. Symmetry Properties of the Surface

Let us define more precisely what is meant by symmetry-breaking and symmetry-preserving surfaces. Consider a uniform translation $\tau$ of the crystal lattice that maps $\alpha$-sites into $\beta$-sites. In an infinite system without free surfaces or a finite system with periodic boundary conditions, the Hamiltonian $\mathscr{H} = \mathscr{H}\{\sigma_i\}$, Eq. (1), is *invariant* under the transformation

$$\sigma_i \to \sigma_i' = \sigma_{i+\tau} \tag{3}$$

This symmetry is spontaneously broken below $T_c$, where the mean magnetization densities $m_\alpha$ and $m_\beta$ transform into each other under Eq. (3), so that $\phi_b \to -\phi_b$. For a system with a free surface, where one imposes periodic and free boundary conditions in the directions parallel and normal to the surface, respectively, the invariance of the Hamiltonian still holds if $\tau$

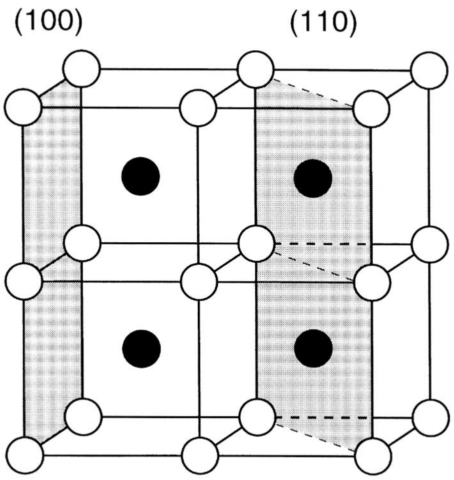

**Fig. 1.** Ordered ($B2$) structure of a bcc binary ($AB$) alloy. Sites belonging to sublattices $\alpha$ and $\beta$ are denoted by open and full circles, respectively. The hatched planes represent the (100) and (110) surface orientations.

can be taken *parallel* to the surface as is the case for the (110) orientation (Fig. 1). Then the surface is called *symmetry-preserving*. One may convince oneself that a surface with Miller indices $(n_1 n_2 n_3)$ is symmetry-preserving if and only if $n_1 + n_2 + n_3$ is even. (By convention, we use the cubic unit cell of the bcc lattice here.) The order parameter, which becomes a local quantity $\phi = \phi_n$ depending on the discrete layer index $n$, vanishes identically above $T_c$ since the $\phi \to -\phi$ symmetry of the bulk system is retained and no enhanced surface interactions have been included in Eq. (1). In contrast, if either one of the lattice planes parallel to the surface belongs to a single sublattice, as is the case for the (100) surface (Fig. 1), *no* translation $\tau$ parallel to the surface exists and the surface is called *symmetry-breaking*. Generally, a $(n_1 n_2 n_3)$ surface is symmetry-breaking if $n_1 + n_2 + n_3$ is odd. Then the Hamiltonian is no longer invariant under Eq. (3) but changes by an amount proportional to the total number of surface sites. Thus the $\phi \to -\phi$ symmetry of the bulk system is generally broken, and the order parameter will be nonvanishing at least locally near the surface even if $T \geqslant T_c$.

The symmetry properties of the surface must also show up in the context of suitable continuum (Ginzburg–Landau) models. Let $\phi_s$ be the value of the order parameter at the surface. For symmetry-preserving surfaces, the surface contribution to the Landau free energy will contain only *even* powers of $\phi_s$. In contrast, arbitrary *odd* powers are expected to occur for symmetry-breaking surfaces due to the loss of the $\phi \to -\phi$ symmetry. In particular, the coefficient of the linear term may be identified with an "effective" ordering surface field $g_1 \neq 0$. Of course, in order to estimate the magnitude of $g_1$ and its dependence on physical parameters such as temperature and bulk composition, the continuum theory must be derived from a microscopic model (see Section 3).

### 2.3. Mean-Field (Bragg–Williams) Approximation

Owing to the spatial inhomogeneity along the $z$ axis perpendicular to the surface, exact treatments of the model [Eq. (1)] are very hard, and one usually has to rely on approximate techniques such as the mean-field (MF) or Bragg–Williams approximation. The MF equations read (with $k_B$ denoting Boltzmann's constant)

$$m_i = \tanh\left[\frac{1}{k_B T}\left(H_i - |J| \sum_j^{(i)} m_j\right)\right] \tag{4}$$

where $H_i = H$, $H_i = H + H_1$ for bulk and surface sites, respectively. The sum $\sum^{(i)}$ runs over all NN sites of $i$. The local magnetizations $m_i$ vary with the index $n = 1, 2, \ldots$, labeling the lattice planes along the $z$ axis, but are the same on each sublattice within a layer. Thus, for the (110) surface, *two* variables are needed to describe the state of each layer,

$$m_i \equiv \begin{cases} m_{n,\alpha} & \text{for } i \in \text{layer } n, \text{ sublattice } \alpha \\ m_{n,\beta} & \text{for } i \in \text{layer } n, \text{ sublattice } \beta \end{cases} \tag{5}$$

The local order parameter $\phi_n$ is conveniently defined by

$$\phi_n \equiv \tfrac{1}{2}(m_{n,\alpha} - m_{n,\beta}) \tag{6}$$

For the (100) surface, one may write

$$m_i \equiv m_n \qquad \text{for } i \in \text{layer } n \tag{7}$$

since each lattice plane belongs to a single sublattice. The definition of the local order parameter requires more care. The obvious choice $\phi_n \equiv \frac{1}{2}(-1)^{n+1}(m_n - m_{n+1})$ is physically reasonable but causes considerable problems in the continuum limit, as explained in detail in Ref. 3. It is favorable to adopt the more symmetric definition

$$\phi_n \equiv \tfrac{1}{2}(-1)^{n+1}\left[m_n - \tfrac{1}{2}(m_{n+1} + m_{n-1})\right] \tag{8}$$

which treats the preceding and succeeding layers on an equal basis.

The MF equations [Eq. (4)] have been studied in Ref. 3 for both (110) and (100) surfaces via the "nonlinear-mapping" technique [10]. It has been shown that in the case of the (100) surface, a nonvanishing order parameter profile appears for $T > T_c$. The characteristic length scale that governs its exponential decay at large $z$ *diverges* as $T \rightarrow T_c$. Precisely at $T = T_c$, the decay takes the form $z^{-\beta/\nu}$ (where $\beta = \nu = \frac{1}{2}$ within MF theory), which is one of the signatures of the normal transition. In the case of the (110) surface, the local order parameter [Eq. (6)] vanishes for $T > T_c$, but one, nevertheless, obtains a nontrivial magnetization profile $m_{n,\alpha} = m_{n,\beta} \neq 0$, describing the alternation of $A$-rich and $B$-rich layers along the $z$ direction. Within MF theory the decay length associated with this profile remains *finite* as $T \rightarrow T_c$.

## 3. CONTINUUM (GINZBURG–LANDAU) MODEL

In proceeding to a suitable continuum description one must be aware of several novel features arising for Ising antiferromagnets or binary alloys, which are not present in simpler systems equivalent to the Ising ferromagnet. First, the Landau expansion of the surface free energy should look different for distinct orientations, due to the loss of the $\phi \rightarrow -\phi$ symmetry for symmetry-breaking surfaces (cf. Section 2.2). Second, one has to take into account so-called "nonordering" (or noncritical) densities. In the alloy picture these are needed to account for spatially varying profiles of, e.g., the local concentration that could *not* be described by the order parameter alone.

For $T \neq T_c$, nonordering densities introduce *additional* length scales that may *compete* with the order parameter correlation length $\xi_b$. It has been shown in a study of wetting in fcc Ising antiferromagnets that this competition may even lead to nonuniversal critical wetting exponents and that the number of nonordering densities depends on the orientation of the surface [8].

To become more specific, let us recall the Ginzburg–Landau model derived and critically examined in Ref. 3 for the case of the *symmetry-breaking* (100) surface. It is based on a free-energy functional of the form,

$$\mathcal{F}\{\phi\} = \int_0^\infty dz \left\{ \frac{C}{2} \left( \frac{d\phi}{dz} \right)^2 + V(\phi(z)) \right\} + f_s(\phi_s) \tag{9}$$

where $\phi_s \equiv \phi(0)$. The Landau expansions of $V(\phi)$ and $f_s(\phi_s)$ read

$$V(\phi) = \frac{A}{2}\phi^2 + \frac{B}{4}\phi^4 + \mathcal{O}(\phi^6), \qquad f_s(\phi_s) = -g_1\phi_s + \frac{C}{\lambda}\phi_s^2 + \mathcal{O}(\phi_s^3) \tag{10}$$

As expected, arbitrary odd powers of $\phi_s$ occur in the expansion of $f_s(\phi_s)$. In view of the above discussion it is remarkable that the Ginzburg–Landau functional [Eq. (9)] does *not* depend on an additional spatially varying nonordering density. The reason is that lattice planes belonging to sublattice $\alpha$ and $\beta$ alternate along the [100] (or $z$) direction. Hence, the order parameter profile uniquely determines the segregation profile, and vice versa. In contrast, the nontrivial segregation profile present for the (110) surface above $T_c$ provides a typical example of a spatially varying nonordering density $\psi$ appearing in the corresponding free-energy functional [11]. The "segregation field" $H_1$ then couples linearly to $\psi$, but no terms linear in the local order parameter and thus no ordering surface field are present.

Deriving the continuum theory from the lattice model has the virtue of relating the "phenomenological" coefficients in Eq. (10) explicitly to the "microscopic" parameters,

$$K \equiv \frac{4\,|J|}{k_B T}, \qquad h \equiv \frac{H}{4\,|J|}, \qquad h_1 \equiv \frac{H_1}{4\,|J|} \tag{11}$$

which are dimensionless measures of the spin coupling strength and the bulk and surface magnetic fields. The "bulk" coefficients $A$, $B$, and $C$ are independent of surface properties and depend on $K$ and $h$ only: $A = A(K, h)$ etc. As usual, $A$ varies linearly with the reduced temperature $t = (T - T_c)/T_c = (K_c - K)/K$ near $T_c$ (at fixed magnetic field $h$), whereas $B$ and $C$ are positive constants to lowest order in $t$ (see Ref. 3). The "surface" parameters are found to be

$$\lambda = 1, \qquad g_1(K, h, h_1) = h_1 + m_{\mathrm{dis}}(K, h) \tag{12}$$

where $m_{\mathrm{dis}} = m_{\mathrm{dis}}(K, h)$ is the magnetization density of the disordered state, which is thermodynamically stable only for $T > T_c$. The so-called extrapolation length $\lambda$ (whose inverse $c_0 \equiv 1/\lambda$ is known as the surface enhancement) is positive as it should be if the surface interactions are not enhanced.

In order to understand better the expression for $g_1$, it is helpful to recall some general symmetry properties of the Ising Hamiltonian [Eq. (1)] which should be respected by the continuum theory. If one replaces $h$ and $h_1$ by its negative, the local mean magnetization and the local order parameter (6) behave as $m_i \to -m_i$, $\phi_n \to -\phi_n$, implying that the ordering surface field should change sign, too:

$$g_1(K, -h, -h_1) = -g_1(K, h, h_1) \tag{13}$$

For bulk field $h=0$ and arbitrary $h_1$, the Ising antiferromagnet is *exactly* equivalent to an Ising ferromagnet since flipping all Ising spins on one sublattice and changing the sign of $K$ leaves the partition function invariant. For the semiinfinite ferromagnet, however, an ordering field $g_1$ is merely equivalent to a surface magnetic field acting on the spins of the first layer and one easily finds [10]

$$g_1(K, 0, h_1) = h_1 \tag{14}$$

Equation (12) fulfills the conditions in Eqs. (13) and (14). The values of $K$, $h$, and $h_1$ for which $g_1(K, h, h_1)$ should vanish can be inferred as follows. Above $T_c$ and for $g_1=0$, the OP profile vanishes, implying that the magnetization profile is a constant $m_n \equiv m_{\text{dis}}(K, h)$. By Eq. (4), the mean internal fields acting on spins in the surface plane $n=1$ and in layers $n>1$ are $H+H_1-4\,|J|\,m_2$ and $H-4\,|J|(m_{n-1}+m_{n+1})$, respectively. The flat profile $m_n \equiv m_{\text{dis}}$ can be a solution only if the internal field is a constant, independent of $n$, which requires that $h_1 = -m_{\text{dis}}(K, h)$. For $T<T_c$ and fixed magnetic field $h$, three bulk solutions of the MF equations exist. Writing $m_{\alpha,\beta} = m \pm \phi$, these are the two ordered phases $m = m_{\text{ord}}$, $\phi = \pm\phi_b \neq 0$, and the disordered state $m = m_{\text{dis}}$, $\phi = 0$, which corresponds to a local maximum of the Landau free energy and is thus thermodynamically unstable. The lattice MF equations for the semiinfinite system generally admit several solutions below $T_c$, with the equilibrium profile being given by the solution minimizing the total free energy. The case $g_1=0$ is distinguished by the fact that the vanishing OP profile $\phi_n \equiv 0$, i.e., $m_n \equiv m_{\text{dis}}$, should always be a (thermodynamically unstable) solution. Moreover, two symmetric (stable) solutions transforming into each other under $\phi_n \to -\phi_n$ and satisfying $\phi_n \to \pm\phi_b$ for $n \to \infty$ exist. Applying the same reasoning as for $T>T_c$, we conclude that the flat profile $m_n \equiv m_{\text{dis}}$ can be a solution only if $h_1 = -m_{\text{dis}}$.

## 4. WETTING PHASE DIAGRAMS

The physical picture behind the wetting behavior at a (100) surface is the following. Below $T_c$, two ordered bulk phases $\pm\phi_b$ coexist. If, e.g., the effective ordering surface field $g_1$ is positive, the surface favors the phase $\phi_b > 0$, i.e., $A$ atoms tend to occupy $\alpha$-planes $n = 1, 3, \ldots$, while $B$ atoms reside preferentially on the $\beta$-planes $n = 2, 4, \ldots$. However, it may occur that deeper in the bulk the role of the two sublattices is interchanged and the order parameter assumes the value $-\phi_b$ there. Then an antiphase boundary separating two regions of ordered phase appears. Antiphase boundaries always occur in real alloys below the ordering temperature. They are the analogs of domain walls in an Ising ferromagnet. Now one may ask how the thickness of this "adsorbed" layer of bulk phase behaves when the temperature is varied. If the interface stays within a finite distance from the surface for $T < T_w$ while moving arbitrarily away into the bulk for $T > T_w$, a wetting transition takes place at $T_w = T_w(h_1, h)$. The thickness of the layer may either grow continuously as $T \uparrow T_w$ (second-order wetting transition) or jump from a finite value below $T_w$ to infinity for $T \geqslant T_w$ in a first-order transition.

We have calculated the wetting phase diagram in the space of physical parameters $1/K \propto T$, $h$, and $h_1$. To this end we employed the full expressions for the bulk and surface Landau free energies $V$ and $f_s$ in Eq. (9) to

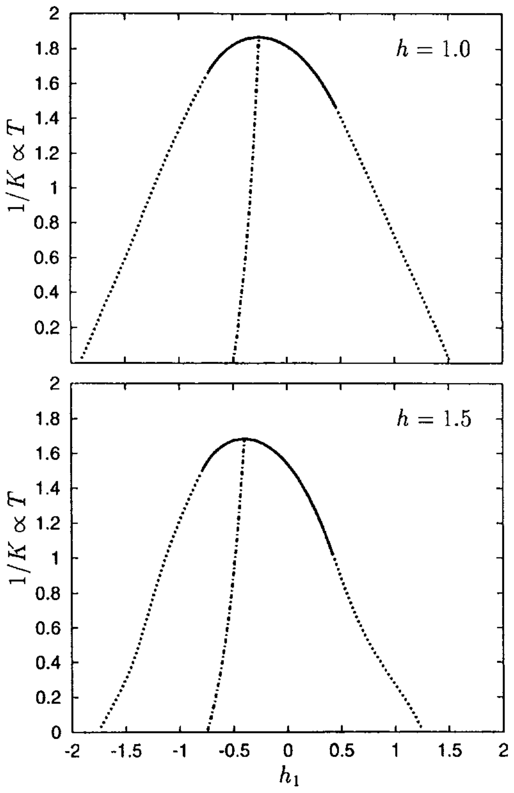

**Fig. 2.** Wetting phase diagrams at fixed bulk fields $h = 1$ and $h = 1.5$, exhibiting continuous (solid lines) and first-order wetting transitions (dashed lines). One has $g_1 > 0$ ($g_1 < 0$) to the right (left) of the dashed–dotted lines, where $g_1 = 0$.

be found in Ref. 3 and used the standard equal-area construction to locate the transitions [12]. Of course, a description in terms of continuum mean-field theory is sensible only above the roughening temperature $T_R$ [13], where $T_R \simeq \frac{1}{3} T_c$ for $h = 1$ [9]. For $T < T_R$ the growth of the wetting layer proceeds via an infinite sequence of layering transitions which are outside the scope of the continuum theory. Figure 2 shows two representative phase diagrams at fixed bulk fields $h = 1$ and $h = 1.5$. The tricritical point separating continuous and first-order transition lines on the right branch of the phase diagram (where $g_1 > 0$) is found to depend strongly on the bulk field for $h$ larger than $\approx 1.5$. If $|h| > 2$, the ordered phases are energetically unstable at $T = 0$ and the bulk phase transition ceases to exist. In order to interpret Fig. 2 an exact ground-state analysis may be carried out similar to the one in Ref. 13, from which one easily finds that complete wetting already occurs at $T = 0$ if $|h_1| \geqslant 1$. Thus continuum mean-field theory is expected to fail if wetting transitions at finite temperatures are predicted for $|h_1| > 1$. In this case one has to resort to the discrete mean-field theory for a more accurate description of the low-temperature part of the phase diagram.

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## REFERENCES

1. H. W. Diehl, in *Phase Transitions and Critical Phenomena*, C. Domb and J. L. Lebowitz, eds. (Academic, London, 1986), Vol. 10, p. 75.
2. A. Drewitz, R. Leidl, T. W. Burkhardt, and H. W. Diehl, *Phys. Rev. Lett.* **78**:1090 (1997).
3. R. Leidl and H. W. Diehl, *Phys. Rev. B* **57**:1908 (1998).
4. F. Schmid, *Z. Phys. B* **91**:77 (1993).
5. H. W. Diehl, *Ber. Bunsenges. Phys. Chem.* **98**:466 (1994).
6. T. W. Burkhardt and H. W. Diehl, *Phys. Rev. B* **50**:3894 (1994).
7. S. Dietrich, in *Phase Transitions and Critical Phenomena*, C. Domb and J. L. Lebowitz, eds. (Academic, London, 1988), Vol. 12, p. 1.
8. D. M. Kroll and G. Gompper, *Phys. Rev. B* **36**:7078 (1987); G. Gompper and D. M. Kroll, *Phys. Rev. B* **38**:459 (1988).
9. F. Schmid and K. Binder, *Phys. Rev. B* **46**:13553 (1992); **46**:13565 (1992).
10. R. Pandit and M. Wortis, *Phys. Rev. B* **25**:3226 (1982).
11. R. Leidl, to be published.
12. J. W. Cahn, *J. Chem. Phys.* **66**:3667 (1977).
13. R. Pandit, M. Schick, and M. Wortis, *Phys. Rev. B* **26**:5112 (1982).