Aust. J. Phys., 1980, **33**, 1017–32

On the Interface Structure in a Simple Cubic Ising System

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Abstract

An examination of the delocalization of the interface in a three-dimensional simple cubic lattice-gas Ising system as a function of the temperature is made using cluster models formulated in terms of the low-order lattice correlations of the Ising system. By regarding the cluster as a sample from the infinite system, the lattice correlations used in the analysis may be computed in a self-consistent manner by taking the correlations defined for the cluster as estimates of the corresponding correlations for the infinite system. The important result to come from the present analysis is that, provided the cluster properly samples the three-dimensional nature of the infinite system, a comparatively small cluster, while not actually yielding an interface critical temperature, can be made to realize a good representation of the interface delocalization as a function of temperature.

1. Introduction

The lattice-gas Ising model with nearest-neighbour interactions provides one of the simplest representations of interfaces between solid and solid, the interface being identified as that region lying between a region of mostly up-spins and a region of mostly down-spins. In the theoretical study of this model the most important result for the three-dimensional case is that of Dobrushin (1972) who showed that at a sufficiently low temperature, and with the appropriate symmetry-breaking boundary conditions, the simple cubic (s.c.) lattice system possesses an interface which is highly localized and remains so up to the two-dimensional critical temperature $T_c(2)$. Furthermore, it can be shown (van Beijeren 1975) that $T_c(2)$ is in fact a lower bound for the stability of the interface. The situation in two dimensions is quite different and we have the important result of Galavotti (1972) who has proved that, for the square Ising model, there always exist large fluctuations which cause the interface to become delocalized at all temperatures. That is, the delocalization of the interface in two dimensions occurs at zero temperature.

The existence of a nonzero temperature below which the three-dimensional Ising interface is localized suggests that this interface might become delocalized somewhere above this temperature—that is, a surface phase transition might occur. Some low-temperature expansions of moments of density gradients for the s.c. system have been made by Weeks *et al.* (1973), and the results obtained do in fact suggest that the interface thickness diverges at a temperature around $0{\cdot}5\,T_c(3)$, which is very close to $T_c(2)$. Leamy *et al.* (1973) have simulated the (100) s.c. lattice-gas interface using Monte Carlo methods and the results obtained support those obtained from the series expansions. We have repeated these Monte Carlo simulations using a

more stable ensemble method of simulation (Johnson 1978*b*) and find that the interface phase transition occurs a little above $0{\cdot}5\,T_c(3)$. The existence of a critical temperature for the interface in three dimensions is rather surprising, particularly in view of the Galavotti (1972) result for two dimensions. However, the truth of the result is reinforced by the argument by analogy, given originally by Burton *et al.* (1951) and presented again by Weeks *et al.* (1973). Here it is proposed that in three dimensions the boundary plane between two aligned spin regions probably behaves like a two-dimensional Ising system for which the critical temperature $T_c(2) = 0{\cdot}502\ldots T_c(3)$. On the other hand, in a two-dimensional system the interface is one dimensional and so the critical temperature is at zero and hence the interface is unstable at all positive temperatures.

Experimentally, it is difficult to observe interfacial phase transitions, particularly in solids, and indirect evidence is often the best that can be obtained. For example, Kidner (1966) showed experimentally that at a sufficiently high temperature, but below the melting points of the metals involved, copper, silver and gold could all diffuse interstitially in lead, and in fact form interstitial solutions, despite the fact that the available (geometric interstitial) space would appear to preclude this. Again, if a gold layer is clamped against a ceramic surface, say, magnesium oxide, and they are both heated to a temperature just below the melting point of gold, held there for an hour or so and then cooled to room temperature, the gold is found to be bonded to the ceramic, the bonding layer being very thin but of high mechanical strength (de Bruin *et al.* 1972). The results of both these experiments can clearly be interpreted in terms of interfacial phase transitions. The mobility of the metal atoms increases as the critical region is reached and this must allow mixing to take place. This mixing is an irreversible process so that, in the metal–ceramic system for example, the bonding would appear to form as a direct result of the interface transition.

In this paper, we discuss some simple cluster models which can readily be used to examine interfacial phase transitions and so obtain estimates of critical temperatures, and for the metal–ceramic bonding system in particular, estimates of the bond strength, as expressed in terms of interfacial excess energy. To examine these models we consider the structure of the (100) interface in an s.c. Ising system as a function of temperature. The layers of lattice sites parallel to the (100) dividing surface are assumed to be unbounded with the lattice site correlations (hereafter simply *correlations*) varying across the layers only. That is, the space variation is across the layers only and so the system is in effect one dimensional. Proceeding away from the dividing surface on the one side, the layers eventually contain all up-spins, while on the other side the layers eventually contain all down-spins.

Consider a cluster of lattice sites, not all necessarily lying in the same layer. First, compute the probability distribution function (p.d.f.) for a given state (configuration) of the cluster particles by taking the p.d.f. for the entire system and (formally) contracting over the states of all the particles lying outside the cluster. In the course of this contracting, in order to estimate the total energy, the interactions between the cluster particles and the nearest-neighbour external particles must be determined. Regarding the cluster as a sample from the infinite system, we assert that the states of the external particles are not arbitrary but depend in probability on the current state of the cluster particles. Accordingly, we estimate the states of the nearest-neighbour external particles (all that is necessary here, since this is the range of the interaction) using p.d.f.s whose moments—that is, correlations—are equal to those

of the cluster. This estimation process is in accord with statistical estimation theory, and is identical with the estimation process we have used in other Ising problems not involving interfaces (Bolton and Johnson 1976; Johnson 1978*a*, 1978*b*). Having computed the p.d.f. for the cluster we may then compute the cluster partition function and the various lattice correlation functions as they apply to the cluster. The next step is to make the problem self-consistent by taking the cluster correlations as estimates of the corresponding correlations for the infinite system. This estimation process is consistent with the assumption that the cluster be a sample from the infinite system. We assume these estimators to be unbiased, although there is some evidence to suggest that this might not be true.* By centring the cluster on the various lattice layers parallel to the dividing surface in turn, and repeating the estimation for the moments each time, we obtain a self-consistent set of nonlinear algebraic equations for a restricted set—that is, a finite set—of correlations, the size of the set depending on the highest order correlation available from the cluster. These equations are generally solvable directly by simple iteration–substitution. In point of numerical computation, since we must sum over all states (configurations) of the cluster particles in order to compute the cluster partition function, there is a practical upper limit to the cluster size that can be considered in this way, and hence to the maximum order of correlation that can be considered. Clusters containing about 20 particles are about the largest that may reasonably be considered, the partition function then being a sum over about 10^6 terms.

The finite number of correlations available from the cluster and their use in estimating the states of the external particles implies a closure at the order of the maximum cluster correlation used in estimating those of the infinite system. This closure can be simply expressed by saying that the fluctuations corresponding to correlations beyond this maximum are independent so that the corresponding covariances are zero. From this it follows that *all*—that is, the infinite set—correlations for the infinite system are defined although, of course, the higher ones will not be independent. For example, if the maximum order of correlation is at the site magnetization $\langle s \rangle$, then all the higher correlations will simply be powers of $\langle s \rangle$. It follows that, since the full set of correlations is defined, a representation of critical phenomena is possible. This is in contradistinction to using either free or periodic boundary conditions on the cluster where the higher order correlations are simply not defined, and hence critical phenomena cannot be defined with the finite set of correlations available.

The clusters we consider in this paper are based on those of one, two and four particles all lying within one layer and with extensions of these clusters to neighbouring layers. None of the clusters considered give rise to a clear transition temperature, such as we found for the infinite 'free' system without interfaces (Johnson 1978*a*), although the slope of the curve of interface thickness as a function of temperature steepens with increasing temperature, the more rapidly the more correlations are taken into account, particularly those within layers rather than those between layers. It is not enough to simply increase the number of particles in the cluster without at the same time increasing the number of correlations that are explicitly considered. Thus, the four-site cluster, with all the sites lying in the same layer and

* In Johnson (1978*a*) it was found that, from these methods with a two-particle sample, the estimate for the critical temperature for the three-dimensional Ising system on an s.c. lattice is slightly lower than the result from the high-temperature series, implying that the estimate of the free energy is too low.

taking into account all five-layer cluster correlations in the estimation of the states of the external particles, gives a thickness curve whose slope increases very much more sharply after $T_c(2)$ than does that for the planar five-particle Bethe cluster using all its correlations, namely the two lowest ones. For each of these planar clusters, the estimation of the states of particles in adjacent layers was made using a one-particle p.d.f. based on the lowest moment for the particular layer. This is a probabilistic extension of mean field estimation. Now, if we consider the two-particle cluster extended over all layers, we find that the probabilistic mean field estimation is in fact accurate to better than 5% up to $T_c(2)$, becoming much less so as the interface becomes delocalized. The four-particle planar cluster with all its correlations taken into account gives an interface thickness curve which steepens after $T_c(2)$ much more rapidly than that obtained from the two-particle cluster even when extended. Even the single two-particle cluster approximation is superior to other cluster methods, for example, the pair approximation used by Weeks and Gilmer (1975) which is based on a simple Bethe (1935) approximation. We conclude that the four-particle cluster is a satisfactory approximation with which to investigate the delocalization with temperature of the interface in an actual physical system. It is true that series approximations for the layers with mean field coupling between the layers could be used and would give quite good results. However, the cluster approximation is more readily applicable to general lattice structures than the series approximations and indeed can be used to examine the details of the metal–ceramic bonding process. This will be described in a later paper.

2. Interface Model

At each vertex i of a connected subset Λ of the (infinite) s.c. lattice $\mathbb{Z}^3$ let there be a spin particle whose state is described by a scalar spin variable $s_i = \pm 1$. Every site of Λ is occupied. The system of particles is to function as an Ising ferromagnet with nearest-neighbour interactions only so that the Hamiltonian $\mathscr{H}(\boldsymbol{s})$ as a function of the spin configuration $\boldsymbol{s} = (s_1, s_2, \ldots)$, specifying the state of every particle on Λ, may be written

$$\mathscr{H}(\boldsymbol{s}) = -\sum_{<ij>} J_{ij} s_i s_j - \sum_{i\in\Lambda, j\in B} J_{ij} s_i s_j - \sum_{i\in\Lambda} h_i s_i, \tag{1}$$

where $\langle ij \rangle$ denotes nearest-neighbour pairs and B refers to the boundary of Λ. The coupling constants J_{ij} are all positive and the h_i are the values of a site-dependent magnetic field.

Let the coordinates of each lattice point be written in the form (i_1, i_2, i_3) with Λ defined by

$$|i_1| < N_1, \qquad |i_2| < N_2, \qquad |i_3| < N_3, \tag{2}$$

and B by the planes $i_p = \pm(N_p+1)$, $p = 1, 2, 3$. We shall refer to the plane of lattice sites $i_3 = n$, $\forall\ i_1, i_2$ as the 'layer' l_n, $-N_3 \leqslant n \leqslant N_3$.

The boundary conditions are the symmetry-breaking conditions

$$s_{i_1,i_2,i_3} = \pm 1, \qquad i_3 = \pm(N_3+1), \qquad \forall\ i_1, i_2. \tag{3}$$

For the moment we shall leave unspecified the conditions on the remaining parts of B.

Restricting our considerations to the isotropic form of J_{ij}, we write $J_{ij} = J > 0$, $\forall\ i,j$. Furthermore, we take the applied magnetic field h_i to have the symmetry-breaking form

$$h_{i_1,i_2,i_3} = \mathrm{sgn}(i_3)\,h, \qquad \forall\ i_1, i_2, \tag{4}$$

although we shall be concerned essentially with the limit $h \to 0$. The surface $i_3 = 0$ may be regarded as the dividing surface between two subsystems Λ^+, Λ^-, such that, if these two were separated, we should have at zero temperature

$$s_i = +1\ (-1), \qquad i \in \Lambda^+\ (\Lambda^-).$$

Using the Hamiltonian (1), we define the (canonical) partition function Q for the particles on Λ as

$$Q = \sum_{s} \exp\{-\beta\,\mathscr{H}(s)\}, \tag{5}$$

where $\beta = 1/k_B T$. Here k_B is Boltzmann's constant and T is the temperature.

We now ascribe to layer l_n, $-N_3 \leqslant n \leqslant N_3$, a set of lattice correlations $\sigma_n^{(k)}$, $\tau_n^{(k)}$, $k = 1, 2, 3, \ldots$, where the $\sigma_n^{(k)}$ are the correlations within layer l_n and the $\tau_n^{(k)}$ are the correlations between sites of l_n and those of other layers $l_{n'}$, $n' \neq n$. The intralayer correlations are defined by

$$\sigma_n^{(1)} = \langle s_i \rangle, \qquad \sigma_n^{(2)} = \langle s_i s_j \rangle, \qquad \sigma_n^{(3)} = \langle s_i s_k \rangle, \ldots, \tag{6}$$

where

$$\langle f(s_i, s_j, s_k, \ldots) \rangle = Q^{-1} \sum_{s} f(s_i, s_j, s_k, \ldots) \exp\{-\beta\,\mathscr{H}(s)\} \tag{7}$$

for any function f. Here $i, j, k, \ldots$ are nearest neighbours on l_n, with i and k being next-nearest neighbours, and so on. While the $\sigma_n^{(k)}$ describe the correlation field within layer l_n, the variation in these quantities with n will be a measure of the correlation between layers and, in particular, the variation in $\sigma_n^{(1)}$ defines the concentration profile across the dividing surface. The interlayer correlations $\tau_n^{(k)}$ are defined in a similar way to the $\sigma_n^{(k)}$, but with $i, j, k, \ldots$ not all in the one layer. However, there is a slight difficulty in definition. If s_k, $k = n-1, n, n+1$, are the spin variables on three nearest-neighbour lattice sites on the same lattice line normal to the dividing surface then, for example, we might define the nearest-neighbour interlayer correlation $\tau_n^{(1)}$ either as

$$\tau_n^{(1)} = \langle s_n s_{n+1} \rangle \qquad \text{(forward definition)}, \tag{8}$$

or as

$$\tau_n^{(1)} = \langle \tfrac{1}{2}(s_{n-1} s_n + s_n s_{n+1}) \rangle \qquad \text{(central definition)}; \tag{9}$$

similarly for the higher order correlations. If the number of layers is large enough so that the concentration profile does not change greatly from layer to layer, the two definitions (8) and (9) will approach one another.

The boundary conditions on the lattice system are such that the layers distant from the dividing surface on the one side contain all up-spins and on the other all down-spins. It follows that we may regard the system as essentially one dimensional with the correlations constant within a layer and varying only from layer to layer. With this assumption we now formulate the interface model in terms of the $\sigma_n^{(k)}$ and $\tau_n^{(k)}$.

Consider a cluster C of lattice sites on Λ, with not all the sites necessarily in the one layer l_n, for some n. If s^C is a configuration of the particles of C, the probability that the cluster particles are in this configuration can be obtained from equation (5) by contracting over the states of the particles outside C. Thus, we have

$$\Pr(s^C) = Q^{-1} \sum_{s}^{C} \exp\{-\beta \mathscr{H}(s)\}, \tag{10}$$

where the summation is over all those configurations s of the particles of Λ for which the particles of C are in configuration s^C. Separating out the interactions of the particles of C, we write

$$\mathscr{H}(s) = \sum_{i \in C} s_i E_i^C + \sum_{i \in \Lambda \setminus C} s_i E_i, \tag{11}$$

where, in particular, E_i^C depends on the interactions of the particles of C with each other as well as with those of C_{nn}, the set of external sites which are nearest neighbours of C. Substituting equation (11) into (10), we find

$$\Pr(s^C) = \sum_{s_{nn}^C} \exp\left(-\beta \sum_{i \in C} s_i E_i^C\right) g(s_{nn}^C), \tag{12}$$

where

$$g(s_{nn}^C) = Q^{-1} \sum_{s'} \exp\left(-\beta \sum_{i \in \Lambda \setminus C} s_i E_i\right), \tag{13}$$

the summation s' being over the configurations of particles of $\Lambda \setminus (C \vee C_{nn})$. From the definition (13) we see that $g(s_{nn}^C)$ is proportional to the probability of finding the nearest neighbours in C_{nn} in state s_{nn}^C, given that the particles of C are in state s^C. Using this fact we now estimate $g(s_{nn}^C)$ and then compute $\Pr(s^C)$ using equation (12).

If we regard the cluster particles as a sample from the infinite system, the external particles must behave statistically in the same way as the sample particles. On this basis, the conventional way of estimating the states of the external particles in a particular layer would be to introduce periodic boundary conditions on C so that each external particle in the same layer behaves in exactly the same way as the equivalent internal particle. Because of the gradient in chemical potential across the layers, we may not apply periodic boundary conditions in this direction and so the states of the external particles in adjacent layers must be estimated in a different way, for example, in a mean field sense. A better estimation process, one which unlike periodic boundary conditions maintains some level of continuity in the correlations across the boundary of C, and which also relates directly to the definition (13) of $g(s_{nn}^C)$, is based on estimating the states of the external particles by means of probability distribution functions (p.d.f.s) whose moments—that is, correlations—are equal to those of the cluster particles. It is then a simple matter to construct the appropriate conditional p.d.f.s and so compute g. The details of this process will be clear from the examples we consider in the next sections. Having estimated the states of the external particles in this way, the next step is to make the whole process self-consistent and, maintaining the spirit of statistical estimation, we regard the cluster correlations as estimates of the corresponding correlations for the infinite system. By locating the cluster C on the various layers in turn and applying the estimation process each time, we obtain a self-consistent set of nonlinear algebraic equations for the correla-

tions. In the following sections we apply this analysis to a number of cluster types, beginning with the single-particle cluster, which yields a probabilistic mean field approximation, and considering finally a four-particle square cluster which, with its set of five correlations, yields a good representation of the interface delocalization. We also consider extensions of these clusters to adjacent layers. The planar clusters necessarily involve only the intralayer correlations, with the interlayer correlations expressed essentially by the variation in these quantities from layer to layer. The extended clusters involve the interlayer correlations quite explicitly. Larger clusters would doubtless lead to better representations of the interface delocalization, but direct evaluation of the partition function is generally not feasible here and expansion in low-temperature series is the only method of dealing with these larger clusters.

3. One-particle Cluster Approximation

The simplest cluster approximation is based on one particle and is realized using one-particle p.d.f.s defined by the $\sigma_n = \sigma_n^{(1)}$ alone. Thus, let $C = C^{(1)}(p)$, $p \in \Lambda$, and let $q \in \Lambda$ be a nearest-neighbour site and lying in the same layer l_n. Then, to this approximation,

$$\Pr(s_q \mid s_p) \equiv \Pr(s_q \mid s_p \mid \Lambda) = \tfrac{1}{2}(1 + \sigma_n s_q) \tag{14}$$

may be interpreted as a conditional probability of the particle at q having spin s_q, given that the spin at p is s_p. The conditional nature of the p.d.f. (14) is to be understood in terms of the equivalence class of the configurations of the particles of l_n as defined by the value of σ_n. The set $[\sigma_n, -N \leqslant n \leqslant N]$ $(N = N_3)$ defines the equivalence class of configurations of the entire system. It follows from this, that if q is in layer $l_{n\pm1}$, then we may take the required probability as

$$\Pr(s_q \mid s_p) = \tfrac{1}{2}(1 + \sigma_{n\pm1} s_q). \tag{15}$$

As we indicated in the Introduction, the use of this one-particle cluster approximation through the p.d.f.s (14) and (15) implies a closure in the sequence of moments for the entire system, the closure here being at the first term σ_n. It follows that the central moment $\langle (s_1 - \langle s_1 \rangle)(s_2 - \langle s_2 \rangle) \rangle$, for example, is zero, as are all higher central moments. For the second moment we find immediately $\langle s_1 s_2 \rangle = \langle s_1 \rangle \langle s_2 \rangle$, so that all the intralayer moments for l_n are simply powers of σ_n, while the interlayer moments for layers l_n, l_{n+1}, for example, are multinomials in σ_n, $\sigma_{n\pm1}$. By its nature the one-particle cluster approximation can give results little better than those of mean field.

In the present s.c. system let the nearest neighbours of $p \in \Lambda$ in layer l_n be (p,k), $k = 1,2,3,4$, the nearest neighbour in l_{n+1} $(p,5)$ and that in l_{n-1} $(p,6)$. Then, using the p.d.f.s (14) and (15) we define $g(s^C_{p,nn})$ through

$$g(s^C_{p,nn}) = A_n \prod_{k=1}^{4} \tfrac{1}{2}(1 + \sigma_n s_{p,k}) \tfrac{1}{2}(1 + \sigma_{n+1} s_{p,5}) \tfrac{1}{2}(1 + \sigma_{n-1} s_{p,6}), \tag{16}$$

where A_n is a constant of proportionality. The representation (16) would appear to be the best possible using only the σ_n, and moreover is one which maintains explicitly the local probability field associated with p and its nearest neighbours.

Substituting the representation (16) in (12), and using the energy expression

$$E^C_p = -J\left(\sum_{k=1}^{4} s_{p,k} + s_{p,5} + s_{p,6}\right) - h_n, \tag{17}$$

we have for the probability of the cluster configuration s^C, on replacing s_p by s_n, since we are dealing directly with spin particles in layer l_n,

$$\Pr(s_n) = A_n \exp(\beta h_n s_n)(1+\sigma_n s_n \tanh K)^4(1+\sigma_{n+1} s_n \tanh K)(1+\sigma_{n-1} s_n \tanh K), \quad (18)$$

where $K = \beta J$. The constant of proportionality A_n has been redefined and is determined by the normalizing condition

$$\Pr(+1)+\Pr(-1) = 1. \quad (19)$$

In order to determine the layer moments σ_n we *assume* for all n that σ_n is equal to $\langle s_n \rangle$, the mean value of s_n with respect to the p.d.f. (18). That is,

$$\sigma_n = \langle s_n \rangle \equiv \sum_{s_n = \pm 1} s_n \Pr(s_n). \quad (20)$$

Equations (20), together with the boundary conditions

$$\sigma_{-(N+m)} = -1, \qquad \sigma_{N+m} = +1, \qquad m > 0, \quad (21)$$

form a self-consistent set of $2N+1$ nonlinear algebraic equations for the layer values of the long-range order σ_n, $-N \leqslant n \leqslant N$. These equations may be solved directly by simple iteration–substitution, starting with the initial values (i.e. low-temperature values)

$$\sigma_n = \pm 1, \quad n > 0, \qquad \sigma_0 = 0, \qquad \sigma_n = -1, \quad n < 0. \quad (22)$$

Note that $\Pr(-1) = 0$ for $n = N+m$ and $\Pr(+1) = 0$ for $n = -(N+m)$, facts that are used implicitly in the solution of equations (20).

4. Two-particle Cluster Approximation

This cluster approximation is based on two particles, both in the one layer, and is realized using the two-particle p.d.f. defined by $\sigma_n = \sigma_n^{(1)}$, $\phi_n = \sigma_n^{(2)}$ and introduced by Johnson (1978*a*). Let $C = \varepsilon^{(2)}(p, q)$ be a nearest-neighbour two-site cluster on Λ with $p, q \in l_n$ for some n, $-N \leqslant n \leqslant N$. Then, with this cluster approximation,

$$\Pr(s_p, s_q) \equiv \Pr(s_p, s_q \mid \Lambda) = (\tfrac{1}{2})^2\{1+\sigma_n(s_p+s_q)+\phi_n s_p s_q\} \quad (23)$$

may be interpreted as a conditional probability of the particles of C being in state (s_p, s_q), given that the other particles on l_n are in a configuration belonging to the equivalence class defined by the pair (σ_n, ϕ_n). Hence the entire layer system is in a state defined by the equivalence class defined by the entire set of (σ_n, ϕ_n), $\forall\, n$. If the state of the particle at p is known, and equal to s_p, then on using equation (14) we may interpret

$$\Pr(s_q \mid s_p) = \tfrac{1}{2}\{1+\sigma_n(s_p+s_q)+\phi_n s_p s_q\}/(1+\sigma_n s_p) \quad (24a)$$

as the probability that the particle at q is in state s_q, given that the particle at p is in state s_p. Further, if the site q is in layer $l_{n\pm1}$ then we should expect to write this as

$$\Pr(s_q \mid s_p) = \tfrac{1}{2}(1+\sigma_n s_p+\sigma_{n\pm1} s_q+\tau_n s_p s_q)/(1+\sigma_n s_p).$$

However, as both cluster particles lie in the one layer l_n, the value of the correlation is not available from the cluster and we shall simply use the one-particle p.d.f.

$$\Pr(s_q \mid s_p) = \tfrac{1}{2}(1+\sigma_{n\pm1}\, s_q). \tag{24b}$$

As with the one-particle cluster, the two-particle cluster and its associated p.d.f.s imply a closure in the sequence of layer moments, this time at those moments involving more than nearest-neighbour correlations. Thus, if 2 is the nearest neighbour of any two sites 1 and 3, 1 and 3 being next-nearest neighbours, and if s_1, s_2, s_3 are the particle states at these sites, then

$$\langle s_1 s_3\rangle = \langle s_1\rangle\langle s_3\rangle = \sigma_n^2, \qquad \langle s_1 s_2 s_3\rangle = 2\sigma_n(\phi_n - \sigma_n^2);$$

similarly for higher moments. Since both σ_n and ϕ_n are necessary to describe the system, we might expect a better representation of the interface delocalization with this cluster than with the one-particle cluster.

Denoting the nearest neighbours of p and q by (p,k), $k = 1 \ldots 6$ and (q,l), $l = 1 \ldots 6$ as in the previous section, we write for the cluster energy E^C

$$\begin{aligned} -\beta E^C &= -\beta \sum_{i\in C} s_i E_i^C \\ &= K s_p s_q + \beta h_n(s_p + s_q) + K \sum_{k=1}^{6}{}' s_p s_{p,k} + K \sum_{l=1}^{6}{}' s_q s_{q,l}, \end{aligned} \tag{25}$$

where the primes on the summations indicate that those k and l values that correspond to q and p respectively are to be omitted.

Using equations (24a) and (15) to estimate the states of the nearest-neighbour particles outside C, we have

$$\begin{aligned} g(\boldsymbol{s}_{nn}^C) = A_n \Bigg(& \prod_{k=1}^{4}{}' \tfrac{1}{2}\{1+\sigma_n(s_p+s_{p,k}) + \phi_n s_p s_{p,k}\}/(1+\sigma_n s_p)\Bigg) \\ & \times \Bigg(\prod_{l=1}^{4}{}' \tfrac{1}{2}\{1+\sigma_n(s_q+s_{q,l}) + \phi_n s_q s_{q,l}\}/(1+\sigma_n s_q) \\ & \times \tfrac{1}{2}(1+\sigma_{n+1}s_{p,5})\tfrac{1}{2}(1+\sigma_{n-1}s_{p,6})\tfrac{1}{2}(1+\sigma_{n+1}s_{q,5})\tfrac{1}{2}(1+\sigma_{n-1}s_{q,6})\Bigg), \end{aligned} \tag{26}$$

with the primes having the same meaning as before. Substituting this equation in (12) and using the energy expression (25), we find for the probability of the cluster configuration $\boldsymbol{s}^C = (s_p, s_q)$

$$\begin{aligned} \Pr(s_p, s_q) = {} & A_n \exp\{K s_p s_q + \beta h_n(s_p+s_q)\} \\ & \times \{G_n^{(1)}(s_p)\, G_n^{(1)}(s_q)\}^3 G_{n+1}^{(2)}(s_p)\, G_{n-1}^{(2)}(s_p)\, G_{n+1}^{(2)}(s_q)\, G_{n-1}^{(2)}(s_q), \end{aligned} \tag{27}$$

where

$$G_n^{(1)}(s) = 1 + \frac{(\phi_n - \sigma_n^2) + \sigma_n(1-\phi_n)s}{1-\sigma_n^2}\tanh K, \tag{28a}$$

$$G_n^{(2)}(s) = 1 + \sigma_n s \tanh K. \tag{28b}$$

Note that $\Pr(s_p, s_q)$ is symmetric in s_p, s_q. As before, the constant A_n is defined by the normalizing condition

$$\sum_{s_p=\pm 1} \sum_{s_q=\pm 1} \Pr(s_p, s_q) = 1 . \tag{29}$$

We now assume the layer moments σ_n, ϕ_n to be defined self-consistently by

$$\sigma_n = \langle s_p \rangle = \langle s_q \rangle = \sum_{s_p=\pm 1} \sum_{s_q=\pm 1} s_p \Pr(s_p, s_q) , \tag{30a}$$

$$\phi_n = \langle s_p s_q \rangle = \sum_{s_p=\pm 1} \sum_{s_q=\pm 1} s_p s_q \Pr(s_p, s_q) . \tag{30b}$$

These two equations, together with the boundary conditions

$$\sigma_{\pm(N+m)} = \pm 1 , \qquad \phi_{\pm(N+m)} = \pm 1 , \qquad m > 0 , \tag{31}$$

form a self-consistent set of $2(2N+1)$ equations for the $2(2N+1)$ unknowns σ_n, ϕ_n, $-N \leqslant n \leqslant N$.

5. Four-particle Cluster Approximation: Square Cluster

The two clusters already considered are what might be called linear clusters—that is, the sites of the cluster all lie on the same lattice line and so might be expected to represent the interface in a two-dimensional lattice system rather than a three-dimensional one. A proper cluster representation of the three-dimensional system is obtained by allowing the cluster to have sites on adjoining lattice lines and so is itself two dimensional. For these more general clusters, correlations characteristic of a two-dimensional Ising system are defined and we should therefore expect a better representation of lattice interface transitions in three dimensions. The simplest cluster which provides these moments is the square cluster. Thus, let

$$C = C^{(4)}(p^1, p^2, p^3, p^4)$$

be a cluster of four sites in layer l_n, each site being the corner of an elemental square on the s.c. lattice. For C we may define five different site-correlation functions associated with l_n. Thus, to the present approximation,

$\sigma_n^{(1)} =$ o, $\sigma_n^{(2)} =$ o o, $\sigma_n^{(3)} =$  , $\sigma_n^{(4)} =$, $\sigma_n^{(5)} =$  , (32)

where the diagrams define the $\sigma_n^{(k)}$ in terms of particle state averages over the sites indicated. For the cluster C, it follows then, with the usual notation, that we may interpret

$$\begin{aligned}
&\Pr(s_{p1}, s_{p2}, s_{p3}, s_{p4} \mid \Lambda) \\
&= (\tfrac{1}{2})^4 \{1 + \sigma_n^{(1)}(s_{p1} + s_{p2} + s_{p3} + s_{p4}) + \sigma_n^{(2)}(s_{p1} s_{p2} + s_{p2} s_{p3} + s_{p3} s_{p4} + s_{p4} s_{p1}) \\
&\quad + \sigma_n^{(3)}(s_{p1} s_{p3} + s_{p2} s_{p4}) + \sigma_n^{(4)}(s_{p1} s_{p2} s_{p3} + s_{p2} s_{p3} s_{p4} + s_{p3} s_{p4} s_{p1}) \\
&\quad + \sigma_n^{(5)} s_{p1} s_{p2} s_{p3} s_{p4}\}
\end{aligned} \tag{33}$$

as the probability that the particles of C are in state $(s_{p1}, s_{p2}, s_{p3}, s_{p4})$, conditional on the particles of l_n being in a state belonging to the equivalence class defined by the set $[\sigma_n^{(k)}, k = 1, 2, 3, 4, 5]$. The closure in the moments here is at the first moment whose correlation length is greater than the cluster diameter.

To use the probability (33) in the estimation of the states of particles on l_n outside C, we first set up a cluster involving two external particles as well as those of C, from which we see that we must estimate the states of pairs of external neighbours rather than those of single particles. Consider a square cluster in l_n consisting of two nearest-neighbour external sites X^1, X^2, which are themselves nearest-neighbour sites of p^1, p^2, say, the four sites together forming an elemental lattice square. Then, on using equation (33) we may define

$$\Pr(s_{X1}, s_{X2} \mid s_{p1}, s_{p2}) = \Pr(s_{X1}, s_{X2}, s_{p1}, s_{p2})/\Pr(s_{p1}, s_{p2}) \tag{34}$$

as the conditional probability of (s_{X1}, s_{X2}) given the state (s_{p1}, s_{p2}). The form (34) uses all the correlations of the cluster C.

To estimate the state of a single external particle, we consider the square cluster (X^1, X^2, p^1, p^2) and write

$$\Pr(s_{X1} \mid s_{p1}, s_{p2}) = \Pr(s_{X1}, s_{p1}, s_{p2})/\Pr(s_{p1}, s_{p2}), \tag{35}$$

where $\Pr(s_{X1}, s_{p1}, s_{p2})$ is obtained from equation (33) by contracting over the states of one of the particles of C, that at p^4 for example, so that

$$\begin{aligned}\Pr(s_{p1}, s_{p2}, s_{p3}) = (\tfrac{1}{2})^3\{1 + \sigma_n^{(1)}(s_{p1} + s_{p2} + s_{p3}) + \sigma_n^{(2)}(s_{p1}s_{p2} + s_{p2}s_{p3})\} \\ + \sigma_n^{(3)} s_{p1}s_{p3} + \sigma_n^{(4)} s_{p1}s_{p2}s_{p3}.\end{aligned} \tag{36}$$

Note that this equation does not involve all the correlations of C.

Denoting the nearest-neighbour external sites of p^i by (p^i, k) as before, then if the cluster particles are in configuration s^C, we can write the energy of the cluster particles as

$$-\beta E^C = -\beta \sum_{i \in C} s_i E_i^C = KE_{\text{int}}^C + KE_{\text{ext}}^C + \beta H^C, \tag{37}$$

where

$$E_{\text{int}}^C = s_{p1}s_{p2} + s_{p2}s_{p3} + s_{p3}s_{p4} + s_{p4}s_{p1}, \tag{38a}$$

$$E_{\text{ext}}^C = \sum_{i=1}^{4}{}' [s_{pi}\{(s_{pi,1} + s_{pi,2}) + (s_{pi,5} + s_{pi,6})\}], \tag{38b}$$

$$H^C = h_n \sum_{i=1}^{4} s_{pi}, \tag{38c}$$

the prime on the summation having the same significance as before.

The states of the external particles may be estimated either singly, using equation (35) or in pairs, using (34). As equation (34) uses all the available cluster correlations, we shall estimate the states of the external particles in pairs. Proceeding as before we find

$$g(s_{nn}^C) = \prod_k \Pr(s_{p^k;X}, s_{p^{k+1};Y} \mid s_{p^k}, s_{p^{k+1}}), \tag{39}$$

where k runs over the sequence $1,2,3,4$ with $4+1=1$. The subscripts X, Y refer to the pair of nearest-neighbour sites external to (p^k, p^{k+1}). There are thus four factors in the product in equation (39). Substituting this equation into (12) and using the energy expression (37), we find for the probability of the cluster configuration $\boldsymbol{s}^C = (s_{p1}, s_{p2}, s_{p3}, s_{p4})$,

$$\begin{aligned}\Pr(\boldsymbol{s}^C) &= A_n \exp(KE_{\text{int}}^C + \beta H^C) \\ &\times \prod_{k=1}^{4} \sum_{s_X=\pm 1, s_Y=\pm 1} (1 + s_X s_{p^k} \tanh K)(1 + s_Y s_{p^{k+1}} \tanh K) \\ &\times \Pr(s_X, s_Y \mid s_{pk}, s_{p^{k+1}}) \prod_{i=1}^{4} G_{n+1}^{(2)}(s_{pi})\, G_{n-1}^{(2)}(s_{pi}), \end{aligned} \tag{40}$$

where $\Pr(s_X, s_Y \mid s_p, s_{p'})$ is given by equation (34) with the moments $\sigma^{(k)}$ taken in layer l_n. The constant A_n is defined by the normalization

$$\sum_{s^C} \Pr(\boldsymbol{s}^C) = 1. \tag{41}$$

We now define the layer moments $\sigma_n^{(k)}$ self-consistently in the usual way, taking

$$\sigma_n^{(1)} = \langle s_{p1} \rangle \equiv \sum_{s^C} s_{p1} \Pr(\boldsymbol{s}^C), \tag{42a}$$

$$\sigma_n^{(2)} = \langle s_{p1} s_{p2} \rangle \equiv \sum_{s^C} s_{p1} s_{p2} \Pr(\boldsymbol{s}^C), \tag{42b}$$

$$\sigma_n^{(3)} = \langle s_{p1} s_{p3} \rangle \equiv \sum_{s^C} s_{p1} s_{p3} \Pr(\boldsymbol{s}^C), \tag{42c}$$

$$\sigma_n^{(4)} = \langle s_{p1} s_{p2} s_{p3} \rangle \equiv \sum_{s^C} s_{p1} s_{p2} s_{p3} \Pr(\boldsymbol{s}^C), \tag{42d}$$

$$\sigma_n^{(5)} = \langle s_{p1} s_{p2} s_{p3} s_{p4} \rangle \equiv \sum_{s^C} s_{p1} s_{p2} s_{p3} s_{p4} \Pr(\boldsymbol{s}^C). \tag{42e}$$

These equations, together with the boundary conditions

$$\sigma_{\pm(N+m)}^{(1)} = \sigma_{\pm(N+m)}^{(4)} = \pm 1, \quad m > 0, \tag{43a}$$

$$\sigma_{\pm(N+m)}^{(2)} = \sigma_{\pm(N+m)}^{(3)} = \sigma_{\pm(N+m)}^{(5)} = +1, \quad m > 0, \tag{43b}$$

form a self-consistent set of $5(2N+1)$ equations for the $5(2N+1)$ unknowns $\boldsymbol{\sigma}^{(k)}$.

6. Bethe Cluster Approximation

Each of the clusters considered so far may be characterized by the property that all of the lattice sites in each cluster are equivalent in the sense that the cluster partition function is symmetric in each of the site variables. From this it follows that the site correlations are uniform across the cluster, and hence the cluster may be regarded as a proper sample from the layer from which it is drawn, since in the present interface model the (thermodynamic) properties of the system vary only from layer to layer and not within layers. If larger clusters, which necessarily have non-equivalent sites, are to be considered, then local constraints in the form of a site-dependent applied magnetic field must be imposed in order to achieve uniformity in the correla-

tions across the sample. Setting up such a cluster with its constraints we may then proceed as before, taking the internal interactions into account in an exact manner and estimating the interactions with the external particles with p.d.f.s which depend only on the lower moments of the cluster. This last point implies that only those correlations that appear in these p.d.f.s will be uniform across the sample. For a system without interfaces and with external interactions estimated by a mean field, this cluster method is essentially the classical Bethe (1935) cluster method. The clusters that might be considered may be obtained in sequence from the simple square lattice by selecting a central site and its neighbours in the first shell, a central site and its neighbours in the first and second shells, and so on. The first cluster has 5 sites with two classes of equivalent sites, and so requires only one constraint, while the second cluster has 13 sites and four classes of equivalent sites and so requires three constraints. This sequence of clusters can be extended, but as the first cluster has $2^5 = 32$ configurations and the second has $2^{13} = 8192$, the second cluster is at the limit of direct numerical computation, even after dividing up the configurations into equivalence classes. However, for the 13 particle cluster it is numerically feasible to use one-particle p.d.f.s only in the estimation of the external states, and even with this the amount of computation is considerable. The indications are that the results for the 13 particle cluster are little better than those for the 5 particle cluster. Accordingly, we shall consider only the 5 particle Bethe cluster.

Consider the 5 particle Bethe cluster on the simple square lattice, consisting of a central site p and four nearest neighbours q_i, $i = 1,2,3,4$ in the first shell. In order to maintain the proper lattice coordination over the cluster we shall assume each site q_i to have three equivalent external nearest neighbours $t_{i,k}$, $k = 1,2,3$. The $t_{i,k}$ do not lie on the original square lattice but rather form the second set of vertices of a directed tree with root on q_i and with every vertex, except the root, having indegree unity and outdegree three. The root has indegree zero and outdegree four. This tree is the so-called Bethe lattice. The present cluster has two classes of equivalent sites, not counting the external sites, which are essentially equivalent to the central site. One class contains the central site p and the other the sites q_i, $i = 1,2,3,4$. We therefore need one constraint and indeed only one may be applied, which may be conveniently imposed as a parametric magnetic field H_q acting at the sites q_i. Assuming no external magnetic field to be applied to the entire lattice, we may write for the cluster Hamiltonian

$$\mathscr{H}(s) = -J \sum_{i=1}^{4} s_{q_i}\left(s_p + \sum_{k=1}^{3} s_{t_{i,k}}\right) - \mu H_q \sum_{i=1}^{4} s_{q_i}. \tag{44}$$

The magnetic field H_q will, in general, be different from zero and is to be determined from the requirement that the cluster correlations, in this case only the one-particle correlations (site magnetizations), $\langle s_p \rangle = \langle s_{q_i} \rangle$ be equal.

If we now estimate the states of the particles on the t sites by means of the two-particle p.d.f. (24a)—thus using *all* the statistical information available—we find for the cluster partition function

$$Q = \sum_{s_p, s_q} \exp\left((Ks_p + \beta h_q) \sum_{i=1}^{4} s_{q_i}\right)\left(\prod_{i=1}^{4} G^{(1)}(s_{q_i})\right)^3, \tag{45}$$

where $\beta h_q = \mu H_q / k_B T$ and $G^{(1)}(s)$ is defined by equation (28a). We now establish uniformity of $\langle s \rangle = \langle s_{q_i} \rangle$, $i = 1,2,3,4$, which yields an equation for h_q.

To apply this cluster to the present interface model, we must first add to the Hamiltonian (44) those terms expressing the interactions between particles of layers l_n and $l_{n\pm1}$. As before, we construct the function g from which we determine the p.d.f. for the cluster configuration in layer l_n. We find

$$\Pr(s_p, s_q) = A_n \exp\left((Ks_p + \beta h_q^{(n)}) \sum_{i=1}^{4} s_{q_i}\right) G_{n+1}^{(2)}(s_p)\, G_{n-1}^{(2)}(s_p)$$
$$\times \prod_{i=1}^{4} G_n^{(1)}(s_{q_i})^3\, G_{n+1}^{(2)}(s_{q_i})\, G_{n-1}^{(2)}(s_{q_i}). \tag{46}$$

Note that $\Pr(s_p, \boldsymbol{s}_q)$ is no longer a symmetric function of all its arguments. The constant A_n is again defined by the normalization

$$\sum_{s_p, \boldsymbol{s}_q} \Pr(s_p, \boldsymbol{s}_q) = 1,$$

and the field h_q, which is layer dependent, is defined by the *internal* consistency condition

$$\langle s_p \rangle = \langle s_{q_i} \rangle \quad \forall\ i, \qquad i = 1, 2, 3, 4. \tag{47}$$

The entire problem is now made self-consistent in the same manner as before, taking σ_n and ϕ_n to be defined self-consistently by the conditions

$$\sigma_n = \langle s_p \rangle \equiv \sum_{s_p, \boldsymbol{s}_q} s_p \Pr(s_p, \boldsymbol{s}_q), \tag{48a}$$

$$\phi_n = \langle s_p s_{q_i} \rangle \equiv \sum_{s_p, \boldsymbol{s}_q} s_p s_{q_i} \Pr(s_p, \boldsymbol{s}_q). \tag{48b}$$

These equations (48) together with the boundary conditions (31) form a self-consistent set of $2(2N+1)$ equations for the $2(2N+1)$ unknowns σ_n, ϕ_n, $-N \leqslant n \leqslant N$.

7. Results of Computations

In examining the properties of the cluster approximations for the interface system we first tested the effectiveness of taking the cluster sites all in the one layer. To this end we considered the two-particle cluster of Section 4 extended over all layers of an 11 layer (i.e. $N = 5$) system. Taking the cluster sites all in the one layer implies, for example, that the interlayer nearest-neighbour correlation $\tau_n^{(1)}$ is equal to $\sigma_n^{(1)} \sigma_{n+1}^{(1)}$, as follows from equation (8), whereas for the extended cluster the accurate form (9) must hold. Expressing the temperature T in units of J/k_B, we found that up to $T \approx 2{\cdot}5$ the error $\tau_n^{(1)}(\text{exact}) - \tau_n^{(1)}(\text{approx})$ is less than 8%. This error increases with temperature, so that at $T = 4{\cdot}0$ the error is 50%. However, this is unimportant since the interface is well delocalized at this stage. It follows that taking the cluster particles in the one layer and using one-particle p.d.f.s for estimating the states of particles in neighbouring layers is adequate up to the (actual) delocalization temperature for the two-particle cluster and *a fortiori* for the four-particle cluster.

The interface thickness $d(T)$ may be defined by means of a linear extrapolation of the density profile at layer l_1 to the 'infinity' layer l_N (Cahn and Hillard 1958). Interpreting this in terms of the long-range order $\sigma_k^{(1)}$, we have

$$d(T) = \sigma_N^{(1)} / \sigma_1^{(1)}. \tag{49}$$

Table 1 gives the behaviour of the thickness $d(T)$ as a function of the temperature T, measured in units of J/k_B, for the various cluster approximations given in the previous sections. All these results are for the case $N = 5$, so that there are 11 layers. It was found that for $N > 5$ the interface thickness was not strongly dependent on N, although the details of the density profile changed as N increased beyond this value.

Table 1. Interface thickness $d(T)$ as a function of temperature for various cluster models
The temperature T is in units of J/k_B

T	(1) One-particle cluster	(2) Two-particle cluster	(3) Two-particle cluster (extended)	(4) Four-particle cluster	(5) Five-particle Bethe cluster
1·00	1·000	1·000	1·001	1·007	1·000
1·50	1·002	1·003	1·012	1·063	1·002
2·00	1·009	1·015	1·060	1·219	1·011
2·10	1·012	1·019	1·075	1·267	1·015
2·20	1·015	1·025	1·093	1·323	1·018
2·30	1·017	1·032	1·113	1·389	1·023
2·40	1·022	1·040	1·135	1·467	1·028
2·50	1·026	1·049	1·160	1·561	1·035
2·75	1·038	1·080	1·236	1·907	1·055
3·00	1·054	1·123	1·336	2·578	1·084
3·25	1·075	1·184	1·471	4·081	1·125
3·50	1·102	1·267	1·661	7·316	1·181
3·75	1·137	1·385	1·949	13·012	1·261
4·00	1·184	1·557	2·430	21·705	1·377

From the table it is clear that the four-particle (square) cluster (column 4) represents the delocalization of the interface with temperature better than any of the other clusters, and in particular, considerably better than the one-particle cluster (column 1), which gives essentially a mean field approximation. It is also superior to the Bethe cluster (pair approximation) of Weeks and Gilmer (1975), their results (Fig. 3 of their paper) lying close to those for the two-particle cluster extended over all layers (column 3). Comparison of the results for the five-particle Bethe cluster (column 5) with those of column 4 shows that the size of the cluster alone is not sufficient to describe the interface delocalization and that higher order correlations must be taken into account explicitly if an acceptable description of the delocalization is to be obtained. A larger cluster with all possible correlations considered, for example the 13 particle Bethe cluster mentioned in Section 6, would presumably give a very good description of the delocalization process. However, the computation appears quite unfeasible. The four-particle cluster, on the other hand, is readily computed even with different couplings within and between layers and seems to be adequate for dealing with, for example, the metal–ceramic bond problem.

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Manuscript received 28 June 1979, accepted 12 March 1980