(1)

ONR

Approximations of Mean Spherical Type for Lattice Percolation Models

James A. Given and George Stell

Department of Chemistry, S.U.N.Y. Stony Brook

1990

Abstract

We develop a general class of approximations of mean-spherical (MSA) type as a method for studying lattice percolation problems. We review the MSA and test certain extensions of it on lattice spin models. The relations between thermal spin models and percolation models are then reviewed in order to identify natural extensions of the MSA to percolation models. These extensions are used to treat both site and bond percolation models. In one 'low-density' formulation of MSA, the threshold for bond percolation on a lattice is found to equal the value at the origin of the corresponding lattice Green's function. This result is extremely accurate for all lattices studied, and in all space dimensions $d \gtrsim$ > or = 3. An accurate treatment is also given of the general site-bond problem. The entire percolation locus for this problem agrees very closely with the results of simulation. We also introduce a new method for studying percolation transitions which is a hybrid of the Kikuchi cluster approximation scheme and the MSA. The method is shown to give extremely good values for percolation thresholds while preserving the valuable features of the standard MSA. In particular, it provides a convenient means of computing the pair connectedness function. We also explore extensions of our approximations to treat directed site and bond percolation.

1. Introduction

Percolation is a phenomenon defined by the formation of macroscopic clusters in a many-body system, given a criterion for pairwise connectedness. It has been studied in recent years from at least two different points of view. Those studying percolation as a particularly accessible, geometrical analog of a phase transition seek an accurate method to locate the percolation threshold and to study the scaling behavior of physical quantities in its vicinity. On the other hand, those who want to study the influence of percolation on bulk material properties and transport processes in disordered materials and liquids want an account of various key quantities that describe clustering, such as the average coordination number of a particle and the mean cluster size, throughout the entire range of system parameters. An approach that addresses both classes of problems is that based on the solution of integral equation approximations for the two-point connectedness function. Several such integral equations have been derived and solved, both for continuum and lattice percolation.[1-8]

One such integral equation approximation which has been studied for various continuum percolation models is the Ornstein-Zernike equation with closure provided by the mean spherical approximation (MSA). This approximation was originally developed[9] for nearest-neighbor thermal spin models and their equivalent lattice-gas analogs. It was subsequently generalized[10] to longer-range lattice models and to continuum fluid models. The MSA for a continuum system of particles at thermal equilibrium can be defined by the equations

$$\begin{aligned} h(x_{12}) &= -1 \qquad && x_{12} \leq a \\ c(x_{12}) &= -\beta v(x_{12}) \qquad && x_{12} > a \end{aligned} \tag{1.1}$$

Here, $h(x_{12})$ and $c(x_{12})$ are, respectively, the full correlation function and the direct correlation function between particles at the vector positions $\vec{x}_1$ and $\vec{x}_2$. Here, $x_{12} = |x_1 - x_2|$ is the scalar distance between such particles, $v(x_{12})$ is their pairwise potential energy, and $\beta = (kT)^{-1}$, where T is the absolute temperature, and k is Boltzmann's constant. The distance a is the distance of closest approach fixed by a hard-core potential which is part of the pairwise interaction. The MSA has been used profitably[11] to treat a wide variety of thermal problems. A major benefit of this approximation is that the resulting equations, e.g., for the equation of state, can be solved analytically for many models of interest.

Recently[4] the MSA was extended to relate the two-point connectedness function $h_c(x)$ and the direct connectedness function $c_c(x)$ of the random sphere percolation model. This is a model of randomly placed spheres which are taken to be directly connected if their pairwise separation is less than a fixed distance a, the sphere diameter. For this model, the MSA is equivalent to the Percus-Yevick, which was first suggested by Coniglio et al[5] in work that extended the cluster- expansion treatment of $h_c(x)$ by Hill.[6] More general models have been introduced by considering systems of particles in thermal equilibrium interacting via a pair potential $\phi(x)$, which introduces correlation between the centers of particles (if one sets $\phi(x) = 0$ the model reduces to the random sphere percolation model). A number of such continuum systems of interest can be solved exactly in the MSA.[7-9] ***** It is also natural to apply the MSA to the functions $h_c(x)$ and $c_c(x)$ in lattice percolation models. A recent study of MSA for lattice site percolation by Hoye and Stell[6] found that both the percolation threshold and critical exponents for percolation on certain lattices in three and higher dimensions are predicted accurately. In this paper, we extend that study by using certain general methods of MSA type to investigate lattice bond and site-bond percolation. The critical exponents are found to be the same as in site percolation, as one expects, while the bond percolation threshold is predicted with remarkable accuracy on all lattices studied, and in all dimensions $d \geq 3$. In this paper, we will work with a very general class of approximations of mean spherical type. These approximations, in general, define a closure of the Ornstein-Zernike equation by providing a pair of assumptions corresponding to the two given in (1.1). In general:

1. The volume surrounding each lattice site is divided in two by choosing a sphere that surrounds that site. The value of the pair correlation function (either $h(x)$ or $c(x)$ can be used), giving the interaction of a site with other sites inside the chosen sphere, is provided explicitly, either by the constraints of the model itself, or by some other approximation. Many approximation schemes provide such values for correlation functions at small separation.

2. The interaction with lattice sites outside the sphere is described by giving an approximate form, for large separation, of the direct correlation function $c(x)$. In the original MSA, as given by (1.1), the radius of the sphere in the scheme just described is taken to be the exclusion radius, defined as the range of the hard-core part of the potential, and the closure is specified at small separation by giving the values of $h(x)$ inside the exclusion sphere. We note that the scheme just outlined has obvious similarities with the effective medium approximation (EMA).[13,14] It also has basic differences; for example, it gives, in general, critical exponents that are non-classical.

This paper is organized as follows: in section 2, we review the general procedure for solving the MSA for thermal lattice models. We illustrate the use of MSA-like approximations by applying these to the Ising model. In section 3, we discuss the relation between thermal models and percolation models in order to identify natural extensions of the MSA framework to percolation. We review the earlier treatment of site percolation. Appropriate variants of the MSA are then applied to both bond and site-bond percolation. In Section 4, we discuss the use of the Kikuchi cluster approximation to obtain the short-distance values of $h(x)$ needed to complete an MSA-like closure. In Section 5, we apply MSA-like approximations to directed site and bond percolation models. Section 6 discusses the present limitations of the approximations discussed in this paper, and gives suggestions for further research. Section 7 summarizes our conclusions.

2. General MSA Formalism

In this section, we review the general Ornstein-Zernike formalism for lattice models. This formalism is identical for thermal and percolation problems. We illustrate its use by applying it to the nearest-neighbor Ising model, as described in lattice-gas terminology.

The Ornstein-Zernike equation is

$$h(x_{12}) = c(x_{12}) + \rho \sum_{x_3} c(x_{13}) h(x_{32}) \tag{2.1}$$

In this section we use the terminology of thermal physics, in which $h(x_{12})$ and $c(x_{12})$ are, respectively, the full pair correlation function and direct pair correlation function. The sum in 2.1 is over all lattice sites. We note that the function $h(x)$ and other functions defined on a lattice depend upon a vector which we denote as x or x_{ij}, this is the separation of sites i and j. An equation identical to (2.1), but with different boundary conditions, governs the relation between the pair connectedness function, given by $g_c(x) = h_c(x) + 1$, and direct connectedness function $c_c(x)$, in a percolation model. This will be discussed in detail in the next section.

We indicate the Fourier transform of a function, e.g. $c(x)$, by placing a caret over the corresponding function symbol. Thus we have

$$c(x) = \frac{\Omega}{(2\pi)^3} \int \hat{c}(k) e^{-ik\cdot x} d^3k \tag{2.2}$$

Here the integral over wave number k is over a single Brillouin zone of the lattice. Also, Ω is the volume of the Wigner-Seitz cell associated to a single lattice site; it is here normalized to unity. Taking the Fourier transform of both sides of (2.1) allows an algebraic solution for $\hat{h}(k)$ in terms of $\hat{c}(k)$:

$$\hat{h}(k) = \frac{\hat{c}(k)}{1 - \rho\hat{c}(k)} \tag{2.3}$$

The strategy for solving (2.1) is this: since $c(x)$ is assumed to be short-ranged, $\hat{c}(k)$ can be written explicitly in terms of a small number of unknown constants, namely the different values of $c(x)$ which are non-negligible. Substituting an assumed form for $\hat{c}(k)$ in (2.3) and Fourier- transforming then gives a solution for $h(x)$. Boundary conditions and constraint conditions specify the remaining constants in the solution. These conditions contain the physical assumptions specific to the model being studied.

Specifically, for the problems of interest in this section, we assume that $c(x_{12})$ is nonzero only if x_{12} is either zero or equal to a nearest-neighbor lattice vector, in which cases $c(x)$ takes the values c_0 and c_1, respectively. Substituting this information in the transform inverse to (2.2) then gives, for hypercubic lattices

$$\hat{c}(k) = c_0 + 2c_1 \sum_{i=1}^{d} \cos k_i a \tag{2.4}$$

Here a is the lattice spacing and d is the dimensionality of the lattice.For the sake of algebraic simplicity, we specialize our discussion to hypercubic lattices and will work, unless otherwise stated, with the three-dimensional simple cubic (SC) lattice. The discussion of this paper applies, however, to general Bravais lattices.

Taking the Fourier transform of (2.3) and adding to both sides the identity

$$\delta_{x,0} = \frac{\Omega}{(2\pi)^3} \int \frac{1 - \rho\hat{c}(k)}{1 - \rho\hat{c}(k)} e^{-ik\cdot x} d^3k \tag{2.5}$$

then gives

$$\delta_{x,0} + \rho h(x) = \frac{\Omega}{(2\pi)^3} \int \frac{1}{1 - \rho\hat{c}(k)} e^{-ik\cdot x} d^3k \tag{2.6}$$

Using (2.4) for $\hat{c}(k)$ allows us to rewrite the denominator of the RHS as

$$1 - \rho\hat{c}(k) = z\rho c_1 \left[(1 + K^2) - d^{-1} \sum_{i=1}^{d} \cos k_i a \right] \tag{2.7}$$

Here z is the coordination number for the lattice, and the quantity K^2 is given by the expression

$$\begin{aligned} K^2 &= z\kappa^2 \\ &= \frac{1 - \rho c_0 - z\rho c_1}{\rho c_1} \end{aligned} \tag{2.8}$$

Substituting (2.7) into (2.6) gives

$$\begin{aligned} \delta_{x,0} + \rho h(x) &= \frac{1}{z\rho c_1} \frac{\Omega}{(2\pi)^3} \int \frac{e^{-ik\cdot x}}{(1 + \kappa^2) - d^{-1} \sum_{i=1}^{d} \cos k_i a} d^3k \\ &\equiv \frac{zG(x)}{z\rho c_1} \end{aligned} \tag{2.9}$$

This last equation defines $G(x)$, which can be identified as the Green's function of the lattice version of the Helmholtz wave equation with wavenumber $K^2 = z\kappa^2$. This function occurs frequently in mathematical physics and has been tabulated.[15,16] We note in particular that for $\kappa^2 = 0$, the function $zG(x)$ is the generating function for random walks on the lattice being studied.

We digress briefly to justify our identification of κ, as defined by (2.8), with the inverse correlation length. For convenience, define $\chi(x) \equiv \delta_{x,0} + \rho h(x)$. Then we have

$$\begin{aligned} \frac{\hat{\chi}(0)}{\hat{\chi}(k)} &= \frac{1+\rho\hat{h}(0)}{1+\rho\hat{h}(k)} \\ &= \frac{1-\rho\hat{c}(k)}{1-\rho\hat{c}(0)} \end{aligned} \tag{2.10}$$

where the second step uses the Ornstein-Zernike equation (2.3). Expanding the RHS of (2.10) in powers of k^2 and substituting (2.4) gives

$$1 + \Lambda_2(ka)^2 + O[(ka)^4] \tag{2.11}$$

with k^2 the norm squared of the vector k and Λ_2 defined by

$$\Lambda_2 = \frac{\rho c_1}{1-\rho\hat{c}(0)} \tag{2.12}$$

For simple hypercubic lattices, Λ_2 can equivalently be identified as[17,18]

$$\Lambda_2 = \frac{\sum_x x^2\chi(x)}{\sum_x \chi(x)} \tag{2.13}$$

That is, Λ_2 is the second spherical moment of the quantity $\chi(x)$ divided by its zeroth moment. To see this, write $\chi(x)$ in terms of its Fourier transform, replace the factors of x with k-derivatives, and note that (2.11) is a Taylor series. Direct comparison then shows that $z\Lambda_2 = \kappa^{-2}$, with κ^2 defined by (2.8). The singular part of the susceptibility near a critical point is proportional to the volume integral of $h(x)$, i.e., to $\hat{h}(0)$. According to (2.3), we can then identify such a point by the condition

$$\rho\hat{c}(0) = 1 \tag{2.14}$$

Note that by (2.8), this is equivalent to the condition $\kappa^2 = 0$. Also, it is reasonable to identify Λ_2 with the square of the correlation length and thus identify $\kappa^{-2} = \xi^2$. The correlation length defined in this manner has the same critical behavior as that based on the assumption that $h(x)$ decays exponentially; the former definition is however more generally applicable. For example, even when $h(x)$ has algebraic decay, as it will when $c(x)$ does, this definition is still applicable, providing that the second moment of $c(x)$ exists.[11a]

Several further relations are useful for the general discussion of critical behavior as described by the Ornstein-Zernike equation. To develop these, we write G_0 and G_1, respectively, for the values of the Green's function $G(x)$, defined by (2.9), evaluated for a lattice displacement vector equal, respectively, to zero, and to the vector difference between a pair of nearest neighbors. We can specify these displacement vectors as $x = 0$, and $|x| = a$, respectively. Note that this causes no ambiguity because, by symmetry, $G(x)$ takes the same value for all nearest neighbor displacement vectors. In the special case that $\kappa^2 = 0$, which defines the critical point, we write these same quantities as $\bar{G}_0$ and $\bar{G}_1$, respectively. Similarly, the values of $h(x)$ at $x = 0$ and $|x| = a$ are written h_0 and h_1, respectively. Setting $|x| = a$ in (2.9) then gives

$$\frac{zG_1}{z\rho c_1} = \rho h_1 \tag{2.15}$$

Dividing (2.9) for $x = |a|$ by the same equation, with $x = 0$, gives

$$\frac{zG_1}{zG_0} = \frac{\rho h_1}{1 + \rho h_0} \tag{2.16}$$

Finally, we can relate G_0 and G_1, for a SC lattice, by using the identity

$$\frac{\Omega}{(2\pi)^3} \int \frac{d^{-1} \sum_{i=1}^{d} \cos k_i a}{(1 + \kappa^2) - d^{-1} \sum_{i=1}^{d} \cos k_i a} e^{-ik\cdot x} d^3 k = zG_1 \tag{2.17}$$

(A similar identity holds for any lattice.) This follows directly by using the symmetry of a Bravais lattice and the definition of G_1. This gives directly, using (2.5) and (2.9)

$$(1 + \kappa^2) zG_0 - zG_1 = 1 \tag{2.18}$$

This relation can be used to eliminate G_1 from (2.16) and give a basic relation for the critical point:

$$\frac{z\bar{G}_0 - 1}{z\bar{G}_0} = \frac{\rho h_1}{1 + \rho h_0} \tag{2.19}$$

We note that the lattice-gas density ρ occurs explicitly only in the combinations ρc_0, ρc_1. Two further constraints must now be supplied to completely specify an MSA-like closure of the Ornstein-Zernike equation. In standard applications of the MSA to pair correlation functions, these are chosen to be the vanishing of the correlation $h(x)$ inside the interaction hard core, and the equation $c(x) = -\beta v(x)$ outside this core. Here $v(x)$ is the interparticle potential and $\beta = 1/kT$. The second of these equations is a "linear response" high-temperature approximation; it is exact to first order in β and the potential $v(x)$. For the Ising model, this implies $h_0 = -1$ and $c_1 = K$ where $K = -\beta J_{LG}$ and J_{LG} is the lattice-gas coupling constant, related to the Ising model coupling constant J_{ISING} by

$$J_{LG} = 4J_{ISING} \tag{2.20}$$

Substituting these relations into (2.15) and (2.19) then gives the condition for criticality

$$\rho(1-\rho)K_{crit} = \bar{G}_0 \tag{2.21}$$

Because we consider the high temperature, zero-field, Ising model only, we have, for the lattice-gas density, $\rho = 0.5$. Thus

$$K_{crit} = 4\bar{G}_0 \sim 1.08 \tag{2.22}$$

for the three dimensional simple cubic (SC) lattice. This should be compared with the value $K_{crit} = .840$ given by the second Bethe-Peirls approximation for this lattice, and also with the value $K_{crit} = .918$ given by high-temperature series analysis,[19] which represents the most precise means available for estimating such quantities.

We derive a variant of this approximation if we recall the definition of $c(x)$ as the direct correlation function and write the low-density approximation

$$\begin{aligned} c(x) &= f(x) \\ &= e^{-K} - 1 \end{aligned} \tag{2.23}$$

This approximation is exact to first order in the lattice-gas density; i.e., it is the first term in the Mayer expansion. Using c_1 from (2.23) gives the criticality condition

$$K_{crit} = -\ln[1 + 4\tilde{G}_0] \tag{2.24}$$

which implies $K_{crit} = .732$. Thus for the SC Ising model in three dimensions, the estimates for the critical point given by the high-temperature approximation (2.22) and the low-density approximation (2.24) are of comparable accuracy. It is (2.22) (or in general the constraint $c(x) = -\beta v(x)$) that has come to be called the mean- spherical approximation (because (2.22) proves to be exact in the mean-spherical and spherical models of a magnetic system.) As we shall see, in some percolation problems, in which $h(x)$ is replaced by the pair connectedness function and $c(x)$ by the direct connectedness function, it turns out that (2.23) (or in general $c(x) = \exp[-\beta v(x)] - 1$) appears to be the more natural and generally useful approximation. This is also found to be the case in studies of continuum percolation.[5]

3. The MSA for Site and Bond Percolation

In this section, we will apply the Ornstein-Zernike formalism of Section 2 to lattice percolation models. First, the case of site percolation is reviewed. We show that a natural approximation for bond percolation reproduces an analytic formula for the critical point that was already shown empirically, by Sahimi[25] and co-workers, to be remarkably accurate. Finally, we give an approximation of MSA type for the general case of random site-bond percolation and reproduce the complete percolation locus for that model.

The formalism of Section 2 can be directly applied to percolation models because these satisfy an Ornstein-Zernike equation of the form (2.1). In particular, one has[2]

$$g_c(x_{12}) = c_c(x_{12}) + \rho \sum_{x_3} c_c(x_{13}) g_c(x_{32}) \tag{3.1}$$

with $g_c(x_{12})$ and $c_c(x_{12})$, respectively, being the connectedness function and direct connectedness function, respectively. The Ornstein-Zernike equation can be taken to be a definition of $c(x)$, and thus has no content, per se. However, we focus here on the 'derivation' of this equation from other formulations that permit a more direct estimate of the value of $c(x)$ and $h(x)$ for small separation. This is valuable because, in any case, one needs an independent representation for $c_c(x)$, or an independent second relation between $h_c(x)$ and $c_c(x)$ in order to have an closed set of equations for these quantities. Below, we shall refer to both the ρ and β expansions, which facilitate estimation of $c_c(x)$ for small argument. In the case of random or uncorrelated percolation, h_c and c_c are temperature-independent, so that only the ρ expansion is available. We focus in particular on mappings of percolation models onto limiting cases of thermal models; these allow us to draw on our experience with MSA-like approximations for the latter. Such mappings allow us to exploit the machinery of liquid-state physics. Also, they are essential when thermal correlations are imposed between the sites or bonds of a percolation model.

In the absence of such correlations, one can calculate series for $c_c(x)$ and $g_c(x)$ in purely graph-theoretic terms, using a formulation due to Essam[20] in terms of self-avoiding walks. For example, for pure site percolation one has

$$g_c(x) = \sum_G d(G)\rho^{v(G)} \tag{3.2}$$

where the sum is over one-irreducible, two-rooted subgraphs G of the lattice being studied, $v(G)$ is the number of vertices in the graph G, and $d(G)$ is a purely combinatoric quantity depending only on the graph G. The function $c_c(x)$ is given by a similar expression, but with the sum restricted to non-nodal graphs.[20]

The techniques of liquid-state physics, such as integral equations, Mayer expansions, etc., are most naturally formulated in the continuum, or more precisely, in lattice-free language that applies to both continuum and lattice models. The same is true of the formulation of percolation theory best suited to adapting these techniques, that due to Hill.[1] We sketch this first. Specifically, we write the Boltzmann factor for a thermal model as a sum of two terms:

$$\begin{aligned}\exp[-v(x_{12})] &= \left\{ \exp[-\beta v(x_{12})]p_b(x_{12}) \right\} + \left\{ \exp[-\beta v(x_{12})][1 - p_b(x_{12})] \right\} \\ &= e^{+}(x_{12}) + e^{*}(x_{12})\end{aligned} \tag{3.3}$$

This induces a corresponding separation of the Mayer function

$$f(x_{12}) = f^{+}(x_{12}) + f^{*}(x_{12}) \tag{3.4}$$

with $f^{+} = e^{+}$ and $f^{*} = e^{*} - 1$. The function $p_b(x_{12})$ defines the separation-dependent probability of a bond between two particles. Its choice is dictated by the physical phenomenon to be modelled. The first term in (3.2) is identified with the particles being directly connected, the second with them not being directly connected. Substitute the sum (3.4) for each Mayer bond in the virial expansions of $h(x_{12})$ and $c(x_{12})$, and expand each Mayer graph into subgraphs whose lines correspond to f^{+} or f^{*} bonds. Define[2,21] the connectedness function $g_c(x_{12})$ to be the sum of all such subgraphs in the expansion of $h(x)$ in which the root points are joined by a chain of f^{+}-bonds; the blocking function $g_b(x_{12})$ is the sum of all the remaining subgraphs. Similarly, one defines the direct connectedness function $c_c(x)$ to be the sum of the corresponding subgraphs contributing to $c(x)$; this is equivalent to the set of subgraphs contributing to $g_c(x)$ that in addition have no nodal points. These definitions are compatible with (3.1). Thus the correlation function has been written as the sum

$$h(x_{12}) = g_c(x_{12}) + g_b(x_{12}) \tag{3.5}$$

of the two-point connectedness function and two-point blocking function. One can show[21] that $g_c(x_{12})$ as defined above formally is in fact the two point connectedness function for a many-body system of particles having correlation function $h(x)$ and density ρ, and being pairwise- connected with separation-dependent probability $p_b(x)$. The connectedness function $g_c(x_{12})$ is the probability distribution associated with finding particles at x_1 and

x_2 in the same connected cluster. Similarly, $g_b(x_{12})$, the two-point blocking function, is the corresponding probability distribution associated with the particles at x_1 and x_2 being in different clusters. We note that our probability-density definition of $g_c(x)$ and the corresponding definition of $c_c(x)$ induced by (3.1) are not dependent on the density series expansions of these quantities; the latter are not fully general. One expects such series to represent $g_c(x)$ and $c_c(x)$ only for ρ and β that characterize non-percolating states; as yet only partial results are available[7,23] for their radii of convergence. We note that, in general, one cannot give a separate physical interpretation in terms of probability densities, of $c_c(x)$, because, unlike $g_c(x)$, it need not be positive definite.

The expansion procedure of Hill can be carried out automatically by using the isomorphism[23] between percolation and the one-state limit of the s-state Potts model. Specifically, the one-state limit of a continuum Potts model[8] with interparticle potential

$$V_{ij} = \phi(x_{ij}) + v(x_{ij})[1 - \delta_{\sigma_i \sigma_j}] \tag{3.6}$$

gives a correlated continuum percolation model with interparticle potential $\phi(x)$ and separation-dependent bond probability $p_b(x)$. If one develops Mayer expansions for the thermodynamic quantities of the model defined by (3.6), and applies the operator $\frac{d}{ds}|_{s=1}$ to them, they yield the basic quantities in the description of the corresponding percolation model. This procedure provides a realization of the general percolation process described below (3.5), with each pair of particles connected with a separation-dependent bond probability given by

$$p_b(x) = 1 - \exp[-\beta v(x)] \tag{3.7}$$

with $v(x)$ as in (3.6). If we write the Ornstein-Zernike equation (2.1) for the specific case of the s-state Potts model, takes the $s \rightarrow 1$ limit and, using identities[8,21]

$$h(x_1, \alpha, x_2, \beta) \rightarrow -g_c(x_{12}) \tag{3.8}$$

$$c(x_1, \alpha, x_2, \beta) \rightarrow -c_c(x_{12}) \tag{3.9}$$

we recover the equation (3.1). Here α and β are any two different spin states.

When we restrict the continuum Potts model to a lattice, by imposing the added restriction that particles only occupy positions whose coordinates are integers, the result is a Potts lattice gas[24] whose one state limit is a very general percolation model. Before doing this, we add to the potential $\phi(x_{ij})$ in (13.6) delta-function potential interaction that prevents overlap of two lattice gas particles, and thus of two sites in the resulting percolation model. We then set the function $p_b(x)$ equal to p_b, a nearest-neighbor bond probability for $|x| = a$, and equal to zero for $x \neq a$. The lattice site and bond percolation models are given by special cases $p_b = 1$, and $\rho = 1$, respectively.

The simplest percolation models are directly related to thermal lattice models. For example, pure bond percolation is the $s \to 1$ limit of the s-state lattice Potts model. Site percolation is the zero-temperature limit of a site-dilute Ising model.[31] It can also be realized as the one-state limit of a Potts model containing multi-site interactions.[31] However, the former mapping seems not to be useful in this context, and the latter has not yet been exploited in this context because of its complexity.

We now use these mappings to construct MSA-like approximations for specific percolation models. We will use the same terminology as in Section 2, but by h_0, h_1, we will mean $g_c(x)$ evaluated at $x = 0$ and $|x| = a$, respectively. Similarly, by c_0, c_1, we denote $c_c(x)$ for $x = 0$ and $|x| = a$, respectively. Site percolation models have already been studied using the MSA[6] approach. In this case it is natural to choose

$$\begin{aligned} h_0 &= 0 \\ h_1 &= 1, \end{aligned} \tag{3.10}$$

the former because we must forbid multiple occupation of sites, as just discussed, and the latter because neighboring occupied sites are always connected. Substituting (3.9) into (2.19) gives the critical site density for percolation

$$\rho_{crit} = \frac{z\tilde{G}_0 - 1}{z\tilde{G}_0} \tag{3.11}$$

This is found numerically to be a good approximation in general.[6]

For hypercubic lattices, the MSA just described gives p_c to high accuracy for $d \geq 4$. However, in three dimensions, the scheme gives $p_c = .341$, where series analysis gives $.312 \pm .003$.[30] This discrepancy indicates that an optimal MSA for site percolation has yet to be found. We note that the effective medium approximation (EMA)[13] for the conductivity of a site-disordered resistor lattice has similar difficulties. The EMA is very similar in spirit to the hybrid approximations to be discussed next. Although this scheme gives excellent approximations in two dimensions, it also predicts[14] a three dimensional site percolation threshold which is too low by 10%.

As already discussed, continuum percolation has many similarities to site percolation as well as bond percolation. Thus the difficulty just discussed may also account for the need to add correction terms[3,5] to the naive MSA for random continuum percolation in order to recover a good estimate of the critical point in this model. These matters are under investigation.

In the case of bond percolation, we keep the first equation of (3.10), but must modify the second. One possibility is to follow the intuitive notion that the direct connectedness function $c(x_{12})$ should be the probability density associated with having a direct bond between the sites at x_1 and x_2

$$c_1 = p_b \tag{3.12}$$

Using the Potts-model correspondence, and keeping only terms to first order in ρ also gives this approximation. This form of the the MSA is appropriate in conditions of low bond-density; in terms of the related Potts model, p_b is also a "high-temperature" expansion variable (see e.g. 3.7). Also, we set $\rho = 1$ because all sites are occupied in bond percolation. This gives for the bond percolation threshold

$$(p_b)_{crit} = \tilde{G}_0 \tag{3.13}$$

Sahimi et.al.[25] noted from numerical comparison that this relation provided an extremely good approximation for all regular lattices, and in all dimensions $d \geq 3$. It is very satisfying that an intuitively reasonable form of the MSA gives just this result. Table 1 shows the quality of the estimate (3.13) for a variety of three-dimensional lattices, as well as hypercubic lattices in higher dimensions.

We could have instead made the approximation

$$c_1 = K \tag{3.14}$$

where K is defined by the correspondence between the Potts model coupling constant, and the bond probability in the percolation model which is its one-state limit:

$$p_b = 1 - e^{-K} \tag{3.15}$$

In other words, if we very formally attempt to treat bond percolation as if it were a thermal model (remembering the Potts-model correspondence), we would be led to try the high-temperature approximation (3.14). This gives the critical condition

$$(p_b)_{crit} = 1 - \exp(-\bar{G}_0) \sim .223 \tag{3.16}$$

This should be compared with (3.13), which gives a value of .252, and the existing series analysis results, which give $.249 \pm .0002$. Thus (3.16) is a reasonable approximation, but it lacks the remarkable accuracy of (3.13). A similar result is found[5] in studies of continuum percolation, where a form for $c(x)$ must be assumed over the entire range of values for which $v(x)$ is nonzero. In that case also, the low-density ansatz (3.12) is found to give a prediction for the threshold which is numerically superior to the high-temperature ansatz (3.14).

We make the observation that approximations for the short-range values of $c(x)$ would be better motivated if in fact that quantity were a probability density; in fact, it seems never to be positive definite. This can be easily checked for the problems studied here because $c(x)$ takes only two values, c_0 and c_1. For both pure site and pure bond percolation, it is always found that for any lattice studied that $\rho c_1 > 0$ and $\rho c_0 < 0$. If this were not true, then critical percolation, in the MSA, would be directly isomorphic to a random walk model[26,27] defined by transition probabilities ρc_0, ρc_1. However, since having a nonzero value for c_0 simply rescales the time coordinate describing the progress of a random walk, one can always rescale the other nonzero values of c_i by $(1 - \rho c_0)$ and get a physically realizable random walk. In fact, we can rewrite the basic equation (2.15) in a way that is applicable to MSA-like approximations in which $c(x)$ is not assumed to vanish for $x > 1$:

$$\frac{zG_1}{(1 - \rho c_0)} = \rho h_1 \tag{3.17}$$

The existence of this formal equivalence is seen to be a general fact about all mean spherical approximations, even those for anisotropic or directed models, as we discuss in Section 5. However, in general, the coefficients c_i oscillate in sign, thus higher-order approximations do not give realizable walks. We note that the normalization condition for the transition rates in such a random walk is just the criticality condition for the model being studied. (see e.g.2.14).

Since the MSA gives a good approximation to the threshold for both pure site and pure bond percolation, it is natural to use it to study the general site-bond percolation model, in which a cluster is defined to be a group of occupied sites connected by occupied bonds. As before, there are several natural approximations that one can use to close the Ornstein-Zernike equation. Note that (3.11) is, a priori, just as reasonable an assumption in the general site-bond problem as in the pure bond problem. Using it in the general problem, however, gives a percolation locus in the (ρ, p_b) plane defined by

$$\rho p_b = \tilde{G}_0 \tag{3.18}$$

which, e.g., in the case of pure site percolation, is immediately seen to be a very poor approximation.

Thus, we instead approximate h_1 by enumerating the smallest graphs that contribute to it, i.e., the smallest bond sets that join two sites that are nearest neighbors. This is equivalent to using the Potts lattice-gas mapping described below (3.8) and calculating the Mayer expansion of that model. On the simple cubic lattic, considering just the two graphs of Figure 1 gives

$$\begin{aligned} h_1(\rho, p_b) &= p_b + (1-p_b) * \left[1-(1-\rho^2 p_b^3)^6\right] \\ &\sim p_b + (1-p_b) 6\rho^2 p_b^3 + O(\rho^4) \end{aligned} \tag{3.19}$$

This approximation for h_1 is exact for site percolation, and gives, for bond percolation, the critical value $(h_1)_{crit} = .258$, whereas the approximation based on (3.11) gives .252 for the same quantity. The percolation locus in the (ρ, p_b) plane as given by the approximation (3.16) is shown in Figure 2. This locus has been obtained by simulation in both two dimensions[28] and three dimensions.[29] The critical locus given by substituting (3.19) in (2.19) is found by calculating the critical site density ρ, for a specific value of p_b, by using the Newton-Raphson method. This approximation is already of high quality and can easily be improved by adding terms, except for the part of the phase plane near the pure site percolation limit; we discuss this problem further in Section 5. It is worth noting that many different schemes are available for estimating the quantity h_1 in both thermal and percolation models. In particular, the method of Kikuchi[31] involves assuming a functional form for the free energy which contains as parameters the values of $h(x)$ for small separation x, and mimimizing this functional to determine these quantities. We discuss this class of approximations in the next section.

4. Hybrids of the Kikuchi Cluster Approximation and MSA

In Section 3, we showed that one can obtain good estimates for phase transition loci from MSA-like approximation schemes if reasonable estimates are available for values of the correlation functions at short-range. In this section, we explore the possibility of using the Kikuchi cluster variational method (CVM)[31] to determine these. In order to complement our discussion in Section 3 of the basis of an MSA approach to percolation models, we also obtain directly a Kikuchi CVM for bond percolation, by using the Fortuin-Kastelyn mapping[23] between percolation and the Potts model. We compare the direct estimates of the critical bond probability given by this method with hybrid estimates given by using the structural information from this method as input to MSA-like approximations. The hybrid estimates are found to be superior. The cluster variational method(CVM), first systematically developed by Kikuchi[31], involves several steps. We outline these here, restricting our discussion to the Ising-like spin models for which the theory was originally developed:

1. Because Ising variables take discrete values, the various small clusters of contiguous spins (pairs, triplets, etc.) can take on only a finite number of possible configurations. After specifying a set of small clusters to serve as a basis set, one chooses as working variables the probabilities of occurrence of each possible configuration of these clusters. If the basis set consists of only one cluster, a nearest-neighbor pair, the corresponding occurrence probabilities are just the values of the spin-spin correlation function at nearest-neighbor separation. We note that these variables are exactly the quantities needed in the MSA-like approximations discussed in this paper. Direct use of these values yields the well-known Bethe approximation.[24]

2. In terms of the working variables, one writes a consistent approximation for the free energy of the system. Requiring that this expression be minimized with respect to the working variables then gives a set of constraint equations to determine the values of the working variables as functions of the system parameters (temperaure, magnetic field, etc.)

3. One can then determine an approximation for the critical point, by requiring that the symmetry-breaking variables display power-law behavior as the singularity is approached.

Instead of following this last step to determine the location of the critical point one can instead use the following hybrid method: use the functional expressions for values of the two-point correlation function at small separation as input to the MSA-like approximations discussed in Section 3. Specifically, the CVM will give expressions for the quantities h_0

and h_1 in the equation

$$\frac{\rho h_1}{1+\rho h_0} = \frac{z\bar{G}_0 - 1}{z\bar{G}_0} \tag{4.1}$$

as given by the MSA. We remark that it is not clear a priori that this method of determining the critical point will be successful, as no single consistent expansion scheme has been employed. For example, the numbers used to evaluate the RHS of (4.1) are obtained by setting $c(x)$ to zero for $|x| > a$; this type of low-density approximation is not a priori consistent with use of an extremely accurate value of h_1.

The algebra involved in realizing the program outlined above has been detailed in the beautiful paper of Kikuchi[31a] and will not be repeated here. We follow the notation used in that paper and merely give the results of our calculations. The variable h_1 used in Section 2 to describe nearest-neighbor values of the Ising model correlation function is related to Kikuchi's variable y_1 by $h_1 = 4y_1 - 1$. If we use the lowest-order CVM, in which the only cluster in the basis set is a nearest-neighbor pair, the result is

$$h_1 = \frac{H^2 - H^{-2}}{6 - H^2 - H^{-2}} \tag{4.2}$$

with $H \equiv \exp[K_{ISING}]$. This result was calculated for a two-dimensional Ising model, but at this low level of approximation, it is entirely consistent to use the relation

$$6K^{(3D)}_{ISING} = 4K^{(2D)}_{ISING} \tag{4.3}$$

noting that the Bethe approximation per se depends only on the combination zK, where z is the coordination number. Substituting (4.2) into (4.1) gives a critical point located at $K_{crit} = .779$, as compared with the value $K_{crit} = .918$ given by series analysis. This is slightly better than the value $K_{crit} = 1.099$ given by the direct Kikuchi method at the same level of approximation. An improved treatment which makes explicit use of the 3D nature of the lattice[31a] gives

$$h_1 = \frac{\phi^2 - 1}{\phi^2 + 6\phi + 1} \tag{4.4}$$

where the auxilliary variable ϕ is defined implicitly by

$$\begin{aligned} H^2 &\equiv \exp[\frac{1}{2}K_{LG}] \\ &\equiv \frac{1}{\phi}\left[\frac{3\phi+1}{\phi+3}\right]^3 \end{aligned} \tag{4.5}$$

Substituting (4.4) into (4.1) gives $K_{crit} = .926$, which is an extremely good approximation!

In order to apply the same approximation scheme to percolation models, we first develop the Kikuchi cluster approximation for bond percolation. Kikuchi[31] applied his method to site percolation by noting that it is equivalent to the zero-temperature Ising model. He treated bond percolation as site percolation on the corresponding alternate lattice. For many common lattices, e.g, the simple cubic latice, this requires an enlarged primitive cell and, presumably, requires including larger clusters in the basis set to give results of comparable accuracy to that obtained for site percolation. We proceed instead by calculating $K_{crit}(s)$ using the CVM for a dilute s-state Potts model, then taking the one-state limit as described in Section 3. Using the Bethe approximation for the two-dimensional square lattice gives for the bond percolation threshold $p_b = .4226$, as compared with the exact result $p_b = .5$. Here we used the correspondence (3.15) between the Potts-model coupling and bond probability.

We now estimate the three- dimensional bond percolation transition by using a procedure parallel to that used above for the Bethe approximation to the Ising model. First we use the direct Kikuchi procedure just described which is based on the Potts-model mapping. Using the scaling $6K_{crit}^{(3D)} = 4K_{crit}^{(2D)}$ as above gives $p_b = .231$ for the transition point in a simple cubic lattice, as compared to the value .252 given by series methods. We now instead use the functional form for the nearest-neighbor connectedness function, as given by the Kikuchi method just described, as input to the MSA defined by (4.1). The Bethe approximation for the Potts-model variable y_1, which is the probability that a nearest-neighbor pair are in different spin states, is given by

$$y_1 = 1./[s + s(s-1)\exp(-2K)] \tag{4.6}$$

We obtain the nearest-neighbor connectedness function h_1 for bond percolation by using the correspondence (3.8) and the relation $h_1 = 4y_1 - 1$. Using the result in the MSA as before gives a critical bond probability $p_b = .242$, a substantially more accurate result.

As a more involved illustration of this hybrid Kikuchi-MSA method, we consider the Wannier approximation, in which the nearest-neighbor pair and elementary plaquette, or square, are taken to be basic clusters. It seems quite difficult to use the direct Kikuchi method described above, in which one first applies the cluster variational method to the s-state Potts model, then takes the one-state limit, as a means for locating the percolation critical point. Indeed, if the spins in the basic clusters are allowed to be in any of s states, with one of the states distinguished as the symmetry-breaking state, there are 20 different configurations of these clusters (see Figure 3). Locating the critical point then involves finding the determinant of a matrix of rank 20. We note in passing that Kikuchi's method[31] of realizing bond percolation as site percolation on an alternate lattice is easily seen to lead to an equally large variable set. The hybrid MSA technique developed in this section is readily applied to this model, however. Since the one-state limit of the Kikuchi method is of some interest in its own right, we describe it in Appendix A. Here we sketch the procedure and discuss the results of using it. After setting the number of states s equal to one, the values of the configuration variables in the symmetric state are quickly obtained. We derive an expression for the pair configuration variable y_{12} as a function of bond density, along with the corresponding form for h_1. Substituting this into the MSA equation (4.1) gives a percolation critical point at bond density $p_c = .249$. This is in remarkable agreement with the best series estimate,[32] $p_c = .249 \pm .0002$!

5. MSA-Like Approximations for Directed Percolation

In this section we apply the class of MSA-like approximations discussed in this paper to directed site and bond percolation models.

In order to gain some perspective on the strengths and limitations of the methods discussed in this paper, we use them to calculate the two-point connectedness function, and the location of the critical point, in directed percolation models. We can define these in general as follows: a distinguished direction is chosen in the space occupied by the lattice being studied. This direction may or may not coincide with one of the principle axes of the lattice. When a vector in this preferred direction is projected onto the bonds of the lattice it induces in them an allowed direction of passage. In the convention adapted here, bonds which are orthogonal to the preferred vector remain non-oriented and thus allow two-way passage or connection. Models containing a class of such bonds will then be called partly directed percolation models. This construction is motivated by one of the basic classes of applications for directed percolation models: transport through random or two-phase materials under the influence of a uniform gradient or bias field. A given lattice may then yield a number of different directed or partly directed models depending on the preferred direction chosen. In terms of MSA-like methods, these models differ from isotropic models in one basic way: random walks on the corresponding lattices either allow only a very restricted class of closed paths, or allow no such paths. The importance of this fact will be explored further when we discuss the results of this section in general terms. Here we focus on developing specific MSA-like approximations.

We may directly adapt the methods already developed to treat directed percolation as regular percolation on a lattice with peculiar conductivity properties. Specifically, we make equations (2.9) and (4.1) the basis of our treatment. The latter will be used unchanged, while for the SC directed lattice (with the (1,1,1) vector the preferred direction), the equation (2.9) becomes

$$\begin{aligned}\delta_{x,0} + \rho h(x) &= \frac{\Omega}{(2\pi)^3} \int \frac{e^{-ik\cdot x}}{1 - \rho c_0 - \sum_i c(x_i) \exp(k \cdot x_i)} d^3k \\ &\equiv G(x)\end{aligned} \tag{5.1}$$

Here the sum is over all sites, at positions x_i, for which $c_i \neq 0$. In general, directed percolation models will have two correlation lengths, both of which become infinite at the critical point.[32] We focus here on the value predicted by MSA for the critical point. We calculated n^{th}-order approximations as follows:

1. We assume that the n values of $c(x)$ corresponding to nearest neighbor, next-nearest neighbor, etc., separation are nonzero; for larger separations x we assume $c(x) = 0$. The nonzero values c_i are related by the random-walk representation (5.1) to nonzero values of step fugacities w_i by

$$w_i = c_i \tag{5.2}$$

Here w_1, w_2, etc. are fugacities for steps to nearest-neighbor, next-nearest neighbor, etc., sites. We have used the fact that $c_0 = 0$ for this model; this can be seen by setting $x = 0$ in (5.1).

2. One then solves n equations of form (4.1) for the step fugacities w_i as functions of the (site or bond) density. Here we use explicit, exact formulas for both the connectedness function h_i and the random-walk generating function zG_i. These are readily found because the directed random paths between any pair of points which contribute to these functions are self-avoiding walks, i.e., they lack loops. Also, the number of such walks is small.

3. Substituting the exact fugacities $w_i(\rho)$ into the criticality condition $\sum_i w_i = 1$ then gives a polynomial equation whose smallest positive root is the critical density.

The critical densities given by successive approximations of this type are listed in Table 2. These numbers seem to converge; however, for both site and bond problems, the resulting critical density is lower than the simulation value by about 8%.

6. Limitations of the MSA and Directions for Further Research

In this section, we analyze possible reasons for the failure of MSA-like methods to yield highly accurate percolation thresholds for some systems.

Why do MSA-like methods give substantially better threshold values for bond percolation models than for site percolation models? Of course, the extension of MSA-like methods in the former case is better motivated than in the latter case; this was the purpose of our development of the Potts-model formalism in Section 3. But we need a more basic understanding to extend these methods further. Here we will explore two possible elements in such an understanding.

The dominant singularity in the Mayer expansion of mean cluster size, and other physical quantities that describe bond percolation models, is the physical percolation threshold. This is not true in general for site percolation models; their dominant singularity tends to be located at a negative real value of density. Dominance by unphysical singularities has also been found in the series expansions of directed site models.[32]

We have no general argument that MSA-like approximations will yield a real, positive density as the dominant singularity. However, this is found to be the case with all the approximations studied in this paper. The dominant singularity in the anti-ferromagnetic lattice Potts model lies on the negative real axis. In the MSA, the Potts model for negative density is mapped onto bond percolation at positive density; thus, in the MSA, the dominant singularity of bond percolation occurs at a positive, physical density. We observe the same fact in the MSA-like approximations studied in Section 5. If one plots the singularities of the mean cluster size, which are just the zeroes of the polynomial equation

$$\rho\hat{c}(k=0,\rho)=1 \tag{6.1}$$

one always finds the dominant singularity at a physical density. The unphysical singularities associated with site percolation also cause difficulties in applying other standard methods for studying phase transitions. Dealing with such structures via approximations of MSA type is thus an open problem.

The slow convergence exhibited by the MSA for 3D directed problems can be understood in two complementary ways. We briefly describe both of them. In the direct form of the MSA described in Section 5 for directed percolation models, the connectedness function is represented as a generating function for directed random walks. The MSA, roughly speaking, uses the balance between random walks that return to their starting point and those that do not to capture the balance between the short range and long-range behavior of $g_c(x)$ at criticality. In directed models in which all walks lack recurrences, this balance is missing because only short walks can contribute to the approximations for $g_c(x)$ at small separation.

Equivalently, one can reformulate the problem of calculating the percolation threshold in terms of random walks with recurrence, but in $(d-1)$ dimensions. If a directed 3D percolation cluster is projected onto the plane perpendicular to the preferred direction, each site can be identified with a two-dimensional vector $r_\perp$, its position in the perpendicular plane with respect to the origin of that cluster. Then define[32]

$$\begin{aligned} S(\bar{r}_\perp) &= \int dr_\parallel g_c(r_\parallel, r_\perp = \bar{r}_\perp) \\ &= \int dk_\perp \exp[-ik_\perp \cdot \bar{r}_\perp] \hat{g}_c(k_\perp, k_\parallel = 0) \end{aligned} \tag{6.2}$$

to be the expected number of sites contained in the cluster and located at lateral positions $\bar{r}_\perp$. Proceeding as in Section 3 then shows that $S(\bar{r}_\perp)$ is given by the generating function of a random walk process in $(d-1)$ dimensions. This process occurs, in general, on a directed lattice (for the 3D SC lattice the corresponding process occurs on the 2D directed cyclic trianglular lattice), but involves random walks with nonzero probability of return to the origin. However, this formulation shows that the MSA describes a directed 3D process in terms of a 2D process. Since the MSA is in general inapplicable in two dimensions, this gives another view of the failure of the MSA in this case. From this analysis, however, one expects the MSA to give accurate critical densities for higher-dimensional (> 3) directed percolation.

7. Conclusions

The MSA approach to site percolation has been successfully extended to both bond percolation and general site-bond percolation. The bond percolation threshold given by this method is found to coincide with an analytic estimate already shown to be of high accuracy. For the general site-bond percolation model on the SC lattice, the percolation locus calculated from this approximation agrees quite well with that given by simulation. Better agreement will require a general, reliable method for treating site percolation models, possibly using the corresponding Potts-model mapping.[22]

A class of approximations of MSA type have been applied to directed site and bond percolation models. These approximations give moderate accuracy, but will require basic improvements to give highly accurate predictions. Some reasons for this have been identified.

A major advantage of this approach to percolation is that the resulting integral equations can be solved analytically to give the connectedness function $g_c(x_{12})$. Summing this function over all possible separation vectors x_{12} then gives the mean cluster size. The results described in this paper can be generalized in a number of directions without giving up this advantage. For example, the bond probability, which in this paper was taken to be non-zero only for particles with nearest-neighbor separation, can be taken to have certain, non-trivial, long-range forms while still allowing exact solution for the connectedness function.

It would be valuable to have efficient computational procedures for the accurate determination of $g_c(x_{12})$ in a general correlated percolation problem. The hybrid procedure discussed in Section 4, in which the Kikuchi method is used to calculate the short-range values of $g_c(x12)$, and these are then used in the MSA, shows great promise in preliminary studies reported here. It would be useful to find a direct Kikuchi approximation for bond percolation, so as to eliminate the added algebraic complexity introduced by the Potts-model map, if this is possible.

Also, in some models it may be necessary to use clusters substantially larger than those tractable by analytic means. For these models, an analog to the numerical methods used in the phenomenological renormalization group would be valuable.

These matters are presently under study.

Acknowledgements

We thank the Office of Naval Research for their support of this work.

Appendix A. Four-Site Kikuchi Approximation for h_1

In this appendix, we sketch the Wannier, or four-site, approximation for bond percolation on the simple cubic (SC) lattice.

In the Wannier, or four-site, approximation, the bond and square composed of nearest neighbor sites are chosen as the set of small clusters used as a basis for building up correlations. For a general, s-state Potts model, there are 20 different configurations of the spins in these clusters. These are shown in Figure 3. The variables giving the probability of occurrence of each site, bond and square configuration are denoted by x_i, y_{ij}, and z_{ijkl}, respectively, where the subscripts give the values of the site variables involved. In terms of these variables, the Kikuchi method gives, for the free energy of the system:

$$\begin{aligned} \beta F = {} & (\frac{1}{2}z)K \sum_{i,j} y_{ij}(1-\delta_{ij}) \\ & - \left\{ 9\sum_{ij} [y_{ij}\ln y_{ij} - y_{ij}] - 7\sum_{i} [x_i \ln x_i - x_i] - 3\sum_{ijkl} [z_{ijkl}\ln z_{ijkl} - z_{ijkl}] \right\} \\ & - C\left[\sum_i x_i - 1\right] - \sum_i D_i \left[\sum_j y_{ij} - x_i\right] - \sum_{ij} E_{ij}\left[\sum_{kl} z_{ijkl} - y_{ij}\right] . \end{aligned} \tag{A.1}$$

Here z is the coordination number and K is the Potts coupling constant. The first term in this expression is the energy per spin, the term in curly brackets gives the entropy per spin, and the last three terms incorporate constraints due to the normalization of variables.

The expression (A.1) is minimized under the conditions

$$7\ln x_i - C + D_i = 0 \tag{A.2}$$

$$\frac{1}{2}zK(1-\delta_{ij}) - 9\ln y_{ij} - D_i + E_{ij} = 0 \tag{A.3}$$

$$\sum_{4c.p.} \left[3\ln z_{ijkl} - E_{ij}\right] = 0 \tag{A.4}$$

where the sum in the equation (A.4) is over the four cyclic permutations of $(ijkl)$. It is not difficult to solve these equations in the symmetric phase. In the limit $s \to 1$, the variables with all indices equal take the value unity; in this limit they give the correlations of a non-interacting spin model. The one-state limit of variables whose indices are not all equal is also well-defined, however, and gives the correlation functions of bond percolation.[7,8] For example, the one-state limit of y_{12} gives the nearest-neighbor value of the blocking function; this is the lattice analog of (3.8). This quantity is given by

$$\begin{aligned} y_{12}^3 &= x^4/(1-p_b) \\ &= [3x^2 - 3x^3 + x^4]^3 \end{aligned} \qquad (A.5)$$

where the auxilliary variable $x = \exp[\frac{1}{12}E_{12}]$ with E_{12} the Lagrange multiplier in (A.1). Equation (A.5) determines the nearest-neighbor corelation function $h_1 = 1 - y_{12}$ as a function of the bond density p_b. Substituting this into (2.19) gives, for the bond percolation threshold in the SC lattice, $p_b = .246$, which is in excellent agreement with the series estimate $p_b = .249 \pm .0002$.[25]

References

[1] T. Hill, J. Chem. Phys. **23**, 617, (1955)

[2] A. Coniglio, U. DeAngelis, and A. Forlani, J. Phys. **A10**, 1123 (1977); A. Coniglio, U. DeAngelis, A. Forlani, and G. Lauro, J. Phys. **A10**, 219 (1977)

[3] Y. Chiew and E.D. Glandt, J. Phys. **A16**, 2599 (1983)

[4] T. DeSimone, S. DeMoulini, and R. Stratt, J. Chem. Phys. **85**, 391 (1986)

[5] J. Xu and and G. Stell, J. Chem. Phys. **89**, 1101, (1988)

[6] J.J. Hoye and G. Stell, J. Phys. **A18**, L951 (1985)

[7] J. Given and G. Stell, J. Stat. Phys. **59**, 981 (1990)

[8] (a.) J. Given and W. Klein, J. Chem. Phys. **90**, 1116 (1989); (b.) J. Given, J. Chem. **90**, 5068 (1989); see also the extensive simulation results reported in reference 34.

[9] H.W. Lewis and G.H. Wannier, Phys. Rev. **88**, 688 (1952)

[10] J.L. Lebowitz and J. Percus, Phys. Rev. **144**, 257 (1966);

[11] a) G. Stell, Phys. Rev. **184**, 135 (1969); b) J. Hoye and G. Stell, Adv. in Chem. Phys. **48**, 183 (1981)

[12] Y. Chiew, G. Stell, and E.D. Glandt, J. Chem. Phys. **33**, 761 (1985)

[13] S. Kirkpatrick, Rev. Mod. Phys. **45**, 574 (1973)

[14] G. Ahmed and J.A. Blackman, J. Phys. C **12**, 837 (1979)

[15] A.A. Maradudin, E.W. Montroll, G.H. Weiss, R. Herman, and H.W. Miles, "Green's Functions for Monatomic, Simple Cubic Lattices", (Academie Royale de Belgique, Bruxelles, 1960)

[16] G.S. Joyce, J. Chem. Phys. **12**, 1390 (1971)

[17] M.E. Fisher and R.J. Burford, Phys. Rev. **156**, 583 (1967)

[18] See the appendix and additional remarks on p. 244 in : G. Stell, "Correlation Functions and Their Generating Functionals", in **Phase Transitions and Critical Phenomena**, Vol. 5B, ed. by C. Domb and M.S. Green, (Academic, N.Y., 1972)

[19] G.S. Rushbrooke and H.I. Scoins, Proc. Roy. Soc. (London) **A230**, 74 (1955)

[20] J. Essam, "Percolation and Cluster Size", from *Phase Transitions and Critical Phenomena*, C. Domb and M.S. Green, eds., (Academic Press, N.Y., 1972), p. 230 ff.

[21] J. Given and G. Stell, Physica **A161**, 152 (1989)

[22] F.Y. Wu, Rev. Mod. Phys. **54**, 235 (1982)

[23] C. M. Fortuin and P.W. Kastelyn, Physica **57**, 536 (1972); C. M. Fortuin, Physica **58**, 393 (1972)

[24] A. Coniglio and W. Klein, J. Phys. **A13**, 2775 (1980)

[25] M. Sahimi, B.D. Hughes, L.E. Scriven, and H.T. Davis, J. Phys. **A16**, 167 (1983)

[26] G. Stell, J. Phys. A **17**, L855 (1984)

[27] G. Stell, "Models for Disordered Media, Including Some New Connections Among Composite Media, Fluid State, and Random Flight Theory", Springer Lecture Notes in Math Series, Vol. 1035, p. 347

[28] P. Agrawal, S. Redner, P.J. Reynolds, and H.E. Stanley, J. Phys. **A12**, 2073 (1979)

[29] M. Yanuka, J. Colloid Interface Sci. **134**, 198 (1990)

[30] D.S. Gaunt and M.F. Sykes, J. Phys. **A16**, 783 (1983)

[31] R. Kikuchi, Phys. Rev. **81**, 988 (1951); R. Kikuchi and S.G. Brush, J. Chem. Phys. **47**, 195 (1967)

[32] R. Kikuchi, J. Chem. Phys. **53**, 2713 (1970)

[32] J. Adler, Y. Meir, A. Aharony, A.B. Harris, Phys. Rev. **B41**, 9183 (1990)

[32] K. De Bell and J. Essam, J. Phys. A **16**, 385 (1983); ibid. J. Phys. A **16**, 3553 (1983)

[33] M.F. Sykes, D.S. Gaunt, and M. Glen, J. Phys. **A14**, 683 (1976); V.A. Vyssotsky, S.B. Gordon, H.L. Frisch, and J.M. Hammersley, Phys. Rev. **123**, 1566 (1961)

[34] D.M. Heyes, Mol. Phys. **69**, 559 (1990); D.M. Heyes and J.R. Melrose, Mol. Phys. **66**, 1057 (1989)

FIGURE CAPTIONS

1. The lowest-order graphs in the density expansion of h_1, the nearest-neighbor connectedness function, as given by (3.19). This quantity is required in the MSA for a general site-bond percolation model.

2. The percolation locus for random site-bond percolation on the 3D simple cubic (SC) lattice, as given both by simulation (solid line), and by the MSA of Section 3 (dotted line).

3. Configurations whose probabilities of occurrence form the working variables for the Wannier or square approximation to the properties of the s-state Potts model. By convention, '1' here denotes the symmetry-breaking state; '2', '3', etc., denote any other distinct states. The $s = 1$ limit of these variables give the two and four-point correlation functions of bond percolation at small separation.

$h_1 =$

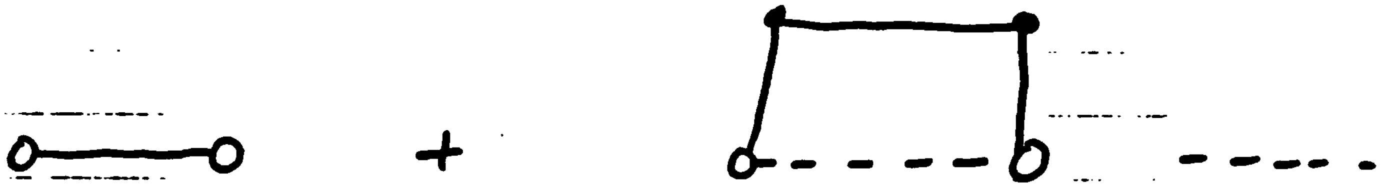
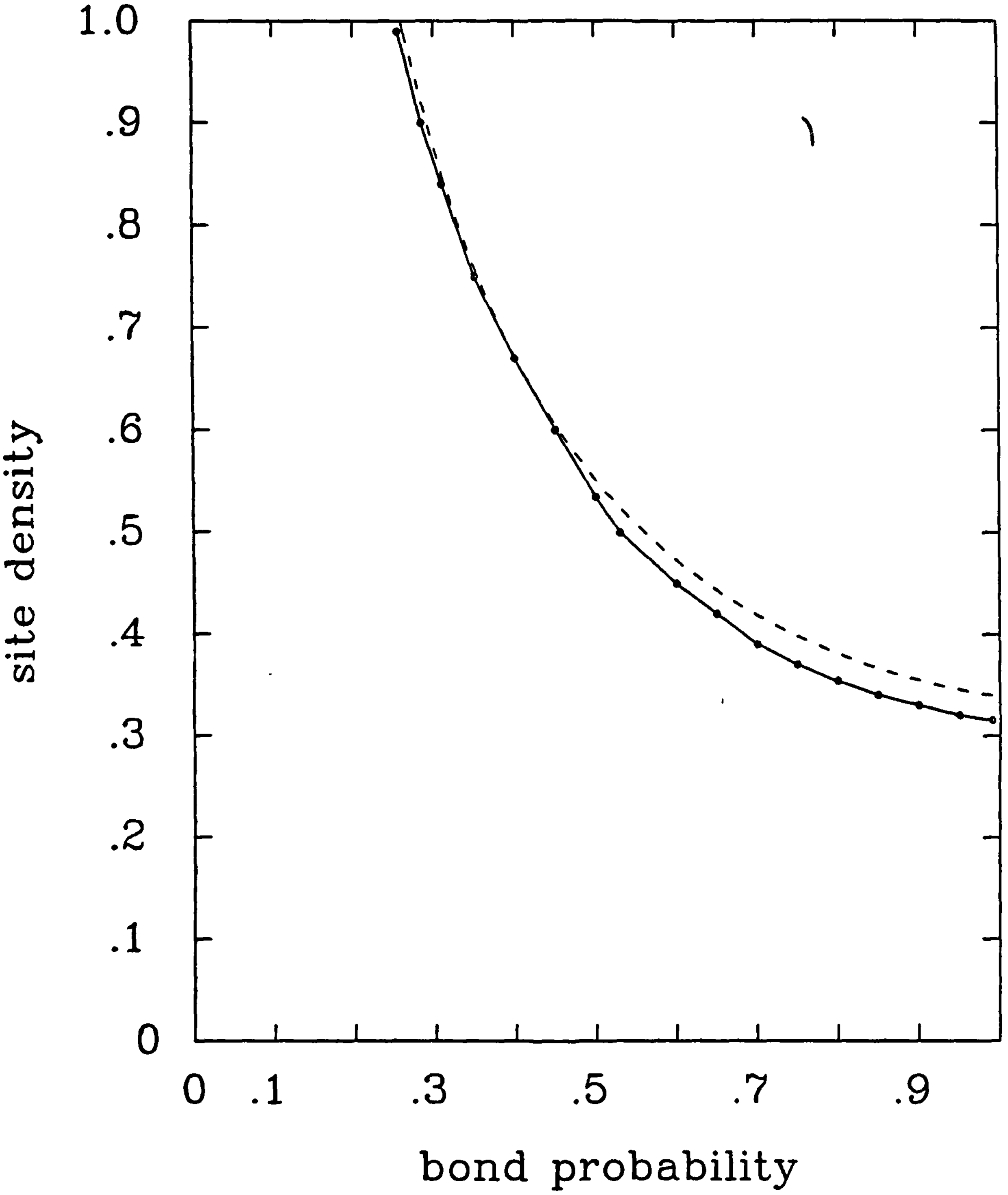


Figure 1.



RANDOM SITE BOND PERCOLATION 3D SC lattice
solid curve — SIMULATION
broken curve — MSA

@ PLOC

②

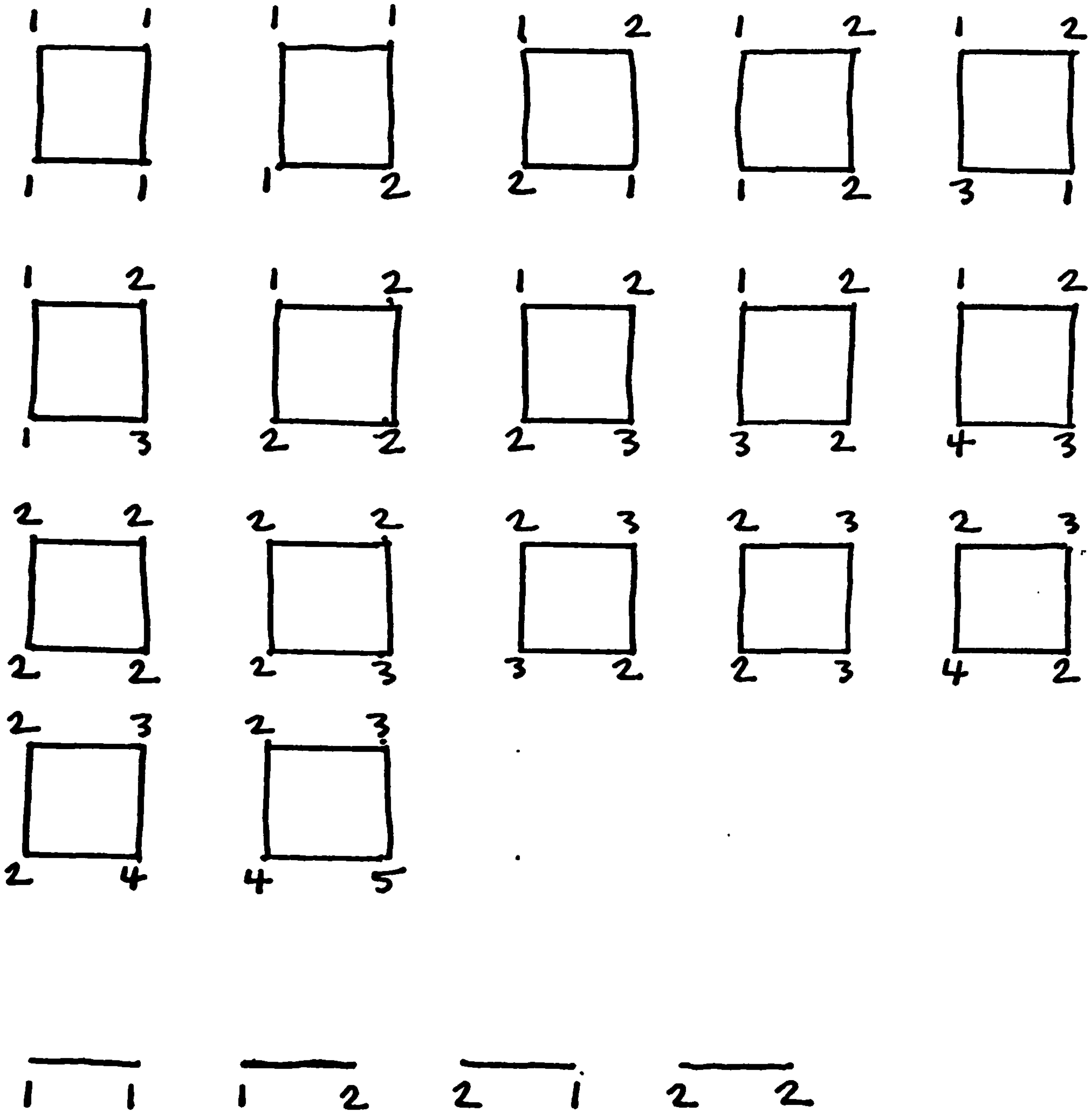

1 1 1 1
1 1 1 2
1 2 2 1
1 2 1 2
1 2 3 1
1 2 1 3
1 2 2 2
1 2 2 3
1 2 3 2
1 2 4 3
2 2 2 2
2 2 2 3
2 3 3 2
2 3 2 3
2 3 4 2
2 3 2 4
2 3 4 5
1 1
1 2
2 1
2 2

FIG. 3

Table Captions

1. Approximations to the bond percolation threshold given by the low density MSA discussed in Section 3. The sources for the numerical estimates are: [a]Adler *et. al.* (1990), [b] Sykes *et. al.* (1976), [c]Vyssotsky *et. al.* (1961). This table was adapted from reference 25 and revised.

2. Approximations to the 3D directed site and bond percolation thresholds given by the MSA scheme discussed in Section 4. The slow convergence is believed to be a result of the two-dimensional nature of the problem in the MSA.

Table 1. Approximations to Bond Percolation Threshold Given by (3.18)

Lattice	series expansions	$\bar{G}_0$
simple cubic	0.2488 ± 0.0002^a	0.25273
body-centered cubic	0.18025 ± 0.00015^a	0.17415
face-centered cubic	0.119 ± 0.001^b	0.11206
hexagonal close-packed	0.124 ± 0.005^c	0.11206
4D simple cubic	0.16005 ± 0.00015^a	0.156
5D simple cubic	0.11819 ± 0.00004^a	0.115

Table 2. Approximations to Directed Percolation Threshold Given by Equation (3.18)

Order of Approximation	Bond Percolation	Site Percolation
1	0.333	0.333
2	0.348	0.395
3	0.352	0.396
4	0.356	0.396
5	0.362	0.396
(EXACT)	0.384	0.432