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The Kirkwood–Salsburg Equations for Random Continuum Percolation

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We develop two different hierarchies of Kirkwood–Salsburg equations for the connectedness functions of random continuum percolation. These equations are derived by writing the Kirkwood–Salsburg equations for the distribution functions of the s-state continuum Potts model (CPM), taking the $s \to 1$ limit, and forming appropriate linear combinations. The first hierarchy is satisfied by a subset of the connectedness functions used in previous studies. It gives rigorous, low-order bounds for the mean number of clusters $\langle n_c \rangle$ and the two-point connectedness function. The second hierarchy is a closed set of equations satisfied by the generalized blocking functions, each of which is defined by the probability that a given set of connections between particles is absent. These auxiliary functions are shown to be a natural basis for calculating the properties of continuum percolation models. They are the objects naturally occurring in integral equations for percolation theory. Also, the standard connectedness functions can be written as linear combinations of them. Using our second Kirkwood–Salsburg hierarchy, we show the existence of an infinite sequence of rigorous upper and lower bounds for all the quantities describing random percolation, including the mean cluster size and mean number of clusters. These equations also provide a rigorous lower bound for the radius of convergence of the virial series for the mean number of clusters. Most of the results obtained here can be readily extended to percolation models on lattices, and to models with positive (repulsive) pair potentials.

KEY WORDS: Kirkwood–Salsburg equations; continuum percolation; connectedness functions; radius of convergence; rigorous bounds; continuum Potts model.

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1. INTRODUCTION

This paper is a contribution to an ongoing project[2] of calculating the properties of random and correlated percolation models by extending methods already developed in the thermal theory of liquids. Typical properties of interest are mean cluster size and mean number of clusters. We develop here some hierarchies of Kirkwood–Salsburg type and use them to extract information about random continuum percolation. This introduction gives a perspective on our approach to continuum percolation; the Kirkwood–Salsburg hierarchy will be introduced in Section 3, where it is first used.

Our motivations for this work are twofold. First, we wish to develop a computational theory of percolation phenomena that does not require the rather drastic simplifying assumption of a lattice geometry. Apart from the calculation of critical exponents, many of the interesting quantities that describe percolation can be best obtained from models with continuum geometry. Continuum models have an additional advantage over lattice models: in calculating their properties, one can make use of the powerful techniques of liquid-state theory that have been developed over the past several decades. Our second motivation for developing the theory explained here lies in our interest in calculating the bulk properties of composite materials. If such a material is composed of substances having radically different material properties (for example, if one of its phases is much more conductive than the others), it can show one or more percolation thresholds as its composition is varied. The development of accurate approximations and bounds for such properties that account for percolation phenomena is a challenging open problem. We believe that the connectedness functions studied in this paper, which are essentially distribution functions that account for connected paths, will be an essential ingredient in such bounds and approximations.

One way of adapting the techniques of liquid-state statistical physics for use in percolation theory is to exploit the connection between continuum percolation and the continuum Potts model (CPM). This is a generalization of the connection established by Fortuin and Kastelyn[7] between lattice bond percolation and the lattice Potts model. Klein[9] described the extension of this correspondence to the continuum; Given and Klein developed a Born–Green hierarchy for the connectedness functions. We have explored the application of various techniques to this model, in order to extract information about percolation, including series methods[8] and scaled particle theory.[13] We will first sketch the connec-

[2] The literature is rapidly growing. For representative references including those of particular relevance to our approach here see refs. 2–13.

tion with continuum percolation provided by the CPM. We then show how this connection helps realize computationally the theoretical insights of Hill[6] and Coniglio *et al.*[2]

The CPM is a many-body thermal system consisting of particles that are of s species, or, equivalently, are in any of s different internal states or "spin" states. These particles have pairwise interaction

$$V_{ij} = v(x_i, x_j)[1 - \delta_{\alpha_i \alpha_j}] + \phi(x_i, x_j) \tag{1.1}$$

Here $v(x_i, x_j)$ is a nonnegative pair potential acting between pairs of particles of unlike species (or, equivalently, internal states or "spin" states) indexed by α_i. The $\phi(x_i, x_j)$ is a pair potential common to all species or states. In the classical description we consider here, particles are typically characterized by their position, momentum, and spin state; the partition function for this model involves integration over the former two coordinates and a summation over the latter. Thus, the particle states can be described by the α_i and the vectors $x_i = (r_i, \Omega_i, p_i)$, where r_i is a center-of-mass position vector, p_i is a momentum vector, and Ω_i is an orientation. Model pair interactions often involve only the r_i in addition to the species designation α_i and for simplicity we shall assume hereafter that x_i means r_i unless we specifically note otherwise. Furthermore, we will assume that the functions v and ϕ in (1.1) depend only on the absolute distances $|x_i - x_j|$, which we will denote as x_{ij} (or as just x when no confusion will result). It is useful to note here that this model is an s-state generalization of the Widom–Rowlinson model,[1] in which $\phi \equiv 0$, and v is usually taken to be a hard-sphere interaction. This model has been extensively employed in the theory of liquids as a model of phase separation. It will suffice for our purposes, however, to consider the special case in which the fugacities of all s phases are equal.

All the quantities that describe continuum percolation can be obtained from the corresponding quantities characterizing this model in the limit in which s, the number of states, tends to one. In this limit, the system described by the interaction (1.1) becomes a percolation model in which particles are distributed according to distribution functions corresponding to the potential $\phi(x)$ and are pairwise connected with a separation-dependent bond probability

$$p_b(x_i, x_j) = 1 - \exp[-\beta v(x_i, x_j)] \tag{1.2}$$

Such models have been widely studied by both series expansions[2,3] and integral equation techniques[4,5] ever since a formalism for their study was

provided by Hill.[6] This is based on separating the pairwise Boltzmann factor corresponding to thermal interaction $\phi(x)$ into two parts,

$$\exp(-\beta\phi) = e^{\pm} + e^{*} \tag{1.3}$$

with

$$e^{\pm} = e^{-\beta\phi(x)} p_b(x) \tag{1.4}$$

$$e^{*} = e^{-\beta\phi(x)}[1 - p_b(x)] \tag{1.5}$$

The function $e^{\pm}$ is called the connectedness part and e^{*} is called the blocking part of the Boltzmann factor. Each is the product of a thermal Boltzmann factor and a bonding (or nonbonding) probability. Note that we assume at this point that the systems we deal with are homogeneous and isotropic; thus $p_b(x)$, $\phi(x)$, and other functions of the position of two particles are assumed to depend only on the scalar separation of these particles. The Mayer f function is then separated in a corresponding manner into the sum of a connectedness bond and a blocking bond

$$f = f^{\pm} + f^{*} \tag{1.6}$$

with $f^{\pm} = e^{\pm}$ and $f^{*} = e^{*} - 1$. In order to define percolation quantities, one then substitutes for the Mayer functions in the virial expansions of physical quantities, expands, and retains the subgraphs with at least a single path of connectedness bonds joining each pair of root points. These expansions have been described in detail.[2,3] The CPM approach we consider here is equivalent to this earlier approach. To see this, we write the Mayer bond for the general interaction (1.1) as

$$\begin{aligned} f(x) &= e^{-\beta\phi(x)}\{p_b(x)\,\delta_{\alpha_i\alpha_j} + [1 - p_b(x)]\} - 1 \\ &= f^{\pm}\delta_{\alpha_i\alpha_j} + f^{*} \end{aligned} \tag{1.7}$$

with $p_b(x)$ the bond probability (1.2), and $f^{\pm}$ and f^{*} just defined. The Kronecker delta in (1.7) and, in general, the spin variables of the CPM will serve as a technical device to select out just those contributions to the thermal distribution function specified by Hill's definition of the connectedness function. This correspondence has been elaborated in detail in ref. 8. It allows one to calculate efficiently higher-order terms in the virial expansions of percolation quantities[8] by using the Potts-model spin algebra as a device for selecting the proper terms automatically. It also provides us with a powerful means of deriving expressions to which we would otherwise not be led.

For simplicity, we generally work with random percolation in this

paper; $\phi(x)$ will then be set to zero. We will often make pedagogical use of what is perhaps the simplest model described within our framework, that of random-sphere percolation, in which we choose

$$p_b(x) = \begin{cases} 1, & 0 < x < 1 \\ 0, & \text{otherwise} \end{cases} \tag{1.8}$$

However, our results are quite general; they can be extended immediately to lattice percolation models, and many can be extended to correlated percolation models with positive potential $\phi(x)$. We discuss this further in the concluding section. We hope to address the important case of attractive interaction between particles in a future publication.

In this paper, we derive a closed hierarchy of Kirkwood–Salsburg equations for random percolation. They allow us to give a rigorous lower bound for the convergence of the virial series of percolation theory, including those for the mean number of clusters, and for the connectedness functions. These functions, which are analogous to distribution functions in thermal models, give the probability that groups of particles are connected into clusters.

This paper is organized as follows: in Section 2, we define the connectedness functions and various related functions needed in this paper. The Kirkwood–Salsburg equations for the CPM are written down in Section 3. Two different methods then yield hierarchies of Kirkwood–Salsburg equations for connectedness functions. The first, which is based on projection methods, gives Kirkwood–Salsburg equations only for a subset of the partial connectedness functions. The second involves a special choice of basis functions, which we call generalized blocking functions. These functions, which are denoted by $g_b(1,..., n; P)$, where P is a partition of the integers $(1,..., n)$, are defined by the probability that particles whose indices are separated by the partition P are *not* connected. In terms of these functions, we give the first closed Kirkwood–Salsburg hierarchy for percolation theory. In Section 4, this hierarchy is used to provide an infinite sequence of rigorous upper and lower bounds for all the basic functions of percolation theory, including the connectedness functions, the mean number of clusters $\langle n_c \rangle$, and the mean cluster size $S(\bar{\rho})$, where $\bar{\rho}$ is the expected number density of particles. In Section 5, specific upper and lower bounds are developed for $\langle n_c \rangle$ and for the two-point connectedness function. These are expressed in terms of the density $\bar{\rho}$ and integrals of the bond probability $p_b(x_{ij})$. Section 6 discusses two extensions of our basic bounding procedure capable of supplying bounds for the mean cluster size. The first of these is developed far enough to yield explicit bounds. In Section 7 we use the Kirkwood–Salsburg hierarchy to provide a rigorous

lower bound for the radius of convergence of the virial series for $\langle n_c \rangle$. Section 8 gives our conclusions and directions for further research. Appendices A and B verify some technical lemmas needed to show that the Kirkwood–Salsburg hierarchies for percolation in fact yield rigorous bounds. Appendix C develops a different bounding procedure which yields monotone convergent sequences of bounds.

2. CONNECTEDNESS FUNCTIONS AND GENERALIZED BLOCKING FUNCTIONS

In this section, we define both the n-point connectedness functions and n-point blocking functions of continuum percolation theory. We will show how both sets of functions may be derived from the one-state limit of the CPM distribution functions. Various subsets of the connectedness functions have appeared in previous work on percolation theory; we will need the complete set of them for this study. The n-point blocking functions are actually special linear combinations of the connectedness functions. We will define them separately, and explain why they are the natural basis set for studying percolation models. We also use the Möbius inversion theorem to give explicitly the coefficient matrix relating the two sets of functions.

The spin-dependent, n-point distribution function for the continuum Potts model (CPM), which is written $\rho(1\alpha_1, 2\alpha_2, ..., n\alpha_n)$, is the expectation density associated with finding a particle at x_1 in spin state α_1, another particle at x_2 in spin state α_2, etc. We will find it convenient to work instead with the distribution functions $g_t(1\alpha_1, ..., n\alpha_n)$ defined by

$$\rho_t(1\alpha_1, ..., n\alpha_n) = \left[\prod_{i=1}^{n} \rho(i\alpha_i) \right] g_t(1\alpha_1, ..., n\alpha_n) \tag{2.1}$$

We use the subscript t to refer to thermal distribution functions; the subscripts b and c will refer, respectively, to the blocking and connectedness functions to be defined presently. For the homogeneous systems discussed here, in the absence of external fields, $\rho(i\alpha_i)$ is a constant ρ; thus, going from the $\{\rho_t\}$ to the $\{g_t\}$ in this case is a trivial renormalization. Note also that for brevity we write 1 for x_1, for x_2, etc.

The one-state limit of these functions is related to the set of partial connectedness functions of percolation. These functions, which are written $g_c(1, 2, ..., n; P)$ with P an arbitrary partition of the integers $(1, ..., n)$, are defined as follows: $\bar{\rho}^n g_c$ is the expectation density associated with finding a set of n distinct particles centered at the positions $(x_1, ..., x_n)$ connected in clusters according to the partition P. That is, a pair of the particles at positions $(x_1, ..., x_n)$ are in the same connected cluster if and only if their indices

are grouped together in the partition P. We emphasize that any number of additional particles besides those at $(x_1,..., x_n)$ may be contained in the same clusters as these latter particles. For the simplest types of connectedness functions, one often omits the argument P from the function g_c, and specifies the grouping of particles by using slash marks to separate the connected groups of particles. In particular, the function $\bar{\rho}^n g_c(1,..., n)$, often simply called *the* connectedness function, is the expectation density associated with finding particles at x_1 through x_n all in the same cluster. It has been found useful, in terms of obtaining closed hierarchies of equations,[11,12] to work with the function $\bar{\rho}^n g_c(1/2,..., n)$, defined as the expectation density associated with finding particles at x_1 through x_n, with those at x_2 through x_n all in the same connected cluster, and the particle at x_1 in a *different* cluster. The case $n=2$ is also the simplest example of a blocking function, which we define next.

The blocking function $\bar{\rho}^n g_b(1,..., n; P)$ is the expectation density for finding particles at positions $(x_1,..., x_n)$ such that no pair of them whose indices are not grouped together in the partition P are contained in the same cluster. Note that, according to this definition, no pair of particles *need* be connected; configurations of the system in which no pair of the particles at $(x_1,..., x_n)$ are connected will contribute to all blocking functions.

We review the construction used by Fortuin and Kastelyn to analytically continue the Potts model to general, noninteger s. We must extend this construction to the continuum and apply it to the distribution functions. The CPM expectation density can be written

$$\rho_t(1\alpha_1,..., n\alpha_n) = \sum_{N=n+1}^{\infty} \frac{z^N}{(N-n)!} \sum_{\{\alpha_i\}}^{N} \frac{1}{\Xi} \int \sum_{i=n+1}^{N} dx_i \times \exp\left(-\beta \sum_{i<j}^{N} V_{ij}\right) \tag{2.2}$$

where Ξ is the CPM grand partition function and V_{ij} is the interaction (1.1). We have chosen here to work in the grand canonical ensemble in order to establish most economically Kirkwood–Salsburg expansions.[6] Such an expansion for the CPM will involve power series in the density $\rho(z, s)$, taken here to be a function of the fugacity z and s, the number of spin states. Consider the case $\phi(x)=0$ of (1.1). If we simply take the limit $s \to 1$ in our CPM before performing any other operations, we have, in this limit, $\rho(z, s)|_{s=1} \to \bar{\rho} = z$. The fugacity and density are equal in this limit, as expected for an ideal gas; the Potts model interaction disappears in this limit because there is no interaction between particles in the same state.

The sum in the rhs of (2.2) is over all s values of the spins $\alpha_{n+1},..., \alpha_N$. The total Boltzmann factor may be expanded

$$\prod_{i<j} e^{-\beta V_{ij}} = \prod_{i<j} e^{-\phi_{ij}} \prod_{i<j} \{p_b(x_{ij})\, \delta_{\alpha_i \alpha_j} + [1 - p_b(x_{ij})]\} \tag{2.3}$$

with $p_b(x_{ij})$ given by (1.2).

When the product (2.3) is expanded out, it gives a sum of terms, each of which is identified with a graph G and associated with a probabilistic event as follows: for a fixed position in configuration space $(x_1,..., x_N)$ associate a graph having vertices at these positions. With a probability $p_b(x_{ij})$, connect the points i and j with a bond; otherwise do not. These two events are associated respectively with choosing the first and second terms from the corresponding bracket in (2.3) when expanding that product. Since, for any potential $v(x)$, the terms $p_b(x)$, as defined by (1.2), and $[1 - p_b(x)]$ add to unity, this is a consistent interpretation of our expansion as a probabilistic weighting of the phase space elements that contribute to g_t. The first factor in (2.3) is not expanded; thus, each phase space element receives a Boltzmann weight corresponding to the potential $\phi(x)$. Note that each factor $p_b(x_{ij})$ is accompanied by a Kronecker delta $\delta_{\alpha_i \alpha_j}$; thus, two particles that are connected must be in the same spin state. Conversely, two particles in different spin states must not be connected, directly or indirectly. The sum over spins $\alpha_{n+1},..., \alpha_N$ then gives each graph G a weight s^{n_c}, where n_c is the number of distinct clusters in the graph G that do not contain any of the particles at $(x_1,..., x_n)$.

We now make several observations about the expansion just performed. First, the number of states s appears only in the weight factor s^{n_c}, which becomes unity in the $s \to 1$ limit. Also, the spins $\alpha_1,..., \alpha_n$ are not summed over. This implies that the quantity $g_t(1\alpha_1,..., n\alpha_n)$ is well defined in the limit $s \to 1$, *even if* $\alpha_1,..., \alpha_n$ are not equal. If we now consider this expansion to *define* the function g_t of (2.2), the parameter s, which originally had a physical interpretation as the number of states in the CPM, can be divorced from this interpretation to become a mathematical quantity capable of taking on a continuum of values. In the limit $s \to 1$, all phase space elements, or graphs, in which two of the external particles in different spin states are in the same connected cluster will make no contribution to this expansion. Other graphs receive their usual Boltzmann weights, multiplied by the product, for that graph, of the bond probabilities associated with it. Note that in general, a phase space element, i.e., a configuration of particles, can make nonzero contribution to a number of different graphs, i.e., schemes for connecting particles. These results can be summarized as follows: the $s \to 1$ limit of the CPM distribution function is a blocking function as defined above, for the associated percolation model.

A valuable notation is provided by rewriting $g_t(1\alpha_1,..., n\alpha_n)$ as $g_t(1,..., n; P)$, where the partition P groups together indices i and j iff $\alpha_i = \alpha_j$. This is possible because the CPM distribution functions depend not on the values $(\alpha_1,..., \alpha_n)$, but only on whether these are the same or different pairwise. We have then,

$$g_t(1,..., n; P) \to g_b(1,..., n; P) \tag{2.4}$$

as $s \to 1$, where the partition P on the rhs also groups together two indices i and j only if $\alpha_i = \alpha_j$.

The expansion just described is especially transparent in the case of sphere percolation, defined by (1.8). In this case, each configuration of particles can be connected by bonds with nonzero probability in exactly one way, i.e., two particles are connected in a graph iff they are closer together than 1. The weighting factor due to bond probabilities equals unity in this case. Thus, adding the hard-sphere Potts interaction corresponding to (1.8) to a thermal model with interaction $\phi(x)$ and taking $s \to 1$ acts as a "projection operator" on the thermal distribution functions, projecting out graphs or contributions with specified connectedness properties. [In a slight abuse of mathematical terminology, we will continue to use this term in the case of a general bond probability $p_b(x)$ even though we have not introduced any operator P such that $PP = P$.]

For obtaining equations for the quantities of percolation theory from the CPM, it is convenient to use the projection idea in a systematic way.[9–12] We explain this technique briefly as follows: as just shown, the one-state limits of the distribution functions are blocking functions. The blocking functions can, with effort, then be expressed at sums of connectedness functions. But certain frequently encountered connectedness functions can be obtained directly from the CPM distribution functions. This involves multiplying a CPM distribution function by a quantity that depends on its external spin arguments, summing over those arguments, taking an s derivative, and setting s equal to unity. When this method is available, it allows automatic derivation of equations for percolation quantities: one writes down, for the case of the CPM, any standard set of relations from chemical physics that hold for distribution functions, and applies the operations just described to both sides. We give two examples, involving the functions $g_c(1,..., n)$ and $g_c(1/2,..., n)$ which have been derived elsewhere.[11]

The connectedness function $g_c(1,..., n)$ can be expressed as follows:

$$g_c(1,..., n) = \frac{d}{ds}\bigg|_{s=1} \sum_{\{\alpha_i\}} \prod_{i=1}^{n} (1 - \delta_{\alpha_i \gamma})\, g_t(1\alpha_1,..., n\alpha_n) \tag{2.5}$$

Here γ is an arbitrary spin state and the sums are over all possible values of α_1 through α_n. If we expand the quantity $g_t(1\alpha_1,..., n\alpha_n)$ of (2.5) as described below (2.3), substituting the separation $(f^{\pm}\delta_{\alpha_i\alpha_j}+f^*)$ for each Mayer function, the only subgraphs contributing to (2.5) will be those with a path of $f^{\pm}$ bonds joining each pair of root points. To see this, note that each such chain forces the root points it connects to be in the same spin state (because of the factor $\delta_{\alpha_i\alpha_j}$ accompanying each $f^{\pm}$ bond). This collapses the spin sums in (2.5) which would otherwise each give a factor $(s-1)$ and cause this term to vanish in the one-state limit. Thus, the operations performed on g_t in (2.5) serve to "project out" connected contributions. The function $g_c(1/2,..., n)$ can be expressed as follows:

$$g_c(1/2,..., n)=\frac{d}{ds}\bigg|_{s=1}\sum_{\{\alpha_i\}}\prod_{i=2}^{n}(1-\delta_{\alpha_1\alpha_i})\, g_t(1\alpha_1,..., n\alpha_n) \tag{2.6}$$

The identities (2.5) and (2.6) were proven in ref. 12. These projection operators simply form the proper linear combinations of blocking functions to give connectedness functions.

We now develop an explicit relation between the connectedness and blocking functions in the general case. To do this, we note that it is possible to develop connectedness functions for the CPM that will reduce to the functions already defined for percolation in the $s\to 1$ limit. Given a criterion for pairwise connectedness such as (1.8), we can sort configurations in the ensemble average defining $g_t(1\alpha_1,..., n\alpha_n)$ according to the connections existing between the particles at positions $(1,..., n)$. This is what is implied by the term projection operator used above. For example, define $G_c(1,..., n)$ to be the restriction of the ensemble average defining $g_t(1\alpha_1,..., n\alpha_n)$ to configurations in which each pair of particles are joined by at least one chain of pairwise connected particles. Fortuin and Kastelyn[7] noted that this function is identical to $g_c(1,..., n)$, except that each configuration contributing to the latter is weighted in the former by a factor s^{n_c}, where n_c is the number of clusters not containing any of the particles at x_1 through x_n. In the limit $s\to 1$, this becomes $g_c(1,..., n)$. Finally, we note that these functions are easily related to the CPM distribution functions.[14] For example,

$$g_t(1\alpha, 2\alpha)=\frac{1}{s}G_c(1, 2)+\frac{1}{s^2}G_c(1/2) \tag{2.7}$$

This is easily seen: the left-hand side (lhs) of this equation is the probability that the particles at x_1 and x_2 are both in spin state α. Since all spin states are equally likely and because any two particles in the same connected cluster must be in the same spin state, the probability of this event is $1/s$

if the two particles are connected, and $1/s^2$ if they are not. By similar reasoning, one has

$$g_t(1\alpha, 2\beta) = (1/s^2)\, G_c(1/2) \tag{2.8}$$

Setting $s = 1$ in (2.7) and (2.8) and also using (2.4) then gives a linear relation between blocking and connectedness functions. In order to treat the general case, we note that the set of all partitions of the integers $(1,..., n)$ has a natural partial ordering: $P' \leqslant P$ whenever the partition P' is a refinement of the partition P. Assume that the partition P divides the integers $(1, 2,..., n)$ into sets $P_1, P_2,...$, and that the refinement partition P' breaks these into $N(P_1), N(P_2),...$ subsets, respectively. Then one can show that

$$g_t(1,..., n; P) = \sum_{P' \leqslant P} \prod_i s^{-N(P_i)} G_c(1,..., n; P') \tag{2.9}$$

The one-state limit of (2.9) is

$$\lim_{s \to 1} g_t(1,..., n; P) \equiv g_b(1,..., n; P)$$

$$= \sum_{P' \leqslant P} g_c(1,..., n; P') \tag{2.10}$$

Using the properties of partial orderings,[15,16] the relation (2.10) can be inverted to give

$$g_c(1,..., n; P) = \sum_{P' \leqslant P} \mu(P, P')\, g_b(1,..., n; P') \tag{2.11}$$

where $\mu(P, P')$ is the Möbius function for the partial order on partitions defined below Eq. (2.8). The Möbius function for any partial order can be defined recursively[15] as follows:

$$\mu(P', P) = \begin{cases} 1, & P = P' \\ -\sum_{P' \leqslant P'' < P} \mu(P', P''), & P' < P \\ 0, & \text{otherwise} \end{cases} \tag{2.12}$$

Some low-order examples of relation (2.11) are

$$g_c(1, 2) = \lim_{s \to 1} [g_t(1\alpha, 2\alpha) - g_t(1\alpha, 2\beta)] \tag{2.13}$$

$$g_c(1/2, 3) = \lim_{s \to 1} [g_t(1\alpha, 2\beta, 3\beta) - g_t(1\alpha, 2\beta, 3\gamma)] \tag{2.14}$$

Here α, β, and γ are any three different spin states. Although a general, closed-form expression for the Möbius function in (2.11) has been derived,[16] it will not be needed here.

Two further properties of these functions will be important in the following. Because the blocking function is a constrained sum over the same configurations that contribute to $g_t(1,..., n)$, the distribution function with pairwise potential $\phi(x)$, one has

$$0 \leqslant g_b(1,..., n; P) \leqslant g_t(1,..., n) \tag{2.15}$$

Note that when $\phi(x) = 0$, $g_t(1,..., n) = 1$. Also, from the definition (2.10), one has

$$g_b(1,..., n; P') \leqslant g_b(1,..., n; P), \qquad P' \leqslant P \tag{2.16}$$

3. KIRKWOOD–SALSBURG EQUATIONS FOR PERCOLATION

In this section, we derive two sets of equations of Kirkwood–Salsburg type for random continuum percolation. The first uses the projection operators of Section 2 and relates two sets of connectedness functions defined in that section. These will be used in Section 4 to derive upper and lower bounds on percolation quantities. The second, which is a closed hierarchy for the generalized blocking functions of Section 2, will be used to bound the radius of convergence of series expansions in percolation.

The Kirkwood–Salsburg equations[6] are a special case of a very general set of integral equations for the distributions of a many-body system. They are derived by focusing on a specific particle (we use particle 1) and expanding the ensemble average defining $g_t(1,..., n)$ in powers of the interaction strength of that particle. Specifically, one develops a cluster expansion in which the effects of particle 1 on all the different groups of k particles, $k > 1$, are systematically taken into account. As a result, the expansion of $g_t(1,..., n)$ has terms depending on $g_t(1,..., n+k)$, $k > 1$, for all values of k. These equations are thus not suited to direct computation except in mean-field approximation, in which the entire set of distribution functions are expressed in terms of the one- and two-point functions. They are, however, well suited to establishing general properties of the fluid distribution functions. In particular, a basic inclusion–exclusion structure of the cluster expansion involved has been used to establish upper and lower bounds for distribution functions.[20] The recursive nature of this hierarchy has been used to provide bounds for the radius of convergence of virial expansions.[22]

The basic mathematical structure underlying the Kirkwood–Salsburg

expansion of distribution functions is quite old; it is implicit in Boltzmann's treatment of the hard-sphere fluid.[17] The central development of Boltzmann's argument is a geometric inclusion–exclusion relation for the volume available in a hard-sphere fluid for insertion of an additional particle. This volume is expressed as the total system volume minus the total volume contained in the exclusion spheres of at least one particle, plus the total volume contained in the exclusion spheres of at least two particles, and so on. Stell[17] used this argument to obtain bounds on the pressure of hard-particle systems. Recently, the same basic argument has been found useful in a variety of attempts to characterize the geometry of random materials. Torquato and Stell[18] srudied the matrix functions $S_n(1,..., n)$ for a system of permeable spheres of one material dispersed in a matrix of another material. The functions S_n, which give the probability that the points x_1 through x_n are all contained in the matrix phase, were shown to satisfy a Kirkwood–Salsburg hierarchy. Fanti *et al.*[19] provide a Kirkwood–Salsburg expansion, in terms of the set of total connectedness functions $g_c(1,..., n)$, for the mean volume V_s of clusters of size s in a continuum percolation model.

These developments have certain desirable features in common, due to their reliance on the inclusion–exclusion argument described above. Kirkwood–Salsburg expansions derived in this manner are alternating series whose terms decrease monotonically in magnitude. The partial sums of such a series provide, alternatively, upper and lower bounds for the quantity being expanded, and these bounds converge monotonically. Unfortunately, in treating thermodynamic functions and distribution functions for systems of interacting particles, it is only the special case of hard particles, which have well-defined boundaries and an interaction defined by a geometric excluded-volume effect, that these inclusion–exclusion arguments apply. For a general, repulsive interaction, analytic arguments, such as the remainder theorem for a Taylor series expansion[20] seem to be necessary to show that partial sums of the Kirkwood–Salsburg equations provide bounds. These arguments give no information about monotone convergence of the bounds. In treating continuum percolation, we find such analytic arguments necessary even for systems of particles with sharply defined boundaries [e.g., the system of randomly centered spheres defined by (1.4)], basically because of the nontrivial combinatoric structure of the Kirkwood–Salsburg equations that describe percolation models. Further perspective on these questions is provided in Section 8.

The Kirkwood–Salsburg hierarchy of integral equations for the CPM is a special case of a hierarchy defined for any system with pairwise additive potential energy. It presents no special difficulties; thus, we write it down directly, noting that integrations over particle positions and

momenta must be accompanied by sums over spin states. These equations are

$$\frac{\rho(\alpha_1)}{z(\alpha_1)} = 1 + \sum_{m=1}^{\infty} \frac{\rho^m}{m!} \sum_{\alpha_2} \cdots \sum_{\alpha_{m+1}} \int \prod_{k=2}^{m+1} f(x_1, x_k, \alpha_1, \alpha_k) \otimes g_t(2\alpha_2, \ldots, m+1\alpha_{m+1})\, dx_2 \cdots dx_{m+1} \tag{3.1}$$

$$g_t(1\alpha_1, \ldots, n\alpha_n) = \left(\frac{z}{\rho}\right) \prod_{k=2}^{n} [1 + f(x_{1k}, \alpha_1, \alpha_k)] \Bigg[g_t(2\alpha_2, \ldots, n\alpha_n) + \sum_{m=1}^{\infty} \frac{\rho^m}{m!} \sum_{\alpha_{n+1}} \cdots \sum_{\alpha_{n+m}} \int \prod_{k=n+1}^{n+m} f(x_1, x_k, \alpha_1, \alpha_k) \otimes g_t(2\alpha_2, \ldots, n+m\alpha_{n+m})\, dx_{n+1} \cdots dx_{n+m} \Bigg] \tag{3.2}$$

This expansion was first discussed in ref. 11. Here we have extracted a factor of ρ^n from the n-point expectation density to get the usual marginal distribution function for a fluid. The CPM density ρ and fugacity z are written as functions of spin state α_1. However, since we here take the fugacities of different spin states to be equal, and because we make no reference to broken-symmetry states of the CPM, the density ρ will be independent of spin state. This last condition must be violated in order to consider the structure of the infinite cluster; this will be reserved for a future publication. Also, in the first term on the rhs of (3.1) the function $g_t(2, \alpha_2)$ is equal to unity for homogeneous systems, such as our CPM.

Equations of the form (2.10) show that linear combinations of Eqs. (3.2) will give, in the one-state limit, Kirkwood–Salsburg equations for the connectedness functions. In general, these are quite complicated. Even in the case of random continuum percolation, a closed, linear hierarchy (one containing only one partial connectedness function of each order) does not seem to exist. Hierarchies tend to involve the entire set of partial connectedness functions. One can, however, derive a valuable set of Kirkwood–Salsburg equations which involve only the connectedness functions (2.5) and (2.6). We develop these equations next.

We want to develop Kirkwood–Salsburg equations for the functions $g_c(1/2, \ldots, n)$. To do this, we multiply both sides of (3.1)–(3.2) by the projection operator

$$\prod_{j=2}^{n} (1 - \delta_{\alpha_1 \alpha_j}) \tag{3.3}$$

sum over spins $\alpha_1, \alpha_2, \ldots, \alpha_n$, take an s derivative, and set s equal to unity. Note that by definition the product (3.3) is equal to unity in the case $n = 1$, i.e., for Eq. (3.1). In evaluating the result, we need to note both the spin

dependence of the Mayer function (1.7), and the identities (2.5) and (2.6). Performing the operations just indicated on the lhs of (3.2) gives the function $g_c(1/2,..., n)$ as desired, as seen from Eq. (2.6). To evaluate the rhs, first perform the sum over α_1. Here, the fugacity z will be equal to $\bar{\rho}$, the percolation density, for the case of random percolation and momentum-independent x_i to be discussed here. Because the distribution functions on the rhs are independent of α_1, all s terms in the sum over this variable are equal. We then extract a factor of s (which can then be set equal to unity, since each term on the rhs is proportional to $s-1$), and the s derivative must cancel this factor. For convenience, we also set $\alpha_1 = \gamma$. Using the identity (2.5), the first term on the rhs can be identified with the connectedness function $g_c(1, 2,..., n)$. Every other term on the rhs also becomes a connectedness function. To see this, note that each successive term contains one more factor $(1-\delta_{\alpha_1\alpha_k})$ from the corresponding Mayer function. Each successive term also contains a g_t function with one more argument (x_k, α_k), and the x_k integral is accompanied by a sum over α_k. Thus, each rhs term contains a copy of the identity (2.5) for a different value of n.

Finally, we note that the spin dependence of the first product on the rhs of (3.2) does not affect these considerations. To see this, rewrite this product using Eq. (1.7):

$$\prod_{k=2}^{n} \{p_b(x_{1k})\,\delta_{\alpha_1\alpha_k} + [1 - p_b(x_{1k})]\} \tag{3.4}$$

When this product is multiplied by the projection operator (3.3) and the spin sums are performed, the first term in each factor of (3.4) drops out. The result is

$$\prod_{k=2}^{n} [1 - p_b(x_{1k})] \tag{3.5}$$

Equations (3.1)–(3.2) thus become

$$\frac{d}{d\bar{\rho}} \langle n_c \rangle = 1 + \sum_{m=1}^{\infty} \frac{(-\bar{\rho})^m}{m!} \int \prod_{k=2}^{m+1} p_b(x_{1k})\, g_c(2,..., m+1) \times dx_2 \cdots dx_{m+1} \tag{3.6}$$

$$g_c(1/2,..., n) = \prod_{k=2}^{n} [1 - p_b(x_{1k})] \Bigg[g_c(2,..., n) + \sum_{m=1}^{\infty} \frac{(-\bar{\rho})^m}{m!} \int \prod_{k=n+1}^{m+n} p_b(x_{1k})\, g_c(2,..., n+m) \times dx_{n+1} \cdots dx_{n+m} \Bigg] \tag{3.7}$$

In Eq. (3.7), the function $g_c(x_2)$ occurring in the first term of the sum on the rhs is equal to unity. This hierarchy expresses the functions $g_c(1/2,..., n)$ in terms of the connectedness functions $g_c(1,..., n)$ alone. In evaluating the lhs of (3.6), we use the relation

$$\left.\frac{d}{ds}\right|_{s=1}\left(\frac{\rho}{z}\right)=\frac{d}{d\bar{\rho}}\langle n_c\rangle-1 \tag{3.8}$$

between the number of clusters per unit volume in continuum percolation and the density in the CPM. This relation follows by comparison of the virial series for the two quantities.[8] It will be discussed in more detail in Section 5.

To illustrate the complexity that arises in most applications of projection operators to this hierarchy, one can use similar techniques to derive Kirkwood–Salsburg equations for the connectedness functions $g_c(x_1,..., x_n)$ themselves. One simply multiplies (3.2) by the projection operator in (2.5), carries out the spin sums, and performs the operation $(d/ds)|_{s=1}$. To characterize this expansion, it is useful to adopt the concept of a "hybrid cluster." When discussing a connectedness function $g_c(2,..., n, n+1,..., n+m; P)$ that occurs in the expansion of $g_c(2,..., n)$, we refer to a percolation cluster as "hybrid" if it contains at least one of the particles at positions $(2,..., n)$ and at least one of the particles at positions $(n+1,..., n+m)$.

The Kirkwood–Salsburg hierarchy for the connectedness functions (2.5) can now be written

$$\begin{aligned} g_c(1,..., n) &= \sum_S \prod_{k\in S} p_b(x_{1k}) \prod_{k\in S'} [1-p_b(x_{1k})] \\ &\quad \otimes \sum_P \Bigg[g_c(2,..., n; P)(-)^{H(P)} \\ &\quad + \sum_{m=1}^{\infty} \frac{(-\bar{\rho})^m}{m!} \int \prod_{k=n+1}^{n+m} p_b(x_{1k})(-)^{H(P)} \\ &\quad \times g_c(2,..., n+m; P)\, dx_{n+1}\cdots dx_{n+m} \Bigg] \end{aligned} \tag{3.9}$$

Here the first sum is over all subsets S of the integers $(2,..., n)$, and S' is the complement of S in this set. The second sum is over all partitions P of the arguments of the connectedness functions involved, such that each of the particles located at these arguments is either (1) connected directly or indirectly to at least one particle in the set S, or (2) contained in a hybrid cluster.

Here $H(P)$ is the number of hybrid cluster in the configuration specified by the partition P.

The irregular pattern of minus signs on the rhs of (3.9) due to the factor $(-)^{H(P)}$ makes it difficult to extract useful bounds for this equation. Also, the complexity of this expression makes it difficult to work with, although the situation may be different for correlated percolation problems in which the correlating potential contains a hard core. In such problems, the expansions discussed here all terminate in a finite number of terms, as in the thermal Kirkwood–Salsburg hierarchy.

For purposes of calculating upper and lower bounds for the connectedness functions, it is best to work with the Kirkwood–Salsburg hierarchy for the blocking functions $g_b(1,..., n; P)$, which were defined in Section 2. This will be derived next.

Consider Eq. (3.2). The spin sums may be carried out formally by recognizing that the distribution functions g_t are not functions of the α_i individually, but depend only on whether these arguments are the same or different pairwise. We exploit this fact, as in Section 2, by replacing the arguments $\{\alpha_i\}$ by the partition P of the integers $(1,..., n)$, which groups together particles whose spin indices are equal. This is explained in greater detail above Eq. (2.1). The distribution function on the lhs of (3.2) then becomes a function of the partition P of the integers $(1,..., n)$. Correspondingly, each distribution function on the rhs becomes a function of a partition P' of integers $(2,..., n+m)$, which is consistent with the partition P, in the sense that it agrees with P when both are restricted to the integers $(2,..., n)$. Each such partition will correspond to many terms on the rhs of (3.2). In particular, if there are b_1 different spin indices in the set $(\alpha_1, \alpha_2,..., \alpha_n)$ and b_2 *new* indices in the set $(\alpha_{n+1},..., \alpha_{n+m})$ that are not among the first set, the multiplicity of the corresponding g_t function is

$$(s-b_1)(s-b_1-1)\cdots[s-b_1-(b_2-1)] \tag{3.10}$$

This corresponds to a partition P into b_1 different sets and a partition P' into either (b_1+b_2-1) different sets, if x_1 is in a subset of 1 in partition P, or (b_1+b_2) subsets, if x_1 is in a subset of P containing several other indices. After summing over spins and taking the $s \to 1$ limit, (3.2) becomes

$$\begin{aligned} g_b(1,..., n; P) = \prod_{k=2}^{n} \{p_b(1,k)\,\delta_{\alpha_1\alpha_k} + [1-p_b(1,k)]\} \Bigg[& g_b(2,..., n; P) \\ & + \sum_{m=1}^{\infty} \frac{(-\bar{\rho})^m}{m!} \sum_{P'} \bar{d}(P, P') \int \prod_{k=n+1}^{n+m} p_b(1,k) \\ & \otimes g_b(2,..., n+m; P')\, dx_{n+1} \cdots dx_{n+m} \Bigg] \end{aligned} \tag{3.11}$$

Here, the weight $\bar{d}(P, P')$ is the $s \to 1$ limit of (3.10), namely

$$\bar{d}(P, P') = \begin{cases} (b_1 - 1)\, b_1(b_1 + 1) \cdots (b_1 + b_2 - 2)(-)^{b_2}, & b_2 \geqslant 1 \\ 1, & b_2 = 0 \end{cases} \tag{3.12}$$

In order to derive the results of Section 4, it is necessary to include in the hierarchy (3.11) an equation relating the mean number of clusters $\langle n_c \rangle$ to the set of functions $\{g_b\}$. This could be done by rewriting Eq. (3.6), using identities of the form (2.11). However, an equation for $\langle n_c \rangle$ is more easily derived from (3.2) in the case $s = 1$ by taking an s derivative of both sides before setting $s = 1$ [see Eq. (3.8)]. This gives an equation for the density derivative of $\langle n_c \rangle$ of the form (3.11), but with the weighting factors $\bar{d}(P, P')$ of terms on the rhs now given by

$$\bar{d}(P, P') = \begin{cases} 0, & b_2 = 0 \\ 1, & b_2 = 1 \\ (-)^{b_2 - 1}\, (b_2 - 1)!, & b_2 > 1 \end{cases} \tag{3.13}$$

4. FORMAL SEQUENCES OF EXACT BOUNDS FROM THE KIRKWOOD–SALSBURG EQUATIONS

In this section, we present three arguments based on the formal series expansions of Section 3 that lead to sequences of rigorous upper and lower bounds for the basic quantities of percolation. These bounds will be combined using recursive elimination in Section 5 to give explicit bounds involving only the bond probability $p_b(x_{ij})$ and density $\bar{\rho}$. Our first argument shows that successive truncations of Eqs. (3.6)–(3.7) have remainder terms that alternate in sign; these truncations thus furnish upper and lower bounds for the mean number of clusters $\langle n_c \rangle$ and for an important subset of the partial connectedness functions. These bounds are simple because of the relative simplicity of (3.6)–(3.7). However, higher-order bounds of this type involve connectedness functions which are not themselves included in the subset bounded through the use of (3.6)–(3.7). Thus, the bounding procedure resulting from this equation is not closed.

Our second argument shows that successive truncations of the hierarchy (3.11) for the generalized blocking functions also have remainder terms which alternate in sign. Since, as we showed in Section 2, the generalized blocking functions form a complete basis for the set of connectedness functions, Eq. (3.11) then provides upper and lower bounds of arbitrarily high order for any of these. Since practical computation of these

bounds is more involved than computation of the bounds resulting from (3.6)–(3.7), the former are best used to extend and complement the latter.

Our final argument establishes that a sequence of sufficiently high-order bounds that can be derived from Eq. (3.11) will converge monotonically to the quantities they bound. This argument is included both for its mathematical interest and because the developments it involves may be of value in other contexts.

Our basic starting point for the derivation of bounds for percolation quantities is the thermal Kirkwood–Salsburg hierarchy (3.1)–(3.2) for the CPM. The Kirkwood–Salsburg equations consist, in general, of a Taylor series expansion of the n-particle distribution functions in powers of the coupling strength of a specific particle. Now, if a system has purely repulsive potential interactions, its Mayer function is negative definite. Applying the remainder theorem to the Taylor-series structure of these equations shows that the remainder terms given by successively higher-order truncation alternate in sign. This observation was exploited some time ago to derive upper and lower bounds for correlation functions, both for a hard-sphere system[20] and for a nonadditive mixture of hard-sphere species.[21] The CPM is such a mixture. Furthermore, the alternation in sign of successive remainder terms is conserved by the operations that transform these equations into the pair (3.6)–(3.7). The argument establishing this point is technical and has been relegated to Appendix A. Basically, the result follows because the remainder term has the same structure as an arbitrary term from the rhs of (3.6)–(3.7). The term of order m on the rhs of (3.6) and (3.7) is easily seen to have the sign $(-)^m$ because the integrand in that equation is positive. The remainder term inherits this definiteness in sign.

Obtaining higher-order bounds involves keeping an increasing number of terms in (3.6)–(3.7) and thus requires one to estimate higher-order connectedness functions. If care is taken to choose either upper or lower bounds for these according to the direction of the inequality, the connectedness functions can be successively eliminated, giving upper and lower bounds that depend only on the percolation density $\bar{\rho}$ and on the separation-dependent bond probability $p_b(x)$. One would ideally like to have arbitrarily high-order bounds for any of the partial connectedness functions, in order to eliminate these from (3.6)–(3.7). An argument similar to that just described shows, however, that the Kirkwood–Salsburg expansion for a general connectedness function will *not* yield upper and lower bounds. To see this, examine Eq. (3.9) and note that, in the sum over partitions, the general term can be positive or negative, because of the factor $(-)^{H(P)}$. This implies that the corresponding remainder term will be of indefinite sign, and thus will not provide bounds.

One can, however, derive arbitrarily high-order bounds for the generalized blocking functions $g_b(1,..., n)$. This is not obvious from consideration of the Kirkwood–Salsburg hierarchy (3.11) derived for those functions, because the coefficients $\bar{d}$ of different terms on the rhs of those equations can have either sign [see Eq. (3.12)]. The integrands on the rhs of (3.12) are, however, positive definite. To see this, one can substitute (2.10) for each of the blocking functions, expand, and combine terms. The result is, in general, a linear combination of connectedness functions, each with coefficient $+1$. This result will be established in detail, and its probabilistic interpretation will be discussed in Appendix B. Here we note simply that successive truncations of (3.11) will give upper and lower bounds on the blocking function $g_b(1,..., n)$. Because these bounds are provided for all such functions, the recursive elimination of the $\{g_b\}$ can be carried out to arbitrarily high order, yielding kth-order upper bounds of the form

$$g_b(1,..., n) \leqslant \sum_{i=1}^{k} g_{1i}(1,..., n)\, \bar{\rho}^i + \bar{\rho}^{k+1} S_k(1,..., n) \tag{4.1}$$

and corresponding lower bounds. Here, the series on the rhs is a partial sum of the virial series for g_b. The virial coefficients g_{1i} are sums of Mayer integrals with $p_b(x)$ bonds; these have been described in detail.[3,8]

Because the blocking functions form a complete basis for expansion of the connectedness functions, one can write kth-order bounds for the latter as linear combinations of the corresponding bounds (4.1) for the former. This method of calculating bounds is more general, although less direct, than that provided by Eq. (3.6)–(3.7). Thus, the most efficient bounds for $\langle n_c \rangle$ and $g_c(1, 2)$ are probably those given by combining the two methods. This is in fact necessary to obtain bounds for the n-point connectedness functions with $n \geqslant 3$.

We note that, in general, successive bounds given by truncating the expansion (3.7) need not improve in quality monotonically. The alternation in sign of terms in (3.7), together with the interpretation of the connectedness functions as probability densities, suggests that a geometric interpretation of these equations using an inclusion–exclusion argument should be available. This is the case for many applications of the Kirkwood–Salsburg expansion technique, as discussed at the beginning of Section 3. The Kirkwood–Salsburg bounds resulting from such an inclusion–exclusion argument converge monotonically, and this property has great practical value. We do not provide such an interpretation here, and thus do not prove in general the monotonicity of the bounds discussed here. We do, however, provide partial results in this direction. We indicate here a means of construction for a series of upper and lower bounds that, except possibly

for the first N_1 bounds in the series, converge monotonically. Here N_1 is a fixed integer which depends on the g_b function being bounded. This construction is only sketched here; it is described in detail in Appendix C.

First, we note that the blocking functions, from their definitions, satisfy a basic set of inequalities. One has

$$g_b(1,..., n; P) \geqslant g_b(1,..., n, n+1; P) \tag{4.2}$$

for $|x_{1k}| < \sigma$; $k = 1,..., n+1$. This is true because the blocking function on the lhs of this equation is defined to be the probability of *not* having any pair of particles connected whose indices are separated by the partition P. Having an additional $(n+1)$th particle near the set $(1,..., n)$ can only increase the probability of finding such a connection. Thus, (4.2) follows.

Next, we collect the terms in (3.11) with positive and those with negative $\vec{d}$ weight as g_{1p} and $(-g_{1n})$, respectively, and write

$$g_1 = g_{1p} - g_{1n} \tag{4.3}$$

The bound (4.2) can be used to show that for n sufficiently large, the order-n term in g_{1p} and g_{1n} will dominate the corresponding order-$(n+1)$ term. This shows, then, that high-order truncations of both g_{1p} and g_{1n} give, alternatively, upper and lower bounds for these functions. Appropriate combinations of these then give monotonically converging bounds for the $\{g_b\}$.

Note that the property (4.2), which is essential for showing that the higher-order terms in g_b decrease monotonically, is specific to the blocking functions; the connectedness functions do not obey such a relation, as is easily seen.

5. SPECIFIC BOUNDS FOR THE BLOCKING FUNCTION AND MEAN CLUSTER NUMBER

In this section, the KS hierarchy (3.6)–(3.7) will be used to obtain a sequence of exact upper and lower bounds on both the mean cluster number and the two-point connectedness function. Other methods of obtaining bounds will also be discussed.

The lowest order KS equation for percolation is of the form

$$\frac{d}{d\bar{\rho}} \langle n_c \rangle = 1 - \bar{\rho} \int p_b(x_{12})\, dx_2 + \frac{1}{2} \bar{\rho}^2 \int p_b(x_{12})\, p_b(x_{13})\, g_c(x_{23})\, dx_2\, dx_3 + R_3^{(1)} \tag{5.1}$$

where $R_3^{(1)}$ is a negative term of order ρ^3. The definiteness of sign of such remainder terms follows from the argument of Appendix A. Using the procedure outlined above with this equation then leads to bounds on the $\bar{\rho}$ derivative of $\langle n_c \rangle$, which, using the obvious boundary condition $\langle n_c \rangle = 0$ for $\bar{\rho} = 0$, can be integrated. The resulting bounds on $\langle n_c \rangle$ will be written using the abbreviations

$$A_2 = \int p_b(x)\, dx \tag{5.2a}$$

$$A_3 = \int p_b(x_{12})\, p_b(x_{13})\, p_b(x_{23})\, dx_2\, dx_3 \tag{5.2b}$$

They are

$$\langle n_c \rangle \leqslant \bar{\rho} \tag{5.3a}$$

$$\langle n_c \rangle \geqslant \bar{\rho} - \frac{1}{2}\bar{\rho}^2 A_2 \tag{5.3b}$$

$$\langle n_c \rangle \leqslant \bar{\rho} - \frac{1}{2}\bar{\rho}^2 A_2 + \frac{1}{6}\bar{\rho}^3 A_2^2 \tag{5.3c}$$

$$\langle n_c \rangle \leqslant \bar{\rho} - \frac{1}{2}\bar{\rho}^2 A_2 + \frac{1}{6} A_3 \bar{\rho}^3 + \frac{1}{8}\bar{\rho}^4 A_2 (A_2^2 - A_3) \tag{5.3d}$$

The inequality (5.3a) is obvious; it would be an equality if all clusters were singlets. Equation (5.3c) was obtained by using the trivial upper bound $g_c(x) \leqslant 1$, whereas (5.3d) was achieved by using the upper bound (5.9b), to be derived below. Note that, as $\bar{\rho} \to 0$, (5.3b) and (5.3c) rigorously imply that

$$\langle n_c \rangle \to \bar{\rho} - \tfrac{1}{2}\bar{\rho}^2 A_2 \tag{5.4}$$

and in fact give the stronger result

$$\frac{\langle n_c \rangle}{\bar{\rho} - \frac{1}{2}\bar{\rho}^2 A_2} = 1 + O(\bar{\rho}) \tag{5.5}$$

This is no surprise; it is fully consistent with the formally exact virial-series expansion in $\bar{\rho}$. The point is that the result is *rigorously* exact. Equation (5.5) tells us that a description of $\langle n_c \rangle$ on the level of the second virial coefficient becomes arbitrarily precise in the limit $\bar{\rho} \to 0$ and is exact through $O(\bar{\rho})$.

Bounds for $g_c(x_1, x_2)$ are obtained by the same process. The second equation of the KS hierarchy (3.7) is

$$g_c(x_1/x_2) = [1 - p_b(x_{12})]\left[1 - \bar{\rho}\int p_b(x_{13})\, g_c(x_2, x_3)\, dx_3 + \frac{1}{2}\bar{\rho}^2 \int p_b(x_{13})\, p_b(x_{14})\, g_c(x_2, x_3, x_4)\, dx_3\, dx_4 + R_3^{(2)}\right] \tag{5.6}$$

where $R_3^{(2)}$ is a negative remainder term of order $\bar{\rho}^3$.

The bounds obtained from this equation are

$$g_c(x_1/x_2) \leqslant 1 - p_b(x_{12}) \tag{5.7a}$$

$$\begin{aligned} g_c(x_1/x_2) &\geqslant [1 - p_b(x_{12})]\left[1 - \bar{\rho}\int p_b(x_{13})\, g_c(x_2, x_3)\, dx_3\right] \\ &\geqslant [1 - p_b(x_{12})]\left[1 - \bar{\rho}\int p_b(x_{13})\, dx_3\right] \\ &\geqslant [1 - p_b(x_{12})](1 - \bar{\rho}A_2) \end{aligned} \tag{5.7b}$$

The bound (5.7a) also follows immediately from probability theory: the probability that the particles at x_1 and x_2 are not connected is the product of the probability that they are not *directly* connected and the probability that they are not *indirectly* connected. Bounding the latter by 1 gives (5.7a). The bounds (5.7) can be used with the exact relation

$$g_c(x_1/x_2) + g_c(x_1, x_2) = 1 \tag{5.8}$$

to give equivalent bounds for $g_c(x_1, x_2)$. For example,

$$g_c(x_1, x_2) \geqslant p_b(x_{12}) \tag{5.9a}$$

$$g_c(x_1, x_2) \leqslant p_b(x_{12}) + [1 - p_b(x_{12})]\,\bar{\rho}A_2 \tag{5.9b}$$

We see also that as $\bar{\rho} \to 0$,

$$g_c(x_1, x_2) \to p_b(x_{12}) \tag{5.10}$$

Substituting (5.9b) into (5.7b) gives

$$g_c(x_1/x_2) \geqslant [1 - p_b(x_{12})]\left[1 - \bar{\rho}\int p_b(x_{13})\, p_b(x_{23})\, dx_3 - \bar{\rho}^2 A_2^2 + \bar{\rho}^2 A_2 \int p_b(x_{13})\, p_b(x_{23})\, dx_3\right] \tag{5.11}$$

6. RIGOROUS BOUNDS FOR THE MEAN CLUSTER SIZE

Because it diverges at the percolation phase transition, the mean cluster size $S(\bar{\rho})$ is perhaps the best-studied quantity describing a continuum percolation model. Thus, rigorous bounds on this quantity are of great interest. In this section, we will develop two elaborations of the method of Section 5 that allow us to give bounds on $S(\bar{\rho})$. We first write the quantity $S(\bar{\rho})$ in terms of an integral over the two-point connectedness function, and attempt to derive bounds for this integral directly using the Kirkwood–Salsburg expansion (3.7). Difficulties that arise in this method are discussed in some detail while using it to derive some low-order bounds for $S(\bar{\rho})$. We then propose an alternative method of deriving bounds on $S(\bar{\rho})$ that uses the equivalent, for percolation, of the compressibility relation. Benefits and drawbacks of this method are also noted. Note that we use the notation $g_c(x)$ for the two-point connectedness function and $g_b(x)$ for the two-point blocking function.

The volume integral over the two-point connectedness function $g_c(x)$ is directly related to the mean cluster size $S(\bar{\rho})$ by

$$S(\bar{\rho}) = 1 + \bar{\rho} \int g_c(x_{12})\, dx_{12} \tag{6.1}$$

To see this, note that the probability density for finding a particle at x_2 conditional to one being located at x_1 is just $\bar{\rho} g_c(x_{12})$. Integrating this density over all x_2 gives the average size of the cluster containing the particle at x_1. Since this particle is chosen arbitrarily, (6.1) follows.

The case $n = 2$ of the Kirkwood–Salsburg hierarchy (3.7) gives upper and lower bounds for $g_c(1, 2)$ as discussed in Section 5. Naively, one might hope simply to integrate these bounds over the spatial variable x to derive bounds on $S(\bar{\rho})$. This, however, is problematic. To see this, note first that the complexity of percolation models requires that more than one connectedness function be defined for a fixed number of particles. The technical difficulties with which this paper is concerned arise largely from the fact that Kirkwood–Salsburg bounds on any one of these functions involve the others. Specifically, as seen in Eq. (5.7), a lower bound for the blocking function $g_c(1/2)$ requires an upper bound for the connectedness function $g_c(1, 2)$. However, because of the normalization

$$g_c(1, 2) + g_c(1/2) = 1 \tag{6.2}$$

these two types of bounds are equivalent. Thus, one requires an "initial" upper bound for $g_c(1, 2)$ prior to using this procedure. This function has the trivial bound of unity, but this bound is not integrable. This difficulty

recurs in higher orders of the bounding procedure. Nevertheless, one can extract information about $S(\bar{\rho})$. Using the bound (5.9a) in (6.1) gives

$$S(\bar{\rho}) \geqslant 1 + \bar{\rho} A_2 \tag{6.3}$$

with A_2 given by (5.2a).

Equations (5.7) and (5.8) yield

$$g_c(1, 2) \leqslant p_b(x_{12}) + [1 - p_b(x_{12})]\, \bar{\rho} \int p_b(x_{13})\, g_c(x_{23})\, dx_3$$

$$\leqslant p_b(x_{12}) + \bar{\rho} \int p_b(x_{13})\, g_c(x_{23})\, dx_3 \tag{6.4}$$

After integrating both sides over x_2, this inequality can be solved for the integral of $g_c(x)$:

$$\int g_c(1, 2)\, dx_2 \leqslant \frac{A_2}{1 - \bar{\rho} A_2} \tag{6.5}$$

In this series of inequalities, (6.5)–(6.9), we assume $1 - \bar{\rho} A_2 \geqslant 0$. Substituting this into (6.1) gives

$$S(\bar{\rho}) \leqslant \frac{1}{1 - \bar{\rho} A_2} \tag{6.6}$$

To refine this inequality, we integrate the first line of (6.4) to give

$$\int g_c(x_{12})\, dx_2 \leqslant A_2 + \bar{\rho} A_2 \int g_c(x_{12})\, dx_2$$

$$- \bar{\rho} \int p_b(x_{12})\, p_b(x_{13})\, g_c(x_{23})\, dx_2\, dx_3 \tag{6.7}$$

We can derive a lower bound on the last term by using (5.9a). This gives the bound

$$-\bar{\rho} \int p_b(x_{12})\, p_b(x_{13})\, g_c(x_{23})\, dx_2\, dx_3 - \bar{\rho} A_3 \tag{6.8}$$

Substituting (6.7)–(6.8) in (6.1) gives the bound for $S(\bar{\rho})$:

$$S(\bar{\rho}) \leqslant (1 - \bar{\rho}^2 A_3)/(1 - \bar{\rho} A_2) \tag{6.9}$$

It seems difficult to go beyond this directly. To proceed further, it may be more profitable to exploit a different bounding procedure for $S(\bar{\rho})$, which we now describe.

In an earlier paper[8] on the relationship between the CPM and percolation, we were led to explore the one-state limit of the CPM compressibility relation. This is a relation between the isothermal compressibility χ_T and spin-dependent distribution function $h_t = g_t - 1$. It is

$$\chi_T = 1 - \rho \sum_{\alpha_1, \alpha_2} \int h_t(x_{12}, \alpha_1, \alpha_2)\, dx_{12} \tag{6.10}$$

If one takes an s derivative of both sides of this relation and sets $s = 1$, the result is

$$\left.\frac{d}{ds}\right|_{s=1} \chi_T = \bar{\rho}\left[\int g_c(x)\, dx - \int h'(x)\, dx\right] \tag{6.11}$$

Here the function $h'(x)$ is defined by

$$h'(x_1, x_2) = \left.\frac{d}{ds}\right|_{s=1} [g_t(x_1\alpha, x_2\alpha) - 1] \tag{6.12}$$

This function $h'(x)$ is a new distribution function, first introduced into percolation theory in ref. 9. If the CPM pressure is differentiated with respect to s and s is set equal to unity, the result is $\langle n_c \rangle$, the mean number of clusters; the same operation applied to the CPM compressibility gives a related quantity

$$\left.\frac{d}{ds}\right|_{s=1} \chi_T = \frac{d}{d\bar{\rho}}\bar{\rho}\left[\frac{d}{d\bar{\rho}}\langle n_c \rangle - 1\right] \tag{6.13}$$

Note that bounds for $\langle n_c \rangle$ in the form of a polynomial in density immediately give similar bounds for the quantity on the lhs of (6.13).

One can see from (6.1) and (6.11)–(6.13) that, because sequences of upper and lower bounds for $\langle n_c \rangle$ are already provided in Section 5 of this paper, a similar sequence for the function $h'(x)$ would also give bounds for $S(\bar{\rho})$. We now provide such a sequence. Consider Eq. (3.2) for $n = 2$ with $\alpha_1 = \alpha_2 = \alpha$ an arbitrary spin state. Taking an s derivative of this equation and setting $s = 1$ gives, on the lhs, the function $h'(x)$. The terms on the rhs can be analyzed by the same methods used to analyze the terms of (3.11). Indeed, the resulting equation has exactly the form of (3.11), but with the weight factors $\bar{d}$ of (3.12) defined instead by

$$\bar{d}(P, P') = \begin{cases} 0, & b_2 = 0 \\ 1, & b_2 = 1 \\ (-)^{b_2 - 1}(b_2 - 1)!, & b_2 > 1 \end{cases} \tag{6.14}$$

with b_2 defined above (3.10). Thus, it is natural that a simple extension of the arguments used in Appendix B to analyze (3.1) also characterize terms on the rhs of this equation. We first give the resulting Kirkwood–Salsburg equation for $h'(x)$, then we explain this result. The equation is

$$h'(x_{12}) = -\left[\frac{d}{d\bar{\rho}}\langle n_c\rangle - 1\right] + \sum_{m=1}^{\infty} \frac{(-\bar{\rho})^m}{m!} \int \prod_{k=3}^{m+2} p_b(x_{1k})\, g_c\left(\frac{2}{3},\ldots, m+2\right) dx_3 \cdots dx_{m+2} \tag{6.15}$$

We analyze the result of applying the operation $(d/ds)|_{s=1}$ to (3.2) by expanding the CPM distribution functions on the rhs of this equation in graphs, following the discussion in Appendix B. Each of the spin variables $(\alpha_3,\ldots, \alpha_n)$ is summed over. Each has a factor $(1-\delta_{\alpha_1\alpha_i})$ in the integrand. Thus, each will generate a factor of $(s-1)$ if the spin sum is not collapsed by connecting the corresponding particle to one whose spin variable is not summed over. But here no such variables are available, since the spins in question are forbidden to be in state α_1 [by the factor $(1-\delta_{\alpha_1\alpha_i})$] and α_2 is equal to α_1. Thus, the best that can be done is to connect all the particles of $(x_3,\ldots, x_n)$ in one cluster, leaving only a single independent spin sum to generate an $(s-1)$ factor. The s derivative then eliminates this factor. Thus, terms of the form shown on the rhs of (6.15) will survive the s derivative and $s\to 1$ limit; the others will not.

Note that, in the limit $x_{12}\to\infty$, the function $h'(x_{12})$ must approach zero [according to Eq. (6.11), its volume integral is finite]. It is easily seen that (6.15) is consistent with this statement. If the limit $x_{12}\to\infty$ is taken, the terms in the sum on the rhs of (6.15) approach the corresponding terms on the rhs of (3.6), that is, their sum exactly cancels the first term in the rhs of (6.15). Unfortunately, however, the same argument shows that terms on the rhs of (6.15) do not separately vanish in the limit $x_{12}\to\infty$. Thus, the Kirkwood–Salsburg inequalities resulting from (6.15) must be combined with those from (3.6) to give the needed bounds on the integral of $h'(x)$ needed in turn to bound the mean cluster size (6.1). The resulting bounds are not very efficient. However, this line of approach, combined with the proper rearrangement of the series (6.15), still seems to us to offer the best possibilities for deriving stronger bounds on the mean cluster size.

We note in passing that Eq. (6.15) yields an immediate zero-separation theorem for the function $h'(x)$. Indeed, in the limit $x_{12}\to 0$, all terms on the rhs of (6.15) except the first are equal to zero by definition of the functions in those terms. Thus, the first term on the rhs of (6.6) is the value taken

on by $h'(x)$ at $x=0$. By extension of the arguments presented in Appendix A, the partial sums of (6.15) furnish alternate upper and lower bounds for $h'(x)$. In particular, the first term is also an upper bound for $h'(x)$, in addition to being its value at $x=0$. Thus, we gain a basic indication that this function may be monotone decreasing, at least in the case of random sphere percolation studied here.

7. CONVERGENCE PROOF FOR THE VIRIAL SERIES

In this section we obtain a lower bound for the radius of convergence of the virial series for the generalized blocking functions $g_b(1,\ldots,n;P)$. This will be done by exploiting the expansion (3.11) and reducing the problem to a similar problem already solved in the thermal theory of mixtures.[20–22] Because an equation for the mean number of clusters $\langle n_c \rangle$ has already been included in this hierarchy, we also obtain bounds on the virial series for this quantity. The argument of this section is very general; it applies to either random or correlated percolation with an arbitrary (finite-range) bond probability function $p_b(x)$.

For simplicity, we first carry out this development for the case of sphere percolation, in which the bond probability is taken to be

$$p_b(x)=\begin{cases}1, & x\leqslant\sigma\\ 0 & x>\sigma\end{cases} \tag{7.1}$$

We then sketch the argument for the general case.

The mean number of clusters per particle in random continuum percolation is given by the virial series[8]

$$\frac{\langle n_c\rangle}{\bar\rho}=1+\sum_{n=1}^{\infty}\frac{1}{n+1}\beta'_n\bar\rho^n \tag{7.2}$$

where the β'_n are related to the irreducible Mayer cluster integrals β_n of the CPM by

$$\beta'_n=\left.\frac{d}{ds}\right|_{s=1}\beta_n \tag{7.3}$$

An equation for the quantity $\langle n_c\rangle$ has been included in the hierarchy of integral equations given by (3.11) [see the discussion below (3.12)].

We now obtain a lower bound on the radius of convergence of the various virial series in percolation theory by placing upper bounds on the rate of growth of the coefficients in these series. The Kirkwood–Salsburg equations (3.11) will be used to do this. It will be convenient to rewrite

(3.11) in terms of the analog, for percolation, of the cavity distribution functions. These functions are defined by

$$y_b(1,..., n; P) = \bar{\rho}^n g_b(1,..., n; P) \Big/ \prod [1 - p_b(x_{ij})] \tag{7.4}$$

They result from dividing out of the blocking function $g_b(1,..., n; P)$ a factor $[1 - p_b(x_{ij})]$ for each pair (i, j) of particle indices (from the set 1 through n) that are separated by the partition P. These functions are just the $s \to 1$ limit of the CPM cavity distribution functions. They have the benefit of being continuous functions of their arguments x_i.

Within its radius of convergence, the cavity function $y_b(1,..., n)$ can be expanded in a virial series

$$y_b(1,..., n; P) = \sum_{l=0}^{\infty} \rho_{n,l}(1,..., n; P)\, \bar{\rho}^l \tag{7.5}$$

If the expansions (7.5) are substituted into the Kirkwood–Salsburg equations for the $y_b(1,..., n; P)$ and the coefficients of equal powers of $\bar{\rho}$ are equated, the result is

$$\begin{aligned} \rho_{n,l}(1,..., n; P) = \sum_{k=0}^{l} \frac{(-)^k}{k!} \sum_{P'} \bar{d}(P, P') \\ \otimes \int \cdots \int \frac{e_{n-1+k}(2,..., n+k; P')}{e_{n-1}(2,..., n; P)} \rho_{n-1+k,l-k}(2, 3,..., n+k; P') \\ \otimes \prod_{j=n+1}^{n+k} p_b(x_{1j}) \end{aligned} \tag{7.6}$$

Here the e_m functions inside the integral are CPM Boltzmann factors for the group of particles whose arguments they bear; they consist of a factor of $[1 - p_b(x)]$ for each pair of indices separated by the partition P'. In the ratio of e_k functions, each factor occurring in the denominator also occurs in the numerator; this is true because the sum over partitions p' only contains those that are extensions of the partition P of $(1,..., n)$.

We now make a basic observation. The recursive bounding procedure we have set up is almost identical to that used to prove convergence of virial expansions for the distribution functions of thermal mixtures. The main difference is the sum, in (7.6), over partitions P'. This sum results from the fact that a set of particles can be organized into clusters in many different ways. This extra multiplicity of terms will, naively, appear to result in a zero radius of convergence for the series involved. Combinatorially, the different clusters act like different species, whose number

is, *a priori*, unlimited. This analogy should not be pushed too far, however; different clusters really act like extended particles whose density is limited by repulsive forces that act between them. These "forces" are probabilistic in origin; they reflect the fact that two clusters that are densely interlaced are likely to directly connect together and become one cluster. We exploit this effect as follows: when the arguments of all y_b functions are restricted to a finite domain, most terms on the rhs of (7.6) will either vanish or be small.

These equations can now be used recursively to bound the coefficient functions $\rho_{n,l}$. Note that these equations relate $\rho_{n,l}$ with $n+l=m$ to $\rho_{n,l}$ with smaller values of m. Thus, if one has bounds

$$\max_P |\rho_{n,m-n}(1,..., n; P)| \leqslant K_{n,m-n} \tag{7.7}$$

these equations can be used to establish such bounds for successively larger values of m.

Before determining these bounds, we make one further observation. The ρ functions occurring on the rhs of (7.6) may have spatial arguments not contained in the ρ function on the lhs of that equation. All such arguments are restricted by factors of $p_b(x_{1k})$ to lie closer to x_1 than σ. Thus, the Kirkwood–Salsburg equations (3.11) form a closed hierarchy for the $\{y_b\}$, when the arguments $x_2,..., x_n$ are all restricted to lie closer to x_1 than a distance R. Here we choose $R=\sigma$. In the case of sphere percolation, a sphere of radius σ can contain at most 12 particles, no pair of which is directly connected. Thus, only blocking functions corresponding to a partition into 12 or less clusters will occur on the rhs. This is the analogue, for sphere percolation, of the fact that the thermal Kirkwood–Salsburg equations for a hard-sphere system truncate after 12 terms. The number of terms on the rhs of Eqs. (3.11) is thus the same as that in the Kirkwood–Salsburg equations for a mixture of 12 species. The bounds on the radius of convergence we derive for (7.2) will also be the same as in this case. Note that the weight factors $\bar{d}(P, P')$ are uniformly bounded by a constant (12! will suffice) and can thus be ignored in what follows. To see this, note that the argument just given allows us to limit our consideration to partitions P, P' into 12 or less clusters. Substituting $b_1+b_2\leqslant 12$ into the expression (3.12) for $\bar{d}$ gives the bound just stated.

One then obtains a convergence bound as follows: if (7.7) is true for $m=M-1$, then (7.6) implies

$$|\rho_{n,M-n}(1,..., n)| \leqslant \sum_{k=0}^{M-n} \frac{1}{k!} K_{n-1+k,M-n+k}(12A_2)^k \tag{7.8}$$

where A_2, as defined in (5.2a), is the volume integral of the bond probability. Therefore, (7.7) will also be true for $m = M$ if

$$K_{n,M-n} \geqslant \sum_{k=0}^{M-n} \frac{1}{k!} K_{n-1+k,M-n-k}(12A_2)^k \tag{7.9}$$

We can satisfy the inequality (7.9) and thus inductively satisfy the bounds (7.7) by choosing

$$K_{n,l} = s(s+l)^{l-1} \frac{(12A_2)^l}{l!} \tag{7.10}$$

In particular, (7.7) also bounds the growth of the virial coefficients. Thus, using the root test for convergence, we derive a nonzero lower bound for the radius of convergence R of that series:

$$R \geqslant \frac{1}{12A_2} \tag{7.11}$$

or

$$\rho\sigma^3 \geqslant \frac{1}{16\pi} = 0.0199 \tag{7.12}$$

We also give, for random percolation, a convergence bound which is complementary to (7.12). The order-m term on the rhs of (3.11) contains a sum of blocking functions, each with m position arguments or indices not contained in the blocking function on the lhs. In Appendix B, we recast this sum as a sum of connectedness functions, each with coefficient unity. There we show that the coefficient of a function $g_c(1,..., n+m; P')$ will be zero unless each of the indices $(n+1,..., n+m)$ is placed by the partition P' in a group together with at least one of the indices $(1,..., n)$. In other words, each partition on the rhs is a partition into the same number of groups as the partition P on the lhs. If we now recast the order-m term as a sum of blocking functions, we find that most of them have cancelled out, namely those with a partition P' not satisfying the constraint just stated. The ones that remain have been diminished in magnitude by losing some of their connectedness functions in the cancellation process just described. A glance at (2.10) shows that this can only diminish their magnitude. Thus, we get an upper bound for $g_b(1,..., n; P)$ from (3.11) by replacing each of these diminished blocking functions by a full blocking function and changing its sign if necessary; this is just the Schwartz inequality. We can now repeat the recursive bounding procedure of (7.6)–(7.11). We carry out a separate

recursion for each value of J, where J is the number of groups into which the partition P divides its indices. The above argument shows that functions $g_b(1,..., n; P)$ with different values of J are not coupled by this procedure. The resulting bound is then identical to that obtained for a mixture of J species with identical fugacities, namely

$$R \geqslant \frac{1}{JA_2} \tag{7.13}$$

For $J < 12$, this bound is better than (7.11). Note that no restriction was made on the domain of g_b in deriving this proof; neither did we place any constraints on the choice of $p_b(x)$.

In the case of positively correlated percolation with a finite-range repulsive potential $\phi(x)$, one can easily generalize the first convergence bound given in this section, i.e., that leading to (7.11). The second bound developed is, however, not yet available for this case.

8. CONCLUSIONS

The connectedness functions of percolation models offer a structure similar to, if more complex than, that of the distribution functions that characterize thermal models. As such it is gratifying to learn that many of the techniques used to study distribution functions have analogs for connectedness functions. In this paper, we develop, and extract information from, two hierarchies of Kirkwood–Salsburg type for the connectedness functions of random continuum percolation. We offer several suggestions for further research.

For a hard-sphere fluid, the partial sums of the fugacity series for the pressure provide upper and lower bounds on that quantity. The analog for random continuum percolation would be the statement that partial sums of the virial series for the mean number of clusters $\langle n_c \rangle$ give bounds on that quantity. Is this statement true? The proof by Penrose[25] for the thermal problem breaks down for percolation, essentially because the $\bar{d}$ weights of Eq. (3.13) are not positive definite. Still, the result may be true. If so, it would have great practical importance for the use of these bounds: virial coefficients for percolation[3,8] are far easier to calculate than bounds of the type developed in Section 5. The main reason for this is that virial coefficients for percolation involve only the specific linear combinations of Mayer graphs usually called modified Mayer graphs. The bounds of Section 5, on the other hand, will, in general, involve all of the separate Mayer graphs for percolation.

Kirkwood–Salsburg hierarchies can be constructed for lattice models

as well as continuum models. The hierarchies developed in this paper can be applied to random lattice percolation simply by replacing volume integrals by sums over lattice points. They would then describe a site–bond percolation process with site density $\bar{\rho}$ and bond density p_b. Certainly, lattice percolation models are a valuable testing ground for the higher-order bounds established in this paper, because the Mayer expansions on a lattice have been established to high order. Note, however, that multiple occupancy of sites is allowed in this random percolation model because of the absence of interaction. To recover the prohibition of multiple occupancy of sites, which is normally adopted in lattice percolation models, one must set

$$\phi(x_i, x_j) = \delta(x_i - x_j) \tag{8.1}$$

Strictly speaking, this takes us into the realm of correlated percolation, although only in a trivial way, since the interaction (8.1) does not establish long-range order.

Finally, can the methods described here be extended to correlated percolation with an arbitrary potential $\phi(x)$? This would permit valuable contact with the mathematical literature,[23,24] in which correlated percolation processes are frequently defined by considering two particles to be directly connected if they are closer together than the range of the interaction. Preliminary results are available. Equations (3.11) have the alternating bound property for an arbitrary positive potential $\phi(x)$. Thus, they provide an infinite sequence of upper and lower bounds for any positively correlated percolation model. We show this at the end of Appendix B. The convergence proof of Section 7 is easily extended to provide a bound on the radius of convergence for an arbitrary positive, finite-range potential. In particular, this includes the well-studied case of PCS percolation,[18] in which particles have a hard core surrounded by a larger inclusion sphere defining pairwise connectedness. A separate study of numerical applications of the methods developed here is being prepared.

APPENDIX A. ON THE REMAINDER TERM IN THE KIRKWOOD–SALSBURG EQUATIONS (3.6)–(3.7)

In this Appendix, we show that the remainder terms given by successive truncations of Eqs. (3.6)–(3.7) alternate in sign, thus establishing the upper and lower bounds calculated in Section 4. Terms on the rhs of (3.6)–(3.7) clearly alternate in sign. The remainder term shares the structure of these terms and thus inherits their definiteness in sign.

The thermal Kirkwood–Salsburg equations may be developed systematically as a Taylor series in a small parameter λ which is identified with the interaction strength of a particular particle, which is here chosen to be particle 1. The remainder term resulting from truncation of these equations after l terms is then given directly by the remainder theorem of calculus. Equations (3.6)–(3.7) are derived from the thermal Kirkwood–Salsburg hierarchy by applying the projection operator (3.3). Their remainder term is derived in the same way. It is[3]

$$R_{l+1} = (-\bar{\rho})^{l+1} \sum_{\{\alpha\}} \prod_{k} (1-\delta_{\alpha_1\alpha_k}) \int_0^1 d\lambda \frac{(1-\lambda)^l}{l!} \frac{\Xi(\lambda)}{\Xi(0)} \prod_{i=2}^{k} e^{-\gamma(x_i,\lambda)} \otimes \int \prod_{i=k+1}^{k+l+1} f(x_{1i})\, e^{-\gamma(x_i,\lambda)} g_l(2,\ldots,k+l+1)\, dx_{k+1} \cdots dx_{k+l+1} \quad \text{(A.1)}$$

To establish the sign of this term, we first simplify it, then carry out the spin sum. Except for the integration over λ (which involves only positive quantities) this remainder term differs from a typical term on the rhs of (3.6)–(3.7) only in the presence of the factors $e^{-\gamma}$. Once we show that these factors are positive definite, and that their spin dependence does not affect the value of (A.1), the result follows by the same argument that shows that the rhs terms of (3.6)–(3.7) alternate in sign.

These factors are defined by

$$e^{\gamma(x_i,\lambda)} = [1 + \lambda f(x_{1i})] \quad \text{(A.2)}$$

with the CPM Mayer function given by

$$f(x_{1i}) = -p_b(x_{1i})(1-\delta_{\alpha_1\alpha_i}) \quad \text{(A.3)}$$

Each such factor occurring in (A.1) is paired with a factor $(1-\delta_{\alpha_1\alpha_i})$. The ones outside the integral get such a factor from the projection operator; the ones inside the integral get this factor from the Mayer functions. Because of this, we can make the replacement

$$e^{\gamma(x_i,\lambda)} \to [1 - \lambda p_b(x_{1i})] \quad \text{(A.4)}$$

This quantity (as well as its reciprocal) is positive definite. The function g_l under the integral sign is then transformed into a connectedness function exactly as in the terms on the rhs of (3.5). Since this function is positive definite, the sign dependence of the remainder term results entirely from the product inside the integral sign. Thus, the remainder term has the sign $(-)^{l+1}$.

[3] Our notation follows that in ref. 20. See Eq. (3.10) of that paper.

B. PROPERTIES OF THE INTEGRANDS IN THE KIRKWOOD–SALSBURG HIERARCHY (3.11)

In this Appendix, explicit expressions are derived for the integrands in the Kirkwood–Salsburg hierarchy (3.11). These show immediately that these integrands lie between zero and unity, and that they, in fact, define probability densities that are readily characterized. In perticular, we show that the nth-order term on the rhs of (3.11) has the sign $(-)^n$. This property will extend to the remainder term of (3.11) (the remainder after the first n terms) and thus show that truncations of (3.11) give alternating upper and lower bounds. This is the same sequence carried out in Appendix A for Eqs. (3.6)–(3.7). We show how to extend this argument to the case of correlated percolation at the end of this Appendix.

The basis of our argument is this: as we saw in Section 3, we can get a useful Kirkwood–Salsburg hierarchy only in terms of the blocking functions. However, we can best understand the content of a typical term on the rhs of (3.11) by evaluating it in terms of connectedness functions. To do this, we return to Eq. (3.2), expand each distribution function on the rhs following Fortuin and Kastelyn, carry out the spin sums, and characterize the terms that survive the $s \to 1$ limit which is needed to give Eq. (3.11).

Thus, we first express the CPM distribution functions $g_l(1\alpha_1,..., n\alpha_n)$ as an ensemble average over the system characterized by the Hamiltonian (1.1) [with $\phi(x)=0$]. The total Boltzmann factor can be written

$$\prod_{i<j} e^{-\beta H_{ij}} = \prod_{i<j} \{p_b(x_{ij})\, \delta_{\alpha_i\alpha_j} + [1 - p_b(x_{ij})]\} \tag{B.1}$$

with $p_b(x_{ij})$ given by (1.2). We now expand this product and identify each term with a graph having a particular connectedness structure, just as in the argument following Eq. (2.2). We will show that the surviving graphs are precisely those which make up a particular subset of the n-point connectedness functions. Since the sum of *all* the n-point connectedness functions gives the n-point distribution function (equal to unity for random percolation), this will establish the claims made above.

If the expansion of (B.1) is substituted into (3.11), all terms will vanish except for those in which each of the particles at internal positions $x_{n+1},..., x_{n+m}$ (those integrated over) are connected to at least one of the particles at external positions $x_2,..., x_n$. To see this, note that each of the spin variables $\alpha_{n+1},..., \alpha_{n+m}$ is summed over the integrand, and that the integrand contains factors $(1-\delta_{\alpha_1\alpha_j})$ corresponding to each. Thus, each such sum will give a factor of $(s-1)$ and the corresponding term will vanish. Only a factor of Kronecker delta equating an external and internal spin variable will collapse the spin sum over the latter, and thus give a non-

zero contribution to the rhs. Only direct or indirect bonds between the corresponding particles produce this factor. This argument shows that in the $s \to 1$ limit, only the part of the CPM distribution function will survive that corresponds to the probability density just described. Because the connectedness functions describe disjoint sets of events, this probability density can be written as a sum of such functions, each with coefficient unity. We can now repeat the argument of Appendix A to show that Eq. (3.11) has the alternating bound property.

The argument for correlated percolation is similar. We first write the Mayer bond for the full pairwise Hamiltonian (1.1):

$$f(x) = -e^{-\beta\phi(x)} p_b(x)(1 - \delta_{\alpha_i \alpha_j}) + (e^{-\beta\phi(x)} - 1) \tag{B.2}$$

We now expand the product of f bonds in the integrand on the rhs of (3.11). For each of the resulting terms, we carry out the spin sums and interpret the result as a sum of connectedness functions. Essential in the process is the fact that, for positive potentials $\phi(x)$, Eq. (B.2) expresses the Mayer bond as a sum of two negative-definite terms. The conclusions in this case are identical to those above.

C. A SEQUENCE OF MONOTONE CONVERGENT BOUNDS FOR BLOCKING FUNCTIONS

In this Appendix, we show the existence of a sequence of bounds for the generalized blocking functions that, except possibly for a small number of low-order bounds, will converge monotonically to these functions. It is felt that the techniques used in this argument can be sharpened considerably; we present the argument as much for this reason as for the specific results demonstrated here.

The generalized blocking functions used in this paper to develop integral equation hierarchies are, for several reasons, a fortunate choice of basis functions for describing the structure of percolation. One of these is the existence, for these functions, of a powerful set of inequalities. One has

$$g_b(1,..., n; P) \geqslant g_b(1,..., n+1; P') \tag{C.1}$$

Here P' is any partition of $(1,..., n+1)$ consistent with P, in the sense that it coincides with P when restricted to $(1,..., n)$. Equation (C.1) is valid because the blocking functions are defined as the probability that a group of connections are *absent*, namely those that would join two particles whose indices are separated by the partition P. Adding more particles to one of the subsets indexed by P, and thus more constraints, can only

reduce the corresponding probability. An elementary theorem of analysis asserts:

Theorem 1. If successive terms in an alternating series decrease in magnitude to zero, then the successive partial sums of that series give monotonically convergent upper and lower bounds to the sum of the series.

We want to use this theorem to establish a monotone sequence of bounds for the sequence for the series in (3.11) and thus for the blocking functions. In this Appendix, for simplicity, we will focus on the case $n=2$, i.e., on bounds for the function $g_c(1/2)$. Two considerations are involved in doing this: first, showing that the magnitudes of terms in the density expansion in (3.11) eventually decrease; second, treating the fact that the $\bar{d}$ weights in (3.11) may be of either sign. The monotone decrease of the magnitudes of these terms would be established if (C.1) could be used to show that each contribution to the term of order m on the rhs of (3.11) dominates a group of contributions to the term of order $(m+1)$. We call the latter the "descendants" of the former. They will be contributions derived from it in the sense of (C.1), that is, by adding a particle to one of the subsets defined by the partition P. By (3.12), a contribution and its descendants will have the same $\bar{d}$ weight.

If a g_b function partitions its arguments into b_1 subsets, the Kirkwood–Salsburg expansion (3.11) of that function will express it in terms of g_b functions that partition their arguments into no more than b_1+12 subsets. The argument following Eq. (6.8) establishes this. For the case $b_1=2$ considered here, i.e., for the two-point function $g_c(1/2)$, the expansion of the rhs of (3.11) will involve partitions P' into $b_1+12=14$ subsets. Thus, for $m>14$, contributions of order $m+1$ can always be paired with contributions of order m having partitions with the same number of subsets. This is useful because we want to compare only contributions having the same $\bar{d}$ weight. Also, because of the term $m!$ in the denominators of each term, the sum of contributions of order $m+1$ will be less than the sum of contributions of order m provided that each contribution has no more than 14 descendants. Thus, the magnitudes of successive terms in the density expansion of (3.11) will decrease, possibly after a finite number of terms of non-monotone behavior.

If one then divides this density expansion into a sum of those contributions with $\bar{d}$ negative and those with $\bar{d}$ positive, denoted g_{1p} and g_{1n}, respectively, the lemma cited at the start of this Appendix will apply. One can thus write $g_c(1/2)$ as a difference of these two functions, and find a sequence of decreasing upper bounds on the former, and monotone increasing lower bounds on the latter (again except possibly for the first 14 terms). Their successive differences will give monotone decreasing upper

bounds on $g_c(1/2)$. The corresponding process gives monotone increasing lower bounds. This same procedure gives monotone convergent bounds for any g_b function, except possibly for the first $b_1 + 12$ bounds in the sequence.

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