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Percolation theory in a gas

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Received 23 May 1977

Abstract. A low density expansion for the pair connectedness in a gas is obtained by methods similar to those used for a solid. In the case of an ideal lattice gas a change of variable enables the usual expansion for a solid to be re-derived. The new formulation allows the use of renormalisation techniques and k -space diagrams. The possibility of interactions is also considered.

1. Introduction

A standard site percolation model on a crystal lattice is such that each site independently of all others is designated either 'occupied' or 'vacant'. The term occupied has a variety of interpretations depending on the use of the model (Essam 1972). The pair connectedness P_{ab} of two sites a and b is the probability that there is a nearest-neighbour path of occupied sites connecting them (conventionally the sites a and b are counted as part of the path). Low-density expansions in powers of p , the probability of occupation, are usually obtained (Cox and Essam 1976) using the result

$$P_{ab}(p) = \sum_{g \in \mathcal{G}_{ab}} d(g)p^v \quad (1)$$

where \mathcal{G}_{ab} is the set of two-rooted subgraphs of the lattice (treating the sites as vertices, the nearest-neighbour pairs as edges and a and b as root points) and v is the number of vertices in g . The ' d -weight', $d(g)$ (Arrowsmith and Essam 1977), is zero unless g is connected and the derived graph obtained by including the edge $[a, b]$ has no articulation points. The graphs which are not excluded by these conditions are known as *one-irreducible*. If \mathcal{C} is a list of such graphs (no two of which are isomorphic, except that a graph in which the root points are asymmetrically placed appears twice, the initial and final roots being labelled 1 and 2 respectively) equation (1) may be written

$$P_{ab}(p) = \sum_{g \in \mathcal{C}} \frac{d(g)}{s(g)} m(g)p^v. \quad (2)$$

Here $m(g)$ is the number of ways of mapping the vertices of g onto the lattice sites such that no two vertices are mapped onto the same site, $1 \rightarrow a$, $2 \rightarrow b$, and adjacent vertices are mapped onto nearest-neighbour pairs. The symmetry number $s(g)$ is the number of ways of mapping g onto itself with the root points fixed.

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Efficient computer programs have been constructed to obtain $m(g)$ for small graphs (Martin 1974) but theoretical development is hindered by the non-factorisation of $m(g)$ for graphs which may be formed by series parallel combination of smaller graphs. Such a factorisation occurs for $s(g)$ and $d(g)$ but the difficulty with $m(g)$ is caused by the restriction of one-to-one mapping.

The expansion described here is for a gas, the particles of which may be in a continuum or on the sites of a lattice (lattice gas) but in the latter case multi-occupation is allowed. The expansion is in powers of the density ρ , and is similar to (2) but in the case of the lattice gas the mapping is now many-to-one. The resulting factorisation of $m(g)$ allows the use of renormalisation techniques and k -space diagrams.

The expansions for the continuum are of interest in their own right since previous work on the continuum model has been restricted to the cluster size distribution. Haan and Zwanzig (1977) obtained low-density expansions for this distribution and analysed the mean cluster size. Monte Carlo calculations of the distribution have also been made (Roberts 1967, Roberts and Storey 1968, Fremlin 1976).

By interpreting p as the probability that a site is occupied by at least one particle, p and ρ may be simply related and expansion (2) is recovered.

Recently the Mayer expansion for an imperfect gas (Uhlenbeck and Ford 1962) has been extended to include the pair connectedness (Coniglio *et al* 1977). The present method gives an equivalent result for the ideal gas and is intermediate between the Mayer theory and existing percolation theory. For the interacting gas our result is expressed in terms of the many-particle distribution functions. The standard Mayer theory may then be used to obtain low-density expansions for the latter (Uhlenbeck and Ford 1962).

2. General formulation for the pair connectedness and cluster size

Consider a gas of n particles distributed in a region Ω of volume V and let $D_n(\mathbf{r}_1, \dots, \mathbf{r}_n)$ be the probability density for finding the particles at $\mathbf{r}_1, \dots, \mathbf{r}_n$. In the case when all the particles are identical we shall need the s -particle distribution functions $n_s(\mathbf{r}_1, \dots, \mathbf{r}_s, n)$ as defined by Uhlenbeck and Ford (1962):

$$n_s(\mathbf{r}_1, \dots, \mathbf{r}_s, n) = (n)_s \int \dots \int d\mathbf{r}_{s+1} \dots d\mathbf{r}_n D_n(\mathbf{r}_1, \dots, \mathbf{r}_n) \quad (3)$$

and has the interpretation of being the probability density for finding *any* s particles in positions $\mathbf{r}_1, \dots, \mathbf{r}_s$. The number density ρ is defined to be n/V . For the ideal gas $D_n = V^{-n}$ and $n_s = (n)_s V^{-s}$. In the thermodynamic limit, $n \rightarrow \infty$, $V \rightarrow \infty$, with ρ fixed, $n_s \rightarrow \bar{n}_s(\mathbf{r}_1, \dots, \mathbf{r}_s)$ and this limit is equal to ρ^s for an ideal gas.

The discussion will be concerned with paths through the system with the particles used as 'stepping stones'. Define the indicator

$$\gamma_{ij}(\mathbf{r}_i, \mathbf{r}_j) = \begin{cases} 1 & \mathbf{r}_j \in \omega(\mathbf{r}_i) \\ 0 & \text{otherwise,} \end{cases} \quad (4)$$

where $\omega(\mathbf{r}_i)$ is the region which can be reached in a single step from \mathbf{r}_i . For a continuum, $\omega(\mathbf{r}_i)$ is usually a sphere of radius R centred on \mathbf{r}_i and for a lattice gas $\omega(\mathbf{r}_i)$ is usually the cells which are adjacent to the cell which contains \mathbf{r}_i . In both these cases γ is independent of the particle labels i and j and is symmetric under interchange of \mathbf{r}_i

and r_j , however we envisage situations in which γ may not have one or both of these properties.

A walk between particles 1 and 2 is an ordered sequence of particles beginning with 1 and ending with 2, the intermediate particles being chosen from the remaining $n - 2$ particles. Let W be the set of all such walks. In a given configuration of particles a walk w is said to be open if for each step $\gamma_{ij}(\mathbf{r}_i, \mathbf{r}_j) = 1$. Let $\gamma(w) = 1$ or 0 according as w is open or closed. Now

$$\prod_{w \in W} (1 - \gamma(w)) \equiv \sum_{W' \subseteq W} (-1)^{|W'|} \prod_{w \in W'} \gamma(w) = \begin{cases} 1 & \text{if no walk is open} \\ 0 & \text{if at least one walk is open.} \end{cases} \tag{5}$$

The pair connectedness $P_{12}(\mathbf{r}_1, \mathbf{r}_2)$ of particles 1 and 2 is the probability density that they are at \mathbf{r}_1 and \mathbf{r}_2 and that at least one walk between 1 and 2 is open; it is therefore given by

$$P_{12}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\phi \subset W' \subseteq W} (-1)^{|W'|+1} \left\langle \prod_{w \in W'} \gamma(w) \right\rangle \tag{6}$$

where $\langle \ \rangle$ is an average over all positions of the particles 3, . . . , n using the probability density $D(\mathbf{r}_1, \dots, \mathbf{r}_n)$.

The connecting graph $G(W')$ corresponding to the set of walks W' , is the directed graph $(\mathcal{V}, \mathcal{A})$ where \mathcal{V} is the subset of particles used by at least one of the walks and \mathcal{A} is the subset of ordered pairs which constitute a step of at least one of the walks. $G(W')$ is rooted at 1 and 2 and directed from 1 to 2 and has no multi-arcs; however the arcs (i, j) and (j, i) may both appear. Equation (6) may be simplified by grouping together all W' having the same $G(W')$ (when considered as abstract labelled graphs) and weighting each labelled graph with its 'directed d -weight'

$$\vec{d}(g) = \sum_{\substack{\phi \subset W' \subseteq W \\ G(W')=g}} (-1)^{|W'|+1}. \tag{7}$$

It has been shown (Arrowsmith and Essam 1977) that $\vec{d}(g) = 0$ whenever g is cyclic and in this context the arcs (i, j) and (j, i) constitute a cycle of length two. It was also shown that for a graph which is acyclic and coverable by self-avoiding paths from 1 to 2

$$\vec{d}(g) = (-1)^{i(g)+1} \tag{8}$$

where $i(g) = a - v + 2$, the number of algebraically independent paths from 1 to 2. Here $a = |\mathcal{A}|$. By construction, all $G(W')$ are coverable, and if we let \vec{L}_{12} be the class of all such acyclic labelled graphs with ordinary vertices having labels chosen from 3, . . . , n then (6) becomes

$$P_{12}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{g \in \vec{L}_{12}} (-1)^{i(g)+1} \langle \gamma(g) \rangle \tag{9}$$

where

$$\gamma(g) = \prod_{(i,j) \in \mathcal{A}} \gamma_{ij}(\mathbf{r}_i, \mathbf{r}_j). \tag{10}$$

If $\gamma_{ij}(\mathbf{r}_i, \mathbf{r}_j)$ is symmetric we may group together all directed graphs which correspond to the same undirected graph and write

$$P_{12}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{g \in L_{12}} d(g) \langle \gamma(g) \rangle. \quad (11)$$

Here the 'd-weight' is the sum of the 'directed d-weights' over all directed graphs which correspond to the undirected graph g , and L_{12} is the corresponding class of labelled undirected graphs.

In the case when all the particles are identical it is more appropriate to consider the pair connectedness $P(\mathbf{r}_1, \mathbf{r}_2)$ which is the probability density that any two particles are at \mathbf{r}_1 and \mathbf{r}_2 and there is a path between them. Also in this case we may collect together all labelled graphs which are the same when the labels are ignored since $\langle \gamma(g) \rangle$ is independent of the labelling. Equation (9) now reads

$$P(\mathbf{r}_1, \mathbf{r}_2) = (n)_2 P_{12}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{g \in \tilde{\mathcal{C}}} \frac{\tilde{d}(g)}{\tilde{s}(g)} (n)_v \langle \gamma(g) \rangle \quad (12)$$

where $\tilde{\mathcal{C}}$ corresponds to \tilde{L}_{12} but now each member of $\tilde{\mathcal{C}}$ carries labels which are a specific permutation of $1, \dots, v$ and conventionally 1 and 2 are the initial and final vertices. $\tilde{s}(g)$ is the symmetry number of g (considered as a directed graph). In terms of the s -particle distributions

$$P(\mathbf{r}_1, \mathbf{r}_2) = \sum_{g \in \tilde{\mathcal{C}}} \frac{\tilde{d}(g)}{\tilde{s}(g)} \int \dots \int d\mathbf{r}_3 \dots d\mathbf{r}_v n_v(\mathbf{r}_1, \dots, \mathbf{r}_v, n) \gamma(g). \quad (13)$$

The equation for the symmetric case corresponding to (12) is obtained by removing the arrows. The low-density expansions of $n_v(\mathbf{r}_1, \dots, \mathbf{r}_v, n)$ for a gas with pair potentials is described by Uhlenbeck and Ford (1962) and their article enables contact to be made with the Mayer expansion of Coniglio *et al* (1977).

Equation (13) is valid for a finite system with n finite so that all walks are of finite length ($\leq n$ steps). In going to the thermodynamic limit we let n and V go to infinity keeping $\rho = n/V$ fixed and a given walk $w \in W$ is only considered open if it lies within a sphere of fixed radius centred on \mathbf{r}_1 and containing \mathbf{r}_2 . Finally the radius of the sphere is allowed to become infinite. This procedure is important when considering the region of density where there are infinite clusters.

The mean cluster size $S(\mathbf{r}_1)$ is the expected number of particles accessible by a walk from a given particle (particle 1 say) including that particle. This may be expressed in terms of the conditional pair connectedness

$$P(\mathbf{r}_2|\mathbf{r}_1) = P(\mathbf{r}_1, \mathbf{r}_2)/n_1(\mathbf{r}_1, n) \quad (14)$$

which is the probability density that there is a particle at \mathbf{r}_2 which is accessible by a walk from a particle given to be at \mathbf{r}_1 . Clearly

$$S(\mathbf{r}_1) = 1 + \int d\mathbf{r}_2 P(\mathbf{r}_2|\mathbf{r}_1) \quad (15)$$

and for a homogeneous gas in the thermodynamic limit this will be independent of \mathbf{r}_1 .

3. Formulation in k space

In this section we assume that we have gone to the thermodynamic limit and that the gas is homogeneous so that $n_1(\mathbf{r}_1, n) = \rho$. We also assume that $\gamma_{ij}(\mathbf{r}_i, \mathbf{r}_j)$ is a function $\hat{\gamma}$ of $\mathbf{r}_j - \mathbf{r}_i$ and hence $P(\mathbf{r}_2|\mathbf{r}_1)$ is a function \hat{P} of $\mathbf{r}_2 - \mathbf{r}_1$. Taking Fourier transforms we have

$$\gamma_{ij}(\mathbf{r}_i, \mathbf{r}_j) = \hat{\gamma}(\mathbf{r}_j - \mathbf{r}_i) = \frac{1}{(2\pi)^d} \int d\mathbf{k}_{ij} \exp[-i\mathbf{k}_{ij} \cdot (\mathbf{r}_j - \mathbf{r}_i)] \tilde{\gamma}(\mathbf{k}_{ij}) \quad (16)$$

and hence

$$\begin{aligned} \tilde{P}(\mathbf{k}) &= \int d\mathbf{r}_2 \exp[i\mathbf{k} \cdot (\mathbf{r}_2 - \mathbf{r}_1)] \hat{P}(\mathbf{r}_2 - \mathbf{r}_1) \\ &= \frac{1}{\rho} \sum_{g \in \mathcal{G}} \frac{\vec{d}(g)}{\vec{s}(g)} \frac{1}{(2\pi)^{ad}} \int \dots \int \prod_{(i,j) \in \mathcal{A}} d\mathbf{k}_{ij} \tilde{n}_v(\boldsymbol{\kappa}_1, \dots, \boldsymbol{\kappa}_v) \tilde{\gamma}(g) \end{aligned} \quad (17)$$

where d is the dimensionality.

$$\tilde{n}_v(\boldsymbol{\kappa}_1, \dots, \boldsymbol{\kappa}_v) = \int \dots \int d\mathbf{r}_2 \dots d\mathbf{r}_v \tilde{n}_v(\mathbf{r}_1, \dots, \mathbf{r}_v) \prod_{i \in \mathcal{V}} \exp[i\boldsymbol{\kappa}_i \cdot (\mathbf{r}_i - \mathbf{r}_1)] \quad (18)$$

with

$$\boldsymbol{\kappa}_i = \sum_{(i,j) \in \mathcal{A}} \mathbf{k}_{ij} - \sum_{(j,i) \in \mathcal{A}} \mathbf{k}_{ji} + \mathbf{k}(\delta_{2,i} - \delta_{1,i}) \quad (19)$$

and

$$\tilde{\gamma}(g) = \prod_{\alpha \in \mathcal{A}} \tilde{\gamma}(\mathbf{k}_\alpha) \quad (20)$$

(note that $\sum_{i \in \mathcal{V}} \boldsymbol{\kappa}_i = \mathbf{0}$).

4. Special models

In this section we consider the ideal gas and lattice gas and make contact with standard percolation theory for a lattice system.

4.1. The ideal gas

In § 2 we noted that for an ideal gas in the thermodynamic limit $n_s \rightarrow \rho^s$. In this limit, equation (13) therefore simplifies to

$$P(\mathbf{r}_2|\mathbf{r}_1) = \sum_{g \in \mathcal{G}} \frac{\vec{d}(g)}{\vec{s}(g)} \rho^{v-1} \int \dots \int d\mathbf{r}_3 \dots d\mathbf{r}_v \gamma(g). \quad (21)$$

A nodal point on a two-rooted graph is one through which all paths between the roots must pass. If g is a nodal graph (i.e. has at least one nodal point) the integral factorises and we can take advantage of this to reduce the size of the class of graph to be summed over. Let $\tilde{\mathcal{N}}$ be the subset of \mathcal{G} which is non-nodal. The direct conditional pair connectedness $C(\mathbf{r}_2|\mathbf{r}_1)$ is defined by (21) with \mathcal{G} replaced by $\tilde{\mathcal{N}}$. Now consider the nodal terms in (21) and choose the nodal point closest to 1 to be 3. Since \vec{d} and \vec{s} may

be written as products over their non-nodal parts, the part of the sum coming from the nodal graphs contains a factor $C(\mathbf{r}_3|\mathbf{r}_1)$ and we may write

$$P(\mathbf{r}_2|\mathbf{r}_1) = C(\mathbf{r}_2|\mathbf{r}_1) + \int d\mathbf{r}_3 C(\mathbf{r}_3|\mathbf{r}_1)P(\mathbf{r}_2|\mathbf{r}_3) \tag{22}$$

or in terms of Fourier transforms

$$\tilde{P}(\mathbf{k}) = \frac{\tilde{C}(\mathbf{k})}{1 - \tilde{C}(\mathbf{k})}. \tag{23}$$

We note that $\tilde{C}(\mathbf{k})$ is given by (17) with \mathcal{C} replaced by $\tilde{\mathcal{N}}$ and for the ideal gas in the thermodynamic limit

$$\tilde{n}_v(\boldsymbol{\kappa}_1, \dots, \boldsymbol{\kappa}_v) = (2\pi)^{d(v-1)} \rho^v \prod_{i \in \mathcal{V}} \delta(\boldsymbol{\kappa}_i) \tag{24}$$

so that the wavevector at each vertex is conserved.

The mean cluster size is given by

$$S = 1 + \tilde{P}(\mathbf{0}) = (1 - \tilde{C}(\mathbf{0}))^{-1}. \tag{25}$$

Equation (23) has been obtained for the more general case of an imperfect gas with pairwise interactions by Coniglio *et al* (1977).

4.2. Lattice gas

The continuum formalism may be taken over to the lattice situation by constructing the Wigner–Seitz cell for each lattice point. Let $c_l (\in L)$ be the cell containing lattice point l and let $\omega(\mathbf{r}_i)$ be the set of cells adjacent to the cell containing \mathbf{r}_i . Thus

$$\gamma_{ij}(\mathbf{r}_i, \mathbf{r}_j) = \gamma_{ij}^*(c_i, c_j) = \begin{cases} 1 & c_j \text{ adjacent to } c_i \\ 0 & \text{otherwise} \end{cases} \tag{26}$$

and $\gamma(g)$ depends only on the cells in which the particles are situated. Replacing $\int d\mathbf{r}_i$ by $\sum_{c_i \in L} \int_{\mathbf{r} \in c_i} d\mathbf{r}_i$ in (13) we obtain the probability $P_{12}^*(c_1, c_2)$ that particles 1 and 2 are in c_1 and c_2 and are connected by a path, in the form

$$P_{12}^*(c_1, c_2) = \sum_{g \in \mathcal{G}} \frac{\tilde{d}(g)}{\tilde{s}(g)} (n-2)_{v-2} \sum_{c_3 \in L} \dots \sum_{c_v \in L} \hat{n}_v(c_1, \dots, c_v, n) \gamma(g) \tag{27}$$

where $\hat{n}_v(c_1, \dots, c_v, n)$ is the probability of finding particles 1, ..., v in cells c_1, \dots, c_v respectively.

We consider two cases which turn out to be related.

(i) Suppose that the interactions are such that not more than one particle can occupy a given cell and that otherwise the potential is zero. This corresponds to the standard ‘site problem’ on a lattice described in the introduction. In this case

$$\hat{n}_v(c_1, \dots, c_v, n) = \begin{cases} \frac{1}{(N)_v} & \text{for } c_1 \neq c_2 \neq \dots \neq c_v \\ 0 & \text{otherwise} \end{cases} \tag{28}$$

where N is the number of lattice sites. If $P^*(c_1, c_2)$ is the probability that c_1 and c_2 are

occupied by any two particles and are connected by a path then

$$P^*(c_1, c_2) = \sum_{g \in \mathcal{G}} \frac{\vec{d}(g)}{\vec{s}(g)} \frac{(n)_v}{(N)_v} \sum_{\substack{\{c_3, \dots, c_v\} \in L^{v-2} \\ c_i \neq c_m}} \gamma(g). \tag{29}$$

In the thermodynamic limit

$$P^*(c_1, c_2) = \sum_{g \in \mathcal{G}} \frac{\vec{d}(g)}{\vec{s}(g)} m(g) p^v \tag{30}$$

where $m(g)$ is the number of mappings defined in § 1 and $p = n/N$ the probability of occupation. Equation (30) reduces to (2) when directed graphs corresponding to the same undirected graph are grouped together.

In this example (15) reduces to the usual result (Essam 1972)

$$S(c_1) = 1 + p^{-1} \sum_{c_2 \in L \setminus c_1} P^*(c_1, c_2) \tag{31}$$

for the expected number of occupied cells connected to c_1 .

We note that the ‘bond problem’ may be included by drawing cells surrounding each bond and defining adjacency by the incidence of the bonds.

(ii) Now suppose that there are no interactions. In this case

$$\hat{n}_v(c_1, \dots, c_v, n) = N^{-v} \tag{32}$$

and defining $\bar{P}(c_1, c_2)$ to be the probability that two particles known to be in cells c_1 and c_2 are connected by a path, we have

$$\begin{aligned} \bar{P}(c_1, c_2) &= N^2 P_{12}^*(c_1, c_2) \\ &= \sum_{g \in \mathcal{G}} \frac{\vec{d}(g)}{\vec{s}(g)} \frac{(n-2)_{v-2}}{N^{v-2}} \sum_{c_3 \in L} \dots \sum_{c_v \in L} \gamma(g) \end{aligned} \tag{33}$$

which in the thermodynamic limit becomes

$$\bar{P}(c_1, c_2) = \sum_{g \in \mathcal{G}} \frac{\vec{d}(g)}{\vec{s}(g)} \bar{m}(g) \rho^{v-2} \tag{34}$$

where $\bar{m}(g)$ is now the number of mappings of g when multi-occupation is allowed and $\rho = n/N$.

Examples (i) and (ii) may be related by defining p to be the probability that a cell is occupied by *at least one* particle, thus

$$p = 1 - e^{-\rho}. \tag{35}$$

$\bar{P}(c_1, c_2)$ is now the probability of at least one path of occupied cells connecting c_1 and c_2 given that they are occupied. Clearly therefore

$$\bar{P}(c_1, c_2) = p^{-2} P^*(c_1, c_2) |_{p=1-e^{-\rho}}. \tag{36}$$

Thus if a low-density expansion is obtained for \bar{P} up to ρ^k then P^* may be obtained up to ρ^{k+2} by substitution.

Because of the possibility of multi-occupation $\bar{m}(g)$ factorises for nodal graphs and in parallel with (22)

$$\bar{P}(c_1, c_2) = \bar{C}(c_1, c_2) + \rho \sum_{c_3 \in L} \bar{C}(c_1, c_3) \bar{P}(c_3, c_2). \tag{37}$$

The passage to \mathbf{k} space follows similarly, the \mathbf{k} sums now being over the Brillouin zone for the lattice.

We note that equation (22) has no parallel in the case of P^* (unless it is merely used as a definition of C^*) and the use of the ρ expansion rather than the p expansion to obtain P^* is a major advance. Similarly $\tilde{P}^*(\mathbf{k})$ has no simple graphical interpretation when the p expansion is used but it may be trivially derived from $\tilde{P}(\mathbf{k})$.

Because of the factorisation, further renormalisation is possible for both lattice and continuum models along the lines described by Wortis (1974) for the Ising model. This enables an expansion in terms of elementary graphs to be made.

5. Extension to many-particle connectedness functions

For simplicity we consider the case of identical particles but imagine the particles to be labelled. Define the l -particle connectedness function $P_l(\mathbf{r}_1, \dots, \mathbf{r}_l)$ to be the probability density that there are particles at $\mathbf{r}_1, \dots, \mathbf{r}_l$ and that there is at least one path connecting the particle at \mathbf{r}_1 to each of the particles at $\mathbf{r}_2, \dots, \mathbf{r}_l$. Let W_i be the set of walks which begin with the particle labelled 1 and end with the particle i ($\neq 1$) and define

$$\gamma_i = \sum_{\phi \subset W_i \subseteq W_i} (-1)^{|W_i|+1} \prod_{w \in W_i} \gamma(w) \tag{38}$$

then

$$P_l(\mathbf{r}_1, \dots, \mathbf{r}_l) = (n)_l \left\langle \prod_{i=2}^l \gamma_i \right\rangle. \tag{39}$$

The connecting graph $G(\bigcup_{i=2}^l W_i')$ will now have l roots and all arcs containing vertex 1 will be incident outwards. The d -weight of an l -rooted directed graph g is defined by

$$\vec{d}(g) = \prod_{i=2}^l \sum_{\phi \subset W_i \subseteq W_i} (-1)^{|W_i|+1} : G\left(\bigcup_{i=2}^l W_i'\right) = g. \tag{40}$$

D K Arrowsmith (1977, private communication) has shown that again cyclic graphs have zero d -weight and coverable acyclic graphs have $\vec{d}(g) = (-1)^{c(g)}$ where $c(g)$ ($= a - v + 1$) is the cyclomatic number. Combining (38), (39) and (40) we obtain the generalisation of (13):

$$P_l(\mathbf{r}_1, \dots, \mathbf{r}_l) = \sum_{g \in \mathcal{G}_l} \frac{\vec{d}(g)}{\vec{s}(g)} \int \dots \int d\mathbf{r}_{l+1} \dots d\mathbf{r}_v n_v(\mathbf{r}_1, \dots, \mathbf{r}_v, n) \gamma(g) \tag{41}$$

where \mathcal{G}_l is the set of l -rooted directed graphs with roots labelled $1, \dots, l$ and the intermediate vertices which are considered indistinguishable are labelled $l+1, \dots, v$ for the purpose of integration. In calculating $\vec{s}(g)$ only symmetry operations on the internal vertices are counted.

The integral of the conditional l -particle connectedness is related to the moments of the distribution of s (the number of particles connected to the particle at \mathbf{r}_1 including that particle) by

$$\int d\mathbf{r}_2 \dots d\mathbf{r}_l P_l(\mathbf{r}_2, \dots, \mathbf{r}_l | \mathbf{r}_1) = \langle (s-1)_{l-1} \rangle \tag{42}$$

where

$$P_l(\mathbf{r}_2, \dots, \mathbf{r}_l | \mathbf{r}_1) = P_l(\mathbf{r}_1, \dots, \mathbf{r}_l) / n_1(\mathbf{r}_1, n). \quad (43)$$

In the thermodynamic limit for a homogeneous gas, the Fourier transform

$$\tilde{P}_{l+1}(\mathbf{k}_1, \dots, \mathbf{k}_l) = \int \dots \int d\mathbf{r}_2 \dots d\mathbf{r}_{l+1} \prod_{m=1}^l \exp[i\mathbf{k}_m \cdot (\mathbf{r}_{m+1} - \mathbf{r}_1)] P_{l+1}(\mathbf{r}_2, \dots, \mathbf{r}_{l+1} | \mathbf{r}_1) \quad (44)$$

is given by (17) with $\tilde{\mathcal{C}}$ replaced by $\tilde{\mathcal{C}}_l$ and

$$\kappa_i = \sum_{(i,j) \in \mathcal{A}} \mathbf{k}_{ij} - \sum_{(j,i) \in \mathcal{A}} \mathbf{k}_{ji} + \sum_{m=1}^l \mathbf{k}_m (\delta_{m+1,i} - \delta_{1,i}). \quad (45)$$

The case of a lattice gas may be treated as in § 4.

6. Summary and applications

We have derived a general expression for the l -particle connectedness function (equation (41) and equation (13) for $l=2$) for a system of particles the positions of which are given by a set of arbitrary distribution functions (equation (3)). The condition (equation (4)) which specifies when two particles are connected may also be chosen freely. The theory therefore includes both lattice and continuum percolation theory. The latter may be thought of as applying to clustering in a gas but also applies to non-crystalline solids. Since the distributions are arbitrary it is possible to include the correlations which would occur in an interacting system.

The formulation may be used as a basis for rigorous results. Existence and analyticity properties in the infinite-volume limit may be obtained and the Ornstein-Zernike form established for the pair connectedness at sufficiently low density (D B Abraham 1977, private communication).

In the case when the particles are distributed independently a partial factorisation of the integral in (41) is possible thereby allowing renormalisation techniques to be used. For example equation (23) represents a partial renormalisation and is a generalisation of the $\mathbf{k}=0$ result of Haan and Zwanzig (1977). This is a major advance over the previous lattice theory (Essam 1972) in which excluded volume effects had to be allowed for.

Three applications of renormalisation are envisaged. Standard approximations in imperfect gas theory (e.g. the hypernetted chain approximation (Rice and Gray 1965)) can be used. It may be possible to extend current expansions of the pair connectedness for lattice systems (Dunn *et al* 1975, Cox and Essam 1976) since a much smaller graph list is required. Equations (17) and (45) may be used as a starting point for renormalisation group theory (Essam and Place 1977).

References

- Arrowsmith D K and Essam J W 1977 *J. Math. Phys.* **18** 235-8
 Coniglio A, De Angelis A and Forlani A 1977 *J. Phys. A: Math. Gen.* **10** 1123-39
 Cox M A A and Essam J W 1976 *J. Phys. C: Solid St. Phys.* **9** 3985-91
 Dunn A G, Essam J W and Ritchie D S 1975 *J. Phys. C: Solid St. Phys.* **8** 4219-35

- Essam J W 1972 *Phase Transitions and Critical Phenomena* vol. 2, eds C Domb and M S Green (London: Academic) p 197
- Essam J W and Place C M 1977 to be published
- Fremlin D H 1976 *J. Physique* **37** 813-7
- Haan S W and Zwanzig R 1977 *J. Phys. A: Math. Gen.* **10** 1547-55
- Martin J L 1974 *Phase Transitions and Critical Phenomena* vol. 3, eds C Domb and M S Green (London: Academic) p 97
- Rice S A and Gray P 1965 *The Statistical Mechanics of Simple Liquids* (New York: Interscience) p 94
- Roberts F D K 1967 *Biometrika* **54** 625-8
- Roberts F D K and Storey S H 1968 *Biometrika* **55** 258-60
- Uhlenbeck G E and Ford G W 1962 *Studies in Statistical Mechanics* vol. 1, eds G E Uhlenbeck and J de Boer (Amsterdam: North Holland) p 163
- Wortis M 1974 *Phase Transitions and Critical Phenomena* vol. 3, eds C Domb and M S Green (London: Academic) p 113