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1977 J. Phys. A: Math. Gen. 10 1123

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Pair connectedness and cluster size

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Received 8 February 1977

Abstract. A theory of the pair connectedness is developed for fluid as well as lattice systems when the presence of physical clusters of particles in the system is explicitly taken into account. Activity and density expansions, an Ornstein-Zernicke relation and the Percus-Yevick approximation are established in analogy with the theory of the pair-correlation function. A simple application to the percolation problem is given; for a lattice the results are compared with the known solution of the Bethe lattice.

For a fluid system the theory is used to investigate the relation of percolation and condensation in a Van der Waals gas: the result shows that an infinite cluster of particles is formed in the gaseous phase, along the coexistence curve, before the critical point is reached.

1. Introduction

The role, in real systems, of physical clusters of particles, first investigated by Hill (1955), has been considered in connection with a large variety of problems such as the percolation problem (Shante and Kirkpatrick 1971, Essam 1972), the random resistors (Kirkpatrick 1973), the nucleation problem (Binder 1975) and the dilute ferromagnet (Elliot and Heap 1962, Rapaport 1972).

The equilibrium distribution of physical clusters has recently been studied by Murmann (1975). In a recent paper (Coniglio *et al* 1977a, to be referred to as I) Hill's original work was extended and a general theory of the equilibrium distribution of physical clusters (for fluid and lattice systems) was started.

Activity expansions were obtained for the mean number of clusters of s particles and some preliminary considerations on the relation of percolation (formation of an infinite cluster) to condensation were given. The point is whether or not a gas-liquid transition corresponds to a large growth of the clusters' size, as this assumption is common to many phenomenological theories of condensation (for a good historical survey of these theories see Domb 1976).

In the present work we extend the general theory of cluster distribution with a theory of the pair connectedness. This function, related to the probability that two particles belong to the same physical cluster, is well known for lattice systems (Essam 1972) and plays the same role in percolation theory as the correlation function in the theory of phase transitions. This extension of the theory will prove particularly suitable in the discussion of percolation and condensation as it leads to a density expansion for the mean cluster size. The plan of the paper is as follows. In § 2 the pair connectedness

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is introduced and activity and density expansions obtained; in § 3 an Örnstein–Zernicke relation is established (definition of a direct pair connectedness) and an approximate form (Percus–Yevick) given.

In § 4 the relation between pair connectedness and mean cluster sizes, well known for lattice systems, is extended to fluid systems: as a consequence activity and density expansions for S are established.

In § 5 the lowest-order approximation of the theory is established and the percolation problem is solved in this approximation: for a lattice the result is compared with the known solution of the Bethe lattice.

In § 6 the problem of percolation and condensation is investigated consistently, i.e. in the same order of approximation for both the direct correlation function (leading to the Van der Waals equation of state) and the direct pair connectedness (leading to the mean size of clusters): in this approximation an infinite cluster of particles is formed in the gaseous phase, along the coexistence curve, before the critical point is reached (figure 1).

The ‘fluid’ formalism is used throughout the paper but all results can be used for lattice systems by an appropriate ‘change of language’.

2. Pair connectedness

For a system of N particles with potential energy

$$E(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i < j} u(r_{ij}) \quad (1)$$

we have discussed in I the equilibrium distribution of physical clusters of particles; these were defined, starting from Hill’s original work, in terms of $f^+(r) = \exp(-\beta u^+(r))$ bonds ($\beta = 1/k_B T$ where T is the temperature and k_B the Boltzmann constant) with

$$\exp(-\beta u(r)) = \exp(-\beta u^+(r)) + \exp(-\beta u^*(r)) \quad (2)$$

the ‘effective’ potentials between bound and unbound particles $u^+(r)$ and $u^*(r)$ respectively being defined as

$$u^+(r) = \begin{cases} +\infty & u(r) > 0 \\ u(r) - k_B T \ln F(r) & u(r) \leq 0 \end{cases} \quad (3)$$

$$u^*(r) = \begin{cases} u(r) & u(r) > 0 \\ u(r) - k_B T \ln(1 - F(r)) & u(r) \leq 0 \end{cases}$$

where $F(r)$ is given by the incomplete Γ function

$$F(r) = \Gamma(\frac{3}{2}, -\beta u(r)) / \Gamma(\frac{3}{2}). \quad (4)$$

Use of equations (1) and (2) in the system’s partition function leads to its decomposition into clusters of particles with f^+ bonds (bound particles) and $f^* = \exp(-\beta u^*) - 1$ bonds (unbound particles). As a result physical clusters can easily be obtained from Mayer’s mathematical clusters (defined in terms of $f = \exp(-\beta u) - 1$ bonds) by replacing each f bond with $(f^+ + f^*)$ and selecting from the resulting graphs those where the particles are at least pair-wise bound (linked by f^+ bonds). We will now make use of this formulation

of physical clusters to establish activity and density expansions for the pair connectedness: this is a well known function for lattice systems and we extend it here to fluids. All our results will then be valid for fluid as well as lattice systems.

For a system of N particles, volume V and density $\rho = N/V$ with potential energy (1) we define the pair connectedness $P(r_i, r_j)$ such that

$$\rho^2 P(r_i, r_j) dr_i dr_j \tag{5}$$

is the probability that particles i and j are in volume elements dr_i and dr_j respectively and are physically bound, i.e. belong to the same cluster (in our formalism: there is a path of f^+ bonds between i and j). For a lattice system the function $P(r_i, r_j)$ reduces to the probability $\rho^2 P_{ij}(p)$ that (for a given lattice with a density p of occupied sites) site i and site j are connected by a chain of occupied sites. Our choice of normalization is such that $P(r_i, r_j)$ is dimensionless in analogy with the pair-correlation function while $\rho^2 P(r)$ is the analogue of the pair-distribution function: in the current literature (see e.g. Essam 1972) it is this last function which is referred to as pair connectedness for lattice systems but our choice will be seen to be the most convenient in later sections.

To obtain an activity expansion for the pair connectedness we can start with the canonical pair-correlation function $g_N(1, 2)$ (from here on we simply write i instead of r_i): in a real fluid

$$\rho^2 g_N(1, 2) d1 d2 \tag{6}$$

is the probability to find particles 1 and 2 in volume elements $d1$ and $d2$ respectively, independently of the positions of the remaining particles (see e.g. Hill 1956). We can think of this probability as the sum of two contributions: the probability that particles 1 and 2 belong to the same physical cluster and the probability that they do not belong to the same cluster. Recalling equation (5) we can then write

$$g_N(1, 2) = P_N(1, 2) + D_N(1, 2) \tag{7}$$

where $P_N(1, 2)$ is the canonical pair connectedness and $D_N(1, 2)$ has the meaning of a 'blocking' function, i.e.

$$\rho^2 D_N(1, 2) d1 d2 \tag{8}$$

is the probability that particles 1 and 2 are in volume elements $d1$ and $d2$ and do not belong to the same cluster (it is not possible to find a 'physical' path between 1 and 2). The pair-correlation function has, in the thermodynamic limit, an activity (z) expansion given by (see e.g. Rice and Gray 1965)

$$g(1, 2) = 1 + \frac{1}{\rho^2} \sum_{n \geq 2} B_n(1, 2) z^n \tag{9}$$

where

$$B_n(1, 2) = \frac{1}{(n-2)!} \int \dots \int U(1, 2, \dots, n) d3 \dots dn \tag{10}$$

where $U(1, \dots, n) \equiv U(\{n\})$ are Ursell's U functions:

$$U(\{n\}) = \sum_{C_n} \prod_{i < j} f_{ij} \tag{11}$$

where f_{ij} are Mayer's f functions and the sum is over all connected graphs C_n of n

labelled points. In the same limit an activity expansion for the pair connectedness can be obtained (see appendix 1) starting from equation (7). The result is:

$$P(1, 2) = \frac{1}{\rho^2} \sum_{n \geq 2} B_n^+(1, 2) z^n \tag{12}$$

where

$$B_n^+(1, 2) = \frac{1}{(n-2)!} \int \dots \int U^+(1, 2|3, \dots, n) d3 \dots dn \tag{13}$$

and U^+ can be obtained from $U(\{n\})$ with the following recipe: in the graphs of $U(\{n\})$ replace each f bond with $(f^+ + f^*)$ and out of the resulting graphs select all those with *at least* one path of all f^+ bonds between 1 and 2. This subset of graphs is $U^+(1, 2|3, \dots, n)$. Let $U^*(1, 2|3, \dots, n) = U(\{n\}) - U^+(1, 2|3, \dots, n)$. From equations (7), (9) and (12) it is clear that the blocking function has an expansion:

$$D(1, 2) = 1 + \frac{1}{\rho^2} \sum_{n \geq 2} B_n^*(1, 2) z^n \tag{14}$$

with $B_n^*(1, 2) = B_n(1, 2) - B_n^+(1, 2)$ or:

$$B_n^*(1, 2) = \frac{1}{(n-2)!} \int \dots \int U^*(1, 2|3, \dots, n) d3 \dots dn. \tag{15}$$

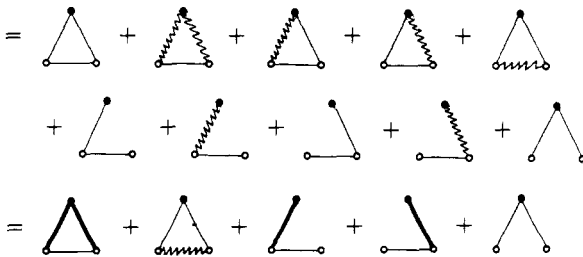
The first few coefficients in the expansions (9) and (12) are shown diagrammatically below. Here a bold line stands for an f bond while the full and wavy lines represent f^+ and f^* bonds respectively; the open circles are particles 1 and 2 and the full circles are field points to be integrated over.

$$B_2(1, 2) = U(1, 2) = \text{---} \text{---}$$

$$B_2^+(1, 2) = U^+(1, 2) = \text{---} \text{---}$$

$$B_3(1, 2) = \int U(1, 2, 3) d3 = \text{---} \text{---} \text{---} + \text{---} \text{---} \text{---} + \text{---} \text{---} \text{---} + \text{---} \text{---} \text{---}$$

$$B_3^+(1, 2) = \int U^+(1, 2|3) d3$$



Equation (12) gives the activity expansion of the pair connectedness with a recipe (equation (13)) to obtain the expansion coefficients from the corresponding coefficients (equation (10)) in the activity expansion of the pair-correlation function.

We will now show how to derive a density expansion for the pair connectedness from the density expansion for the pair-correlation function. Our conclusion will be that equation (7) retains its validity in terms of density expansions with the same recipe to

obtain the coefficients in the expansion of $P(1, 2)$: take the coefficients (diagrams) in the density expansion of the total correlation function $h(1, 2) = g(1, 2) - 1$, substitute each f bond with $(f^+ + f^*)$ and out of the new diagrams select those with *at least* one path of all f^+ bonds between 1 and 2. Consider, in fact, the density expansion of the total correlation function (see e.g. Münster 1969):

$$h(1, 2) = f_{12} + (1 + f_{12}) \sum_{m \geq 1} \beta_{m,2} \rho^m \tag{16}$$

where the $\beta_{m,2}$ are irreducible cluster integrals of the second kind: the corresponding graphs are such that they become multiply connected (stars) through addition of the direct $f(1, 2)$ bond. These graphs do not contain articulation points whereas the graphs in the activity expansion are simply connected, i.e. they contain articulation points. It is easy to show (Stell 1964, Wortis 1974) that if we sum in the activity expansion all the graphs departing from an articulation point the result is the density in that point: therefore we can obtain the density expansion (16) simply by replacing all the terms departing from any articulation point in the activity expansion with a factor ρ . Now we can think of the diagrams in the activity expansion as basic $\beta_{m,2}$ and $f_{12}\beta_{m,2}$ diagrams with all possible diagrams attached to each vertex: since particles 1 and 2 always belong to the basic diagrams it is only the f bonds of *these* diagrams which are decomposed into f^+ and f^* bonds in order to extract $P(1, 2)$. Since the basic diagrams are transferred without alterations into the density expansion the diagrammatic separation implicit in equation (7) is maintained in the summation process leading to the density expansion. The new coefficients of $P(1, 2)$ will then be given by those basic diagrams with *at least* one path of all f^+ bonds between 1 and 2 and this is just the anticipated recipe to extract $P(1, 2; \rho)$ from $h(1, 2; \rho)$. Thus we write (from equation (16)):

$$P(1, 2) = e^{-\beta u^{+(1,2)}} \left(1 + \sum_{m \geq 1} \beta_{m,2} \rho^m \right) + e^{-\beta u^{*(1,2)}} \sum_{m \geq 1} \beta_{m,2}^+ \rho^m \tag{17}$$

where $\beta_{m,2}^+$ is obtained from $\beta_{m,2}$ with the usual recipe. A density expansion for the pair connectedness has been given by Essam (1972, see also Cox and Essam 1976) for a lattice system with zero interaction. The particular importance of a density expansion for the pair connectedness will become clear in the next section.

3. Direct pair connectedness

In this section we show how, in complete analogy with the Örnstein–Zernicke theory (see e.g. Münster 1969), it is possible to obtain the pair connectedness by summation of a particular class of diagrams in its density expansion. A general diagram in the expansion (17) will consist of paths of f^+ and f^* bonds joining 1 and 2 through a certain number of field points (with at least one of these paths being made of all f^+ bonds): we define *nodal point* as a field point such that *all* paths between 1 and 2 pass through that point. A nodal diagram is then a diagram containing at least one nodal point. It is then possible to separate the diagrams associated with $P(1, 2)$ into two distinct subsets: nodal and non-nodal diagrams. Let $C^+(1, 2)$ be the function associated with the subset of non-nodal diagrams (we shall call this function direct pair connectedness in analogy with the direct correlation function) and $N^+(1, 2)$ the function associated with the

subset of nodal diagrams; then:

$$P(1, 2) = C^+(1, 2) + N^+(1, 2). \tag{18}$$

Now let us look at the nodal diagrams. In the set $N^+(1, 2)$ there are nodal points, there is at least one path of f^+ bonds between 1 and 2 and no graph of this set will contain the direct $f^+(1, 2)$ bond (since the path $f^+(1, 2)$ passes through no field point). Let 3 be the nodal point closest to 1: all paths from 1 pass through 3, in particular the path (or paths) of all f^+ bonds. Then between 1 and 3 there are all diagrams without nodal points and with at least one path of all f^+ bonds: that is $C^+(1, 3)$. Between 3 and 2 then there will be all possible diagrams (with or without nodal points) but with at least one path of f^+ bonds: that is $P(3, 2)$. The set of nodal diagrams $N^+(1, 2)$ is therefore obtained if we combine each diagram of the set $C^+(1, 3)$ with each diagram of the set $P(3, 2)$ i.e. $N^+(1, 2)$ is given by the convolution integral:

$$N^+(1, 2) = \rho \int C^+(1, 3)P(3, 2) d3 \tag{19}$$

multiplied by the particle density associated with the field-point 3.

Equation (18) therefore becomes:

$$P(1, 2) = C^+(1, 2) + \rho \int C^+(1, 3)P(3, 2) d3 \tag{20}$$

in complete analogy with the Örnstein-Zernicke relation for the total correlation function:

$$h(1, 2) = C(1, 2) + \rho \int C(1, 3)h(3, 2) d3. \tag{21}$$

The Fourier transform of the pair connectedness is therefore completely determined by the Fourier transform of the sum of only non-nodal diagrams of $P(1, 2)$ through:

$$\tilde{P}(K) = \frac{\tilde{C}^+(K)}{1 - \rho \tilde{C}^+(K)}. \tag{22}$$

The importance of the direct pair connectedness and equation (22) can immediately be appreciated: it is now possible to find an approximate, explicit, form for $P(1, 2)$, the Percus-Yevick (PY) approximation. In the theory of fluids the PY form of the pair correlation function $g_{PY}(r)$ is a well known approximation which seems to work quite satisfactorily for some range of the density. Its form is (see e.g. Rice and Gray 1965):

$$f_{PY}(1, 2) e^{\beta u(1,2)} = 1 + N(1, 2) \tag{23}$$

where $N(1, 2)$ is the function associated with the subset of nodal diagrams in the density expansion of $g(1, 2)$. We can separate these diagrams into two distinct subsets

$$N(1, 2) = N^+(1, 2) + N^*(1, 2) \tag{24}$$

where $N^+(1, 2)$ has been defined (see equation (1)) and $N^*(1, 2)$ are all nodal diagrams such that there is no path of all f^+ bonds between 1 and 2. Then from equation (23) we have:

$$g_{PY}(1, 2) = (1 + f_{12})(1 + N_{12}) = (1 + f_{12}^+ + f_{12}^*)(1 + N_{12}^+ + N_{12}^*) \tag{25}$$

which can be written as:

$$g_{PY}(1, 2) = f_{12}^+ + f_{12}^+ N_{12} + f_{12}^* N_{12}^+ + N_{12}^+ + (\text{diagrams which contain no path of all } f^+ \text{ bonds between 1 and 2}). \quad (26)$$

Recalling equation (7) and the definition of pair connectedness we conclude that the first terms in equation (26) are nothing but the PY approximation to the pair connectedness:

$$P_{PY}(1, 2) = f_{12}^+ + f_{12}^+ N_{12} + f_{12}^* N_{12}^+ + N_{12}^+ \quad (27)$$

which, using equations (18) and (23) can be written as:

$$P_{PY}(1, 2) = e^{-\beta u^+(1,2)} g_{PY}(1, 2) e^{\beta u(1,2)} + e^{-\beta u^*(1,2)} (P_{PY}(1, 2) - C_{PY}^+(1, 2)). \quad (28)$$

This equation, together with equation (22), can be solved (by iteration) for systems where the PY approximation $g_{PY}(r)$ is known to obtain the PY approximation to the pair connectedness. Another well known approximation in fluid theory is the HNC (hypernetted chain) equation (see e.g. Rice and Gray 1965): the diagrams involved in this approximation however cannot be easily separated to extract the ones belonging to the pair connectedness. We do not pursue the subject any further here.

4. Mean size of physical clusters

The pair connectedness can be used to determine the mean size of physical clusters S . This typical percolation quantity is given by (Essam 1972):

$$S = \frac{\sum_s s^2 n_s}{\sum_s s n_s} \quad (29)$$

where n_s is the equilibrium number of physical clusters of s particles whose activity expansion has been derived in I:

$$n_s = V \sum_{N \geq s} z^N \sum_{|N|} N_s b_{|N|} \quad (30)$$

where $|N|$ is a partition of N such that $\sum_{s=1}^N s N_s = N$ and $b_{|N|}$ can be obtained from Mayer's integrals b_N (see I for details):

$$\sum_{|N|} b_{|N|} = b_N = \frac{1}{N! V} \int \dots \int U(\{n\}) d1 \dots dN.$$

For a lattice it is easy to see (Essam 1972) that the mean size S can be obtained directly from the lattice pair connectedness P_{ij} by:

$$S = 1 + \frac{\rho}{\mathcal{N}} \sum_{i \neq j} P_{ij} \quad (31)$$

where ρ is the density of occupied sites and \mathcal{N} the total number of sites. Here our aim is to extend the formalism to fluid systems and we therefore look for the appropriate generalization of equation (31). Intuitively the summation over lattice sites should be replaced by an integration: this turns out to be true but the proof is not straightforward

and is given in appendix 2. The result is:

$$S = 1 + \rho \int P(r) dr. \quad (32)$$

Introducing the Fourier transform $\tilde{P}(K)$ of the pair connectedness equation (32) reads:

$$S = 1 + \rho \tilde{P}(0). \quad (33)$$

Using equation (22), S can be written in terms of the direct pair connectedness as:

$$S = \frac{1}{1 - \rho \tilde{C}^+(0)} \quad (34)$$

to be compared with the isothermal compressibility χ_T :

$$\rho k_B T \chi_T = \frac{1}{1 - \rho \tilde{C}(0)} \quad (35)$$

where $\tilde{C}(K)$ is the Fourier transform of the direct correlation function. The direct pair connectedness can immediately be used to determine the percolation critical density ρ_p : this is the solution of the equation

$$\rho_p \tilde{C}^+(0, \rho_p, T) = 1. \quad (36)$$

In general equations (34) and (35) can be used consistently (same diagrammatic approximation for the direct functions) to study the behaviour of the mean size of physical clusters in the neighbourhood of the critical point ($\chi_T \rightarrow \infty$) and along the condensation curve of a gaseous system. In § 5 we use them to investigate the relation of percolation to condensation for a gas in the Van der Waals approximation: this was left as an open question in I where percolation and condensation (in the sense of Mayer) were first compared.

5. Percolation

To lowest order $C^+(1, 2) = f^+(1, 2)$ and equation (36) gives for the percolation critical density:

$$\rho_p = 1/\tilde{f}^+(0) \quad (37)$$

where

$$\tilde{f}^+(K) = \int e^{-\beta u^+(r)} e^{i\mathbf{K}\cdot\mathbf{r}} d\mathbf{r}. \quad (38)$$

To the same order the pair connectedness and mean cluster size are (see equations (22) and (34)):

$$\tilde{P}(K) = \frac{\tilde{f}^+(K)}{1 - \rho \tilde{f}^+(K)} \quad (39)$$

$$S = \frac{\rho_p}{\rho_p - \rho}. \quad (40)$$

For completeness we also give the result of the calculation of the mean number of clusters to this order:

$$\sum_s \rho_s = \rho - \frac{1}{2} B_2^+ \rho^2; \quad B_2^+ = \int B_2^+(1, 2) \, d\mathbf{r}_{12}.$$

This can be obtained from the activity expansion of the partial densities ρ_s in the tree approximation (summation of tree diagrams). For small values of wavenumber K we can write:

$$\tilde{f}^+(K) = \tilde{f}^+(0)(1 - \alpha K^2) \tag{41}$$

and then:

$$\tilde{P}(K) \sim \frac{1}{\rho\alpha(\xi^{-2} + K^2)} \tag{42}$$

with the ‘connectedness length’ given by:

$$\xi = \left(\frac{\rho\alpha}{\rho_p - \rho} \right)^{1/2}. \tag{43}$$

From equation (42) we obtain the asymptotic (large- r) behaviour of the pair connectedness in d dimensions:

$$P(r) \sim e^{-r/\xi} / r^{d-2}. \tag{44}$$

For an Ising model with coordination number q and nearest-neighbour interaction J we have from I:

$$\tilde{f}^+(K) = \sum_{\mathbf{R}_{ij}} f_{ij}^+ e^{i\mathbf{K}\cdot\mathbf{R}_{ij}} \tag{45}$$

where

$$f_{ij}^+ = e^{\beta\epsilon} \theta_{ij}; \quad \epsilon = 4J \tag{46}$$

and

$$\theta_{ij} = \begin{cases} 1 & \text{if } i \text{ and } j \text{ are nearest neighbours} \\ 0 & \text{otherwise.} \end{cases} \tag{47}$$

From (37) we then have:

$$\rho_p = \frac{1}{q} e^{-\beta\epsilon}. \tag{48}$$

This is less, for all values of β , than the percolation density

$$\rho_p^{\text{Bethe}} = \frac{1}{q-1} \frac{(q-1)^2 e^{-\beta\epsilon}}{(q-2)^2 + e^{-\beta\epsilon}(2q-3)} \tag{49}$$

in the Bethe lattice although the two results are both increasing functions of temperature (Coniglio 1976, Odagaki 1975, Kikuchi 1970) as expected. This behaviour as a function of temperature has not been proved in general, as far as we know, for the percolation density but only for the percolation activity (Lebowitz and Penrose 1976). Notice that from equations (40) and (48) it follows that the mean cluster size is a decreasing function of temperature: in particular at low densities, where the present

approximation is valid. As for the critical indices equation (40) shows that S diverges at ρ_p with critical index $\gamma_p = 1$ in agreement with the result on the Bethe lattice (Fisher and Essam 1961); equation (43) shows that ξ diverges at ρ_p with critical index $\nu_p = 1/2$ and equation (44) shows that at $\rho = \rho_p$:

$$P(r) \sim 1/r^{d-2+\eta_p} \quad (50)$$

with critical index $\eta_p = 0$.

The last two critical indices do not coincide with the corresponding indices of the Bethe lattice where $\nu_p = \eta_p = 1$ (Coniglio 1976). Notice that Toulouse (1974) has suggested that a critical dimensionality $d_c = 6$ obtains from the classical critical indices $\nu_p = 1/2$, $\gamma_p = 1$, $\beta_p = 1$ (where β_p is related to the percolation probability): these indices are often all attributed, incorrectly, to the Bethe lattice. Finally we point out that the percolation density of the Bethe lattice (equation (49)) reduces to the lowest-order approximation (equation (48)) in the limit $q \rightarrow \infty$.

6. Percolation and condensation

In I we started a study of the relation between formation of an infinite cluster of particles and condensation of the system. This problem was dealt with by explicit calculation of the mean cluster number and mean cluster size in the chain approximation (summation of chain diagrams in the activity expansions). Of course we had to treat condensation in the sense of Mayer (pressure–activity plane) since the percolation quantities were functions of the activity z . The percolation activity z_p and condensation activity z_c were found to coincide as far as the interaction between clusters was not completely taken into account. The complete calculation (full interaction) of the mean cluster size was not given in I and the coincidence of percolation and condensation in the chain approximation was left as an open problem.

For completeness we might mention here that the complete calculation of S in the chain approximation can be easily carried out via the pair connectedness and the result is $z_p \neq z_c$.

The results of the present work however make possible a further study of the problem as a function of density rather than activity: we can therefore treat condensation in the pressure–density plane rather than in the sense of Mayer.

In this section we study the percolation of a gaseous system undergoing condensation. The question is: on a given isotherm is the percolation density ρ_p lower or higher than the transition density ρ_G ?

The simplest equation of state which does contain all the necessary features (condensation and critical point) is the Van der Waals equation

$$P + a\rho^2 = \frac{k_B T \rho}{1 - b\rho} \quad (51)$$

where the parameters a and b are given in terms of the critical point values:

$$\rho_c = \frac{1}{3b}; \quad k_B T_c = \frac{8}{27} \frac{a}{b}; \quad P_c = \frac{1}{27} \frac{a}{b^2}. \quad (52)$$

The point now is to find the percolation density consistently, i.e. in the same approximation as equation (51). Consistency can easily be obtained starting with

equations (34) and (35). It is known that integration of equation (35), recalling that

$$\chi_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T \tag{53}$$

leads to the virial expansion for the pressure (see e.g. Munster 1969):

$$\beta P = \rho - \int \rho \tilde{C}(0) d\rho = \rho + \sum_{n=2} B_n \rho^n. \tag{54}$$

In other words: an approximation in the virial series (order m in the density) is equivalent to stopping at order $m = 2$ in the density expansion of the direct correlation function.

Thus the approximation of the second virial coefficient

$$\beta P = \rho + B_2(T)\rho^2 \tag{55}$$

is consistent with:

$$C(r) = f(r) \tag{56}$$

and therefore

$$C^+(r) = f^+(r) \tag{57}$$

i.e. the percolation density consistent with an equation of state (55) is given by equation (37). For a potential equal to hard core plus attractive part:

$$u(r) = \begin{cases} +\infty & r < r_0 \\ -u_0 \left(\frac{r_0}{r} \right)^6 & r \geq r_0 \end{cases} \tag{58}$$

equation (55) is almost exactly equivalent to equation (51) with:

$$b = \frac{2}{3}\pi r_0^3; \quad a = u_0 b \tag{59}$$

(see e.g. Pathria 1972).

We can therefore obtain the percolation density $\rho_p(T)$ by evaluating $\tilde{f}^+(0)$ with the potential (58).

We have (see equations (3) and (4)):

$$f^+(r) = e^{-\beta u^+(r)} = \begin{cases} 0 & r < r_0 \\ F(r) \exp\left(\beta u_0 \left(\frac{r_0}{r}\right)^6\right) & r \geq r_0 \end{cases} \tag{60}$$

where

$$F(r) = \frac{2}{\pi^{1/2}} \int_0^{\beta u_0 (r_0/r)^6} y^{1/2} e^{-y} dy = \Gamma\left(\frac{3}{2}, \beta u_0 (r_0/r)^6\right) / \Gamma\left(\frac{3}{2}\right) \tag{61}$$

where $\Gamma(x, y)$ is the incomplete Γ function. Then:

$$\tilde{f}^+(0) = \frac{4\pi}{\Gamma\left(\frac{3}{2}\right)} \int_{r_0}^{\infty} \exp\left(\beta u_0 \left(\frac{r_0}{r}\right)^6\right) \Gamma\left(\frac{3}{2}, \beta u_0 \left(\frac{r_0}{r}\right)^6\right) r^2 dr \tag{62}$$

which, to first order in $\beta u_0 (r_0/r)^6$ (consistently with the evaluation of $B_2(T)$), gives

$$\tilde{f}^+(0) = \frac{4\pi}{9\Gamma\left(\frac{3}{2}\right)} r_0^3 (\beta u_0)^{3/2}. \tag{63}$$

Eliminating r_0 and u_0 through the relations (59), introducing the variable $x = T/T_c$ and using (52) we finally have:

$$\frac{\rho_p(x)}{\rho_c} = 0.64x^{3/2} \quad (64)$$

for the percolation density as a function of the temperature.

In the neighbourhood of the critical point ($\rho_G \approx \rho_c$, $T \approx T_c$) expanding equation (51) in the variables $\rho_c - \rho$ and $T_c - T$ we find:

$$\frac{\rho_G(x)}{\rho_c} = \frac{3}{3 + 1.92(1-x)^{1/2}} \quad (65)$$

Then:

$$\frac{\rho_p(x)}{\rho_G(x)} = 0.21x^{3/2}[3 + 1.92(1-x)^{1/2}] < 1 \quad (66)$$

leading to the conclusion: the percolation point is always located (on a given isotherm) before the transition point (in the neighbourhood of the critical point).

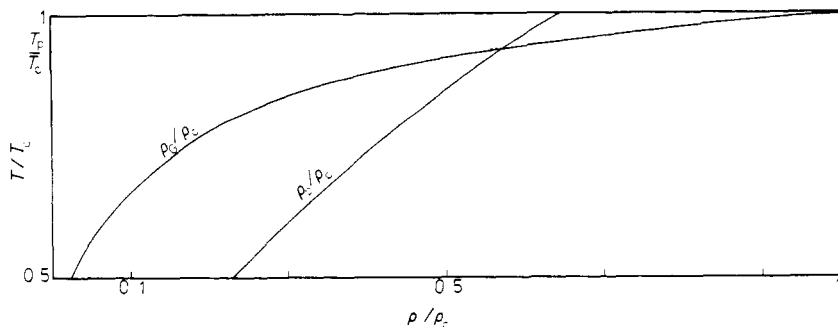


Figure 1. Reduced gas-liquid coexistence curve ρ_G/ρ_c against T/T_c of a Van der Waals gas and percolation curve ρ_p/ρ_c against T/T_c in the same approximation (second virial coefficient). ρ_c and T_c are the density and temperature of the critical point from the Van der Waals equation. Above the 'percolation' temperature T_p an infinite cluster is formed in the gaseous phase before condensation.

For a comparison of the whole coexistence curve $\rho_G(T)$ with the percolation curve (64) it is convenient to write equation (51) in terms of the reduced variables P/P_c , ρ/ρ_c , x :

$$\frac{P}{P_c} + 3\left(\frac{\rho}{\rho_c}\right)^2 = \frac{8x}{3 - \rho/\rho_c} \frac{\rho}{\rho_c} \quad (67)$$

The coexistence curve $\rho_G(x)/\rho_c$ can then be obtained numerically from equation (67) by equating the Gibbs potentials $\mu(\rho_G, T) = \mu(\rho_L, T)$ of the gas and liquid phases at those points where $P(\rho_G, T) = P(\rho_L, T)$.

The result is shown in figure 1 together with equation (64) for the reduced quantities: it is therefore valid for a large class of substances (law of corresponding states).

Figure 1 shows the existence of a temperature T_p where percolation and condensation coincide: an infinite cluster is formed in the system before condensation only for $T > T_p$.

The same result has been found for three-dimensional lattices (Müller-Krumbhaar 1974, Sykes and Gaunt 1976) and for the Bethe lattice (Coniglio 1976) while for two-dimensional lattices it is always $T_p = T_c$ (Coniglio *et al* 1977b).

7. Conclusions

We have developed a theory of the pair connectedness, for fluids and lattices, in complete analogy with the theory of the pair-correlation function.

This allows a treatment of the percolation problem, in discrete as well as continuous systems, parallel to the Örnstein–Zernicke theory of phase transitions.

Via the pair connectedness, activity and density expansions for the mean cluster size have been obtained. Series expansions for the mean cluster number and the percolation probability are under investigation.

The problem of percolation and condensation in a fluid has been solved in the Van der Waals approximation: an infinite cluster of particles may appear in the gaseous phase before condensation.

This problem might be worth further investigation in higher-order approximations: of particular interest would be the knowledge of some observable quantity connected with the mean cluster size.

Appendix 1

We wish here to prove that the pair connectedness has the activity expansion given by equation (12).

We start with equation (7) and look for an explicit expression for $P_N(1, 2)$. The canonical pair-correlation function can be written as (see Rice and Gray 1965):

$$g_N(1, 2) = \frac{V^2}{Z_N} \int \dots \int W(\{N\}) d\{N-2\} \tag{A.1}$$

where Z_N is the configurational integral and $W(\{N\})$ are Ursell's W functions:

$$W(\{N\}) = \prod_{i < j} (1 + f_{ij}) = \sum_{G_N} \prod_{i < j} f_{ij} \tag{A.2}$$

the sum going over all graphs G_N of N labelled points.

If we now replace each f bond in the graphs of $W(\{N\})$ with $(f^+ + f^*)$ we obtain a new set of graphs which can be separated into two subsets: one, which we call $W_{12}^+(\{N\})$, such that each graph contains at least one path of all f^+ bonds between 1 and 2 and the second, $W_{12}^*(\{N\})$, such that no graph will contain a path of all f^+ bonds between 1 and 2. Then:

$$W(\{N\}) = W_{12}^+(\{N\}) + W_{12}^*(\{N\}). \tag{A.3}$$

But since (see equation (1)) $W(\{N\}) = \exp(-\beta E(\{N\}))$ is the statistical weight of the configuration $(1, 2, \dots, N)$ then $W_{12}^+(\{N\})$ is the statistical weight of a configuration $(1, 2, \dots, N)$ such that 1 and 2 belong to the same cluster.

Recalling the meaning of $P_N(1, 2)$ we can therefore write, in analogy with equation (A.1):

$$P_N(1, 2) = \frac{V^2}{Z_N} \int \dots \int W_{12}^+(\{N\}) d\{N-2\}. \tag{A.4}$$

The argument leading from (A.1) to an activity expansion of the pair-correlation function can now be used to obtain the expansion of the pair connectedness: for clarity we briefly recall its main steps.

The procedure (for details see Rice and Gray 1965) is to expand the set $W(\{N\})$ according to:

$$\begin{aligned} W(\{N\}) &= U(1)W(2, 3, \dots, N) + \sum_P U(1, i)W(2, 3, \dots, i-1, i+1, \dots, N) + \dots \\ &+ \sum_P U(1, i_1, \dots, i_{n-1}) W(2, \dots, i_j-1, i_j+1, \dots, N) + \dots \tag{A.5} \\ &\text{all } j \in 1, \dots, n-1 \end{aligned}$$

where $U(\{N\})$ are Ursell's U functions (see equation (9)) and \sum_P means the sum over all ways of choosing particles i, i_1 , etc out of the remaining $N-1$ particles (1 has been singled out). When this expansion is inserted in (A.1) two types of contribution may arise in the general term of order n according as the set (i_1, \dots, i_{n-1}) does, or does not, include 2.

The contribution of the terms which do not include 2 is shown to be unity (in the thermodynamic limit). The terms including 2 are (to order n):

$$\begin{aligned} &\int \dots \int U(1, 2, i_1, \dots, i_{n-2}) W(3, \dots, i_j-1, i_j+1, \dots, N) d\{N-2\} \quad \text{all } j \in 1, \dots, n-2 \\ &= \int \dots \int U(1, 2, i_1, \dots, i_{n-2}) d\{n-2\} \\ &\quad \times \int \dots \int W(3, \dots, i_j-1, i_j+1, \dots, N) d\{N-n\} \\ &= Z_{N-n} \int \dots \int U(1, 2, i_1, \dots, i_{n-2}) d\{n-2\} = Z_{N-n} (n-2)! B_n(1, 2) \tag{A.6} \end{aligned}$$

since the configurational integral of K particles is:

$$Z_K = \int \dots \int W(\{K\}) d\{K\}$$

and $B_n(1, 2)$ has been defined in equation (8).

Taking into account the number of terms of order n and summing over n we obtain, in the thermodynamic limit, the activity expansion (equation (9)).

If we now repeat the argument starting from (A.4) it is clear that in the general term of order n we have to consider only the contribution arising when 1 and 2 are connected: in fact, if there is no path of f bonds between 1 and 2 it will be impossible to find a path of f^+ bonds.

So we only have to consider terms of the form (A.6) but, because of the meaning of $W_{12}^+(\{N\})$, the expansion can only contain graphs with at least one path of all f^+ bonds

between 1 and 2, that is:

$$W_{12}^+(\{N\}) = U^+(1, 2)W(3, \dots, N) + \sum_P U^+(1, 2|i_1, \dots, i_{n-2})W(3, \dots, i_j - 1, i_j + 1, \dots, N) + \dots \quad (A.7)$$

where $U^+(1, 2|3, \dots, n)$ is the subset of graphs obtained from the graphs in $U(1, 2, \dots, n)$ selecting those with at least one path of f^+ bonds between 1 and 2 (after the substitution of each f bond with $f^+ + f^*$).

The terms of order n in $P_N(1, 2)$ are therefore of the form:

$$Z_{N-n} \int \dots \int U^+(1, 2|i_1, \dots, i_{n-2}) d\{n-2\} = Z_{N-n}(n-2)!B_n^+(1, 2) \quad (A.8)$$

where $B_n^+(1, 2)$ has been defined (see equation (13)).

The same argument leading to (9) leads now to the expansion (12).

Appendix 2

We show that for fluid as well as lattice systems the mean size of physical clusters can be obtained from the pair connectedness $P(r)$ by:

$$S = 1 + \rho \int P(r) dr. \quad (A.9)$$

Recalling equation (32) and the expression of the density of finite clusters

$$\rho = \sum_s s \rho_s, \quad (A.10)$$

where $\rho_s = n_s/V$ is the partial density of clusters of s particles, equation (A.9) is equivalent to:

$$\rho^2 \int P(1, 2) d1 d2 = \sum_{s \geq 2} s(s-1)n_s.$$

Introducing the activity expansions (16) and (33) for $P(1, 2)$ and n_s we have

$$\sum_{N \geq 2} z^N \int B_N^+(1, 2) d1 d2 = V \sum_{s \geq 2} s(s-1) \sum_{N \geq s} z^N \sum_{|N|} N_s b_{|N|}. \quad (A.11)$$

In I the coefficients $b_{|N|}$ were obtained from Mayer's cluster integrals b_N :

$$b_N = \frac{1}{N!V} \int U(1, 2, \dots, N) d\{N\} \quad (A.12)$$

and we can therefore write:

$$b_{|N|} = \frac{1}{N!V} \int U_{|N|}(1, 2, \dots, N) d\{N\}. \quad (A.13)$$

Using equation (14) we can then write equation (A.11) as:

$$\sum_{N \geq 2} z^N \frac{N(N-1)}{N!} \int U^+(1, 2|3, \dots, N) d\{N\}$$

$$= \sum_{s \geq 2} s(s-1) \sum_{N \geq s} \frac{z^N}{N!} \sum_{|N|} N_s \int U_{|N|}(1, \dots, N) d\{N\}. \tag{A.14}$$

The two series are equal if the coefficients of each power of z are equal. The validity of equation (A.9) is therefore established once we prove that:

$$N(N-1) \int U^+(1, 2|3, \dots, N) d\{N\} = \sum_{s=2}^N s(s-1)N_s \sum_{|N|} \int U_{|N|}(1, \dots, N) d\{N\}. \tag{A.15}$$

Consider now the quantity:

$$\binom{N}{2} \int U^+(1, 2|3, \dots, N) d\{N\}.$$

Because of the integration over all the particles it is:

$$\int U^+(1, 2|3, \dots, N) d\{N\} = \int U^+(i, j|N-2) d\{N\} \tag{A.16}$$

where (i, j) is any of the possible couples of particles $1, \dots, N$. Then:

$$\binom{N}{2} \int U^+(1, 2|3, \dots, N) d\{N\} = \sum_{i \neq j} \int U^+(i, j|N-2) d\{N\}. \tag{A.17}$$

In the last sum are all the graphs of $U(\{N\})$ with at least one path of all f^+ bonds between i and j , that is with particles i and j belonging to the same physical cluster, for any of the possible couples i, j which can be formed from particles $1, 2, \dots, N$. The same graphs are clearly obtained if we consider directly the physical clusters

$$\sum_{|N|} \int U_{|N|}(1, \dots, N) d\{N\}$$

with no particular attention to any selected couple of particles: but then we have to multiply each partition by the number of ways of choosing any two particles physically bound (at least one path of all f^+ bonds) in that given partition; in a cluster of s particles there are $s(s-1)/2$ ways of choosing a bound couple and if there are N_s clusters of s particles there will be $s(s-1)N_s/2$ ways: the total number of ways (in the given partition) is obtained summing over all possible clusters of $2, 3, \dots, N$ particles:

$$\sum_{s=2}^N \frac{s(s-1)}{2} N_s.$$

Summation over all partitions then gives the total number of ways of choosing any two particles physically bound, i.e. all the graphs in the sum in equation (A.17):

$$\sum_{i \neq j} \int U^+(i, j|N-2) d\{N\} = \sum_{|N|} \sum_{s=2}^N \frac{s(s-1)}{2} N_s \int U_{|N|}(1, \dots, N) d\{N\}. \tag{A.18}$$

From (A.17) and (A.18) equation (A.15) is obtained thus concluding our proof.

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