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PERCOLATION OF RANDOMLY CENTERED RODS AND SPHERES

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Abstract

The percolation properties of randomly centered rods and spheres are studied. The approach is based on the detailed study of frequencies of cluster occurrences. For random rods, the analytic expressions are derived for all cluster frequencies. It is then shown that one-dimensional systems of random rods exhibit critical behaviour with $\rho_c = \infty$, $\gamma = 1$. For randomly centered spheres, we designed a numerical method for calculating the cluster frequencies. The approach is based on the principles of the Monte Carlo method. It can cope with clusters containing up to seven particles, which should suffice for the evaluation of accurate values of critical density and critical exponents.

1. Introduction

The statistical mechanics of the gaseous and liquid state is mainly devoted to thermal problems. In thermal problems one tries to reveal structural and dynamical characteristics of the system provided that the Hamiltonian which defines the interactions between the particles is known. Structural characteristics are usually defined in terms of distribution functions. At low fluid densities, the distribution of particles can be interpreted in terms of clustering behaviour. The concept of clusters was introduced by Mayer [1] and led to a rich mathematical formalism.

In addition to the Mayer clusters, which are of more formal character, Hill [2] introduced the concept of physical clusters, sets of particles which are physically connected by dispersion forces and do not have enough kinetic energy to fall apart. One can extend the definition of clusters to a proximity definition, where the clusters are declared to be connected if each particle within a cluster has at least one particle in the neighbourhood so that their separation is less than a certain distance. However, as soon as one accepts the proximity criterion, the physical basis becomes obscured because in general there is no clear-cut criterion to define the distance at which the particles are said to be connected. This feature leads to percolation problems [3] which can be superimposed on the thermal problems. The percolation problem is usually defined as follows: Find the threshold density at which the clusters begin to percolate, which means that they attain macroscopic extensions. Due to the fact that the definition of connectedness invokes a certain degree of arbitrariness, we can see that each Hamiltonian can give rise to several percolation problems. The simplest percolation problem can be defined for the simplest system: randomly centered points. The thermal problem of this system is

trivial because it corresponds to the ideal gas. In what follows, we shall see that even such a simple system defines a percolation problem of considerable complexity.

2. Percolation of random rods and spheres

In order to define the percolation problem of random points in one, two, or three dimensions, one needs to define the minimum distance (d) at which the points are connected. One can consider the percolation problem to be solved when the percolation threshold density and the corresponding critical indices are determined.

In order to reach this goal, one can try to determine the frequencies of cluster occurrences. Let us first calculate the probability that a subvolume v will be devoid of points. If $v \ll V$, then the probability for such a configuration is $1 - v/V$ to the power N. This expression can be transformed in the following way:

$$P(v) = (1 - v/V)^N = [(1 - v/V)^{V/v}]^{Nv/V}. \tag{2.1}$$

In the limit when v/V goes towards to zero, one can write

$$P(v) = \exp(-\rho v), \tag{2.2}$$

where ρ is the number density of points.

On the basis of this result, it is not difficult to determine the cluster frequencies. The singlets are those points which are free of neighbours within a "sphere" of radius d. The volume V_0 of such a "sphere" is $2d$, πd^2 and $4\pi d^3/3$ in 1, 2 and 3 dimensions, respectively. Consequently, the relative abundance of singlets $n_1 = N_1/N$ is equal to $P(v = V_0)$, which gives in terms of (2.2)

$$n_1 = \exp(-\rho V_0). \tag{2.3}$$

Following the same line of argument, one can write down the expression for the frequency of a p-point cluster:

$$n_p = (\rho^{p-1}/p!) \int \mathrm{d}^3 \boldsymbol{r}_2 \ldots \mathrm{d}^3 \boldsymbol{r}_p \exp(-\rho v(\boldsymbol{r}_2, \ldots, \boldsymbol{r}_p)). \tag{2.4}$$

Point no. 1 is supposed to be located at the origin ($\boldsymbol{r}_1 = 0$). The integrals over $p - 1$ coordinates should run over all the configurations which do not disconnect the p-cluster. The excluded volume $v(\boldsymbol{r}_2 \ldots \boldsymbol{r}_p)$ is equal to the minimal volume, which should be devoid of points other than $1 \ldots p$ in order to keep the cluster isolated.

2.1. PERCOLATION OF RANDOMLY CENTERED RODS

In one dimension, the percolation problem can be thoroughly solved. Instead of random points, we can speak about random rods of length d. Each point lies in

the center of the rod, and two points are connected if the corresponding rods overlap. The integrals appearing in the expression for cluster frequencies can be solved analytically for any p, obtaining

$$n_p(\rho) = \exp(-2\rho d)\,(1 - \exp(-\rho d))^{p-1}. \tag{2.1.1}$$

If one introduces the fraction of occupied volume u as another density variable,

$$u = 1 - e^{-d\rho}, \tag{2.1.2}$$

the cluster frequencies can be expressed in even more compact form:

$$n_p(u) = (1 - u)^2 u^{p-1}. \tag{2.1.3}$$

It is easy to calculate the mean cluster size

$$\langle p \rangle = \sum_p p^2 n_p / \sum_p p\, n_p\,; \tag{2.1.4}$$

since $\sum_p p n_p = 1$, one obtains

$$\langle p \rangle = (1 + u)/(1 - u).$$

If this expression is compared with the standard form $\langle p \rangle \propto (u_c - u)^{-\gamma}$, one immediately realizes that the percolation occurs at $u_c = 1$ and that the critical exponent γ is equal to 1. The threshold value $u_c = 1$ means that the clusters of randomly centered rods percolate when the entire volume becomes occupied, which again means that the number density must become infinite.

Furthermore, in complete analogy with the one-dimensional lattice [4], one can also determine the critical exponents τ and σ, which turn out to have the values 2 and 1, respectively.

2.2. PERCOLATION OF RANDOMLY CENTERED SPHERES

In three dimensions, the percolation problem of random spheres does not appear as trivial as in the one-dimensional case. In the literature, one can trace three approaches towards the solution of this problem: integral equation techniques [5–8], computer simulation [9, 10], and series expansion [11]. In lattice percolation, the series expansion approach gives the most accurate results. In continuum percolation, the series expansion is competitive to computer simulation and turns out to be more efficient than integral equation approaches. In this work, we develop an alternative numerical method which may lead to a better understanding of continuum percolation in non-correlated systems. The approach is based on the evaluation of the frequencies of cluster occurrences. Haan and Zwanzig [11] developed the formalism to calculate

the coefficients of power series expansion of cluster frequencies in number density. This approach is limited by the availability of cluster integrals. For randomly centered spheres in three dimensions, Haan and Zwanzig succeeded in reconstructing the coefficients up to fourth power in density, while Given and Stell [6] discussed the possibilities of extending the series. However, it is not possible to proceed very far because the diversity of possible cluster topologies becomes excessively abundant beyond $p = 5$. It is our aim to develop a numerical procedure which will function beyond this point.

For $p = 2$ and 3, the integrals expressing the cluster frequencies can be cast into a compact form:

$$n_2(\rho) = 2\pi\rho d^3 \exp\left(-4\pi\rho d^3/3\right) \int_0^1 x^2 \exp\left(-\pi\rho d^3 (x - x^3/12)\right) dx, \quad (2.2.1)$$

$$n_3(\rho) = \frac{8\pi^2\rho^2 d^6}{6} \int_0^1 x^2 dx \int_0^1 y^2 dy \int_{-1}^1 dz \exp(-\rho v(x,y,z))$$

$$+ 2 \int_0^1 x^2 dx \int_{1-x}^1 y^2 dy \int_{\frac{1-x^2-y^2}{2xy}}^1 dz \exp(-\rho v(x,y,z)). \quad (2.2.2)$$

$v(x, y, z)$ is the excluded volume. The variables x, y and z refer to the distances r_{12}, r_{23} and the cosine of the angle between the vectors $\boldsymbol{r}_{12}$ and $\boldsymbol{r}_{23}$. The methods of calculation of the excluded volume will be discussed in due course. If the exponential function in (2.2.1) and (2.2.2) is expanded in a power series in the number density and the integrals are carried out, one can obtain the coefficients in the density expansion. We checked that our results agree with the coefficients obtained by Haan and Zwanzig.

For the clusters beyond $p = 3$, there is no simple way to evaluate the integrals appearing in (2.4), but one can apply the Monte Carlo method.

The most simple and straightforward way to evaluate the integral

$$I = \int d\boldsymbol{r}_2 \ldots d\boldsymbol{r}_p \exp(-\rho v(\boldsymbol{r}_2 \ldots \boldsymbol{r}_p)) \quad (2.2.3)$$

is the crude Monte Carlo method.

According to this method, any finite-dimensional integral within finite limits can be evaluated as the average value of the integrand multiplied by the total volume of the space spanned by the integration variables. In our case, the integration variables are the coordinates of $p - 1$ points provided that one point is located at

the origin of the coordinate system. The integration domain should be chosen in such a way that no connected p-cluster topology is left out. This condition is satisfied when the points are located within the sphere of radius $(p-1)d$ with volume U. The points outside this domain can not contribute to a connected cluster. On the basis of the above-mentioned arguments, (2.2.3) can be written as follows:

$$I = U^{p-1} \sum e^{-\rho v(r_2 \ldots r_p)} / N_{TOT} . \tag{2.2.4}$$

This equation can be applied directly as it stands. One generates N_{TOT} random p-tuplets, discards the disconnected clusters, calculates the excluded volume for each connected cluster, and performs the summation. The calculation remains feasible up to $p = 5$, but beyond this number the fraction of connected clusters becomes too small and the method is no longer efficient. In order to extend the applicability of the method we also developed a more advanced algorithm, due to which (2.2.4) is evaluated in two steps. In the first step, one evaluates the number N_C of connected clusters relative to the total number N_{TOT} of randomly generated p-tuplets. In the second step, one evaluates the average $\langle e^{-\rho v} \rangle = \sum e^{-\rho v} / N_C$ within the set of connected clusters. The two results can be combined to obtain

$$I = U^{p-1} \left(\frac{N_C}{N_{TOT}} \right) \left(\sum e^{-\rho v} / N_C \right). \tag{2.2.5}$$

The quantity N_C/N_{TOT} can be calculated in a computer run where random p-tuplets are generated and tested for connectedness. This is a fast numerical procedure and because it is free of the evaluation of the excluded volume, one can afford to test billions of p-tuplets using a moderate amount of computer time.

The average $\langle e^{-\rho v} \rangle$ can be calculated by means of the standard Metropolis Monte Carlo procedure used for hard body potentials with disconnected clusters being equivalent to the configurations with infinite potential and the connected ones to those with zero potential energy. One starts with an arbitrary configuration of points forming a connected cluster. Afterwards, one generates a sequence of random moves of points. If a new configuration of points represents a disconnected cluster, it is rejected, and the weight with which the parent configuration (the one from which the new configuration is derived by random moves) enters into the averaging procedure is incremented by 1. In the averaging procedure, the initial part of the sequence of configurations should be discarded and the averaging over the productive run gives us $\langle e^{-\rho v} \rangle$.

As far as the determination of the excluded volume is concerned, one can use the analytic expressions for the volumes of intersecting spheres up to $p = 4$ [13, 14]. For high p values, we used the following algorithm.

For p spheres composing a connected cluster, M random points were generated, uniformly distributed within each sphere. For each point, the number of spheres to

which the point was common was determined. In this way, the counters $M_1 \ldots M_i \ldots M_p$ with $\sum M_i = pM$ were obtained. M_i counts the number of points belonging to i spheres. The excluded volume is then given as follows:

$$v(r_2 \ldots r_p) = 4\pi d^3 \left(\sum M_i / i \right) / (3M).$$

If M was taken of the order of magnitude of 10^4, the accuracy of $v(r_2 \ldots r_p)$ becomes a fraction of a percent.

3. Results and discussion

As the main numerical results of this paper, we consider the cluster frequencies for $p = 2$ to 7 as a function of number density. The calculations were performed by means of the crude Monte Carlo method ($p = 3, 4, 5$) or by the Metropolis MC method ($p = 5, 6, 7$). The ratio N_C/N_{TOT} (see eq. (2.2.5)) was determined on the basis of 10^9 configurations, while the lengths of the productive runs were much shorter ($\approx 10^5$) because of the time-consuming computation of the excluded volume. The results are depicted in fig. 1, where also the error bars are drawn. The errors were estimated on the basis of scattering of the results referring to partial summations.

On the basis of these data, we made two kinds of efforts towards the determination of the percolation threshold density ρ_c and the critical exponent γ:

(i) series expansion method,

(ii) extrapolation of the peak position in $n_p(\rho)$.

The computational task pertaining to the series expansion method [11] is based on the determination of the coefficients in the density expansion of the mean cluster size (see 2.1.4):

$$\langle p \rangle = \sum a_k \rho^k. \tag{3.1}$$

If the coefficients a_k are known, one can determine the percolation threshold density and the critical exponent by means of the "ratio" method or some other numerical aid such as Padé analysis. The numerical values of the coefficients a_k stem from the knowledge of $n_p(\rho)$, which again can be expressed as a power series:

$$n_p(\rho) = \sum_{k=0}^{\infty} b_{pk} \rho^k. \tag{3.2}$$

Combining eqs. (3.1), (2.1.4) and (3.2), one obtains

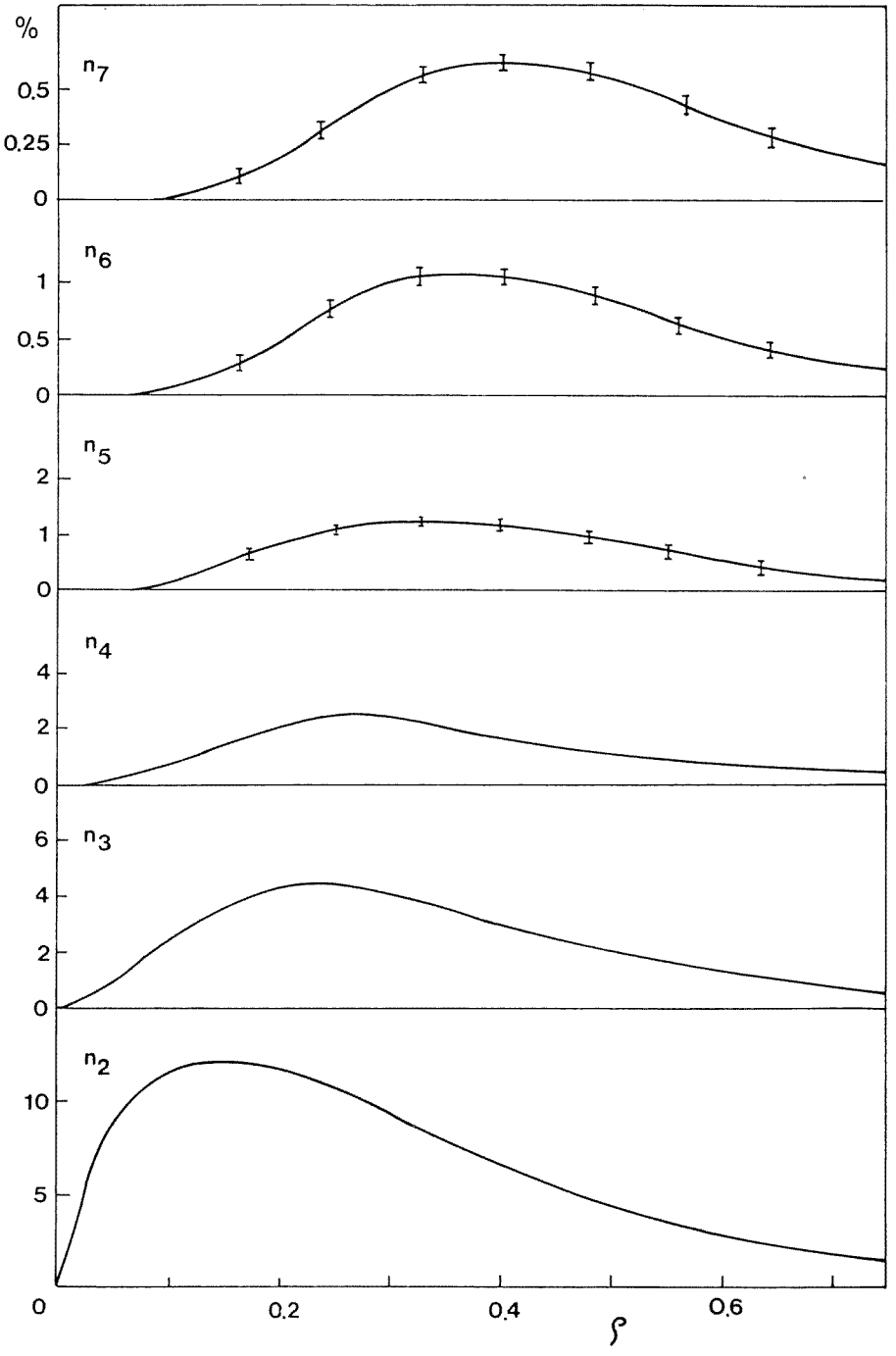

Fig. 1. Cluster frequencies for different cluster sizes as a function of number density. Note the differences in scale factor on the ordinate axis. The maxima approach asymptotically the tentative percolation threshold density at $\rho_c d^3 = 0.68$ (see also fig. 3).

$$a_k = \sum_{p=1}^{k+1} p^2 b_{pk} \,. \tag{3.3}$$

The coefficients b_{pk} for random spheres were evaluated by Haan and Zwanzig in terms of cluster integrals for $1 < p < 5$ and $0 < k < 4$, which is exactly sufficient to determine the coefficients a_k for $0 < k < 4$. Our results go beyond this point, as can be seen in fig. 1, because $n_p(\rho)$ are calculated up to $p = 7$. The results on which the graphs of fig. 1 are based do not allow us to calculate the coefficients a_k beyond $k = 4$ because the accuracy of the data is too low. In order to obtain a_5, for example, eq. (3.3) tells us that one needs to know b_{p6}, $1 < p < 6$. When the summation in (3.3) is performed, one realizes that the terms alternate in sign and that the factor p^2 amplifies the contribution and also the error of higher terms. We found that the relative uncertainty of the coefficient a_5, which was evaluated on the basis of the data presented in fig. 1, is more than 50%, which means that it can not help when determining ρ_c and γ. On the other hand, the determination of ρ_c and γ on the basis of a_1 to a_5 by the ratio method is also questionable, as can be seen in fig. 2, where

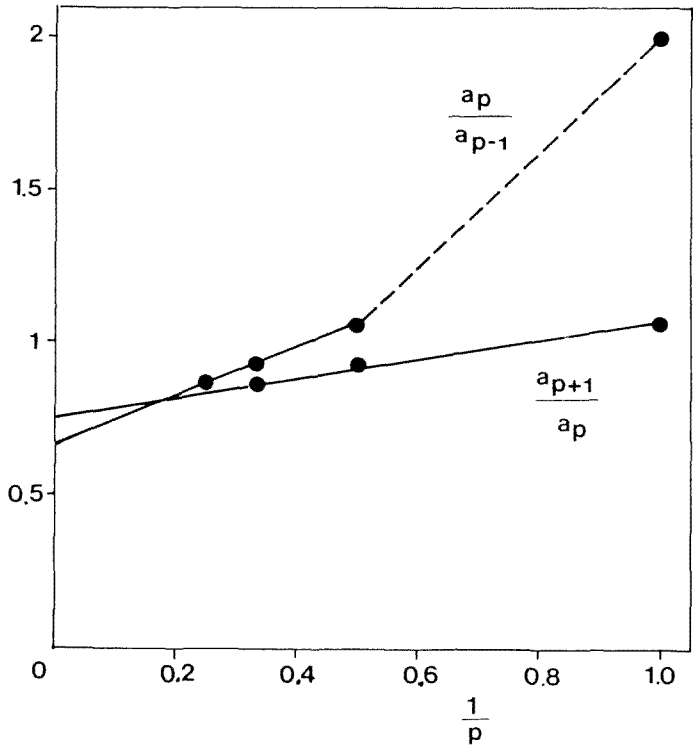

Fig. 2. If ρ_c is determined on the basis of the "ratio" method, the ambiguity exists whether a_{p+1}/a_p should be drawn versus $1/p$ or $1/(p+1)$. If only the data are available for low p values, the discrepancy between the two results is appreciable.

it is shown that the ratio method in the series expansion may give ambiguous results if one remains below $p = 5$.

The above-mentioned drawbacks were a strong motivation to design an alternative numerical procedure on which basis one could quantify the percolation problem. This is method (ii), which exploits the fact that by means of the Metropolis MC procedure one can determine rather accurately the locations of the maxima $\rho_{max}(p)$ of $n_p(\rho)$. If a log–log plot of the position of the maxima relative to a tentative value of ρ_c versus p is drawn (see fig. 3), one finds that $\rho_c - \rho_{max}(p)$ behaves as $p^{-\omega}$. The

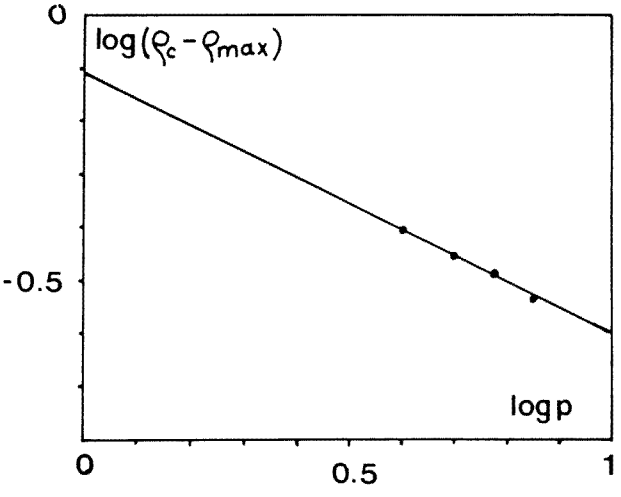

Fig. 3. In fig. 1, one can see that the maxima of $n_p(\rho)$ approach the critical density ρ_c. In order to quantify this feature, a log–log plot is drawn: log of the distance between the maximum of $n_p(\rho)$ and the tentative value of ρ_c ($=0.68/d^3$) versus log p. The analysis reveals the relation $\rho_c - \rho_{max} \propto p^{-\omega}$, where $\omega = 0.5 \pm 0.03$.

approximate value of ω is 0.5 ± 0.03 and for the present we have no simple explanation about its origin. If we draw a diagram of $\rho_{max}(p)$ as a function of $p^{-0.5}$ (fig. 4), the intercept of the line with the ordinate gives the value of the percolation threshold density $\rho_c d^3 = 0.68 \pm 0.01$. This result is consistent with the results of the series expansion method [11] and simulation results.

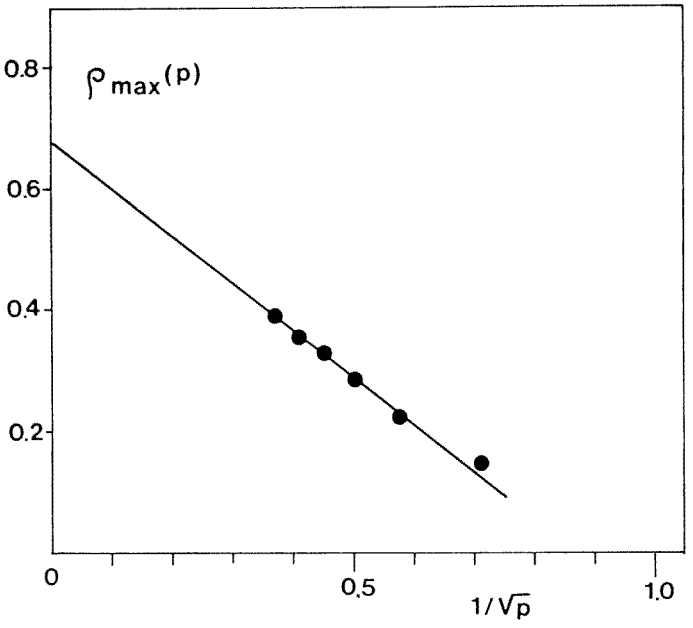

Fig. 4. The location of the maxima of $n_p(\rho)$ as a function of $1/\sqrt{p}$. The extrapolation $p \to \infty$ gives us the percolation threshold density ($\rho_c d^3 = 0.68 \pm 0.01$).

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