Systematic derivation of percolation thresholds in continuum systems

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Analytic expressions for the critical percolation density in the continuum are derived using the direct-connectedness expansion method. Demonstrating a systematic application of this method for systems of permeable cubes or spheres, it is concluded that the present expansion is quite practical for the derivation of critical parameters of continuum systems. Correspondingly we also utilize the method to find the percolation threshold of the so-far unstudied continuum systems of oriented hypercubes. The results obtained are in excellent agreement with Monte Carlo simulations.

Percolation in the continuum has drawn considerable attention in recent years[1] although more rigorous and accurate percolation parameters have been determined by lattice models.[2,3] The first attempt to rigorously derive critical parameters in continuum systems was made by Haan and Zwanzig[4] twelve years ago. Their approach was based on the application of graph theory to a lattice-bond-like percolation problem where the existence of a bond is defined by permeable-object overlap. In view of the lengthy cluster enumeration involved[5,6] and its latticelike analogy, this method was not too appealing, and thus its use has not been subsequently attempted for any continuum system. Furthermore, Ref. 4 does not specify the graphs used and their corresponding statistical weights, nor does it explain how the quoted "best results" were selected. In particular, the use of high-order overlap integrals in that work does not allow an easy derivation of continuum parameters for objects other than cubes and spheres. At about the same time Coniglio *et al.*[7] have shown that in general there is a simple relation between the direct-pair connectedness $C^+(\mathbf{r})$, which is analogous to the direct-pair correlation function (well known from fluid theory[8,9]), and the mean cluster size, which is a fundamental concept of percolation theory.[2] The fact that this relation is derivable in the context of classical fluid theory and is hence natural for continuum systems has motivated several researchers[10–12] to examine whether this relation can be used for the actual determination of critical parameters. Consequently, two approaches were taken for the utilization of the above relation. The first was based on the Percus-Yevick approximation[10,11] while the other was based on an order-by-order calculation[12] of a density expansion of $C^+(\mathbf{r})$. In the first approach, although the qualitative features of the percolation threshold behavior were nicely reproduced,[11] the quantitative results were very poor. For example, the percolation thresholds of various systems of spheres were[10,11] 30% higher than the correct values. The other approach[12] has been shown to be beneficial for the study of trends in the behavior of thresholds, in particular for permeable objects, but no actual computation of parameters, with it, has been presented.

In view of the fact that the latter approach (which is the only rigorous one that naturally applies to the continuum) has not been tested yet for the derivation of critical parameters, it appeared worthwhile to try it for known and unknown continuum percolation problems. The main drawback evident in this approach is that the convergence of the corresponding expansion is slow and that only its first few terms are available (mainly due to the difficulty in computing the overlap integrals beyond what is available from virial expansions[4]). On the other hand, it seemed plausible to us that Padé approximants of the first few terms obtained by this order-by-order approach may yield reasonably good critical parameters. In this letter we report then the results of the first derivation of critical parameters within this approach. Specifically, percolation thresholds were found here for systems for which Monte Carlo values are well known (systems of permeable spheres and cubes) as well as for systems for which Monte Carlo values have not been presented before and are presented here (hypercubes).

The percolation thresholds of systems composed of permeable regular convex objects, such as spheres or cubes ("centrosymmetrical" objects[13]), have been known for many years.[14–16] They were shown by many Monte Carlo studies[14–21] to be determined by relations of the type[18]

$$N_c V_{ex} = B_c \ , \tag{1}$$

where N_c is the critical density of the objects, V_{ex} is their excluded volume[1,18] the volume in which two object centers have to be in order for the objects to overlap), and B_c is the critical average number of bonds per object. The quantity B_c, which was found to be an invariant of systems composed of a given kind of objects, has been argued[16,18] to be the basic topological parameter of the system. For example, for spheres[16–21] $B_c = 2.8 \pm 0.05$ while for cubes.[4,15,21] $B_c = 2.6 \pm 0.1$. For simple centrosymmetrical objects, we know that $V_{ex} = 2^d V$, where V is the volume of the object and d is the dimensionality of the system.[1,4,13] Following the generalized use of the V_{ex} concept,[18] Bug *et al.*[12] have proposed that a rigorous

derivation of the percolation threshold for a system of permeable objects is possible by the above-mentioned approach. The derivation is based on the expansion of $\hat{C}^+(0)$ [the zero wave-vector Fourier transform of $C^+(\mathbf{r})$] in terms of the object density ρ, where the coefficients of the expansion are defined by

$$\hat{C}^+(0)=\sum_{n=2}^{\infty}\hat{C}_n{}^+(0)\rho^{n-2}\ . \tag{2}$$

In the case of permeable objects, one would like to express the density in terms of B_c [see Eq. (1)], i.e., by $B_c=\rho_c V_{\rm ex}$. Thus, it is natural[12] to express the expansion given by Eq. (2) using dimensionless coefficients k_n such that

$$\rho\hat{C}^+(0)=\sum_{n=2}^{\infty}k_n\rho^{n-1}V_{\rm ex}^{n-1}\ . \tag{3}$$

Since at the percolation threshold[12]

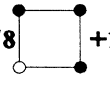
$$\rho_c\hat{C}^+(0)=\sum_{n=2}^{\infty}k_nB_c^{n-1}=1$$

(see below), the task of the theory is to calculate the values of the coefficients k_n. Fortunately, the integrals involved in the calculation of k_n are the same as those used for the calculation of the well-known virial coefficients[22-24] b_n of the corresponding impenetrable objects. However, explicit values of the integrals are only available up to $n=7$ for hypercubes[25] and $n=5$ for spheres.[23] On the other hand, the statistical weights of the integrals are different in the percolation problem [i.e., in $\hat{C}_n^+(0)$] and in the virial expansion problem (i.e., in b_n). As far as we know, for the percolation problem, attempts have been made[26] to calculate these weights, so far, only up to $n=4$. The method of the present work is then to make better use of the available integrals by determining the statistical weights of the lowest-order terms sufficiently to evaluate reliably the percolation thresholds with accuracy exceeding that of existing Monte Carlo results.

Let us now turn to a short account of the calculation procedure that we applied. The virial coefficients b_n are well known[23-25] to be given in terms of sums of diagrams which symbolize cluster integrals, such as[23]

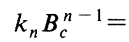
$b_2=$ **-1/2**  $=\int f(\mathbf{r}_{1,2})d\mathbf{r}_{1,2}$

$b_3=$ **-2(1/6)**  $=\int\int f(\mathbf{r}_{1,2})f(\mathbf{r}_{1,3})f(\mathbf{r}_{1,3})d\mathbf{r}_{1,3}d\mathbf{r}_{2,3}$ (4)

$b_4=$ **-3[1/8**  **+1/8**  **+1/8** 

+1/24  **]**

where $f(\mathbf{r}_{i,j})$ are the Mayer f functions. The coefficients b_n may be expressed as sums of diagrams according to the rule[23-25]: $b_n=\{$sum of all topologically distinct diagrams which have n points and are at least doubly connected$\}\cdot(1-n)/n$. In percolation problems, one is interested in connectedness[7] between two points and thus the coefficients $C_n^+(\mathbf{r}_{1,2})$ are given[7,12] by the {sum of all diagrams of $n-2$ black points and 2 white points (roots), labeled 1 and 2, which are at least doubly connected and have at least one path of f^+ links between point 1 and point 2}. Generally,[7,12] one defines $f=f^++f^*$, and for permeable objects (no potential in the problem), one further finds[12] that $f^+(\mathbf{r})=-f^*(\mathbf{r})$ where $f^+(\mathbf{r})$ represents a connection (or a contact) criterion. In the case of permeable objects, $f^+(\mathbf{r})$ is given a value of 1 within the excluded volume and 0 outside this volume.[12] For example, the first two diagrams (or integrals) for the percolation problem will be given now by[12]

$\int$  $d\mathbf{r}_{1,2}\equiv\int f^+(\mathbf{r}_{1,2})d\mathbf{r}_{1,2}=V_{\rm ex}$,

$\int$ $d\mathbf{r}_{1,2}\equiv\int f^*(\mathbf{r}_{1,2})f^+(\mathbf{r}_{1,3})f^+(\mathbf{r}_{2,3})d\mathbf{r}_{1,3}d\mathbf{r}_{1,2}$ (5)

$\equiv k_3V_{\rm ex}^2$.

Comparing the above diagrammatic expansions of b_n [Eqs. (4)] and $C_n(\mathbf{r})$ [Eqs. (5)], one sees immediately that both b_n and k_n involve the same integrals, but they may have different signs and combinatorial weights (due to the extra requirement of the f^+ path in the percolation problem[7,12]).

Following the above considerations we have found the $\hat{C}_n^+(0)$ diagrams [see Eq. (5)] containing up to five points [i.e., up to $\hat{C}_5^+(0)$] in the following way:[27] First, doubly connected (viriallike) diagrams are collected and two points are rooted[12] [become "white," compare Eqs. (4) and (5)]. In each of the diagrams obtained (which are labeled as class i) we permute all the nonrooted (black) points in all possible ways. Of these diagrams, only the topologically distinct ones are kept. Quantitatively this is done by dividing the value of the integral by the symmetry number S_i, which denotes the number of ways to permute the indices of the black points without obtaining a topologically distinct diagram. We further define a degeneracy factor g_i which accounts for the different labeling of the roots as point 1 and point 2. If a permutation of 1 and 2 produces a topologically different diagram, we have $g_i=2$, while otherwise $g_i=1$. Since we count the topologically distinct diagrams, g_i is a multiplicative factor of every diagram. Finally, all f bonds are decomposed into f^++f^* bonds and only diagrams in which 1 and 2 are connected by at least one path of f^+ bonds are registered. For each f diagram then, there are many such new decomposed diagrams. Every new diagram is also assigned a sign which is negative if there is an odd number of f^* bonds in the diagram [see Eq. (5)]. Due to the different signs, many diagrams of the same g_i and S_i cancel out and we are left with N_i uncanceled diagrams. Hence the final weight of a diagram i (i.e., of an integral) such as those on the left-hand side (l.h.s.) of Eq. (5) is

$$W_i=(g_iN_i/S_i)(\pm 1)\ , \tag{6}$$

where the sign is that of the residual N_i diagrams. The value of $\hat{C}_n^+(0)$ is simply $\sum_i W_{n,i}I_{n,i}$, where $I_{n,i}$ is the numerical value of the corresponding integral, and the sum is over the different classes of order n [see, e.g., Eqs. (9) and (10) below].

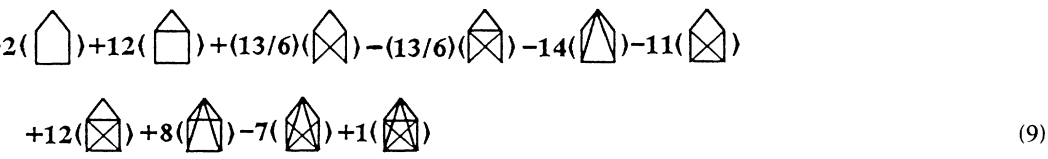
In this paper we are mainly concerned with the case of a system of permeable parallel hypercubes since for this case the values of $I_{n,i}$ are known[25] for all dimensions. The reason for this is that for a hypercube of dimension d, one has

$$f^+(\mathbf{r})=-f^*(r)=\prod_{i=1}^{d}f^+(x_i)\ , \tag{7}$$

where

$$f^+(x_i)=\begin{cases}1, & -\frac{1}{2}<x_i<\frac{1}{2}\\ 0 & \text{otherwise}\ .\end{cases} \tag{8}$$

With this definition $V_{ex}=1$, and since $B_c=\rho_c V_{ex}$, ρ_c here is just the system invariant B_c. Since $\hat{C}_2^+(0)$, $\hat{C}_3^+(0)$, and $\hat{C}_4^+(0)$ were presented previously,[12,26] we give here explicitly only the newly derived weights of $\hat{C}_5^+(0)$. Hence in terms of diagrams [compare Eqs. (4) and (5)], we can write

$\hat{C}_5^+(0)=(V_{ex}^4)k_5=$  (9)

where each diagram now symbolizes a specific indexed diagram. The numerical values of these diagrams, $D_i/(4!)^d$, are just the values obtained by Hoover and DeRocco[25] in the case of d-dimensional cubes, for which $f(x_i)=1$ when $-1<x_i<1$ (i.e., their cube is of volume 1 and the corresponding "excluded volume" is 2^d). Combining the weights found here with the values D_i of Ref. 25, we find then that

$$\begin{aligned}\sum_i W_{5,i}D_{5,i}=&-2(230)^d+12(196)^d+\tfrac{13}{6}(192)^d\\&-\tfrac{13}{6}(180)^d-14(174)^d-11(164)^d\\&+12(152)^d+8(144)^d-7(132)^d+(120)^d\ ,\end{aligned} \tag{10}$$

and thus [following our definition as given by Eq. (8)], the k_5 coefficient of Eq. (3) is given by

$$k_5=\sum_i W_{5,i}D_{5,i}/[(4!)^d(2^d)^4]\ . \tag{11}$$

Using Eq. (11), we obtain that for permeable cubes

$$k_5=-0.033\,47\ . \tag{12}$$

Similarly, our results for the other coefficients of Eq. (3), for $d=3$, are $k_2=1$, $k_3=-0.421\,87$, and $k_4=0.124\,29$.

If we had the rest of the k_n values or evidence that they decrease fast enough with n, we could have solved Eq. (3) for the percolation threshold, ρ_c. This is due to the fact that the dependence of the mean cluster size on ρ, which is given by[7]

$$S=1/[1-\rho\hat{C}^+(0)]\ , \tag{13}$$

is determined at the threshold by the divergence condition

$$\rho_c\hat{C}^+(0)=1\ . \tag{14}$$

However, the above required information is not available and thus we have to find a way to extrapolate the rest of the expansion. This can be done by taking advantage of Eq. (13) and the expected[1,3] critical behavior: $S=A_c(\rho_c-\rho)^{-\gamma}$, where A_c is the amplitude of S. Such problems appear in many critical phenomena studies[4,28] and are often handled by the method of the Padé approximants.[29] This is also the course we have chosen to take here. Following our prime interest in evaluating percolation thresholds as accurately as possible, we used a Padé approximation of S, biased with the known[2,3] values of the critical exponent γ. (It is a well-founded assumption that γ is universal and was shown indeed to be the same for lattice and continuum systems of equal dimension[30,31]). The values obtained by unbiased calculation will be discussed elsewhere.[27] The first stage of finding the desired extrapolation is expanding the series

$$S=1+\sum_{j=1}^{\infty}s_j\rho^j\ , \tag{15}$$

using the k_n values found above and Eq. (13). Equating the coefficients of ρ^i yields[32] the values $s_1=1$, $s_2=0.5781$, $s_3=0.2815$, and $s_4=0.1295$, for the density expansion of S [Eq. (15)]. The second stage is using these s_j terms in order to find[32] the first few terms of the series of a function $h(\rho)$ defined by

$$h(\rho)=[S(\rho)]^{1/\gamma}\ . \tag{16}$$

Finally, we use a Padé approximant[29] with coefficients a_j and b_j such that

$$h(\rho)=\left[\sum_{j=1}^{L}a_j\rho^j\right]\Big/\left[\sum_{j=1}^{M}b_j\rho^j\right]+o(\rho^{L+M+1})\ , \tag{17}$$

where the highest value of $L+M$ is determined by the available information [i.e., the index of the last known term in the series expansion of $h(\rho)$ as defined by Eq. (16)]. In the critical region $h(\rho)$ has the approximate behavior

$$h(\rho)=A_c^{1/\gamma}/(\rho_c-\rho),\quad \rho\to\rho_c\ . \tag{18}$$

TABLE I. B_c values obtained from the biased Padé approximants for a system of spheres.

M \ L	0	1	2	3
1	1.74	3.14	2.66	2.84
2	1.95	2.77	2.79	
3	2.09	2.79		
4	2.09			

TABLE II. B_c values of systems of hypercubes as obtained by the 1/3 Padé approximant and Monte Carlo simulations.

Dimension	Padé	Monte Carlo	γ values used
$d=2$	4.70	4.5±0.1	43/18
$d=3$	2.60	2.63±0.05	1.74
$d=4$	1.91	2.1±0.2	1.44
$d=5$	1.59	1.8±0.2	1.2
$d=6$	1.34	1.4±0.2	1

The value of ρ_c is given then by one of the roots of the denominator of Eq. (17) (and thus we must consider only the $M \geq 1$ approximants). To illustrate the nature of the biased Padé results, we present in Table I the B_c values (ρ_c per excluded volume) for the various possible L/M combinations, as obtained by using the above procedure (with the well-known[33] universal value of $\gamma = 1.74$), in the case of permeable spheres. Recalling the above-mentioned value[21] of $B_c = 2.8 \pm 0.05$ we see that already for $L/M = 1/2$, the result obtained is in agreement with the Monte Carlo B_c value. Examining the results for $L/M = 1/3$ and $L/M = 2/2$, we see that the B_c values obtained converge (as is the case in other critical phenomena studies[2,28]) along the $L = M - 1$ diagonal. From the results shown in Table I, it becomes apparent why one has to calculate the expansion terms at least up to $\hat{C}_5^+(0)$: If we would have used only $\hat{C}_4^+(0)$ in this calculation of the biased Padé approximants, we could only guess that the result obtained by the approximant $L/M = 1/2$ is the correct result. Since we obtained essentially the same values for $L/M = 1/3$ and $L/M = 2/2$ we feel confident that the B_c values converge with increasing $L + M$. We found[27] the convergence to improve with increasing dimensionality; for example, for six-dimensional hypercubes all the approximants with $L + M \geq 2$ yield practically the same B_c value (i.e., $B_c = 1.34$).

Turning to the data obtained for hypercubes, we present here for the sake of brevity[27] only the results obtained for $L = 1$ and $M = 3$. These results, which were obtained by using known[3,33] γ values, are shown in Table II. We found[27] that these values are quite insensitive to small variations in γ. For comparison we also show in Table II the well-known B_c values for systems of two and three dimensions,[14-21] as well as newly obtained Monte Carlo results, for systems of higher dimensions.[21] The comparison between the two sets of results shows that there is excellent agreement between the Monte Carlo B_c values and the values derived here from the Coniglio-Bug approach with biased Padé approximants. The excellent agreement is manifested by the finding that the results agree to within the statistical uncertainty of the Monte Carlo values. The fact that within this uncertainty the Monte Carlo results are systematically higher than the present rigorously derived results is likely to be due to finite-size effects in the simulations.

In conclusion, we have used the pair-connectedness approach of Coniglio *et al.*,[7] utilized it order by order as suggested by Bug *et al.*,[12] and extrapolated the results by Padé approximants. We found that this systematic procedure yields quite accurate values for the percolation thresholds of continuum systems composed of permeable objects.

[1]For a short review see I. Balberg, Philos. Mag. B **55**, 991 (1987).

[2]D. Stauffer, *Introduction to Percolation Theory* (Taylor and Francis, London, 1985).

[3]A. Aharony, in *Directions in Condensed Matter Physics,* edited by G. Grinstein and G. Mazenko (World Scientific, Singapore, 1986), p. 1.

[4]S. W. Haan and R. Zwanzig, J. Phys. A **10**, 1547 (1977).

[5]J. Blease, J. W. Essam, and C. M. Place, J. Phys. C **11**, 4009 (1987).

[6]D. C. Hong and H. E. Stanley, J. Phys. A **16**, L475 (1983).

[7]A. Coniglio, L. De Angelis, and A. Forlani, J. Phys. A **10**, 1123 (1977).

[8]C. A. Croxton, *Liquid State Physics, A Statistical Mechanical Introduction* (Cambridge University Press, London, 1974).

[9]J. P. Hansen and I. R. M. Macdonald, *Theory of Simple Liquids* (Academic, New York, 1976).

[10]Y. C. Chiew and E. D. Glandt, J. Phys. A **16**, 2599 (1983).

[11]T. De Simone, R. M. Stratt, and S. Demoulini, Phys. Rev. Lett. **56**, 1140 (1986); J. Chem. Phys. **85**, 391 (1986).

[12]A. L. R. Bug, S. Safran, and I. Webman, Phys. Rev. Lett. **54**, 1412 (1985); Phys. Rev. B **33**, 4716 (1986).

[13]L. Onsager, Ann. N.Y. Acad. Sci. **51**, 627 (1949).

[14]F. D. K. Roberts and S. H. Story, Biometrika **55**, 258 (1968).

[15]A. S. Skal and B. I. Shklovskii, Fiz. Tekh. Poluprovodn. **7**, 1589 (1973) [Sov. Phys.—Semicond. **7**, 1058 (1974)].

[16]I. Balberg, Phys. Rev. B **31**, 4053 (1985), and references therein.

[17]J. Kurkijarvi, Phys. Rev. B **9**, 770 (1974).

[18]I. Balberg, C. H. Anderson, S. Alexander, and N. Wagner, Phys. Rev. B **30**, 3933 (1984).

[19]V. K. S. Shante and S. Kirkpatrick, Adv. Phys. **20**, 235 (1971).

[20]I. Balberg, N. Binenbaum, and N. Wanger, Phys. Rev. Lett. **52**, 1465 (1984).

[21]N. Wagner and I. Balberg, (unpublished). The values obtained for cubes and spheres in this Monte Carlo simulation are

more accurate than the values reported in previous works such as in Ref. 15. More details of these simulations, which typically used samples of $N_c \cong 20\,000$ hypercubes, will be presented elsewhere.

[22]H. Kamerlingh Onnes, Proc. K. Ned. Akad. Wet. **4**, 125 (1902).

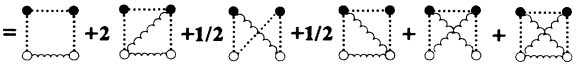
[23]J. E. Kilpatrick, Adv. Chem. Phys. **20**, 39 (1971).

[24]For a review and many references see D. A. McQuarrie, *Statistical Thermodynamics* (University Science Books, Mill Valley, CA, 1973), Chap. 15.

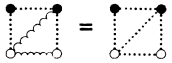
[25]See, in particular, W. G. Hoover and A. G. DeRocco, J. Chem. Phys. **36**, 3141 (1962).

[26]Even the decomposition to this order as was given in Ref. 12 is incorrect. $C_4^+(\mathbf{r})$ should be given by

$C_4^+(\mathbf{r})$



rather than the expression given in Ref. 12. Note that this conclusion is not changed when the diagrams are presented in a different manner, i.e., by replacing two ~~~~ by two ..... e.g.,



[27]More details will be given in a forthcoming paper.

[28]J. W. Essam and M. E. Fisher, J. Chem. Phys. **38**, 802 (1962).

[29]G. Baker and P. Graves-Monris, *Padé Approximants* (Addison-Wesley, New York, 1981).

[30]D. Y. Kim, J. J. Herrmann, and D. P. Landau, Phys. Rev. B **35**, 3661 (1987).

[31]I. Balberg, Phys. Rev. B **37**, 2391 (1988).

[32]*Handbook of Mathematical Functions,* edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1968), p. 15.

[33]J. Adler, J. Phys. A **18**, 1063 (1983).