Continuum percolation of permeable objects

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We study the extent to which excluded volume determines the percolation threshold for permeable elements in the continuum. An expansion due to Coniglio, De Angelis, Forlani, and Lauro exploits a similarity between the statistical mechanics of hard particles and statistics of percolation of permeable objects. This expansion shows that the expectation value of the excluded volume completely determines the threshold at lowest order in element density. Permeable rods in the continuum may be analyzed with the help of Onsager's treatment of virial coefficients for hard rods. Systems of rods provide cases in which higher-order terms will alter the proportionality of threshold to the inverse of the expected excluded volume and cases in which this proportionality remains exact.

I. INTRODUCTION

Continuum percolation is appropriate for discussing the connectedness of systems of elements whose positions are not constrained *a priori* to coincide with the sites (or bonds) of a regular lattice. A natural application is to complex fluids; for example, the critical behavior at a point of gelation.[1] In the past decade, Monte Carlo determinations of the critical percolation density ρ_p for various simply shaped elements have been performed.[2–4] This paper addresses the dependence of this threshold on the excluded volume of the elements. (The excluded volume around a permeable element is a figure whose perimeter consists of all loci of a chosen point on a second element such that the two elements just make contact.) A brief report of the results of Secs. IV–VI was made in letter form.[5] The present paper contains the detailed proofs of these results and places them in context as part of a general method for finding ρ_p as a configurational average.

We will rely on an analytic expression for ρ_p developed by Coniglio *et al.*[6,7] This is a Mayer-type expansion in the density of elements which is based on earlier work by Hill.[8] An alternate analytic expression which determines cluster statistics and critical concentrations is due to Klein;[9] it is an extension of the $q\rightarrow 1$ Potts-model formulation of Kastaleyn and Fortuin.[10] (Both of these methods permit the formal introduction of an interaction between the elements.) A dependence of the second virial coefficient on excluded volume was first discussed by Onsager.[11] In Sec. II we show that the series for ρ_p verifies an informal argument of Sinai quoted by Shklovski in Ref. 12.

The case of percolation of "parallel" elements with no orientational disorder, which is the subject of Sec. II, is of limited interest, though it is relevant to systems capable of nematic ordering, such as liquid crystals. For simple convex figures oriented parallel to one another, volume and excluded volume differ only by a dimensionally dependent factor. However, this is not true of the expectation value of excluded volume in a system with, for example, orientational disorder among elements. A proportionality between percolation threshold and the inverse of the expected excluded volume for elements with orientational disorder has been demonstrated in a simulation of a capped cylinder system by Balberg *et al.*[13] An expansion for the critical density can be written for this disordered system (Sec. III). The lowest-order term in this series predicts the dependence seen by Balberg, but in this case it is not true that all terms in the density expansion scale with the inverse of the expected excluded volume between two elements; higher-order diagrams involve expectation values of multiple, coupled volumes. However,[5] one sees that in the limiting case of very slender capped cylinders, the percolation threshold is inversely proportional to the expectation value of the excluded volume.

II. PARALLEL, MONODISPERSE, PERMEABLE ELEMENTS

Suppose that we seek the percolation threshold for a collection of permeable objects which will be placed randomly in a space of arbitrary dimensionality. We can define an effective interaction as follows:

$$u^{+}(\mathbf{r})\equiv\begin{cases}0 & \mathbf{r}\text{ within excluded volume about origin ,}\\ \infty & \text{otherwise ,}\end{cases}$$
$$u^{*}(\mathbf{r})\equiv\begin{cases}\infty & \mathbf{r}\text{ within excluded volume about origin ,}\\ 0 & \text{otherwise .}\end{cases} \tag{1}$$

With

$$f^{+}(\mathbf{r})\equiv e^{-\beta u^{+}(\mathbf{r})}$$

and (2)

$$f^{*}(\mathbf{r})\equiv e^{-\beta u^{*}(\mathbf{r})}-1\ ,$$

we have

$$f^{+}(\mathbf{r}) \equiv \begin{cases} 1 & \mathbf{r} \text{ within excluded volume ,} \\ 0 & \text{otherwise ,} \end{cases}$$
$$f^{*}(\mathbf{r}) \equiv \begin{cases} -1 & \mathbf{r} \text{ within excluded volume ,} \\ 0 & \text{otherwise .} \end{cases} \tag{3}$$

$f(\mathbf{r})$, the Mayer f function, is defined so that

$$f \equiv f^{+} + f^{*}$$

and thus $f(\mathbf{r})=0$ for all $\mathbf{r}$. The interaction (1) may be compared with those in Hill;[8] it expresses the fact that two elements are considered part of the same cluster if the center of one is located within the excluded volume of the other. This means simply that the actual volumes of the two elements overlap. However, (3) sets no energy price on this overlap. In a sense, the connectedness statement, (1), defines the excluded volume for a chosen system. A set of elements and their excluded volumes (actually, areas in this case) are drawn in Fig. 1. A property of the element of Fig. 1(c) is that its excluded volume is not related to its volume by a simple proportionality. We have

$$A = 2\epsilon L \ ,$$

while

$$A_{\text{exc}} = 2L^2 + 6\epsilon L \ . \tag{4}$$

Thus, excluded volume and volume scale differently with the two parameters, ϵ and L, which identify the element, even in the absence of any anisotropic placement of these elements in the plane.

We now implement a virial expansion for the pair connectedness $P(1,2)$ ($i \equiv \mathbf{r}_i$), defined such that

$$\rho^2 P(1,2) d\mathbf{r}_1 d\mathbf{r}_2 \tag{5}$$

is the probability that particle 1 is in $d\mathbf{r}_1$ and 2 is in $d\mathbf{r}_2$ and the particles are connected (i.e., members of the same cluster). ρ is the mean density of elements. Coniglio *et al.*[7] find that

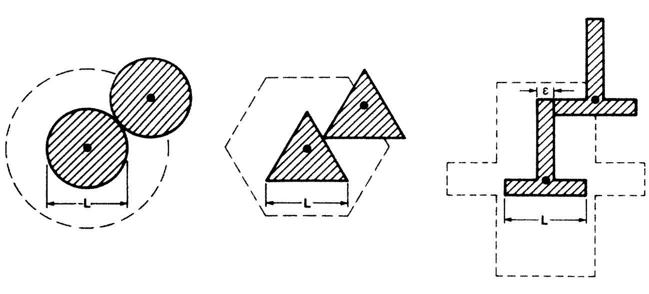


FIG. 1. Excluded volume (or area in two dimensions) around a figure is bounded by a perimeter consisting of all possible loci of the center of a second figure such that the two figures just make contact. (a) The excluded area around a circle of diameter L is a circle of diameter $2L$. (b) The triangle has an excluded area of $(3\sqrt{3}/2)L^2$, 6 times the triangle area. (c) The excluded area is $2L^2+6L\epsilon$. Since the area is $2L\epsilon$, the area may vanish while the excluded volume remains finite.

$$P(1,2) = e^{-\beta u^{+}(\mathbf{r}_{12})}\left[1+\sum_m \beta_{m,2}\rho^m\right] + e^{-\beta u^{*}(\mathbf{r}_{12})}\sum_m \beta^{+}_{m,2}\rho^m \ , \tag{6}$$

where $\mathbf{r}_{12} \equiv \mathbf{r}_1 - \mathbf{r}_2$. The $\beta_{m,2}$ represent diagrams analogous to those in the virial expansion for pair correlation.[14] In that expansion, there appear only "stars"; these are diagrams in which each vertex (particle coordinate) is connected by at least two independent paths made up of f bonds to every other vertex. The diagrams in (6) are made up of all possible combinations of f^{+} and f^{*} bonds with the following prescription: The $\beta_{m,2}$ assume the topology of stars with the addition of a bond between 1 and 2. The $\beta^{+}_{m,2}$ are defined similarly, save for the restriction that there is at least one path of f^{+} bonds between 1 and 2.

A certain subset of the diagrams of (6) will be of use in calculating the percolation threshold. These comprise the "direct pair connectedness." They are denoted $C^{+}(1,2)$ and can be defined from the Ornstein-Zernike-like relation

$$C^{+}(1,2) = P(1,2) - \rho\int C^{+}(1,3)P(3,2)d\mathbf{r}_3 \ . \tag{7}$$

If we call a diagram "nodal" if all paths from vertex 1 to 2 pass through at least one unique intermediate point, then C^{+} will be the subset of nonnodal diagrams connecting points 1 and 2. C^{+} determines the critical percolation density, for[7]

$$S = 1 + \rho\int P(\mathbf{r}_{12})d\mathbf{r}_{12} = 1 + \rho\widetilde{P}(0) \ , \tag{8}$$

where S is the mean cluster size and the tilde denotes the Fourier transform. From (7),

$$\widetilde{C}^{+}(k) = \widetilde{P}(k) - \rho\widetilde{C}^{+}(k)\widetilde{P}(k) \ ,$$

so that

$$S = \frac{1}{1-\rho\widetilde{C}^{+}(0,\rho)} \ .$$

Therefore

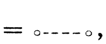
$$\rho_p = [\widetilde{C}^{+}(0,\rho_p)]^{-1} \ , \tag{9}$$

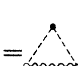
i.e., ρ_p is the density where the mean cluster size S becomes infinite.

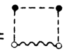
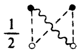
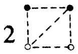
For example, the density expansion for C^{+} begins

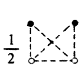
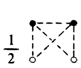
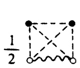
$$\widetilde{C}^{+}(0,\rho) = \widetilde{C}^{+}_2(0) + \rho\widetilde{C}^{+}_3(0) + \rho^2\widetilde{C}^{+}_4(0) + \cdots \ , \tag{10}$$

with

$\widetilde{C}^{+}_2(0) =$  ,

$\widetilde{C}^{+}_3(0) =$  , (11)

$\widetilde{C}^{+}_4(0) =$  $+\frac{1}{2}$  $+2$ 

$+\frac{1}{2}$  $+\frac{1}{2}$  $+\frac{1}{2}$  , where

denotes $f^{+}(\mathbf{r}_{ij})$,

denotes $f^{*}(\mathbf{r}_{ij})$,

and we integrate over all black vertices and over one of the two white vertices.[15] We have departed slightly from the notation of Ref. 6 by removing the ρ dependence from $\widetilde{C}_n^{+}$ and writing it explicitly in (10).

Armed with this expansion, one may look order by order in density to extract the excluded-volume dependence of ρ_p. To zeroth order in density, from (3) and (10),

$$\widetilde{C}_2^{+}=\int_0^{\infty} f^{+}(\mathbf{r}_{12})d\mathbf{r}_{12}=\int_{V_{\text{exc}}} d\mathbf{r}_{12}=V_{\text{exc}} \; . \tag{12}$$

To this order, one approximates the probability that two elements are connected with the probability that they overlap directly. Equations (9), (10), and (12) imply that to this lowest order $\rho_p \cong 1/V_{\text{exc}}$. For many regular, convex elements of volume V (those called "centrosymmetrical" by Onsager[11]) in a given dimension, this approximation predicts critical volume fractions, $\phi_p \equiv V\rho_p$, which are identical. For ellipsoids, cylinders, and regular polyhedra with inversion symmetry, this value is $\frac{1}{8}$. For the d-dimensional analogs of these figures it is $1/2^d$. Empirically,[2-4] this underestimates ρ_p, which is expected since one overestimates $\widetilde{C}^{+}(0,\rho)$.

To the next order,

$$\widetilde{C}_3^{+}=-\int_0^{\infty} f^{+}(\mathbf{r}_{12})f^{+}(\mathbf{r}_{13})f^{+}(\mathbf{r}_{23})d\mathbf{r}_{12}d\mathbf{r}_{13} \; . \tag{13}$$

It is straightforward to show that (13) can be written

$$\widetilde{C}_3^{+}=V_{\text{exc}}^2 k_3 \; , \tag{14}$$

where k_3 is a number invariant under any linear transformation on shapes of the percolative elements. The proof is as follows: Let $\overleftrightarrow{A}$ be a linear transformation on coordinates, $\overleftrightarrow{A}$: $\mathbf{r}\rightarrow\mathbf{r}'$, such that $r_i'=\overleftrightarrow{A}_{ij}r_j$. We operate with $\overleftrightarrow{A}$ on each of the permeable volumes 1, 2, and 3, making a consistent choice for the definition of the "center" of a volume and performing any rotation demanded by $\overleftrightarrow{A}$ with respect to that center. We note as $\overleftrightarrow{T}$ the operation of transforming the volumes 1, 2, and 3 with $\overleftrightarrow{A}$ in this way. This $\overleftrightarrow{T}$ is the "linear transformation on shapes" previously mentioned, and under which k_3 is to be invariant. Then,

$$\overleftrightarrow{T}\widetilde{C}_3^{+}=-\int_0^{\infty} (f')^{+}(\mathbf{r}_{12})(f')^{+}(\mathbf{r}_{13})(f')^{+}(\mathbf{r}_{23})d\mathbf{r}_{12}d\mathbf{r}_{13} \; , \tag{15}$$

where $(f')^{+}(\mathbf{r})$ is unity if $\mathbf{r}$ falls within the excluded volume centered at the origin of a transformed volume element, the magnitude of which is noted V'_{exc}, and is zero otherwise.

Since $\overleftrightarrow{A}$ can be decomposed into a combination of a rotation and a dilation, we consider the serial effects of these two operations on $\widetilde{C}_3^{+}$:

A rotation of each volume element by a uniform angle Ω about its center will clearly have no effect on this quantity. We recall that each element, and hence the excluded volume about each element, is assumed to remain parallel to all others. The rotational part of $\overleftrightarrow{T}$ will merely reorder the terms in the integral (13) as it rotates our reference axes (the axes fixed on element 1) by Ω.

If $\overleftrightarrow{A}$ consists of dilations (is diagonal), consider transforming all vectors in (15) by $\overleftrightarrow{A}$. This is just a change of variable, so

$$\overleftrightarrow{T}\widetilde{C}_3^{+}=-\int_0^{\infty} (f')^{+}(\mathbf{r}'_{12})(f')^{+}(\mathbf{r}'_{13})(f')^{+}(\mathbf{r}'_{23})d\mathbf{r}'_{12}d\mathbf{r}'_{13} \; . \tag{16}$$

By definition, $(f')^{+}(\mathbf{r}')=f^{+}(\mathbf{r})$. Substituting this into (16) and noting that $d\mathbf{r}'_{ij}=(\det\overleftrightarrow{A})d\mathbf{r}_{ij}$, we find

$$\overleftrightarrow{T}\widetilde{C}_3^{+}=(\det\overleftrightarrow{A})^2\widetilde{C}_3^{+} \; . \tag{17}$$

Since rotation matrices are unitary, we find (17) holds for a general linear transformation $\overleftrightarrow{A}$ involving dilation and/or rotation. Thus the two first terms of (10) are found to scale upon transformation as

$$\begin{aligned}\overleftrightarrow{T}\widetilde{C}^{+} &\cong V'_{\text{exc}}+[(V'_{\text{exc}})^2/V_{\text{exc}}^2]\widetilde{C}_3^{+}\\ &\equiv V'_{\text{exc}}k_2+(V'_{\text{exc}})^2k_3 \; ,\end{aligned} \tag{18}$$

where $k_2\equiv 1$, and hence Eq. (14). Any linear transformation on shapes, $\overleftrightarrow{T}$, effects $\widetilde{C}_3^{+}$ by a factor identical to the square of the rescaling factor for the excluded volume. We conclude the argument by examining a general term, t_n, which contributes to $\widetilde{C}_n^{+}$ in the expansion (10):

$$t_n=p\int_0^{\infty} f^{+}(\mathbf{r}_{ij})f^{+}(\mathbf{r}_{kl})\cdots d\mathbf{r}_{12}d\mathbf{r}_{13}\cdots d\mathbf{r}_{1n} \; . \tag{19}$$

The $i,j,\ldots$ are some indices between 1 and n; p is some constant factor. This diagram is created from the prescriptions (6) and (7), but there are two important features of (19) for this argument: First, that one integrates over n-1 distinct radii; the diagram is completely connected. Second, the cutoff function for each radius is some product of f^{+} functions, each of which is a constant (unity) over the excluded volume centered upon some element. In this case, we can perform the transformation $\overleftrightarrow{T}$ on the set of n elements as we did to derive (15) and (16) to obtain

$$\overleftrightarrow{T}t_n=(\det\overleftrightarrow{A})^{n-1}t_n \; . \tag{20}$$

Equation (20) will hold for all terms t_n in $\widetilde{C}_n^{+}$ so that we may write $\widetilde{C}^{+}$ as

$$\widetilde{C}^{+}(0,\rho)=V_{\text{exc}}+\rho V_{\text{exc}}^2k_3+\cdots+\rho^{n-1}V_{\text{exc}}^n k_{n+1}+\cdots \; .$$

Then (9) becomes

$$\rho_p=\frac{1}{V_{\text{exc}}\left[1+\sum_{n=1}\rho_p^n V_{\text{exc}}^n k_{n+2}\right]} \; . \tag{21}$$

The only way that (21) can be true, for example, for all choices of V_{exc} for elements of a given shape, is if

$$\rho_p=C/V_{\text{exc}} \; , \tag{22}$$

where C is defined in terms of integrals over f^{+} functions by the recursive relation

$$C=\left[1+\sum_{n=1} C^n k_{n+2}\right]^{-1} . \tag{23}$$

Equation (22) is our desired result. As we have shown, the constant C is invariant under uniform dilations and rotations of the percolative elements. One may argue that the set of transformations $\{\overleftrightarrow{T}\}$ is not very general, and are not the most interesting for a system which is anisotropic and/or polydisperse. Further, for this class of transformations, both V and V_{exc} scale with the determinant of $\overleftrightarrow{A}$; so one can make the parallel claim that $\widetilde{C}^+$ scales with the rescaling factor of the volume itself. This will always be true for centrosymmetrical objects and such linear operators. However, in the following sections we treat cases of operations which are interesting physically and are not of this simple linear form. When applied to a polydisperse or orientationally disordered system, the volume and the excluded volume (actually an expectation value for the excluded volume) scale quite differently. In some cases, upon transformation the percolation threshold scales with the inverse of the latter and an equation of the form (22) holds. In some cases this is not so. It is the behavior of the numbers k_i under transformations which scale V and V_{exc} differently, which is precisely of interest in identifying the contribution of V_{exc} to ρ_p; this could produce, for example, the sort of scaling seen by Balberg *et al.*[13,16] and Robinson.[17]

Existing data[18] $[C=\phi_p(V_{\text{exc}}/V)]$, indicates that, for spheres, $C=2.80$. For other convex shapes in three dimensions, C is exceptionally close to this value.[4] This is referred to as a "universality" by Balberg *et al.*;[19] they do state that it is approximate.[20] Given the proximity of the various Cs, the source of any discrepancy between C values for similar shapes becomes of interest. Density series indicate that such a discrepancy is a real effect. For example, elements such as square and cube have manifestly different values of k_3. Further, one sees uniformly higher values for cubes versus spheres, and square versus circles, for coefficients of the density series of mean cluster size calculated up to fifth order by Haan and Zwanzig.[18] (Their series can be inverted and the terms reordered to identify the coefficients $\widetilde{C}_n^+$.) If we create, say, a square and a circle which enclose equal volumes, the average radial distance from the center of the square to its border can be easily found to be slightly larger than the circular radius ($1.0172r$). Percolation is facilitated by enhanced overlap, so we might conclude that the "pointy" square would percolate at a slightly lower density; analogously, a parallelpiped percolates at a slightly lower density than an ellipsoid of equal volume, as the trend in the Haan and Zwanzig data would indicate. This intimates that the "universality" is not exact.

A final comment in this section concerns an easy extension of the arguments above to the "inclusive figure" (IF) convention. Rather than defining two elements as connected if they overlap ["overlapping figure" (OLF)], we may define them to be connected if the center of one lies within the volume of the other. The terminology is due to Pike and Seager.[2] Skal and Shkilovski[4] found the IF problem to be most appropriate in describing the hopping conductivity of a lightly doped semiconductor. If we strike the words "excluded" from definitions (1) and (3), we may use the Coniglio method to calculate ρ_p for an IF system. We would then arrive at the conclusion

$$\widetilde{C}^+(0,\rho)=V+\rho V^2 j_3+\cdots+\rho^{n-1}V^n j_{n+1}+\cdots$$

[where the j_i are the counterparts of the k_i in Eq. (21)], so that

$$\rho_p=C'/V . \tag{22$'$}$$

Shklovskii[12] gives an argument due to Sinai which predicts (22′) with C' invariant under linear transformations on the surfaces' bounding volumes. (The Coniglio expansion confirms in a formal way Sinai's intuitive argument.) In cases where percolation is of parallel, centrosymmetrical figures, the constants C and C' are identical and (22) and (22′) imply that

$$\rho_p^{\text{IF}}/\rho_p^{\text{OLF}}=2^d . \tag{24}$$

One can trivially map an OLF problem onto an IF problem where the shapes of the included figures are the excluded volumes of the original problem. For example, the permeable element of Fig. 1(b) has the shape of an equilateral triangle of volume $V=\sqrt{3}L^2/4$. If these elements are constrained to retain a fixed orientation, an element has a hexagonal excluded volume of magnitude $6V$. (This is an example[2] of a simple shape which is not "centrosymmetric.") Then (22′) and (24) imply that if we compare OLF percolation of the triangles to percolation of hexagons of equal volume V,

$$\rho_p^{\text{tri}}/\rho_p^{\text{hex}}=2/3 . \tag{25}$$

Rigorously, the "pointier" triangle must percolate at a lower density than the hexagon.

III. POLYDISPERSITY OR ORIENTATIONAL DISORDER

In the preceding we looked at systems in which the percolating elements were centered at random, but allowed no variation in either size or orientation. Suppose that we seek the percolation threshold for a system of elements with some randomness in either shape or orientation. We can write a general expression for ρ_p by letting $u_{\alpha\beta}^+(\mathbf{r}_{ij})$ be defined as in Eq. (1), except now α is an index which contains information on the orientation and/or morphology of the element at $\mathbf{r}_i$ and β for the element at $\mathbf{r}_j$. This potential is still zero within the excluded volume around the origin and infinite elsewhere, but it is now the excluded volume around an element of "type" α for an element of type β. As in Eq. (1), $f_{\alpha\beta}^*$ is $-f_{\alpha\beta}^+$. We rewrite Eq. (3) as

$$f_{\alpha\beta}^+=e^{-u_{\alpha\beta}^+},\quad f_{\alpha\beta}^*=e^{-u_{\alpha\beta}^*}-1 . \tag{26}$$

Then (9) becomes

$$\begin{aligned}\rho_p&=1/\langle\widetilde{C}^+(0,\rho_p)\rangle\\&=1\Big/\sum_{\{\alpha_i\}}F(\alpha_1,\ldots,\alpha_N)\widetilde{C}^+_{\alpha_1,\ldots,\alpha_N}(0,\rho_p) ,\end{aligned} \tag{27}$$

where F is the joint probability of observing the set $\{\alpha_i\}$

of N states of the N elements in the system. For a percolation application, we assign states independently from element to element, so F becomes $\prod_i F(\alpha_i)$.

The zeroth-order contribution to $\langle \widetilde{C}^+ \rangle$ is

$$\langle \widetilde{C}_2^+ \rangle = \sum_{\alpha,\beta} F(\alpha)F(\beta) \int_0^\infty f_{\alpha\beta}^+(\mathbf{r}_{12})d\mathbf{r}_{12} = \langle V_{\text{exc}} \rangle \ . \tag{28}$$

In the polydisperse or disordered notation, we effect changes in the percolating elements simply by changing the distribution function $F(\{\alpha_i\})$. Thus an operation $\overleftrightarrow{\mathrm{T}}$ on the system may be thought of as working on $F(\{\alpha_i\})$. The index α_i can include a $(d-1)$-dimensional vector indicating the angular orientation of an element with respect to some fixed reference axes, can govern element size, etc. Equation (28) states that the zeroth-order contribution to ρ_p will scale with any transformation on the polydisperse or disordered system exactly as the expectation value of the inverse of the excluded volume will.

The challenge is to understand whether higher-order terms concur with the previous result, or whether their dependence of the parameters of $F(\{\alpha_i\})$ may differ from that of V_{exc}. One finds that $\overleftrightarrow{\mathrm{T}}$ commutes with the taking of the expectation value of $\widetilde{C}^+$. That is, if $\{\alpha_i\}$ are a set of shape or orientation parameters which map to $\{\alpha_i'\}$ under $\overleftrightarrow{\mathrm{T}}$, then

$$\begin{aligned}\overleftrightarrow{\mathrm{T}}\langle \widetilde{C}^+_{\{\alpha_i\}} \rangle &= \prod_{\{\alpha_i\}} F'(\{\alpha_i\})\widetilde{C}^+_{\{\alpha_i\}} \\ &= \prod_{\{\alpha_i'\}} F'(\{\alpha_i'\})\widetilde{C}^+_{\{\alpha_i'\}} \\ &= \prod_{\{\alpha_i\}} F(\{\alpha_i\})\widetilde{C}^+_{\{\alpha_i'\}} \\ &= \langle \overleftrightarrow{\mathrm{T}}\widetilde{C}^+_{\{\alpha_i\}} \rangle \ ,\end{aligned}$$

since by definition $F'(\{\alpha_i'\}) \equiv F(\{\alpha_i\})$. Thus if $\overleftrightarrow{\mathrm{T}}$ is the sort of linear transformation introduced in the preceding section, then ρ_p will again be rescaled only by the determinant of the transformation. If $\overleftrightarrow{\mathrm{T}}$ is not of this form, whether $\langle V_{\text{exc}} \rangle$ dictates the scaling of ρ_p must depend on the particular system one chooses and the particular transformation one makes. This is elaborated upon in the Appendix. Recently, Chiew *et al.*[21] have applied a Percus-Yevick approximation to a system of binary spheres and found that ϕ_p is indeed independent of the distribution function and equal to $\frac{1}{2}$. However, this value is quite distinct from Monte Carlo estimates[2,22] of $\cong 0.35$ for monodisperse spheres. Further, Chiew *et al.* found that ϕ_p is dependent on the distribution if the wholly permeable spheres are replaced by partially permeable spheres (the permeable-sphere model of Ref. 23). In the following two sections, we use the example of a system of rods with variable orientations to show that it is only in special cases that rescaling of the expected excluded volume produces a rescaling of the percolation threshold by the same factor.

IV. RANDOMLY ORIENTED CYLINDERS IN THREE DIMENSIONS

Consider the percolation threshold for a set of cylinders capped with hemispheres in three dimensions. We assume that the axes are aligned (with respect to an arbitrary z axis) at random according to a uniform distribution:

$$\begin{aligned}F(\theta) &= 1/2\theta_\mu, \quad \theta \text{ in } (-\theta_\mu, \theta_\mu) \\ &= 0, \quad \text{otherwise} \ .\end{aligned} \tag{29}$$

It is then the case that for cylinders of length L and caps of radius r[11,13]

$$V = \pi r^2 L + 4\pi r^3/3 \ ,$$

while

$$\langle V_{\text{exc}} \rangle = 8\langle V \rangle + 4L^2 r \langle \sin\gamma \rangle \ , \tag{30}$$

where γ is the angle between the axes of two cylinders. With (28) applied to (30), the zeroth-order dependence of ρ_p on the parameters is mixed, but if r/L is small, then, to zeroth order,

$$\rho_p \propto 1/rL^2 \langle \sin\gamma \rangle \ . \tag{31}$$

(Note that Coniglio's expansion makes no distinction between the threshold for percolation parallel to versus percolation perpendicular to the z axis.)

Now consider higher-order contributions to ρ_p. We look specifically at $\widetilde{C}_3^+$ for the system of cylinders. Such a cluster integral, even before the expectation value is taken, is notoriously difficult to calculate.[24] However, Onsager has estimated the order of magnitude for such a term. His estimate is given for an isotropic system of rods, one for which $\theta_\mu = \pi/2$. However, the geometry it predicts seems to be appropriate also to the anisotropic case, so long as θ remains large with respect to r/L. To greatest order in L this term behaves as

$$\langle \widetilde{C}_3^+ \rangle \sim r^3 L^3 \log(L/r) \ . \tag{32}$$

We continue to look only at the limit of slender cylinders; Eq. (32) is true to lowest order in r/L. Briefly, the r^3L^3 factor arises because, before the expectation value is taken, a typical intersection of excluded volumes between elements 1 and 3 and between 2 and 3 will be a "thin" parallelepiped of dimensions r^2L. The last integration, over the excluded volume between 1 and 2, adds a factor of rL^2 [Eq. (31)]. The $\log(L/r)$ term arises from the process of taking the expectation value; Ref. 11 contains a rigorous exposition.

Equation (32) shows that, to this order in the density expansion, ρ_p will not scale as $1/\langle V_{\text{exc}} \rangle$, for

$$\rho_p \cong \frac{1}{\langle V_{\text{exc}} \rangle + \rho_p \zeta r^3 L^3 \log(L/r)} \ . \tag{33}$$

The factor ζ includes expectation values over relative orientations. Even if one ignores the slowly varying dependence of the $\log(L/r)$ term, one finds that there is no nonzero value of ζ which allows $\rho_p \sim 1/\langle V_{\text{exc}} \rangle$. To a consistent order in r/L, this would be

$$\rho_p \sim 1/(8\pi r^2 L + 4rL^2\langle \sin\gamma \rangle) .$$

The succeeding terms in the series (9) make it clear that, so long as all the terms do not vanish identically, there will be a formal correction to the law $\rho_p \sim 1/\langle V_{\text{exc}} \rangle$. One can apply Onsager's geometrical insight in a rough way to the higher-order terms in the expansion for $\langle \tilde{C}^+ \rangle$. At fourth order and beyond, the terms t_n are varied in the number of elements whose volumes they couple. Since terms at each *succeeding* order require *successively* one further volume integral, and since each term beyond second order has a minimum of one integral over the intersection of multiple excluded volumes, an upper bound exists:

$$\langle \tilde{C}^+_{n+3} \rangle \propto (\tilde{C}^+_3)(rL^2)^n . \tag{34}$$

This is an upper bound in the sense that certain terms (those which are more tightly connected) will scale with higher powers of r or lower powers of L. [Equation (34) omits logarithmic factors, which will certainly be present as well.] Substituting (34) into the expansion for ρ_p makes the point that the threshold cannot depend only on the excluded volume if the series is to be good for all r and L.

An important observation concerning the case of isotropic rods in three (and higher) dimensions[5] is that in the limit $r/L \to 0$ all terms in the series for ρ_p vanish in comparison to the first, $\langle \tilde{C}^+_2 \rangle$. In this limit, it is simply the case that

$$\rho_p \cong 1/\pi r L^2 = 1/\langle V_{\text{exc}} \rangle . \tag{35}$$

This prediction may be checked against Fig. 1 of Balberg *et al.*[13] The region in which ρ_p is fitted with a slope of r^{-1} extends from r/L approximately 0.1 to 0.01. A hypothetical correction of order r/L is not especially small in this range; nevertheless, Eq. (35) agrees with the figure in this region to within 20%. This figure also shows the crossover to r^3 dependence as $L \to 0$ and the capped rods become spheres. In principle, the functional behavior of ρ_p in the crossover regime could be exactly determined from a knowledge of the cluster integrals. In practice, exact solutions of the integrals are too difficult to obtain, although some information about the scaling behavior of these integrals may be gleaned from the data in this range.

Recently, Williams *et al.* have evaluated virial integrals up to fifth order for thin rods numerically. While the results are preliminary,[25] they seem to support the conclusion that all higher-order $\tilde{C}^+_i$ vanish in units of $\tilde{C}^+_2$. Hence, Eq. (35) holds, barring any abnormal divergence of the cluster series, Eq. (9). (Unfortunately we are so far unable to show formally that no such divergence exists at ρ_p.)

In conclusion, an expansion for ρ_p shows that this threshold has dependences on r/L for the three-dimensional stick system which cannot be accounted for by the law $\rho_p \sim 1/\langle V_{\text{exc}}(r,L,\theta_\mu) \rangle$. However, in the limit $r/L \to 0$, the formal corrections vanish term by term. In this case the excluded volume hypothesis becomes exact, and there develops a strict equality between ρ_p^{-1} and $\langle V_{\text{exc}} \rangle$.

V. RANDOMLY ORIENTED STICKS IN TWO DIMENSIONS

For a real system, the interesting (or realizable) transformations may consist of a change in the distribution of orientations of the elements. Polarizable elements in variable fields, nematically ordered liquid crystals at variable temperature, are model systems for this sort of transformation. We consider thin sticks in two dimensions to test variations in orientational disorder. For a monodisperse collection of sticks of length L, one has

$$\langle \tilde{C}^+_2 \rangle = L^2 \langle \sin\theta_{12} \rangle . \tag{36}$$

θ_{12} is the angle between sticks 1 and 2. Figure 1 of Ref. 19 contains a sketch of this parallelogram-shaped V_{exc}.

Consider the simplest distribution which permits angular variation: sticks can lie at one of two angles, θ_1 or θ_2, with respect to some y axis. We redefine the y axis to be symmetric with respect to these two directions:

$$F(\theta) = p\delta_{\alpha,\theta} + (1-p)\delta_{-\alpha,\theta} , \tag{37}$$

with $|\theta_1 - \theta_2| = 2\alpha$. Imagine changing the distribution so that $[F(\theta)]' = F(\theta/\lambda)$; the transformed sticks are constrained to lie at $\alpha\lambda$ or $-\alpha\lambda$. (Without loss of generality, assume these do not exceed $\pi/2$.) For this system

$$\begin{aligned} \langle V_{\text{exc}} \rangle &= L^2 2p(1-p)\sin(2\alpha) \\ &\to \langle V_{\text{exc}} \rangle \sin(2\lambda\alpha)/\sin(2\alpha) . \end{aligned} \tag{38}$$

This simple example has the property that the percolation threshold is altered by the inverse of this factor, so $\rho_p \sim 1/\langle V_{\text{exc}} \rangle$. The reason is as follows: The transformation on angles can be achieved by two successive operations performed on the terms of the series, Eq. (9). These operations are reminiscent of the linear operations $\overleftrightarrow{\mathrm{T}}$ of Sec. II. However, they are not performed on the element volumes themselves, but on the f^+ functions in the expansion for ρ_p. The operations are as follows:

(i) Dilate the x axis of the relative coordinate $\mathbf{r}_{ij}$ in each f^+ in the series for ρ_p [e.g., in every term t_n as in Eq. (A1)]. (This transformation is similar to the "squeezing" performed by Balberg *et al.*;[19] a difference is that, we do not rescale the empty space between elements.) We dilate by a factor of $\tan(\lambda\alpha)/\tan\alpha$. Under this operation, the series (9) predicts that the percolation threshold is reduced by the factor $\rho_p' = \rho_p \tan\alpha/\tan(\lambda\alpha)$, while the volume of each parallelogram-shaped excluded volume is increased by that factor. Because the sticks are of negligible width, terms which involve the overlap of two parallel sticks do not contribute to ρ_p.

(ii) Contract each stick uniformly along both coordinate axes. The transformation (i) sent $\sin\alpha \to \sin\alpha' = \sin(\lambda\alpha)$, $L \to L' = L\cos\alpha/\cos(\lambda\alpha)$. If operation (ii) contracts a stick oriented at $\pm\lambda\alpha$ by a factor $\cos(\lambda\alpha)/\cos\alpha$, then

$$\begin{aligned} &\alpha' \to \alpha'' = \lambda\alpha, \quad L' \to L'' = L , \\ &\rho_p'' = \rho_p'[\cos\alpha/\cos(\lambda\alpha)]^2 = \rho_p[\sin 2\alpha/\sin(2\lambda\alpha)] . \end{aligned} \tag{39}$$

Operations (i) and (ii) transform the series (9) to the series for the new system in which the orientation of the sticks is rescaled but the lengths are left invariant.

Though these operations will rescale stick width, for sticks of vanishing width, this cannot affect ρ_p [whose leading dependence is, from Eq. (36), $1/L^2$]. Thus, for widthless sticks, the rescaling of excluded volume should completely determine the change in threshold. Monte Carlo data[16,17] for the special case $p=\frac{1}{2}$ support this.

For a more general angular distribution, the case is not so clear. We may choose a smooth distribution and first perform a transformation such as (i) above. If, as in Ref. 16, one "squeezes" by a factor noted as $P_{\parallel}/P_{\perp}$, the transformed distribution admits a polydispersity of stick lengths. Lengths are correlated with angles according to

$$L_i'=\frac{L(P_{\perp}/P_{\parallel})}{[\sin^2\theta_i'+\cos^2\theta_i'(P_{\perp}/P_{\parallel})^2]^{1/2}}\ ,$$
$$F'(\tan\theta_i')=F(\tan\theta_i(P_{\perp}/P_{\parallel}))\ . \tag{40}$$

The transformed distribution has a threshold which is altered by an anisotropy factor, $\rho_p'=\rho_p P_{\parallel}/P_{\perp}$. However, there is no second operation on the f^+ analogous to operation (ii) above which will render the system monodisperse again [except for the inverse of (i)]. One cannot alter the angular distribution of the original system for a general $F(\theta)$ and still retain monodispersity if one employs only dilations which act uniformly on each excluded volume of the sum, Eq. (9). It remains an open question whether a nonlinear operation which varies angular distributions alone will alter the percolation threshold rigorously via the excluded-volume rule: $\rho_p'=\rho_p\sin\theta/\sin\theta'$. This does not imply that the excluded-volume theory is not useful for such sticks in two dimensions. Monte Carlo data,[3(b),16,17] for uniform, normal, and log-normal distributions, indicate that at least an "approximate universality" holds.

Finally, it is straightforward to note that the threshold scales with the remaining distribution parameter L, as does the excluded volume. A uniform dilation such as (ii) above takes $L\to\lambda L$, $\langle V_{\rm exc}\rangle\to\lambda^2\langle V_{\rm exc}\rangle$, and, as in Eq. (39), $\rho_p\to\rho_p/\lambda^2$.

VI. STICKS IN THREE DIMENSIONS WITH ORIENTATIONAL CONSTRAINT

Boissonade *et al.*[26] performed a Monte Carlo study of fibers which were centered at random, but constrained to lie parallel to one of three mutually orthogonal axes. The simulation was performed on a lattice; a chain of n sites represented a fiber of aspect ratio n. One consequence of the lattice algorithm is that it blurs a distinction between "permeable" and "nonpermeable" elements which is sharp in the continuum. For example, one can calculate the lattice analog of $\widetilde{C}_2^n$ (call it $\widetilde{D}_2^n$) by inverting a series for the mean cluster size: $S(p)=\sum_r a_r p^r$. Identifying $\phi\sim p\sim\rho n$, we find

$$S(p)=1/(1-\widetilde{D}_2^+ p/n+\cdots)$$

with

$$\widetilde{D}_2^+\equiv\tfrac{4}{3}n^2+\tfrac{16}{3}n-\tfrac{2}{3}\ \text{("hard" cylinders)}\ ,$$
$$\equiv 2n^2+6n-1\ \text{("permeable" cylinders)}\ . \tag{41}$$

In the "permeable" case, one allows members of the same cluster to have lattice sites in common, as well as contact each other in the way of "hard" lattice cylinders. In contrast to Eq. (41), the continuum $\widetilde{C}_2^+$ will vanish for a perfectly hard object, as will all $\widetilde{C}_n^+$. (Hard objects present a vanishing phase space for overlap.) In conclusion, the lattice algorithm of Ref. 26 corresponds to a continuum problem with a hard core surrounding a permeable shell of comparable size.

Boissonade *et al.* found the law

$$p_c\propto 1/n\ . \tag{42}$$

At lowest order in p, Eq. (41) supports this law and predicts corrections to it which are lower order in n. Since the generation of a finite number of terms in the lattice series cannot ensure the applicability of Eq. (42), we consider the analogous continuum problem. For permeable rods, or for rods with a hard core and permeable shell of comparable width, which are constrained to lie perpendicular to one of three coordinate axes, only a fraction of the diagrams in Eq. (27) will contribute to the slender-rod limit. For the first diagram of Eq. (11) [whose configurational average is Eq. (28)], one finds

$$\langle\widetilde{C}_2^+\rangle=\tfrac{2}{3}4rL^2 \tag{43}$$

to lowest order in r/L. Six diagrams of nine contribute to this, and the remaining three, for which the two rods are parallel, are of order r^2L. There is no contributing diagram corresponding to $\langle\widetilde{C}_3^+\rangle$, for Eq. (11) shows that this diagram involves the pairwise overlap of three rods. For this system, pairwise overlap of three rods can only occur if there is also a three-way overlap. Such a diagram will be of leading order r^3L^3 and, as in the case of Eq. (32), will not contribute to ρ_p as $r/L\to 0$. (Diagrams with all three rods parallel with scale as r^4L^2.) For $\langle\widetilde{C}_4^+\rangle$, the leading contribution in r/L will arise from the first two four-vertex diagrams which are sketched in Eq. (11). Further, these contributions will only lead if the configurations they describe consist of rods which are pairwise parallel, and with pairwise intersections that occur at right angles. Any such diagram carriers a combinatoric weight of $\frac{2}{9}$, and will scale as r^3L^6, or $1/\langle V_{\rm exc}\rangle^3$.

In conclusion, diagrams contributing in the slender-rod limit are the subset of diagrams of Eq. (10) for which clusters of rods are (i) coplanar and (ii) have all intersections of sticks occurring at right angles. The coplanarity of this reduced class of diagrams has an obvious property: The operation $L\to\lambda L$ which we applied to a two-dimensional system at the end of Sec. V can be applied here with the same result. That is, we imagine dilating by λ uniformly along both axes in the plane formed by the intersecting sticks in each particular diagram. Then we see that to lowest order in r/L every diagram with $i+1$ vertices which contributes is rescaled by a factor λ^{2i}. Thus, $\langle\widetilde{C}_{i+1}^+\rangle\to\lambda^{2i}\langle\widetilde{C}_{i+1}^+\rangle$; therefore $\rho_p\sim 1/L^2$. Further, we can combine this operation with a dilation normal to the plane of intersection of the sticks in each diagram. This gives the scaling of ρ_p with the small dimension of the rods: $\rho_p\sim 1/r$. Thus the continuum analog of Eq. (42) will be

$$\rho_p \sim 1/L^2 r \tag{44}$$

for this system of rods with discrete angular orientations. For rods with a moderate aspect ratio n, there must be a correction to Eq. (42) which is lower order in n (not higher, as might be predicted from Ref. 27). The small-n region of Fig. 5 of Boissonade *et al.* is consistent with this correction.

VII. CONCLUSIONS

We have applied an expansion for ρ_p developed by Coniglio *et al.* to test the prediction that $1/\langle V_{\mathrm{exc}}\rangle$ completely determines ρ_p for a wide class of permeable elements. Recent results by Balberg *et al.* and Robinson suggest this prediction for the case of percolation of anisotropic objects (cylinders). These objects allow one to distinguish between the percolation threshold scaling with volume and with excluded volume. We find that one may write $\rho_p = C/V_{\mathrm{exc}}$ with V a constant under distortions of the percolating elements which are global linear transformations of the excluded volume of the elements. Nonlinear transformations may yield a different result. For the case of randomly oriented cylinders in three dimensions, the rule $\rho_p(r,L) \sim 1/\langle V_{\mathrm{exc}}(r,L)\rangle$ is not strictly true. However, it becomes true in the stick $(r/L \to 0)$ limit, where the proportionality becomes equality. For the case of sticks in two dimensions, $\rho_p(L) \sim 1/\langle V_{\mathrm{exc}}(L)\rangle$ is true. Further, $\rho_p(L,\theta) \sim 1/\langle V_{\mathrm{exc}}(L,\theta)\rangle$ is true for the special case of $F(\theta)$ a discrete distribution where θ can take on one of two values (or trivially, only one.) It remains to be seen whether this result holds in two dimensions for a distribution where allowed angles number more than two, in particular, for a continuous spectrum of allowed orientations. The density expansion for ρ_p involves difficult integrals even at its second order. The hope is that one may find symmetries which are upheld term by term under nonlinear transformations of interest. Without requiring that the integrals be done, this will determine the effect of such transformations on the percolation threshold.

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APPENDIX

We will argue that ρ_p may receive contributions from terms which do not scale as an appropriate power of the expectation value of the excluded volume, as does $\tilde{C}_2^+$. Consider a general term which contributes to $\tilde{C}_n^+$. It has the form

$$t_n = p \int_0^\infty f^+_{\alpha_i\alpha_1}(\mathbf{r}_{ij_1}) f^+_{\alpha_i\alpha_2}(\mathbf{r}_{ij_2}) \cdots f^+_{\alpha_i\alpha_m}(\mathbf{r}_{ij_m}) \cdots \times f^+_{\alpha_k\alpha_l}(\mathbf{r}_{kl}) \cdots d\mathbf{r}_{12} d'\mathbf{r}_{13} \cdots d\mathbf{r}_{1n} \ . \tag{A1}$$

We have explicitly written all f^+ functions which show a coupling of i to any other element; there are m such elements and they are noted as $\{j_i\}$. If the integral over $\mathbf{r}_{1i}$ is performed first, one first calculates the excluded volume of a type-α_i element around a type-α_j one for all j in the set $\{j_i\}$. Then one takes the intersection of all such excluded volumes, each of which is centered at element j_i. If we continue to integrate (A1), this time over any one of these $\mathbf{r}_j$, we calculate what we may think of as an "effective" excluded volume for this element, j_1, say, with respect to each of the remaining $n-2$ elements to which it is coupled. We say "effective" because we must weight each excluded volume with the result of the original integration which has a dependence on $\mathbf{r}_{j_1}$. If we continue to integrate, as each coordinate is integrated out an intersection of effective excluded volumes is calculated, and they are "effective" since the integration variable is weighted by a function of itself and the remaining variables. This function is a nontrivial result of the previous integrations. In the case of parallel, monodisperse elements, we showed that if one operates with $\overleftrightarrow{T}$ linear, each integration involves accruing an additional factor of $\det\overleftrightarrow{A}$ and, hence, Eq. (20). However, suppose we perform some more general transformation on the distribution $F(\alpha)$ so that the excluded volume between two elements is rescaled? Then we have

$$\langle V_{\mathrm{exc}}\rangle' = \sum_{\alpha,\beta} \int_0^\infty F'(\alpha)F'(\beta) f^+_{\alpha\beta}(\mathbf{r}_{12}) d\mathbf{r}_{12} = k\langle V_{\mathrm{exc}}\rangle \ . \tag{A2}$$

If $F \to F'$ is quite general, there is no compelling reason for the term (A1), upon averaging with the weight $F'(\alpha_1) \cdots F'(\alpha_n)$, to scale as k^{n-1} times its former value; the expectation value for an intersection of "effective" excluded volumes can depend on the transformation in a very different way than would the expectation value of a single, isolated excluded volume. Therefore, when these terms are summed in the series (9), there is no requirement that an excluded-volume "universality" will hold.

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[1] A. Coniglio, H. E. Stanley and W. Klein, Phys. Rev. B **25**, 6805 (1982); D. Stauffer, Physica **106**, 177 (1981).

[2] G. E. Pike and C. H. Seager, Phys. Rev. B **10**, 1421 (1974).

[3] (a) D. H. Fremlin, J. Phys. (Paris) **37**, 813 (1976); (b) I. Balberg, Phys. Rev. B **31**, 4053 (1985).

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

[5] A. L. R. Bug, S. A. Safran, and I. Webman, Phys. Rev. Lett. **54**, 1412 (1985).

[6] A. Coniglio, U. De Angelis, A. Forlani, and G. Lauro, J. Phys. A **10**, 219 (1977). Recent advances in the formalism have been made by G. Stell; see, for example, J. Phys. A **17**, L855 (1984).

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

[8] T. L. Hill, J. Chem. Phys. **23**, 617 (1955).

[9] W. Klein, Phys. Rev. B **26**, 2677 (1982).

[10]P. W. Kastaleyn and C. M. Fortuin, J. Phys. Soc. Jpn. Suppl. **26**, 11 (1969).

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

[12]B. I. Shklovskii, Zh. Eksp. Teor. Fiz. **61**, 2033 (1971) [Sov. Phys.—JETP **34**, 1084 (1972)].

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

[14]D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976), Chap. 13.

[15]$\widetilde{C}_4^+$ is shortened from a longer expression to the form quoted in the text by the special case, Eq. (3).

[16]I. Balberg and N. Binenbaum, Phys. Rev. B **28**, 3799 (1983).

[17]P. C. Robinson, J. Phys. A **16**, 605 (1983).

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

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

[20]For a related universality, see H. Scher and R. Zallen, J. Chem. Phys. **53**, 3759 (1970).

[21]Y. C. Chiew, G. Stell, and E. D. Glandt, J. Chem. Phys. **83**, 761 (1985).

[22]A. L. R. Bug, S. A. Safran, S. G. Grest, and I. Webman, Phys. Rev. Lett. **55**, 1896 (1985).

[23]L. Blum and G. Stell, J. Chem. Phys. **71**, 42 (1980).

[24]Second-order coefficients for anisotropic elements in parallel, T. Kihara, Rev. Mod. Phys. **25**, 831 (1953); fourth-order hard-sphere coefficient, B. R. A. Nijboer and L. Van Hove, Phys. Rev. **85**, 777 (1952).

[25]G. W. Williams (private communication).

[26]J. Boissonade, F. Barreau, and F. Carmona, J. Phys. A **16**, 2777 (1983).

[27]F. Carmona, F. Barreau, P. Delhaes, and R. Canet, J. Phys. (Paris) Lett. **41**, L531 (1980).