Continuum Percolation of Rods

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(Received 9 January 1985)

We determine the aspect-ratio dependence of the critical percolation threshold for various systems of rods. An exact expansion, due to Coniglio *et al.*, tests the conjecture that the threshold is proportional to the inverse of the expected excluded volume. We confirm the conjecture, and show that the proportionality becomes equality, for isotropic rods in three dimensions, in the slender-rod limit. In this limit, the critical region in which nonclassical exponents are valid vanishes.

PACS numbers: 64.60.Cn, 05.40.+j, 71.30.+h

Percolation problems involving anisotropic objects have broad application to the connectedness (hence conductivity, elasticity,. . .) of real, disordered media. Though there is an extensive literature on thermally driven phase transitions in systems of anisotropic particles,[1] the percolation transition has only rarely been treated, by experiment[2] and simulation[3–7]. In this paper, we use a cluster expansion[8,9] for the critical density, ρ_p, to derive analytically the dependence of the percolation threshold on particle anisotropy. The discussion is restricted to rodlike particles (with aspect ratio r/L and orientation in space described by a director $\boldsymbol{\gamma}$), to focus on the recent conjecture[7] that

$$\rho_p \propto \langle V_{\text{exc}} \rangle^{-1}, \tag{1}$$

where V_{exc} is the excluded volume[10] about one of the particles. The expectation value is taken over all allowed particle orientations and sizes in an orientationally disordered, polydisperse system. This conjecture was suggested to the authors of Ref. 8 by a similar approximate law for lattice percolation,[11] and is supported by Monte Carlo evidence.[4,6,7] Our principal result is that the percolation threshold is given by the inverse of the excluded volume for the limiting case of long rods with an isotropic distribution of angles. In this limit of $r/L \to 0$, the size of the "critical region" where the exponents are nonclassical vanishes as well.

For anisotropic objects, the study of the percolation threshold is of interest since its value can span a large range as a function of particle anisotropy and/or orientation. Through experiment or simulation, one observes systematic trends as these parameters are varied. Analytically, one predicts these trends by exploiting symmetries of the density expansion for the percolation threshold. These symmetries permit the result of one threshold measurement to predict the results of a class of experiments. An obvious application is to optimize the net volume of an inclusion which is required for percolation within a host medium.

The analytic expression for ρ_p was developed by Coniglio *et al.*[8,9]; it is a Mayer-type[12] density series based on work by Hill.[13] We apply the expansion to the case of percolation of permeable objects. Experimental systems of interest are not always composed of permeable objects, but of globules with a hard core which is surrounded by an effective "shell" through which an excitation (ionic conduction, diffusion of a marker, . . .) may travel.[14] For such cases, the excluded volume in the expression which follows is taken as the excluded volume produced by the permeable shells alone. One defines the effective two-body potentials as follows: $u^+(\mathbf{r}_{12})=0$ for $\mathbf{r}_{12}$ within the excluded volume about 1, and $=\infty$ otherwise. Similarly, $u^*(\mathbf{r}_{12})=\infty$ for $\mathbf{r}_{12}$ within the excluded volume about 1, and $=0$ otherwise. Thus objects 1 and 2 are members of the same cluster if the center of mass of object 2 lies within the excluded volume of 1; this occurs if and only if their volumes overlap. (The unique shape of the excluded volume will depend on the choice of the center.) The excluded volume is not necessarily proportional to the actual volume of the shapes. Figure 1 shows a two-dimensional example, the excluded area (volume) of the two T-shaped objects in a plane which are constrained to lie parallel to one another. For these shapes, the area is $A=2L\epsilon$ while the excluded area is $A_{\text{exc}}=2L^2+6L\epsilon$. (This figure and its three-dimensional analog provide a counterexample to the observation made in Ref. 7 that for figures in parallel, $V_{\text{exc}} \propto V$.)

Given the definitions $f^+(\mathbf{r}) \equiv \exp\{-\beta u^+(\mathbf{r})\}$, $f^*(\mathbf{r}) \equiv \exp\{-\beta u^*(\mathbf{r})\}-1$, Coniglio *et al.*[9] have shown that

$$\rho_p = \left\{ \sum_{i=2}^{\infty} \tilde{C}_i^+(0,\rho_p)\rho_p^{i-2} \right\}^{-1}. \tag{2}$$

In Eq. (2), $\tilde{C}_i^+$ is an integral over products of the f^+, f^*, and is the percolation analog of the direct pair-correlation function[15]—the "direct pair connectedness."

At lowest order in density, the percolation threshold is given by

$$\rho_p \simeq \{\tilde{C}_2^+\}^{-1} = \{\textstyle\int f^+(\mathbf{r}_{12})\, d^3r_{12}\}^{-1} = \{V_{\text{exc}}\}^{-1}. \tag{3}$$

For a system with polydispersity or orientational disorder, we let $\mathbf{a}_i$ represent the state (dimensions and/or

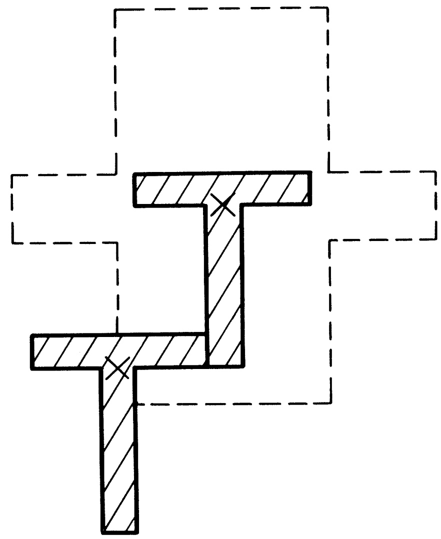

FIG. 1. The excluded volume around a permeable figure is constructed as shown. It is bounded by a perimeter consisting of all possible loci of the center of a second figure such that the two figures just make contact. Each two-dimensional T-shaped object within this system of parallel T's has as its excluded area the region within the dotted perimeter. The magnitude of this excluded area is $A_{\text{exc}}=2L^2+6L\epsilon$, where L is the long dimension, and ϵ the short dimension of each crosspiece which forms the T. Since $A=2L\epsilon$, it is possible to create figures with a diverging excluded area, but a finite area. This is analogously true of the volume and excluded volume of three-dimensional T figures (which are imagined to extend into the paper a uniform depth).

orientation) of particle i. If $P(\mathbf{a}_i)$ is the weight of this state, then to lowest order,

$$\rho_p \simeq \left\{ \sum_{a_1 a_2} P(\mathbf{a}_1) P(\mathbf{a}_2) \int f^{+}_{a_1 a_2}\, d^3 r_{12} \right\}^{-1} = \langle V_{\text{exc}} \rangle^{-1}. \tag{4}$$

Equations (3) and (4) show that at lowest order, ρ_p is sensitive only to the magnitude of the (expected) volume around an element. For many regular, convex elements (those called "centrosymmetrical" by Onsager[10]), the approximation (3) predicts critical volume fractions $\phi_p \equiv V\rho_p$ which are identical: $\phi_p = 1/2^d$ in d dimensions. Empirically[3] this underestimates ϕ_p, which is expected since $\tilde{C}_2^+$ is an overestimate of the complete direct pair connectedness. However, we show below that for long thin rods, the threshold is given to a very good approximation by the lowest-order term.

A system of randomly oriented spherocylinders with varying aspect ratios was simulated in three dimensions by Balberg, Binenbaum, and Wagner.[6] They have noted that for cylinders of length L and caps

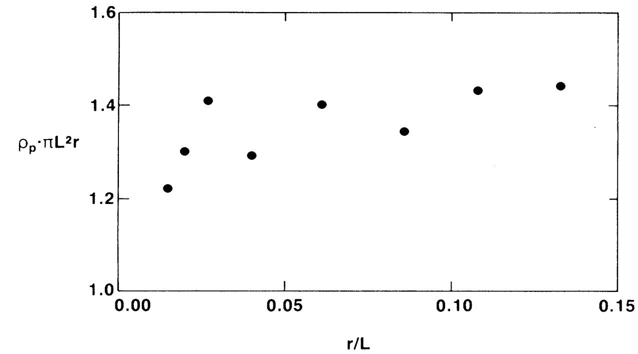

FIG. 2. Small-r data from Fig. 1 of Ref. 6. We have plotted $\rho_p \langle V_{\text{exc}}(r) \rangle$ vs r. There is, for this range of r, a systematic deviation from the excluded-volume rule. In this limit $r/L \to 0$, the plot is predicted to obey this rule and approach a constant value, unity.

of radius r, $V=\pi r^2 L + 4\pi r^3/3$ and $V_{\text{exc}} = 8V + 4L^2 r \langle \sin\gamma \rangle$, where γ is the angle between cylinder axes; $\langle \sin\gamma \rangle = \pi/4$ for an isotropic distribution of angles.[7] At lowest order [Eq. (4)], the density expansion yields $\rho_p \simeq 1/4L^2 r \langle \sin\gamma \rangle$ plus terms of higher order in r/L which we neglect in the limit $r/L \to 0$. The configurational integrals for the higher order $\tilde{C}_i{}^+$ are difficult to calculate for all but the simplest shapes.[16] However, Onsager has estimated the order of magnitude for a term (in the context of a thermal problem) which corresponds to $\tilde{C}_3^+$ for percolation. In the isotropic case, he found[10] that to lowest order in r/L,

$$\langle \tilde{C}_3^+ \rangle \propto r^3 L^3 \ln(L/r). \tag{5}$$

Note that this term, which makes a vanishingly small correction to ρ in the limit $r/L \to 0$, is not of the functional form $\langle V_{\text{exc}} \rangle^{-1}$ [which to a consistent order in r/L is $(L^2 r + 8r^2 L)^{-1}$].

We have applied similar arguments to the general terms in the density expansion and find the following:

(i) Logarithmic factors in L/r will appear in terms of all orders, since these accompany integrations of the form $\int f_{13} f_{23} \cdots d^3 r_{13} \cdots$. Thus, it is likely that ρ_p is not simply proportional to $\langle V_{\text{exc}} \rangle^{-1}$ as conjectured in Ref. 7, but can have other functional dependence on r, L.

(ii) An upper bound exists on the scaling behavior:

$$\langle \tilde{C}_{i+3}^+ \rangle \propto \langle \tilde{C}_3^+ \rangle (rL^2)^i + \ldots. \tag{6}$$

Thus, we find that for isotropically distributed cylinders with $r/L \to 0$, all terms in the series for ρ_p vanish in comparison with the first, $\langle \tilde{C}_2^+ \rangle$. In this limit, we find that $\rho_p \simeq 1/\pi L^2 r$.

This prediction for ρ_p can be checked against the data of Ref. 6. In Fig. 2 we have replotted the data of their Fig. 1 as $\rho_p \pi L^2 r$ vs r. For $\rho_p \propto \langle V_{\text{exc}} \rangle^{-1}$, the plot must be constant; our prediction in the limit $r/L \to 0$

is that the constant is unity. However, Fig. 2 shows that in this range of r/L there is still a systematic deviation from the excluded-volume rule. It seems that smaller aspect ratios are required to attain the $r/L \to 0$ limit.

For situations in which the distribution of stick angles is not uniform, we find that the vanishing of higher-order terms with r/L is still approximately valid. So long as the probability for a stick to lie within any chosen, small steric angle ϕ is of order $\phi/4\pi$, $\langle \tilde{C}_i^+ \rangle$ for $i > 2$ will still vanish as $r/L \to 0$. Thus, $\rho_p \simeq \frac{1}{4}L^2 r \langle \sin\gamma \rangle$ for near isotropic as well as isotropic angular distributions.

The prediction (1) for isotropic sticks stands in contradiction to a recent argument[17] which suggests that $\rho_p \propto 1/L^3$. (The argument seems to rely on an incorrect calculation of the rescaling of ρ_p under the authors' chosen transformation.) Monte Carlo evidence[3,4,6] uniformly supports the excluded-volume prediction, Eq. (1).

Another consequence of the vanishing of higher-order terms in the density expansion is the large range of applicability of mean-field behavior for the critical exponents. The susceptibility/mean-cluster-size exponent for this rod system is determined by[9]

$$S = \langle 1/(1 - \rho\{\sum \tilde{C}_i^+ \rho^{i-2}\}) \rangle. \tag{7}$$

In the limit $r/L \to 0$, the higher-order terms in the expansion are negligible for some ρ outisde of a small neighborhood about $\rho_p^{\mathrm{mf}} = \langle \tilde{C}_2 \rangle^{-1}$. Equation (7) implies that outside of this neighborhood of ρ_p^{mf} which shrinks with r/L, the classical exponent, $\gamma = 1$, is observed. One can show in a similar way that the other exponents take on their classical values in this region as well. Though the mean-field critical point itself scales as $1/L^2 r$, we find that if $\Delta\rho$ is the neighborhood about ρ_p in which a nonclassical exponent may exist, then $\Delta\rho/\rho_p \to 0$ as $r/L \to 0$. Physically, if we imagine L growing as r shrinks (which is consistent with, for example, a constant cylinder volume) each cylinder may interact with others whose centers lie increasingly far from their own. Insofar as a divergence of L may be interpreted as a divergence in the range of interactions between the cylinders, a mean-field theory is expected to be exact.

In addition to the case of rods with random orientations, we have used Eq. (2) to predict ρ_p for several other cases and have compared our predictions with recent Monte Carlo simulations. These are discussed in detail elsewhere.[18] (In the two-dimensional cases below, the excluded "volume" is understood to be an excluded area.)

(1) Rods in two dimensions with two possible orientations $\pm a$: The distribution which admits this angular variation is $P(\gamma) = p\delta_{a,\gamma} + (1-p)\delta_{-a,\gamma}$. A natural transformation to consider in such a system is a change in angle: $P(\gamma) \to P(\gamma/\lambda)$. It can be shown[18] from Eq. (4) that if one performs a linear transformation[19] on each excluded volume which appears in Eq. (1), then $\rho_p \to \{\det \mathbf{A}\}^{-1}\rho_p$. ($\mathbf{A}$ effects the transformation with respect to the center of mass of each object.) The transformation of angles above is linear in this way, and the determinant is $\sin 2\lambda a/\sin 2a$. Since this is the ratio of excluded volumes before and after the transformation, the excluded-volume rule is exact with respect to angular variation. Monte Carlo data[4] for the special case $p = \frac{1}{2}$ support this.

(2) Rods in two dimensions with arbitrary angular distribution: Scaling arguments on the $\tilde{C}_i^+$ show that

$$\rho_p \propto 1/L^2, \tag{8}$$

in agreement with Ref. 4.

(3) Rods in three dimensions with three orthogonal orientations: Boissonade, Barreau, and Carmona[5] performed a Monte Carlo study of fibers on a lattice which were oriented at random, but constrained to lie parallel to one of three mutually orthogonal axes. They found that $\rho_p \propto 1/L^2$. At lowest order in ρ, a lattice version of Eq. (2) supports this law.[18] For the analogous system in the continuum (permeable rods, or rods with a hard core and permeable shell of comparable dimensions which are constrained to lie perpendicular to one of three coordinate axes), we find[20] $\rho_p \propto 1/L^2 r$. For sticks with a moderate aspect ratio, n, there must be a correction to this rule which is lower order in n (not higher as might be predicted from Ref. 17). The small-n region of Fig. 5 of Boissonade, Barreau, and Carmona is consistent with this correction.

In summary, we have shown that the density expansion for the percolation threshold is a useful method for finding the dependence of threshold on particle anisotropy. For long rods with random orientations, we find that $\rho_p = \langle V_{\mathrm{exc}} \rangle^{-1}$ with corrections which vanish in the limit $r/L \to 0$. For other cases (two dimensions, certain discrete orientations,. . .) ρ_p is still proportional to $\langle V_{\mathrm{exc}} \rangle^{-1}$ in the long-rod limit.

The pros and cons of using percolation to model the sol-gel transition are discussed in the work of Stauffer.[21] A continuum (versus lattice) model with the possibility of interactions reduces the number of cons substantially. Our findings are consistent with measurements of the gelation threshold for the rodlike *trans* phase of 4BCMU,[22] though in this system the elasticity exponent is measured to be nonclassical.

Our findings are not consistent with the analysis of conductivity data of Ref. 2 where the percolation threshold for graphite fibers in an insulating matrix was inferred to follow $\rho_p \propto 1/L^3$. This scaling law was deduced from only four data points and it is possible that the system was not in the asymptotic large-L/r limit. In addition, attractive interactions between fibers could lead to clustering. If the number of fibers in a cluster is independent of concentration, then the clusters can be approximated by spheres of size L which would indeed show a percolation threshold scaling as $1/L^3$.

The authors would like to thank G. Grest, Y. Kantor, K. Kremer, T. Witten, and B. White for helpful discussions.

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[19]By "linear" one means a rotation about the object's own center of mass composed with a dilation about that center with respect to fixed Cartesian axes.

[20]One finds that only a fraction of the diagrams in Eq. (4) will contribute to the slender-rod limit. These correspond to clusters of sticks which are (i) coplanar and (ii) have all intersections of sticks occurring at right angles. For example, no diagram corresponding to $\langle \tilde{C}_3^+ \rangle$ may be constructed, and only two diagrams out of a possible six will contribute to $\langle \tilde{C}_4^+ \rangle$. It is shown in Ref. 18 that this reduced class of diagrams produces a critical density which obeys the excluded-volume rule.

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