PHYSICAL REVIEW LETTERS

VOLUME 52 | 23 APRIL 1984 | NUMBER 17

Percolation Thresholds in the Three-Dimensional Sticks System

I. Balberg[a] and N. Binenbaum
RCA Laboratories, Princeton, New Jersey 08540

and

N. Wagner
The Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel
(Received 18 October 1983)

We report the dependence of the percolation threshold of the three-dimensional sticks systems on aspect ratio and on macroscopic anisotropy. This Monte Carlo study is the first determination of percolation thresholds for randomly oriented objects in three-space. The results show that the above dependence is determined by the excluded volume of the sticks. However, the total excluded volume of randomly oriented objects is lower than that of the same objects in parallel alignment.

PACS numbers: 05.40.+j, 05.70.Jk, 71.30.+h

The study of percolation in three dimensions has centered thus far on the percolation in lattices.[1] The only three-dimensional continuum system that has been studied in some detail is the system of hard-core or soft-core (interpenetrating) spheres.[2–4] Other systems which were briefly studied are those of "regular" objects, such as cubes[3,5] or ellipsoids,[5] which are aligned parallel to each other. Here, we report the first study which is concerned with random orientation of the objects in three dimensions. We present results showing the dependence of the percolation threshold on the aspect ratio and the macroscopic orientational anisotropy of the sticks system.

The three-dimensional objects chosen for this study are capped cylinders. They consist of a cylinder of length L and radius r which is capped at the two ends by hemispheres of radius r. The choice of this kind of stick is motivated by the possibility of making a comparison, in the $L/r \rightarrow 0$ limit, with the well established results obtained for spheres.[2–7] This is quite important for checking the three-dimensional model where, unlike the two-dimensional case,[8] no convenient graphic display of the system is feasible. Our soft-core sticks system is also a good description of composites in which elongated conducting particles are flexible enough to contact each other in a manner which geometrically resembles interpenetrating sticks. Much interest was given recently to these composites.[9–12]

The algorithm used in the present study is similar in principle to the one used in two dimensions.[8] The capped cylinders are randomly put in a unit cube and their orientations in space are chosen randomly. Here we have chosen fixed size sticks (of length L and radius r in units of the cube's size) and we are searching for the critical concentration of sticks, N_c, which is required for the onset of percolation across this cube. The anisotropic case considered here is that of uniaxial anisotropy, where the axis of symmetry is the z axis. This means that the angle θ_i between the axis of stick i and the z axis of the cube is chosen randomly in the interval[8]

$$-\theta_\mu \leq \theta_i \leq \theta_\mu, \tag{1}$$

while the other spherical coordinate ϕ_i is always chosen randomly in the interval $0 \leqslant \phi_i \leqslant 2\pi$. Hence for a system of N sticks the macroscopic anisotropy of the system is defined as in the two-dimensional case[8]:

$$P_{\parallel}/P_{\perp} = \sum_{i=1}^{N} |\cos\theta_i| / \sum_{i=1}^{N} [1-(\cos\theta_i)^2]^{1/2}, \qquad (2)$$

where $P_{\parallel} = (L+2r)\sum_{i=1}^{N} |\cos\theta_i|$ is the sum of the sticks' axes projections in the parallel (or longitudinal) direction and $P_{\perp} = (L+2r)\sum_{i=1}^{N} |\sin\theta_i|$ is the corresponding sum in the perpendicular (or transverse) direction. Correspondingly, the critical concentration in the z direction, $N_{c\parallel}$, and the critical concentration in the perpendicular direction, $N_{c\perp}$, are determined for each value of $P_{\parallel}/P_{\perp}$.

As was pointed out above, it is important to check the present results against the well studied case of spheres, in order to establish the reliability of the procedure used. Hence, we have used our procedure in the isotropic case ($\theta_{\mu} = \pi/2$) for a fixed $L = 0.006$ and a variable r in the range $0.01 < r < 0.4$. In this range ($L/r << 1$) the sticks have practically degenerated into spheres. We have determined $N_{c\parallel}$ and $N_{c\perp}$ for each value of r and used $(N_{c\parallel} + N_{c\perp})/2 = N_c$ as the average of the critical concentration. The computed dependence of $1/N_c$ on r was found to be cubic. This dependence is to be expected from the invariant value found for the critrical volume of hard-core spheres[13] as well as the invariant value found for soft-core spheres.[14] Moreover, for a radius of, say, $r = 0.02$ we found a critical concentration of 10 000 spheres. Hence the volume of all these spheres is $(4\pi/3) \times (0.02)^3 10^4 = 0.335$. This is in excellent agreement with the value of 0.35 ± 0.02 obtained in many other studies.[14] (To appreciate the accuracy of our determination of this volume let us mention that it was found for all values of $N_c > 1000$. As expected the lower the N_c the larger the deviation from this value. For example, for $N_c = 100$ our computed value was 0.40.)

Following this agreement we have considered the isotropic case with a fixed L and a variable r in which r is varied so as to scan the wide range of aspect ratios ($L/2r$) from $L/2r << 1$ to $L/2r >> 1$. The dependence of $1/N_c$ on r in this wide range is shown in Fig. 1. The most notable feature in the observed dependence is the variation from a linear to a cubic dependence. The fact that the cubic dependence is observed for very small ensembles of sticks does not jeopardize its reliability since this dependence has been confirmed in the $L/r << 1$ region for large ensembles (see above). The impor-

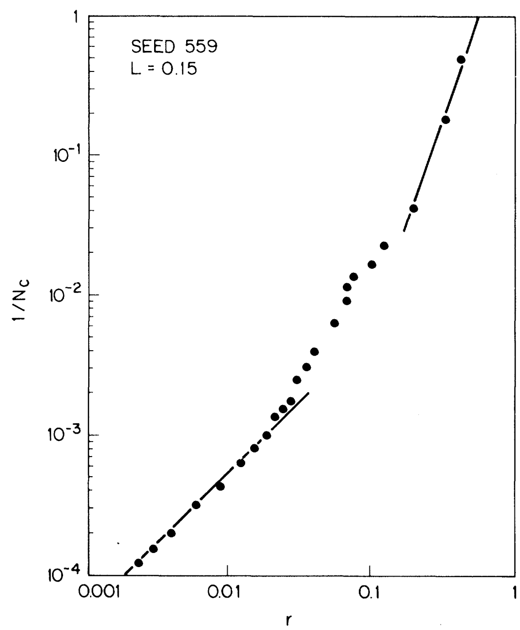

FIG. 1. The dependence of the critical concentration N_c of capped cylinders on their radius r in an isotropic system of sticks.

tant observation is the linear dependence in the $L/r >> 1$ region. This dependence does not follow from Refs. 2 and 4, where it was concluded that $N_c V$ is a dimensionally invariant quantity. Here V is the volume of the object. In our case

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

and thus a linear dependence on r is not expected. To further check this point we have considered a fixed r and a variable L case in which N_c was computed as a function of L. The results which were obtained for $r = 0.015$ and $1 \geqslant L \geqslant 0.01$ show that in the $L/r >> 1$ region the dependence of $1/N_c$ on L becomes quadratic. This is again in disagreement with the $N_c V$ argument. We see then that, in the $L/r >> 1$ region, $1/N_c$ is proportional to $L^2 r$. This result is in accord with our suggestion[8] that it is the object's excluded volume rather than the object's volume which determines the percolation threshold. The excluded volume is the volume around an object in which the center of an identical object should not be present if interpenetration of the two objects is to be avoided.[15,16] It appears that the distinction between the object's volume[13] and its excluded volume, in the context of the percolation threshold, has not been made previously, because almost all previous studies[2-7] were concerned with spheres. For spheres the two arguments are equal since the excluded volume is simply eight times the object's volume. Hence the excluded volume of all the spheres is $8(0.35)\approx 3$. This value has also been found[5] to be "dimensionally invariant" for other objects, yet the corresponding study was limited to the case where the objects were all parallel to each other.

Considering our capped cylinders it can be shown that the excluded volume of each is given by[17]

$$V_{\mathrm{ex}}=(32\pi/3)r^3+8Lr^2+4L^2r\langle\sin\gamma\rangle, \tag{4}$$

where $\langle\sin\gamma\rangle$ is the average of $\sin\gamma$, and γ is the angle between two sticks. The first term in Eq. (4) is just the spherical term discussed above, while the last term is the one discussed by Onsager[15] for the $L/r >> 1$ case. The results presented in Fig. 1 for the $L/r >> 1$ region show that the maximum possible total excluded volume $4L^2rN_c$, associated with our random orientation case, is significantly lower than that for spheres or parallel-aligned objects.[5] This maximum volume is 1.8 rather than the value of 3 discussed above. Our result is not trivial since the critical excluded area of a widthless randomly aligned stick is relatively close (less than about 80%) to the critical excluded area of a circle.[2,17] An intuitive argument for the above difference is based on the fact that the overlap of the excluded volumes in the random case is lower than the two-dimensional-like overlap of the excluded volumes in the aligned case.[17]

Turning to the dependence of the percolation threshold on anisotropy, we should consider the average $\langle\sin\gamma\rangle$ in order to compare the Monte Carlo results with the behavior predicted by the excluded-volume argument [Eq. (4)]. To do this, $\sin\gamma$ has to be integrated over the possible ranges of the spherical coordinates of two sticks. This integral can be readily solved[17] in the isotropic $\theta_\mu=\pi/2$ case yielding a value of $\langle\sin\gamma\rangle=\pi/4$. For other values of θ_μ we computed $\langle\sin\gamma\rangle$ numerically.

Following these considerations we have computed $N_{c\parallel}$ and $N_{c\perp}$ as a function of θ_μ, or of $P_\parallel/P_\perp$, in the region where the L^2r dependence of $1/N_c$ was found for the isotropic case (Fig. 1). The results obtained are shown in Fig. 2. Also shown in this figure is the expected dependence of N_c on $P_\parallel/P_\perp$ (dashed curve) which was obtained from the dependence of $\langle\sin\gamma\rangle$ on θ_μ. The expected N_c was normalized by the "experimental" isotropic value found at $P_\parallel/P_\perp=1$. For $P_\parallel/P_\perp\lesssim 8$, the results and their scatter around the predicted dependence resemble the behavior found for two dimensions[8]: $N_{c\perp}$ is found to be the upper limit to the critical concentration and $N_{c\parallel}$ is found to be the lower limit to this concentration. Taking systems of fewer sticks has shown that the gap between the $N_{c\parallel}$ and the $N_{c\perp}$ values has increased. We also show the case of an extreme anisotropy ($P_\parallel/P_\perp=11.5$) in order to demonstrate that the dependences predicted by Eq. (4) are fulfilled: Once $L^2r\langle\sin\gamma\rangle$ becomes small compared with the other terms in Eq. (4) the dependence on anisotropy is eliminated. We may conclude then, that in the region where the long-stick approximation holds ($4L^2r\langle\sin\gamma\rangle >> 8Lr^2$), the predicted results are between $N_{c\parallel}$ and $N_{c\perp}$ found "experimentally." We see then that, similar to the two-dimensional case, there is an isotropic percolation threshold in uniaxially anisotropic three-dimensional systems.

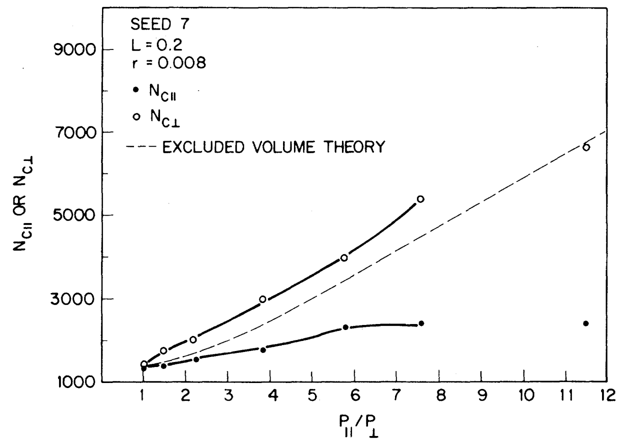

FIG. 2. The dependence of the critical concentration of sticks on the macroscopic orientational anisotropy of the system $P_\parallel/P_\perp$. Both the critical concentration for percolation along the axis of symmetry, $N_{c\parallel}$, and the critical percolation concentration perpendicular to this axis, $N_{c\perp}$, are to be compared with the prediction given by Eq.(4) (the dashed curve).

In conclusion, we have shown that the dependence of the percolation threshold of randomly oriented three-dimensional sticks on their aspect ratio and anisotropy is determined by their excluded volume. The numerical value of the total excluded volume is found to be significantly lower than the invariant excluded volume of spheres and some other parallel-aligned objects. This indicates that orientational randomness has a much stronger effect on the onset of percolation in three dimensions than it has in two dimensions. Similar to the two-dimensional case an isotropic percolation threshold is found for the uniaxially anisotropic three-dimensional systems.

The authors are indebted to C. H. Anderson and S. Alexander for many helpful discussions during the course of this study.

[a]Permanent address: The Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel.

[1]D. Stauffer, Phys. Rep. Phys. Lett. **54**, 1 (1979).

[2]G. E. Pike and C. H. Seager, Phys. Rev. B **10**, 1421 (1976).

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

[4]V. K. S. Shante and S. Kirkpatrick, Adv. Phys. **20**, 325 (1971).

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

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

[7]D. H. Fremlin, J. Phys. (Paris) **37**, 813 (1976).

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

[9]For review papers, see *Carbon Black-Polymer Composites,* edited by E. K. Sichel (Dekker, New York, 1982).

[10]I. Balberg and S. Bozowski, Solid State Commun. **44**, 551 (1982).

[11]F. Carmona, F. Barreau, R. Canet, and P. Delhaes, J. Phys. (Paris), Lett. **41**, 531 (1980).

[12]J. B. Donnet and A. Voet, *Carbon Black* (Dekker, New York, 1976).

[13]H. Scher and R. Zallen, J. Chem. Phys. **53**, 3759 (1970).

[14]In these studies it was either the critical radius (Ref. 2) $r_c = 0.7048 r_s$ where $r_s = (3/4\pi N)^{1/3}$, the average bonds per site (Refs. 5–7) $B_c = 2.7 \pm 0.2$, or the average occupied volume (Refs. 2 and 4) of 0.29 ± 0.02 which have been determined. All these results are the same and can be derived simultaneously (Ref. 2).

[15]L. Onsager, Ann. N. Y. Acad. Sci. **51**, 62 (1949).

[16]P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford Univ. Press, London, 1976).

[17]I. Balberg, C. H. Anderson, S. Alexander, and N. Wagner, unpublished.