Reconsideration of continuum percolation of isotropically oriented sticks in three dimensions

Z. Néda and R. Florian
Department of Physics, Babeş-Bolyai University, strada Kogălniceanu 1, RO-3400, Cluj-Napoca, Romania

Y. Brechet
Laboratoire de Thermodynamique et Physico-Chimie Metallurgique, ENSEEG/INPG, Domaine Universitaire de Grenoble, Boîte Postal 75, 38402 Saint Martin d'Hères Cedex, France

(Received 11 November 1998)

The continuum percolation problem of permeable and isotropically oriented sticks (with the form of capped cylinders) is reconsidered by Monte Carlo simulations in three dimensions. Errors in earlier studies are revealed and results in agreement with the excluded volume rule are presented. Finite-size effects are discussed. [S1063-651X(99)00703-5]

PACS number(s): 64.60.Ak, 02.50.Ng, 05.40.−a

The three-dimensional continuum percolation problem of hard-core or soft-core (permeable) geometric objects was an area of active research in the 1980s [1]. Among the considered geometrical objects a very important category is the case of permeable sticks with the form of capped cylinders (cylinders of length L and radius R capped with hemispheres of radius R) [2]. Recent developments of nano reinforced polymer composites with fibers [3] having aspect ratios $L/R \approx 50$, and the study of both mechanical and electrical percolation of these materials has renewed interest in this field. However, as pointed out in [4] the permeable stick assumption has to be carefully examined when applied to real composite materials.

It was conjectured [5] that the percolation threshold q_p is proportional to the inverse of the expected excluded volume V_{ex}:

$$q_p = \frac{N_c}{V} \propto \frac{1}{V_{ex}}. \tag{1}$$

(We denoted by N_c the number of sticks at percolation and by V the volume of the cube in which the percolation problem is considered.) For sticks with the form of capped cylinders, the excluded volume is given by

$$V_{ex} = \frac{32\pi}{3} R^3 \left[1 + \frac{3}{4}\left(\frac{L}{R}\right) + \frac{3}{8\pi} \langle \sin(\gamma) \rangle \left(\frac{L}{R}\right)^2 \right], \tag{2}$$

where $\langle \sin(\gamma) \rangle$ is the average value of $\sin(\gamma)$ for two randomly positioned sticks, and γ is the angle between them. For the isotropic orientation of rods [$\langle \sin(\gamma) \rangle = \pi/4$] it was shown by a cluster expansion method [6] that the proportionality in Eq. (1) becomes equality in the $R/L \to 0$ slender-rod limit. Monte Carlo (MC) studies for the problem were performed in [2] and analytical predictions were always discussed in comparison with these data. It seems, however, that in the mentioned MC study a classical mistake was made while generating the isotropic distribution of rods and the percolation threshold was strongly affected. Thus the comparison between analytical models and these simulations becomes misleading. In the present paper we intend to point out the mistake made in the earlier MC simulations and give corrected results in comparison with the excluded volume theory.

In [2] the authors claim to obtain the isotropic distribution of the rods orientations by generating their θ and φ polar coordinates randomly with a uniform distribution on the $[-\pi/2, \pi/2]$ and $[0, 2\pi]$ intervals, respectively. Following their two-dimensional study [7], they define the measure of the macroscopic anisotropy of the system as

$$P_{\parallel}/P_{\perp} = \sum_{i=1}^{N} |\cos(\theta_i)| \Big/ \sum_{i=1}^{N} [1 - \cos^2(\theta_i)]^{1/2}. \tag{3}$$

Proceeding, however, in the way described above, the generated configurations will definitely not be isotropic ones, although their anisotropy constant (3) will be one. It is easy to realize that the z axis will be a privileged one, and percolation in this direction reached easier than in the y or x direction. In order to get the right isotropic distribution for the rods orientation, their end points must span uniformly the surface of a sphere, which amounts to a uniform distribution in the whole range of solid angle. This can be achieved only by choosing the θ angle randomly with a weighted distribution and not a uniform one. From the surface element on the unit sphere [$d\sigma = \sin(\theta) d\theta d\varphi$], it is realized immediately that the weight factor is governed by the $\sin(\theta)$ term.

The mistake made by the authors does not affect the $L/R \to 0$ limit, considered to get confidence in their simulation data. However, when calculating the ρ_c critical density at percolation and the V_{ex} excluded volume of the sticks they calculate the average of $\sin(\gamma)$ for the right isotropic case, getting $\langle \sin(\gamma) \rangle = \pi/4$. Calculating $\langle \sin(\gamma) \rangle$ for their "isotropic" configurations, the result would be $\langle \sin(\gamma) \rangle = 2/\pi$.

We see thus that in the limit $R/L \to 0$ where the third term in Eq. (2) is the most important, the results are strongly affected. The paper discussing the validity of the excluded

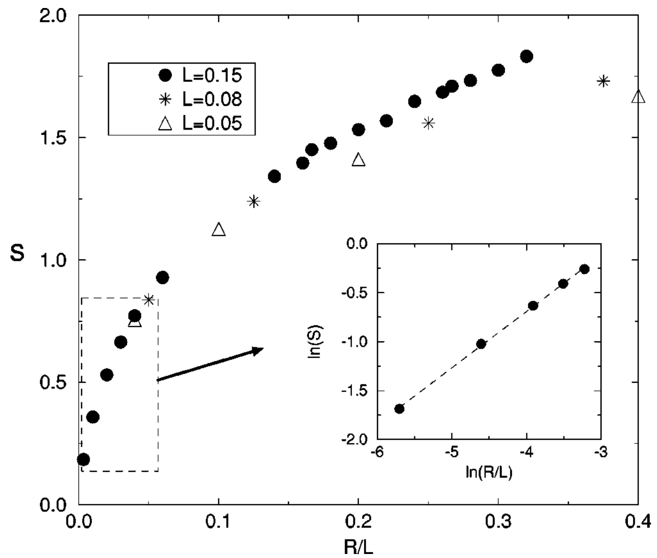

FIG. 1. $s = q_p V_{ex} - 1$ as a function of the R/L aspect ratios of the sticks. Data for three different stick lengths L are presented. The magnified region shows the $s = (R/L)^{0.5764}$ power-law fit (dashed line) for the $R/L < 0.06$ region.

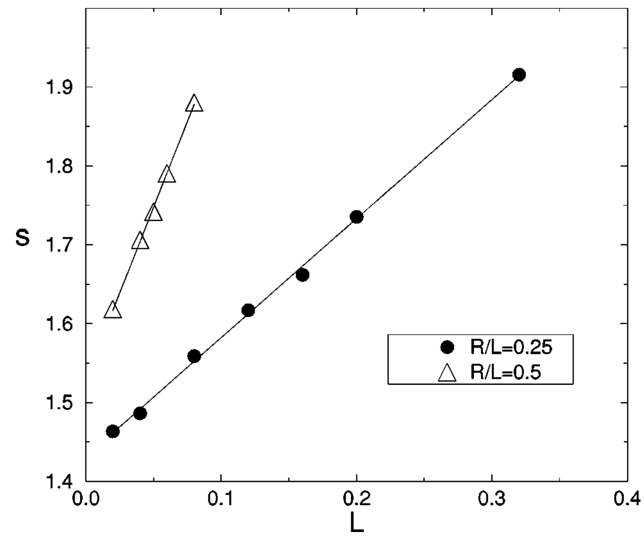

FIG. 2. Finite-size effects: $s = f(L)(s = q_p V_{ex} - 1)$ for two different aspect ratios of the sticks. Continuous lines are the best linear fits. In the $L \rightarrow 0$ limit we obtained $s = 1.431$ and $s = 1.534$ for $R/L = 0.25$ and $R/L = 0.5$, respectively.

volume rule [6] observes the systematic deviation (Fig. 2 in Ref. [6]) but fails in explaining its origin. In [6] the authors argue that the systematic deviation is due to the fact that much smaller aspect ratios are required to approach the right result in the $R/L \rightarrow 0$ limit. A very simple reason for this deviation may be that the generated configurations were simply not isotropic ones. We mention here that it seems the error in generating the right isotropic distribution is repeated also in [8], where the authors study, by Monte Carlo methods, the cluster structure and conductivity of three-dimensional continuum systems. The MC simulation data in [2] has led to erroneous statements in several other papers [9], where some tables and comparison with analytical results should be reconsidered. It is important thus to reconsider the MC simulations and to confirm properly the excluded volume equality from [6].

We have studied the problem inside a cube with sizes 1. In order to preserve homogeneity near the cube's frontiers, the coordinates of the centers of the cylinders were generated uniformly in the interval $[-(L/2+R), 1+(L/2+R)]$. The orientation of the cylinders were isotropic, generating the θ angles with a weighted distribution, and φ with a uniform distribution. We tested the isotropy by determining the percolation thresholds in different directions. The intersection of two capped cylinders was determined by calculating the minimum distance between points on the two axes of the corresponding cylinders and checking if this distance is smaller than $2R$. Each time a new stick was generated, it was assigned to a cluster if it intersected others, or a new cluster was created. We considered the percolation produced when the new cluster spanned the cube from a face to the opposite face. We calculated the critical concentration N_c as the number of sticks inside the cube at percolation; if a capped cylinder was only partially inside the cube, it contributed to N_c with a fractional value less than one, corresponding to the fraction of its volume inside the cube to its total volume. We produced 5000 percolations for each pair of L and R studied, and the average N_c was calculated as the one corresponding to the maximum of the Gaussian distribution fitted on the distribution of the 5000 N_cs determined during simulations. This result was in good agreement with simply the mean of the determined percolation thresholds, but it was much more precise.

The obtained results are summarized in Figs. 1 and 2. In Fig. 1 we plot the quantity $s = q_p V_{ex} - 1$ as a function of R/L for various fixed L values. In the limit $R/L \rightarrow 0$ our simulations suggest the analytically predicted $s = 0$ relation [6]. The convergence for the applicability of this equation is, however, rather slow. In the $R/L \rightarrow 0$ limit ($R/L < 0.06$) for $L = 0.15$ we found s scaling as a function of R/L with an exponent of 0.5764. From Fig. 1 it is also clear that for smaller values of L and same R/L ratios the value of s gets smaller. There are thus important finite-size effects, which are less evident in the $R/L \rightarrow 0$ limit. We checked that in the limit of $L \rightarrow 0$ the $s = 0$ equality still does not hold. This is clear from our large-scale simulation data for $R/L = 0.5$ and $R/L = 0.25$. The data presented in Fig. 2 suggest that in the limit $L \rightarrow 0$, s is linearly converging to 1.431 and 1.533 for $R/L = 0.24$ and $R/L = 0.5$, respectively. Both from Fig. 1 and Fig. 2 one observes that the L dependence of the data is much stronger for higher R/L values and in the limit $R/L \rightarrow 0$, we predict no finite-size effects. Approaching better the $R/L \rightarrow 0$ or $L \rightarrow 0$ limits are technically difficult due to the large number of sticks necessary for percolation.

In conclusion, we corrected the earlier erroneous simulation results for the isotropic case and confirmed the validity of the excluded volume rule. Important finite-size effects were found in the limit of large R/L aspect ratios.

[1] I. Balberg, Philos. Mag. B **56**, 991 (1987).
[2] I. Balberg, N. Binenbaum, and N. Wagner, Phys. Rev. Lett. **52**, 1465 (1984).
[3] V. Favier, R. Dendievel, G. Canova, JY. Cavaille, and P. Gilormini, Acta Mater. **45**, 1557 (1997).
[4] S. P. Obukhov, J. Phys. A **21**, 3975 (1988).
[5] I. Balberg, C. H. Anderson, S. Alexander, and N. Wagner, Phys. Rev. B **30**, 3933 (1984).
[6] A. L. R. Bug, S. A. Safran, and I. Webman, Phys. Rev. Lett. **54**, 1412 (1985).
[7] I. Balberg and N. Binenbaum, Phys. Rev. B **28**, 3799 (1983).
[8] I. Balberg and N. Binenbaum, Phys. Rev. A **31**, 1222 (1985).
[9] I. Balberg, Phys. Rev. B **31**, 4053 (1985); I. Balberg and N. Binenbaum, Phys. Rev. A **35**, 5174 (1987); D. Laria and F. Vericat, Phys. Rev. B **40**, 353 (1989); A. Drory, Phys. Rev. E **54**, 5992 (1996).