New, Heuristic, Percolation Criterion for Continuum Systems

U. Alon,[a] I. Balberg, and A. Drory

Racah Institute of Physics, Hebrew University, Jerusalem 91904, Israel

(Received 11 January 1991)

A heuristic criterion is introduced and applied for derivation of percolation thresholds in continuum systems. The criterion is comprehensive in the sense that it applies to systems with diverse bonding criteria as well as to systems with a correlated distribution of sites. Its usefulness is manifested by the excellent quantitative agreement between the values obtained and available Monte Carlo data.

PACS numbers: 64.60.Ak, 05.40.+j

In the last few years it has been shown that the properties of percolation processes in continuum systems[1] cannot be predicted simply by using results obtained from lattice percolation[2] models. In particular, diversity in geometrical shapes, size distribution, and correlations between objects (such as those due to interactions) cannot be incorporated into these models. There are numerous applications for the understanding of the corresponding systems in many fields, including porous media,[3] conduction in atomically disordered solids,[4] polymers,[5] composite materials,[6] and microemulsions.[7]

The most important parameter to be known for such percolating systems is their percolation threshold, i.e., the critical concentration of the objects at which an infinite connected network appears.[2] While the critical behavior in percolating systems is universal and has been extensively studied,[2] the percolation threshold shows great sensitivity to system parameters.[1] Hence a further "unification" of percolation theory can be served by finding a single analytic approach for the determination of the thresholds. In the continuum, the threshold concentration depends on the shape and orientation of the objects[8] as well as on the correlations[9] between the positions of their centers (hereafter, sites). So far, no general theory, or even a general analytic approach, has been proposed for a comprehensive determination of the percolation threshold in the above variety of continuum systems. The available analytic results are accurate thus far only for simple randomly placed objects,[10] and as for interacting objects, only qualitative agreement between analytic results and computer simulations for the system of hard-core–soft-shell spheres has been obtained.[11] For all other systems[1] and for more realistic interactions[9] only Monte Carlo results are available.

In view of these considerations and the appreciation of the difficulties associated with the development of a rigorous comprehensive theory,[10] it appears that a general, though heuristic, argument which yields accurate values for percolation thresholds in the continuum can be of great use. Such a criterion is suggested in this paper. As far as we know this is the first simple criterion that illuminates the interplay between short-range correlations and macroscopic connectedness in percolating systems. In view of the importance of percolation thresholdlike quantities in the theories of random systems, the insight gained from this criterion may also have an intrinsic value beyond the immediate interest of the present Letter. As we show below, all one actually needs to know, in order to apply the criterion, are the systems' most basic parameters, i.e., the shape of the objects and the interaction potential between them. Surprisingly, while being quite simple, it yields extremely accurate values for the percolation thresholds as demonstrated by the excellent agreement with available Monte Carlo results.

To specify the criterion, we consider systems in which pair connectedness between sites is defined by object overlap (see below). The percolation threshold is the density of sites (object centers) at which an infinite cluster is first formed. We heuristically derive an equation for this density by comparing two fundamental characteristic lengths of the system: The first is the average "bonding distance" l which we define as the mean distance between two connected sites. The other characteristic length, L, is the average distance between sites which have at least two sites connected to them (hereafter referred to as neighbors). Such sites may be considered as the basic building blocks of the infinite-cluster's backbone, since sites with less than two neighbors may, at most, belong to dead ends. Sites with two or more neighbors are surrounded by objects whose centers lie, by definition, at an average distance of l. Therefore we consider an ideal gas of such sites, each surrounded by a sphere of radius l, which effectively represents its mantle of nearest neighbors. We postulate that percolation occurs when these effective spheres begin to overlap, i.e.,

$$L = 2l .$$

Loosely, this criterion corresponds to demanding that, on the average, the multineighborhood sites be connected (at least by a common neighbor) to other such sites, thereby propagating connectedness.

To demonstrate the application of our new criterion, we start our discussion with randomly centered (permeable) objects. For simplicity and because of practical applications, we consider in this work three-dimensional systems. Correspondingly, we define the excluded volume[8] of an object, V_{ex}, as the volume in which two object centers have to be in order for them to overlap (e.g., for a system of spheres of radius R, the excluded volume is a sphere of radius $2R$). The mean distance between connected sites, l, is then given by

$$l^2=V_{ex}^{-1}\int r^2 d^3r\,, \tag{1}$$

where the integration is over the excluded volume. We note that our percolation criterion is not too sensitive to the type of averaging used[10] in the definition of l.

To approximate L, we consider a system of volume $\Omega(\gg V_{ex})$ in which sites are distributed randomly with a density $\rho=N/\Omega$. The number of neighbors per site is known to follow the Poisson distribution:[12] The probability for a site to have k neighbors is $(B^k/k!)\exp(-B)$, where B is the average number of neighbors per site. In the case of permeable objects,[8] $B=\rho V_{ex}$. Hence, ρ', the effective density of sites with at least two neighbors, is

$$\rho'=\rho[1-(1+B)\exp(-B)]\,. \tag{2}$$

The average volume per site of sites with at least two neighbors is now $v=1/\rho'$. Assuming that this volume is spherical, we have

$$L=2(3/4\pi\rho')^{1/3}\,. \tag{3}$$

Our suggested percolation criterion is

$$L=2l\,. \tag{4}$$

Using Eqs. (2)-(4), this criterion becomes

$$B_c[1-\exp(-B_c)(1+B_c)]=(l_0/l)^3\,, \tag{5}$$

where $l_0=(3V_{ex}/4\pi)^{1/3}$ is the radius of a sphere of volume V_{ex}, and B_c is the critical number of bonds per site[8] ($B_c=\rho_c V_{ex}$). We find from Eq. (5) that the only object-dependent parameter which determines the percolation threshold is the dimensionless geometrical parameter l/l_0. Hereafter we name this parameter the "pointedness" of the object. The pointedness is essentially a measure of the object's departure from sphericity: Objects with sharp edges or protrusions have a higher pointedness than more "spherical" ones. According to Eq. (5) the "pointier" the object, the lower the threshold. This is in accordance with previous analytic[10] and Monte Carlo[10,13] results. Using Eq. (1) to calculate l, finding B_c from Eq. (5) is straightforward. We present in Table I the pointedness, the calculated B_c values, and results from Monte Carlo simulations,[4,8,10,13] for permeable spheres and permeable parallel cubes. The comparison of the two sets of B_c values demonstrates the accuracy obtained by the presently suggested percolation criterion. If we repeat the same procedure [Eq. (5)] for two-dimensional systems, the results obtained are quite far off the correct B_c values which are taken from Refs. 10 and 13. On the other hand, we can obtain excellent results for the two-dimensional systems in accordance with our approach which is founded on the basic building blocks of the infinite-cluster backbone. This is done by noting that the B_c values for two-dimensional systems composed of permeable objects are of the order of 4 (higher than those of three-dimensional systems). Hence we conclude that the basic building blocks are sites of higher connectedness than sites in three-dimensional systems. Indeed, by using Eqs. (2) and (5) with the subtraction of the $k\le 4$ terms in the Poisson distribution, we can predict accurately the B_c values for two-dimensional systems. This is well demonstrated by the values given in Table I. We also found such an excellent agreement in other two-dimensional systems. In fact, finding that the latter procedure yields such accurate results indicates that our basic physical picture of the building blocks is sound.

TABLE I. The pointedness, the calculated B_c values, and results from Monte Carlo simulations, for some permeable objects.

	Pointedness	Calculated B_c	B_c from simulations
Spheres	$\sqrt{3/5}=0.7746$	2.796	2.8 ± 0.05
Cubes	$(\pi/6)^{1/3}=0.8060$	2.604	2.6 ± 0.1
Circles	$\sqrt{1/2}=0.7071$	4.42	4.5 ± 0.1
Squares	$\sqrt{\pi/6}=0.7236$	4.35	4.4 ± 0.1

Let us turn now to the problem of calculating the percolation threshold in systems with a correlated distribution of sites (e.g., sites distributed as though they were interacting particles). Connectedness is defined by overlap of permeable shells that surround each site. For this paper's purpose, we define the generalized "excluded volume" as the volume in which the corresponding permeable object centers would have to be in order for their shells to overlap. For example, for a system of hard-core–soft-shell spheres of shell diameter d and hard-core diameter σ, the excluded volume is a sphere of diameter $2d$. The correlations in the site distribution are characterized by the radial distribution function[14] $g(r)$, where $\rho g(r)d^3r$ is the probability of finding a site (an object center) in a volume d^3r at a distance r from a site located at the origin. The bonding distance l is now given by a weighted average over the above defined excluded volume, i.e.,

$$l^2=\left[\int r^2 g(r)d^3r\right]\Big/\int g(r)d^3r\,. \tag{6}$$

This definition of l gives regions within the permeable shell, in which it is more probable to find other sites, greater weight than to less populated regions.

To define L, the mean distance between sites bound to at least two other sites, we must calculate the probability that at a given density a site has either one or no neighbors. We approximate this probability by maintaining a Poisson distribution for the number of neighbors per site: The probability that a site has k neighbors is assumed[15] as above to be $(B^k/k!)\exp(-B)$, but now B—the average number of bonds per site—is given by

$$B=\rho\int g(r)d^3r\,. \tag{7}$$

Correspondingly, the definition of L [Eqs. (2) and (3)] is now given by

$$L=2\left[(4\pi\rho/3)\left\{1-\left[\exp\left(-\rho\int g(r)d^3r\right)\right]\left(1+\rho\int g(r)d^3r\right)\right\}\right]^{-1/3}. \tag{8}$$

Using our percolation criterion Eq. (4), we now derive [as in Eq. (5)] a general equation for the critical density ρ_c:

$$(\rho_c V_{\rm ex})\left\{1-\left[\exp\left(-\rho_c\int g(r)d^3r\right)\right]\left(1+\rho_c\int g(r)d^3r\right)\right\}=(3V_{\rm ex}/4\pi)\left(\int g(r)d^3r\Big/\int r^2 g(r)d^3r\right)^{3/2}. \tag{9}$$

It is now very simple, given $g(r)$, to calculate the percolation density ρ_c for systems of interacting objects. We present the results of such calculations for systems of hard-core–soft-shell spheres and for systems of spheres with a hard core and an attractive square-well potential. For these simple interactions, adequate approximations for $g(r)$ are known[14] and results of Monte Carlo simulation are available[9,11] for B_c.

The zeroth-order approximation of $g(r)$ in powers of density is simply $g_0(r)=\exp[-U(r)/k_BT]$ where $U(r)$ is the pair potential and k_BT the thermal energy.[14] Thus for spheres of hard-core diameter σ, square-well range λ, and depth $U_0=-\epsilon k_BT$, we have

$$g_0(r)=\begin{cases}0, & r<\sigma,\\ e^{\epsilon}, & \sigma<r<\lambda,\\ 1, & r>\lambda.\end{cases} \tag{10}$$

Using the definition of l [Eq. (6)] we obtain

$$\frac{l}{l_0}=\left(\frac{\frac{3}{5}[(1+v^5e^{\epsilon})-(v^5+\eta^5e^{\epsilon})]}{(1+v^3e^{\epsilon})-(v^3+\eta^3e^{\epsilon})}\right)^{1/2}, \tag{11}$$

where again $l_0=[(3/4\pi)/V_{\rm ex}]^{1/3}$, $v=\lambda/d$, $\eta=\sigma/d$, and d is the permeable shell diameter. Turning to the average number of bonds per site [Eq. (7)], we have

$$B(\rho)=\tilde{B}[(1+v^3e^{\epsilon})-(v^3+\eta^3e^{\epsilon})]\,, \tag{12}$$

where $\tilde{B}=(4\pi d^3/3)\rho=V_{\rm ex}\rho$. In the case of no interactions $B(\rho)=\tilde{B}=B$ as expected.[8]

Hence, for a general case including interactions, our new percolation criterion is just

$$(l/l_0)^3=\tilde{B}_c\{1-\exp[-B(\rho_c)][1+B(\rho_c)]\}\,, \tag{13}$$

where $\tilde{B}_c=V_{\rm ex}\rho_c$.

We improved our approximation of $g(r)$ for systems of hard-core–soft-shell spheres by using the Percus-Yevick (PY) approximation,[14,16] $g_{\rm PY}(r)$. For hard-core spheres with a square-well interaction we used then the approximation[14] $g(r)=g_{\rm PY}(r)$, where $g_{\rm PY}(r)$ is the PY correlation function for spheres of corresponding hard-core diameter. The approximations based on the PY correlation function are known to be extremely accurate for low and intermediate hard-core densities.[14]

Our results for the threshold density of a system of hard-core–soft-shell spheres as a function of the hard-core fraction[11,14,17] $\eta=\sigma/d$ are shown in Fig. 1, along with the available Monte Carlo results.[9] Our results for hard-core–soft-shell spheres with an attractive square-well potential are compared with those of a Monte Carlo simulation[9] in Fig. 2.

As we see in Fig. 1, even for the zeroth approximation in $g(r)$, the presently calculated thresholds are very close to the Monte Carlo results for $\eta<0.9$. It is particularly striking that, as shown in Fig. 2, our results accurately follow the wide variations in ρ_c. When η goes to 1, however, our result for ρ_c diverges (unphysically). The zeroth-order approximation of $g(r)$ is adequate because of the low hard-core densities $\rho_c\eta^3$ for all but the highest η. The calculation of ρ_c in this approximation may be easily performed for any potential.

The general behavior in Fig. 1 may be qualitatively understood[9,17] in light of the new percolation criterion.

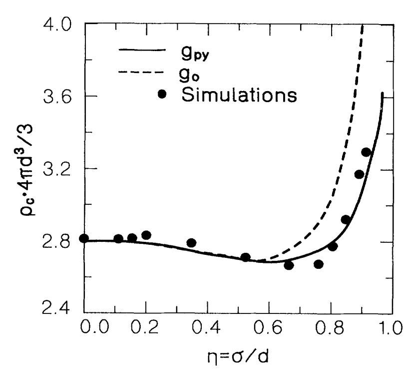

FIG. 1. Presently calculated threshold density for hard-core–soft-shell spheres. The shell diameter is d and the hard-core diameter is $\sigma=\eta d$. The dashed curve represents the present calculation using $g_0(r)$, and the full curve, the present calculation with $g_{\rm PY}(r)$. For comparison we show the simulation results (dots) reported in Ref. 9.

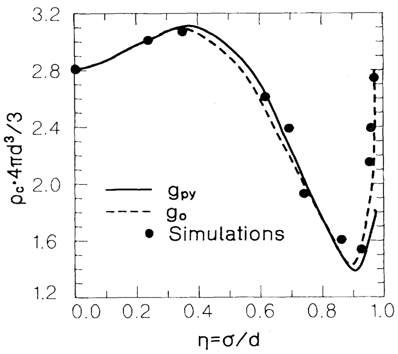

FIG. 2. Presently calculated threshold density, compared with the simulation results of Ref. 9, for a system of hard-core–soft-shell spheres with an attractive square-well potential. Shell diameter is d, hard-core diameter is σ, well diameter is $\lambda = \sigma + 0.1d$, and the well depth is $\epsilon = -U_0/k_BT = 2.08$. Approximations used for $g(r)$: dashed curve, $g_0(r)$; full curve, $g_{PY}(r)$.

Briefly, as η increases, the volume available for overlap decreases, the density of sites with more than one neighbor decreases, and in order to achieve percolation an increase in ρ_c is required. On the other hand, with increasing η the average distance between overlapping objects increases, thus yielding a higher pointedness, and hence a lowering of ρ_c. The second effect is dominant for small hard-core fractions, while the first becomes important for large hard-core fractions. The competition between the two effects produces the minimum observed in Fig. 1. The addition of attractive interactions causes the minimum to deepen and a new maximum in ρ_c to appear at low η. This is a result of the strengthening of the above effects due to increased clustering. The deep minimum in ρ_c validates the use of $g_0(r)$ for strong attractive potentials, even for large hard-core fractions. Thus the new criterion clarifies the role of microscopic correlations in determining the macroscopic connectedness. The depth of the minimum in B_c (shown in Figs. 1 and 2) is associated with the amplitude of the first peak in $g(r)$ where the permeable shell encloses a region whose density is higher than the average density due to the nearest-neighbor shell. This higher effective density offsets the tendency of the decreasing overlap region to increase B_c.

In conclusion, we have calculated the percolation critical density for permeable spheres and cubes, hard-core–soft-shell spheres, and hard-core–soft-shell spheres with an attractive potential. The calculations, which were based on a new percolation criterion, are mathematically simple and yield very accurate values for the critical density.

The authors would like to thank S. Alexander, P. G. de Gennes, and Y. Rosenfeld for helpful discussions.

[(a)]Present address: Physics Department, Nuclear Research Center, Negev, P.O. Box 9001 Beer-Sheva, Israel.

[1]I. Balberg, Philos. Mag. B **55**, 991 (1987).

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

[3]See, for example, *Physics and Chemistry of Porous Media,* edited by D. L. Johnson and P. N. Sen (AIP, New York, 1984).

[4]See, for example, B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors* (Springer-Verlag, Berlin, 1983).

[5]J. E. Sax and J. M. Ottino, Polymer **26**, 1073 (1985).

[6]See, for example, B. Abeles, H. L. Pich, and J. I. Gittleman, Phys. Rev. Lett. **35**, 247 (1975); I. Balberg and S. Bozowski, Solid State Commun. **44**, 551 (1982); F. Carmona, P. Prudhon, and F. Barreau, Solid State Commun. **51**, 225 (1984).

[7]See, for example, K. L. Mittal and R. Lindman, *Surfactants in Solutions* (Plenum, New York, 1984), and in particular, S. Bhattacharya, J. P. Stokes, M. W. Kim, and J. S. Huang, Phys. Rev. Lett. **55**, 1884 (1985).

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

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

[10]U. Alon, A. Drory, and I. Balberg, Phys. Rev. A **42**, 4634 (1990); (to be published). For accurate analytic estimates of B_c, see e.g., S. W. Haan and R. Zwanzig, J. Phys. A **10**, 1547 (1977).

[11]T. DeSimone, R. M. Stratt, and S. Demoulini, Phys. Rev. Lett. **56**, 1140 (1986).

[12]See, for example, S. Chandrasekhar, in *Noise and Stochastic Processes,* edited by N. Wax (Dover, New York, 1954); L. E. Reichl, *A Modern Course in Statistical Physics* (Edward Arnold, New York, 1980).

[13]G. E. Pike and C. H. Seager, Phys. Rev. B **10**, 1421 (1974). See also, B. J. Adler and W. E. Alley, J. Stat. Phys. **19**, 341 (1978); T. Vicsek and J. Kertesz, J. Phys. A **14**, L31 (1981); J. Kertesz and T. Vicsek, Z. Phys. B **45**, 345 (1982).

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

[15]This assumption is borne out, for k up to $2B_c$, by Monte Carlo simulations of a system of hard-core–soft-shell spheres [see Ref. 1 and I. Balberg and N. Binenbaum, Phys. Rev. B **35**, 5174 (1987)].

[16]G. Throop and R. Bearman, J. Chem. Phys. **42**, 2408 (1965).

[17]Balberg and Binenbaum, Ref. 15.