Site percolation in randomly packed spheres

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Three-dimensional structures of equal-sized randomly packed hard spheres (RPHS) have been built on a computer, and the site-percolation threshold has been calculated. The mean coordination of RPHS is 6 and we find a site-percolation threshold of 0.310 ($\pm$0.005). This value of the percolation threshold is the same as the simple cubic lattice, which has an exact coordination of 6. Expressing the percolation threshold for randomly packed hard spheres, in terms of the volume of occupied space, gives a critical-volume fraction of 0.183 ($\pm$0.003).

In recent years the ideas and results of percolation theory have found wide application in the physics of disordered and inhomogeneous systems. The classical results of percolation theory have been related to associated conductivity problems and used in interpreting transport phenomena in amorphous semiconductors,[1] metal ammonia solutions,[2] conducting particles embedded in a continuous insulating medium,[3] conduction in mixtures of continuous insulating and conducting media,[4] and conduction in powder or particulate mixtures[5] (for a more complete list of references see papers cited in Refs. 5 and 6). Of all these, the problem that most easily relates to classical percolation theory is the electrical conduction in particle mixtures, and as a result, this problem has found favor as an illustrative model experiment.[7,8] However, this system is more important than for mere tutorial purposes. There are many solid-state devices that are made from powders, and we are often concerned with conduction mechanisms, an important aspect of which is the role of the percolative nature of the current flow.

The classical problem of site percolation is formulated as follows: If we consider a regular lattice, where each lattice point is considered to be connected to each nearest-neighbor lattice site, then electrical contact or simply connectivity exists from any lattice site to any other site via the bonds between sites. If we now consider a fraction of sites p, selected randomly, to be conducting and the remainder nonconducting, then there exists a critical fraction of sites p_c, below which there is zero probability of finding a connecting path of infinite extent.

The calculation of p_c has been made for a number of the common regular lattices and the results are shown in Table I. It was noted by Scher and Zallen[9] that if we represent the critical percolation in terms of a critical-volume fraction (CVF) instead of a critical site occupation, i.e., by multiplying the critical site occupation (p_c) by the packing density of the lattice, then the common lattices have a CVF that varies by 6% [0.154 ($\pm$ 0.01)] compared to p_c that varies by a factor of 2. This result was the basis of a proposed empirical rule that stated for site percolation there exists a CVF that depends only on the dimensionality and not on lattice structure. Scher and Zallen[9] proposed therefore that the empirical rule should have validity for random systems even to the extent of conducting particles in a continuous medium. The latter application has been contested strongly by Seager and Pike,[6] who nevertheless conceded the likelihood that the empirical rule would be applicable to random mixtures of two media having a "hard-core interaction" such as powder mixtures.

In this paper we examine this possibility in more detail by calculating the site-percolation threshold in three-dimensional structures built by random packing of hard spheres (RPHS).

Randomly packed structures of equal sized hard spheres can be built using ball bearings or some other spherical material to construct a physical model (for a recent review see Ref. 10) or they can be simulated on a computer.[11-13] The ball-bearing models have a well-defined packing density,[14] but the models built by shaking stacks of ball bearings have a degree of order and are more accurately referred to as random mixtures of highly ordered microdomains.[12]

Random packing of hard spheres built with a computer are in some senses a better representation of truly random packing.[12] They also have a well defined density but more importantly they have a well defined distribution of nearest-neighbor touching contacts. The distribution of touching contacts for ball-bearing assemblies has been measured by immersion in various fluids to mark the contacts,[15,16] but these methods are not good at distinguishing touching contacts from near contacts.

TABLE I. Site-percolation threshold and critical-volume fraction for the common three-dimensional lattices and for random-packed hard spheres.

	Coordination z	p_c [a]	Packing density f	CVF [b]
diamond	4	0.425	0.34	0.146
sc	6	0.307	0.52	0.160
sc	6	0.3115 [c]	0.52	0.163
bcc	8	0.243	0.68	0.163
fcc	12	0.195	0.74	0.144
hcp	12	0.204	0.74	0.151
RPHS	6	0.310	0.59	0.183

[a] Reference 21.
[b] Reference 9.
[c] Reference 22.

The computer-generated randomly packed hard-sphere structures used in this paper were built by a method similar to that used by Matheson[12] and Tory *et al.*[11] Spheres are placed one at a time in a randomly chosen, locally close-packed site, such that the new sphere makes contact with three other spheres already in place. The coordinates of the spheres are recorded and three-dimensional structures are built up from an initial two-dimensional layer, which in the first instance is a plane surface and thereafter is a section of spheres from a previously constructed model. The plane surface is used merely to start the process and the region near this plane surface would be excluded from the percolation calculations. During the building, periodic boundary conditions are incorporated, such that any sphere placed at Cartesian coordinates (x, y, z) is also placed at $(x \pm L_x, y \pm L_y, z)$. As the model is built up the computer program assigns a number to each sphere and records the numbers of all the other spheres in contact with it, and thus the entire interconnecting network for the assembly of spheres is stored.

We can summarize this information in the form of a distribution curve of the number of contacts per sphere as shown in Fig. 1. The distribution has a mean of six contacts per sphere and a small but finite amplitude at three contacts and nine contacts, in agreement with the observations of Tory *et al.*[11]

The percolation problem for the RPHS model is formulated in a manner identical to that of the regular lattices, i.e., the spheres are equivalent to the lattice sites and the contacts between spheres are the bonds. The advantage of studying the percolation threshold in this system compared to mixtures of conducting and nonconducting balls[7,8] is that we have an accurate measure of the actual contacts for each sphere and by definition these contacts (or bonds) determine the connecting paths.

The method we have used for determining the critical percolation threshold is similar to Pike and Seager[17] and Levinshtein *et al.*,[18] which is a form directly related to the conductivity problem. Boundary regions are established at two opposite faces of a cube of side l, and percolation is detected by finding a connecting path from a site in one boundary region to a site in the opposite boundary region. To begin with, we consider all the spheres to be removed from the structure. The spheres are then replaced in a random order one at a time. Each sphere replaced is given a cluster identification number. If the new sphere is connected to any other spheres which have also been replaced then these spheres are given a common identification number. Any spheres which

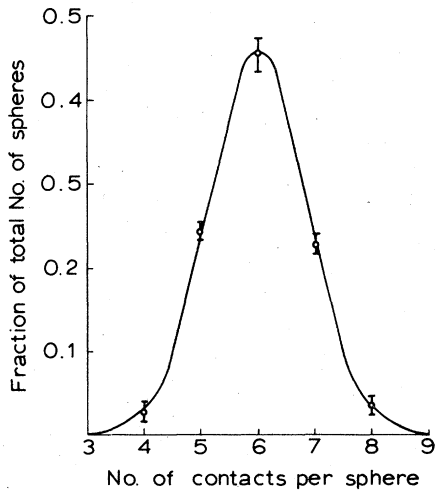

FIG. 1. The distribution of the number of touching contacts per sphere in RPHS.

are replaced and situated in one of the boundary regions are given a cluster identification number of 1; the other boundary region is given a cluster identification number of 2. Whenever a new sphere is replaced which connects two or more existing clusters, then the whole of the new large cluster is assigned the lowest cluster identification number. In this way all those spheres which are connected to one boundary region have a cluster identification number of 1 and those connected to the other boundary region have a cluster identification number of 2. The structure is said to percolate when a sphere is replaced which connects a cluster with identification number 1 with a cluster of identification number 2 and thus the first connecting path is formed from one face of the cube to the opposite face.

The value of p_c which is determined in this way has a range of values due to the finite size of the cube and the smearing of the critical point in such a system. This size dependence has been discussed by Roussenq *et al.*[19] for two dimensions and illustrated by Levinshtein *et al.*[18] for the three-dimensional simple cubic lattice and can be described in terms of a correlation length.

In order to check our computer program and especially to check the suitability of the method to RPHS of rather limited size, we first applied the method in an identical manner to simple cubic lattices of size varying between $4\times4\times4$ and $20\times20\times20$ and compared the results obtained with more accurate determinations in the literature.

In Fig. 2, we show the results we have calculated for the simple cubic lattice. The percolation threshold is measured 60 times for a cube of side $l=4$ and $l=10$ and 30 times for $l=20$, and we have plotted the number of connected configurations as a function of the fractional occupation of sites p. The width of the transition region is greater for the smaller sized cubes. The low end of the transition region can be identified with the finite probability that even below p_c a cluster with linear dimension greater than l exists. The upper end of the transition region can be identified with the finite probability that above p_c the sample will not be connected. In this case the infinite cluster has a "superlattice" or "macromesh"[20] with a mesh size greater than l.

In Fig. 3, we have plotted for the simple cubic lattice the mean value of p_c (which is the same as the median value within experimental error) as a function of l for cubes with and without periodic boundary conditions connecting the faces perpendicular to the boundary region faces. Our results without periodic boundary conditions agree with Levinshtein *et al.*[18] and show a stronger dependence on l than those with periodic boundary conditions. We therefore associate this effect with the decreasing ratio of surface sites to bulk sites with increasing l and the influence of these surface sites which have a lower coordination (5 instead of 6) on the measured p_c. The results with periodic boundary conditions show a dependence on size which is small compared to the uncertainty in p_c and compares well with the best values from the series expansion method, $p_c=0.307$ $(+0.01)$,[21] and the Monte Carlo determination of cluster size, $p_c=0.3115$ (±0.0005).[22]

We now turn to the results for RPHS, which have periodic boundaries built in during the construction. Owing to the computational effort involved, we have limited our RPHS to a size $10\times10\times10$ (in units of sphere diameters). However, since each realization of a RPHS structure is different, we have constructed nine different

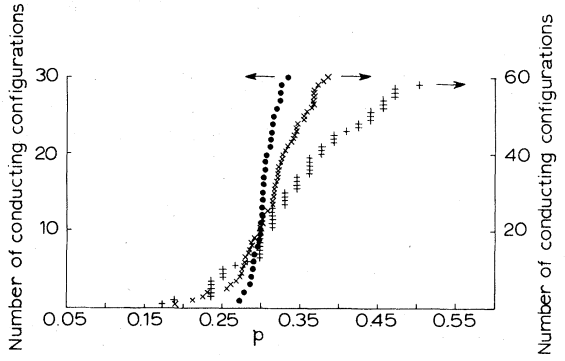

FIG. 2. The number of connected configuration out of a total of 60 measured (30 for $l=20$) as a function of the fraction of occupied sites (p) for a simple cubic lattice of side $l=4$ (+), $l=10$ (×), and $l=20$ (●).

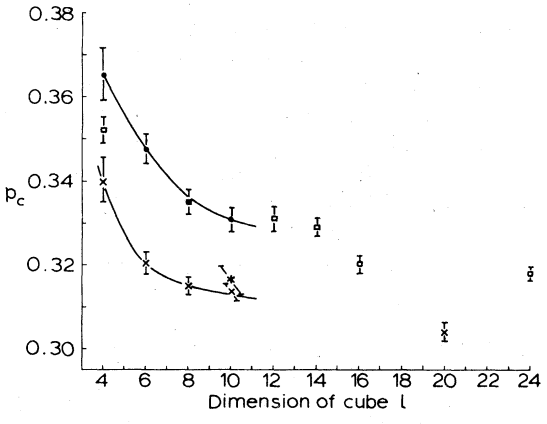

FIG. 3. The percolation threshold (p_c) as a function of the size of the sample cube; ●—without periodic boundaries, ×—with periodic boundaries, *—RPHS for $l=10$, □—Ref. 18.

structures and measured the percolation threshold 60 times on each in the same way as for the regular lattice. In addition we have constructed RPHS of size $6\times6\times6$ and $8\times8\times8$. We find that the size dependence of p_c and the value of p_c itself is the same, within experimental error, as the simple cubic lattice with periodic boundaries. We can conclude therefore that reasonable values for p_c can be obtained for RPHS of size $10\times10\times10$. In practice, we find that our calculated values for the simple cubic lattice of size $10\times10\times10$ are 2% larger than the more accurate values of Sur *et al.*,[22] and so we have corrected the RPHS values by a similar factor before quoting the final result. Thus we conclude that for RPHS $p_c = 0.310\ (\pm 0.005)$. If we express this result in terms of the critical-volume fraction, which we can measure either by multiplying p_c by the packing fraction f (0.58–0.60) or summing directly the volume of the spheres as they are replaced in the structure (the result is the same within experimental error), then we find $x_c = 0.183\ (\pm 0.003)$. This critical-volume fraction is larger than any of the common lattices (see Table I), and thus the empirical rule is not so well obeyed for computer-generated RPHS.

In Fig. 4 we reproduce the measured percolation threshold p_c as a function of the reciprocal of the coordination number of the lattice. All the common lattices fit onto a common trend line. In addition, if we consider bonds to exist to next-nearest neighbors and 3rd-nearest neighbors, then the increased coordination of the lattices gives a new value of p_c, which fits onto another trend line which passes through the origin[23] (this figure can be contrasted with Ref. 8). The empirical rule of Scher and Zallen[9] arises owing to the canceling trend of the packing density as a function of the coordination number. However, the RPHS has a mean coordination and packing density which does not fit into the trend of the regular lattices; the mean coordination is 6 contacts and the packing density is between 0.58 and 0.60. If we identify the mean number of contacts with z, then the RPHS fit onto the curve of Fig. 4, but less well to the CVF rule. One further point can be made as an objection to the use of the CVF empirical rule applied to RPHS. In RPHS there are a large number of near contacts as well as touching contacts. An application of some deforming pressure will make near contacts into good ones, and a resulting change in the percolation threshold will be observed for a negligible change in packing density.

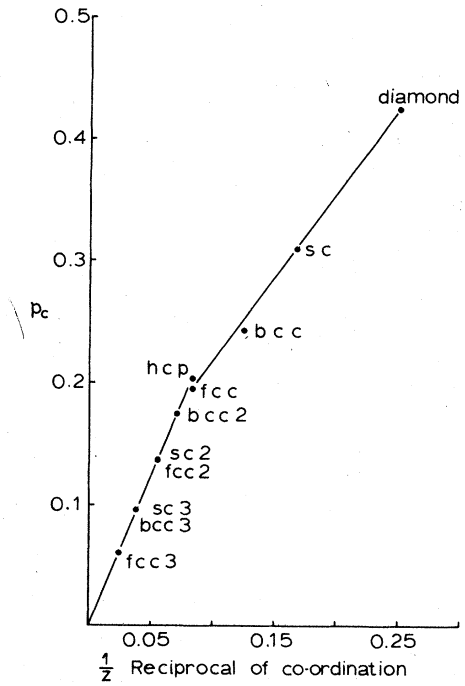

FIG. 4. The percolation threshold as a function of the reciprocal of the coordination. The numbers 2 and 3 after the lattice type indicate coordination to 2nd- and 3rd-nearest neighbors.

Our results for RPHS support the suggestion[8] that Fig. 4 could be used to determine the mean coordination number from a measurement of the percolation threshold p_c in random particulate systems.

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