PHYSICAL REVIEW B VOLUME 21, NUMBER 8 15 APRIL 1980

Comments and Addenda

The section Comments and Addenda is for short communications which are not appropriate for regular articles. It includes only the following types of communications: (1) Comments on papers previously published in **The Physical Review** *or* **Physical Review Letters**. *(2) Addenda to papers previously published in* **The Physical Review** *or* **Physical Review Letters**, *in which the additional information can be presented without the need for writing a complete article. Manuscripts intended for this section must be accompanied by a brief abstract for information-retrieval purposes. Accepted manuscripts follow the same publication schedule as articles in this journal, and page proofs are sent to authors.*

Site percolation in random networks

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(Received 12 December 1979)

The site-percolation threshold has been calculated for randomly coordinated networks based on a model of computer-generated randomly packed hard spheres (RPHS). Each network is generated by allowing each sphere to coordinate to (i.e., be in contact with) every other sphere up to a given coordinating radius r, and the percolation threshold is calculated for different values of r. When the percolation threshold is plotted against the reciprocal of the coordination number, the results are well described by two straight lines intersecting at a point corresponding to a coordination number of 12, in agreement with results of regular lattices. It is suggested that this result forms a useful empirical rule for site percolation in random networks with applications in, for example, random particulate systems.

In a recent paper[1] the author calculated the site-percolation threshold in a random network of equal-sized randomly packed hard spheres (RPHS) using a computer simulation. Such a three-dimensional structure has as well-defined packing density (~0.6) and a distribution of nearest-neighbor touching contacts with a mean value of six per sphere. The site-percolation threshold was found to be 0.310 (±0.005), and the critical volume fraction (CVF) at the percolation threshold was 0.183 (±0.003), a value rather higher than that suggested by Scher and Zallen's empirical rule.[2]

It has been observed that, if the percolation threshold of the common regular lattices is plotted against the reciprocal of the coordination number, then the results are well described by a straight line. The result for the RPHS structure is in agreement with this, and it was suggested that this line could form the basis of an empirical rule for site percolation in random networks and be used, for example, to determine the mean number of conducting contacts from a measurement of the percolation threshold in random particulate systems.

In this paper we examine this possibility in more detail. We have taken the RPHS model as our basic random network and measured the percolation threshold as a function of increasing the coordination radius of each sphere from the initial value of one sphere diameter.

Domb and Dalton[3] showed that, if a similar procedure is applied for the regular lattices, i.e., by allowing coordination to second and third-nearest neighbors, then the values of the percolation threshold, when plotted against the reciprocal of the coordination number, fit a second straight line which passes through the origin.

For randomly packed hard spheres there are no second- or third-nearest neighbors as such, but we can increase the mean coordination number smoothly and continuously by increasing the coordinating radius of each sphere.

The computer program for constructing RPHS structures has been fully described elsewhere.[4] The spheres are placed one at a time in a randomly chosen, locally close-packed site, and three-dimensional structures are built up by a process of sequential deposition. The structures have periodic boundary conditions built in during the construction such that any sphere placed at a point with Cartesian coordinates (x, y, z) is also placed at $(x \pm L_x, y \pm L_y, z)$. RPHS structures built by this method are well characterized with a packing density ~0.6 and a symmetric distribution of contacts with a mean value of six.

The coordinates of each sphere in the assembly is calculated when placed and subsequently recorded in a data file. It is relatively straightforward to determine any desired geometrical property of the assembly by reading this file and per-

forming some simple calculations. In particular we can calculate the number of spheres "in contact" with each sphere in the assembly, for any value of the coordinating radius. Each sphere in the assembly is numbered, and the number of all the other spheres "in contact" with each sphere is determined and stored in a two-dimensional array. This array therefore contains the entire interconnecting network for the assembly of spheres and can be used directly for calculating the percolation threshold.

Figure 1 shows the distribution of coordination numbers for different values of r, the coordinating radius expressed in sphere diameters. These distributions represent the bulk of the assembly, and spheres on the boundaries are excluded. For $r=1$ the distribution gives the distribution of touching nearest-neighbor contacts. As r is increased, the distribution becomes wider, and the mean value of coordination increases. We note, however, that within experimental error the distribution remains symmetric, and the mean and modal values are the same.

The percolation threshold for different values of r was measured in an identical manner to the earlier paper.[1] 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. The separation between the two boundary regions is kept constant for all values of r, and the width of the boundary region is large enough, such that all spheres that are not boundary spheres are fully coordinated, i.e., have the same mean coordination as spheres in the mid dle of the assembly.

The percolation threshold is measured by randomly replacing the spheres one at a time until the addition of a single sphere forms a connected path between the two boundary regions. The percolation threshold measured in this way has a range of values due to the finite size of the structure and the smearing of a critical point in such a system.

Previously[1] we determined the percolation threshold as a function of the size of the sample cube and showed that for our RPHS structures, the value of the percolation threshold and its size dependence was identical to the results for simple-cubic lattices with periodic boundary conditions. Since the value of the percolation threshold for simple-cubic latices is known to quite a high accuracy from previously published calculations,[5] it was found that the mean value obtained with a small-sized cube of dimension $10\times10\times10$ using our method was 2% larger than the more accurate value. We therefore assumed that the value for the RPHS structure was 2% less than we calculated for a cube of size $10\times10\times10$ (in units of sphere diameters).

In the present work we have used the same small-sized structures and have similarly calculated the percolation threshold sixty times in each of nine separate realizations of the RPHS structure, for each chosen value of r. We have corrected all the calculated mean values of the percolation threshold by multiplying by 0.98 in the same way, before quoting the final result. However, we have not independently checked the size dependence of the percolation threshold for these RPHS structures with increased mean coordination, and there is no reason to believe the size dependence in all cases will be identical and equal to the simple-cubic lattices. We have taken this into account by increasing the quoted errors to the values of the percolation threshold (Table I). It should be noted, however, that the resulting values are perfectly adequate for the purposes of this paper.

Figure 2 shows the calculated percolation threshold as a function of the reciprocal of the coordination number (Z) corresponding to the RPHS structures with coordinating radius between $r=1$ (mean number of contacts equals 6.0) and $r=1.9$ (mean number of contacts, 30.2). Included in this figure are the results of the common lattices with nearest-, second-nearest-, and third-nearest-neighbor coordination. For the sake of clarity, error bars are not included in the figure, but can be found from Table I.

The points for the random networks of the RPHS structures are in extremely good agreement with

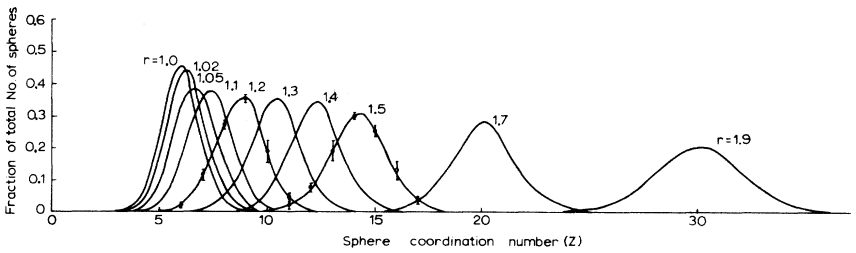

FIG. 1. Distribution of coordination numbers for different values of r, the coordinating radius.

TABLE I. Calculated percolation thresholds and mean coordination numbers for different values of r.

Coordinating radius (sphere diameters)	Mean coordination number	Percolation threshold p_c
1.0	6.00	0.310 (±0.010)
1.02	6.24	0.304 (±0.010)
1.1	7.34	0.274 (±0.009)
1.2	8.73	0.246 (±0.008)
1.3	10.36	0.220 (±0.007)
1.4	12.18	0.198 (±0.007)
1.5	14.24	0.170 (±0.005)
1.7	20.06	0.124 (±0.004)
1.9	30.23	0.086 (±0.003)

those of the common regular lattices. The results for the random networks also seem to be well described by two straight lines intersecting at a point corresponding to a mean coordination number of 12.

The *best* straight-line fit to the points for values of coordination numbers greater than 12 appears not to pass through the origin. However, such minor deviations could be due to a systematic change in the size dependence of the calculated value of p_c, and in any case are within the quoted experimental errors.

Figure 3 shows an expansion of Fig. 2 covering the narrow range from $r=1$ to $r=1.1$. Calculations were made for $r=1.00$, 1.005, 1.01, 1.02, 1.05, and 1.10. These calculations were performed exactly as before, although all points are not included in Table I or Fig. 2. This range of r is of considerable interest if these ideas and the proposed empirical rule are to be applied to the case of random particulate mixtures. In our model this range of r corresponds to the gradual conversion of very near contacts into conducting contacts. The straight line drawn in Fig. 3 is the same line as in Fig. 2. In this diagram the error bars correspond to the original errors in determining p_c for the small-size structures and do not include the reliability of these values at representing the true value of p_c (as above). Again the results show a smoothly decreasing value of p_c for an increasing value of coordination number, in agreement with the trend line of the regular lattices.

It is interesting now to compare results obtained with the computer-generated RPHS, with results obtained on RPHS built as physical models using ball bearings or some other suitable spherical

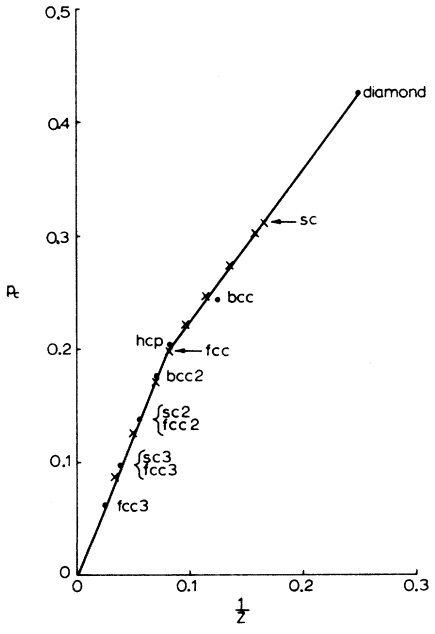

FIG. 2. Site-percolation threshold as a function of the reciprocal of the coordination number. ×-points from RPHS with different r, ●-regular lattices with nearest, second-nearest, and third-nearest neighbors (an arrow indicates a point for regular lattice superimposed on the point for RPHS).

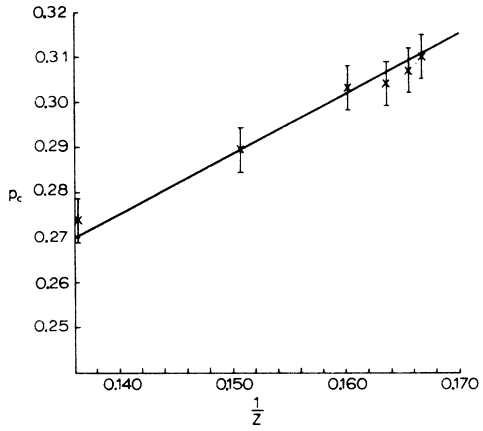

FIG. 3. Site-percolation threshold for RPHS near $r=1$.

material. Such physical models have been extensively studied (see Ref. 6 for a review).

The geometrical properties appear to be slightly different to the RPHS models simulated on a computer, but a useful comparison of the distribution of contacts in the two types of models is extremely difficult and has not been performed. Part of this difficulty has been attributed to an inability to measure the sphere positions in ball-bearing models with sufficient accuracy and the tendency of the paint method of Bernal and Mason[7] to be unreliable. In addition a comparison of the geometrical properties of computer-generated RPHS with ball-bearing models is further complicated by the two states of random packing in ball-bearing models, random loose packing (density = 0.60), and random close packing (density = 0.64).

The percolation threshold has been measured for the ball-bearing-type models. The measurement is made electrically by using mixtures of conducting spheres and insulating spheres, with suitable precautions being taken to ensure random mixing and good electrical contact between touching neighbors.

Fitzpatrick *et al.*[8] report a value of $p_c = 0.27$, corresponding to a measurement with a similar geometry to our computer calculations. They also report a value of $p_c = 0.225$ using a spherical geometry with a single central sphere as one electrode, but we consider the latter geometry does not represent the true percolation problem.

Ottavi *et al.*[9] report a value of $p_c = 0.30$ in a similar experiment. Comparing these results with Fig. 2 suggests that the randomly packed hard-sphere models of Fitzpatrick *et al.*[8] have a mean number of contacts ~7.4 and those of Ottavi *et al.*[9] ~6.3. Fitzpatrick *et al.*[8] used shaken stacks of spheres with a density of 0.64 corresponding to random close packing, while Ottavi *et al.*[9] used random loose-packed spheres with a density of 0.60. It is tempting to assign the difference in the measured percolation threshold to a difference in the effective number of contacts in the two states of random packing.

Bernal and Mason[7] reported for loose random packing a mean of 5.5 touching contacts and 7.1 very near contacts. For close random packing they reported 6.4 touching contacts and 8.5 very near contacts.

The above values of 7.4 contacts for close packing and 6.3 for loose packing, determined from the percolation experiments, form a reasonably consistent picture, bearing in mind the limitations of the direct method of determining contacts.

Another experimental determination of the percolation threshold through electrical measurements in random particulate systems was made by Clarke *et al.*[10] They measured the percolation threshold in random mixtures of submicrometer-sized powder-binder layers of conducting ZnO and insulating ZnS. Surface forces probably dominate the packing of these submicrometer-sized particles, and the reported packing density was only 0.45. However, the measured percolation threshold was 0.30, again suggesting a mean number of contacts close to 6. In these systems of submicrometer-sized particles, there is no direct method of determining the number of contacts, and yet this quantity is clearly important in determining the electrical properties of powder photoconductors with commercial applications.

In conclusion, we have shown that in random networks, the site-percolation threshold is determined by the mean coordination number of the network. The relationship between the percolation threshold and the mean coordination number is found to be well described by two straight lines, when the percolation threshold is plotted against the reciprocal of the coordination number.

We suggest that such a plot can be used to form the basis of an empirical rule for site percolation in random networks. Amongst some of the possible applications of such a rule are random particulate mixtures.

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