Network Approach to Void Percolation in a Pack of Unequal Spheres

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A procedure is developed to map the void space in a packing of unequal spheres onto a network. This enables one to use random networks to study problems with no underlying network defined *a priori*. The procedure is used to calculate the continuum percolation threshold for void space percolation in sets of randomly located, overlapping spheres with unequal radii. Within the statistical uncertainty, this threshold appears to be universal: 0.159 ± 0.002 in two dimensions and 0.030 ± 0.002 in three dimensions. As a possible application, the permeability of a bead pack is discussed. [S0031-9007(96)01040-X]

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The idea of percolation processes was introduced in 1957 to describe a fluid which spreads randomly through a porous medium [1]. Since then, percolation problems have been studied extensively, and a variety of applications has been reported (see, e.g., Ref. [2]). Most of the attention has been given to percolation on regular lattices, even for the study of the properties of disordered continuum systems. However, for such cases it is more appropriate to address the issue of continuum percolation. This is, for instance, of particular interest for subjects like the structure of liquids [3] or the structure of irregular particle packings [4]. Here, one considers the percolation of the material itself (i.e., material percolation). On the other hand, in cases where one is primarily concerned with the properties of the void space, the complementary form of percolation is useful. This so-called void percolation is relevant for the study of, e.g., transport in disordered media [5,6].

As a model for disordered materials one can use a set of randomly located, overlapping spheres. For the case of equal size spheres, the sphere percolation problem has been studied with various techniques, including Monte Carlo simulation, network mapping, and renormalization. The void percolation space problem has received less attention. Kertész estimated the percolation threshold using Monte Carlo techniques [7], and Elam *et al.* used a network mapping to calculate the percolation threshold and critical exponents [8]. The latter work was made possible by Kerstein [9], who proved that the network obtained via the Voronoi tessellation is a good representation of the void space.

Percolation and transport properties of networks obtained by the Voronoi tessellation have since been studied as properties of the network itself [10–12]. Others have used the same methods to study percolation properties of the void space in a realistic sphere packing [6,13–15].

If one wishes to extend this work to packings of spheres of unequal size, results are harder to come by. From theoretical considerations it is known that the sphere percolation threshold depends on the distribution of sphere sizes [16–18]. The critical exponents can also differ. Monte Carlo studies have been performed to confirm this work [19–21]. Although the results in three dimensions are not conclusive, in two dimensions they do confirm the theoretical expectation that the percolation threshold depends on the distribution of the sphere radii. As yet little is known about the percolation properties of the void space in packings of unequal spheres.

In this Letter I report a network mapping for packings of spheres with arbitrary radii. This mapping can be made for the spheres themselves, as well as for the void space in between the spheres. The technique greatly simplifies the study of percolation properties of unequal sphere packings. In particular, one may use it to determine to what extent void percolation thresholds and critical exponents are universal, i.e., independent of, for instance, the distribution of sphere radii. More generally, the technique may be employed in areas where the Voronoi tessellation restricted much of the research to equal size sphere packs. Examples are the structure of liquids, glasses, and colloidal suspensions [3], the structure of particle packings (powders, filtration beds [4,22]), and transport in porous media (conductivity, elasticity, fluid flow [5,6,15]).

I first discuss network mapping and the properties which make it so useful. Subsequently I apply this method to calculate the percolation threshold of the void space in-between spheres with unequal radii. Finally, as an example, I show that inclusion of the percolation threshold into the Kozeny-Carman equation for the permeability of a bead pack leads to a better description of the flow behavior at low porosities.

The mapping.—As mentioned above, for the mapping of the void space between spheres of equal radius one can use the Voronoi tessellation. This tessellation is defined with respect to a given set of points in space, for example, the centers of spheres in a random pack. If the set of points is denoted by $\mathbf{x}_i$, $i = 1, \dots, N$, the Voronoi region containing center $\mathbf{x}_i$ consists of all the points $\mathbf{x}$ for which

$$d(\mathbf{x}, \mathbf{x}_i) < d(\mathbf{x}, \mathbf{x}_j) \qquad \forall\ j \neq i\,,$$

where $d|\mathbf{x},\mathbf{y}|$ denotes the distance between points $\mathbf{x}$ and $\mathbf{y}$. The boundary between the region around $\mathbf{x}_i$ and the adjacent one around $\mathbf{x}_j$ is found by setting $d(\mathbf{x},\mathbf{x}_i) = d(\mathbf{x},\mathbf{x}_j)$, which defines the plane of points at equal distance to $\mathbf{x}_i$ and $\mathbf{x}_j$. This plane is perpendicular to the line connecting $\mathbf{x}_i$ with $\mathbf{x}_j$. If one takes into account all points $\mathbf{x}_j$ other than $\mathbf{x}_i$ itself, the region around $\mathbf{x}_i$ is bounded by a number of plane segments. Such a region is called a polyhedron.

The edges of the Voronoi polyhedra constitute a network of bonds. The points where the edges come together, the "vertices" of the polyhedra, are the sites of the network. Kerstein [9] proved that the void percolation problem is equivalent to the bond percolation problem for those edges of the Voronoi tessellation which are contained within the void. However, his proof is valid only for equal radius spheres. The proof is based on the assumption that a point inside a polyhedron, but outside its associated sphere, lies in the void space. This need not be true in the case of unequal radii.

In Ref. [22] an alternative tessellation was proposed for packings of unequal spheres, in order to be able to construct high density packings. The proposed definition for region i is

$$d(\mathbf{x},\mathbf{x}_i) - r_i < d(\mathbf{x},\mathbf{x}_j) - r_j \qquad \forall\ j \neq i\,,$$

where r_i is the radius of sphere i. This criterion is based on the distance to the surfaces of the spheres, rather than to their center. Although this is a valid definition of a tessellation, it is a very cumbersome one to work with, because the regions that are defined in this way are bounded by curved surfaces. It becomes difficult to calculate properties for the resulting networks.

I therefore propose an alternative which is defined by

$$d(\mathbf{x},\mathbf{x}_i)^2 - r_i^2 < d(\mathbf{x},\mathbf{x}_j)^2 - r_j^2 \qquad \forall\ j \neq i\,.$$

Such a definition has been used in the past to characterize structures in molecular compounds and in packings of multicomponent amorphous material [23,24]. Here I provide evidence that this tessellation is ideally suited for studying the void space in-between spheres, because of its following properties. (1) The boundaries between regions are planar. The boundary between regions i and j is perpendicular to the line connecting $\mathbf{x}_i$ and $\mathbf{x}_j$. (2) For equal spheres this is the Voronoi tessellation. (3) For overlapping spheres the boundary between regions coincides with the plane of intersection of the spheres. (4) For nonoverlapping spheres the boundary between regions always lies between the spheres (which is not valid for the Voronoi tessellation applied to unequal spheres). (5) The proof by Kerstein holds for arbitrary radii.

The latter point can be explained as follows. Consider a point $\mathbf{x}$ inside polyhedron i, but outside its associated sphere. I show that $\mathbf{x}$ lies in the void space. For the proposed tessellation $\mathbf{x}$ has the properties

$$d(\mathbf{x},\mathbf{x}_i) - r_i > 0\,,$$

$$d(\mathbf{x},\mathbf{x}_i)^2 - r_i^2 < d(\mathbf{x},\mathbf{x}_j)^2 - r_j^2 \qquad \forall\ j \neq i\,.$$

From the first line it follows that $d(\mathbf{x},\mathbf{x}_i)^2 - r_i^2 > 0$. Using the second line I conclude that $d(\mathbf{x},\mathbf{x}_j)^2 - r_j^2 > 0$ and hence $d(\mathbf{x},\mathbf{x}_j) > r_j$ for all j. In other words, the point $\mathbf{x}$ lies outside all spheres and hence in the void space.

This tessellation also has a new property: polyhedron i need no longer contain the center of sphere i. In fact, a region can be entirely empty, which is not possible with the Voronoi tessellation. This does not pose a problem, however, because a region will be empty only if its associated sphere is located entirely within one or more other spheres: in those cases one could of course have "thrown away" that sphere in the first place.

The void percolation threshold.—As an application of the new mapping technique, I calculated the percolation threshold for the void space in sphere packings with a bimodal sphere radius distribution. For monodisperse, overlapping, randomly located spheres, this threshold was calculated by Kertész [7] and by Elam *et al.* [8], who found 0.034 ± 0.007 and 0.032 ± 0.004, respectively. So far, no values have been reported for unequal, overlapping, randomly located spheres.

To calculate the percolation threshold, I have used a continuum version of the method discussed in Ref. [2]. The centers of the spheres were randomly located in a unit volume, by use of the random number generator, advocated in Ref. [25]. A fraction of the centers were assigned a radius r_1; the others were assigned a radius r_2. The ratio r_1/r_2 was set at a fixed value, say 0.25, while the absolute values of r_1 and r_2 were chosen such that initially the sum of all sphere volumes was unity. Because of overlap between the spheres, there is still a significant void space in between the spheres. This void space is mapped onto a network, making use of the new tessellation technique. The implementation was done by modifying the Voronoi tessellation algorithm of Moore and Angell [26]. In the runs presented here, periodic boundary conditions were used. With the help of a cluster algorithm [27], it is easy to check whether the resulting network percolates. If it percolates, the sphere radii increase for the next run; if not, they decrease in length. The increase or decrease is calculated by multiplying both r_1 and r_2 by the same factor, thus keeping the ratio r_1/r_2 fixed. In a binary search the multiplication factor a for which the system is at the threshold of percolation is determined. The void space fraction or porosity φ is then calculated as $\exp(-a^D)$, where D is the dimensionality of the system [21]. These steps are performed for many different sets of sphere centers. The results of these runs were averaged.

As a test of the dependence of the percolation threshold, I have used several systems, both in two and in three dimensions. The ratio of sphere radii was varied from 1 to $1/10$ in two dimensions and from 1 to $1/4$ in

TABLE I. The void percolation threshold for various systems. D is the dimension, r_1 and r_2 are the radii of the two types of spheres that were used, f is the fractional number of r_1 spheres, φ is the void space fraction for which the system is at the percolation threshold, and ν is a critical exponent. φ_e is obtained by extrapolation using Eq. (3), and φ_f by a fit to the scaling relation (1). Error estimates concerning the last digits are given between brackets.

D	r_2/r_1	f	φ_e	φ_f	ν
2	1/1		0.160 (1)	0.159 (1)	1.33 (10)
	1/2	0.4164	0.158 (2)	0.157 (2)	1.47 (13)
	1/4	0.2863	0.159 (2)	0.159 (2)	1.36 (8)
	1/10	0.1888	0.160 (2)	0.158 (2)	1.44 (10)
3	1/1		0.031 (2)	0.029 (2)	0.84 (3)
	1/4	0.2070	0.030 (4)	0.027 (3)	0.84 (8)

three dimensions. For each of the systems a number N_1 of spheres with radius r_1 was chosen that would yield good statistics. The fraction $f = N_1/(N_1 + N_2)$ for each system is shown in Table I, together with the results of the runs. For the two-dimensional systems, runs were performed for $N = 100$, 316, 1000, 3162 and 10 000. For each system size, 600 independent realizations were computed, with the exception of $N = 10\,000$, for which 300 realizations were computed. For the three-dimensional systems, the number of realizations was 300 for $N = 100$, 316, 1000 and 3162, whereas it was 100 for the $N = 10\,000$ system. For the three-dimensional system with $r_2/r_1 = 1/4$, the largest system was $N = 3162$.

The percolation threshold $\varphi(N)$ for a system of N spheres depends on N [21]:

$$|\varphi(N) - \varphi(\infty)| \sim N^{-1/(\nu D)}, \tag{1}$$

where ν is a critical exponent. Therefore one has to extrapolate in order to obtain a value for $\varphi(\infty)$. This can be done either by using a value for ν that is known for other systems, or by treating ν as an extra fitting parameter. In the latter case one finds a value for ν as well, at the expense of a larger uncertainty in $\varphi(\infty)$. Another possibility is to use the scaling relation for the standard deviation of φ:

$$\Delta\varphi(N) \sim N^{-1/(\nu D)}. \tag{2}$$

The advantage in using this relation is that one deals with only one unknown, but the drawback is that one needs more statistics for a reliable result.

Based on the above two scaling relations, one can also construct an extrapolation formula that is independent of the exponent ν:

$$\varphi(\infty) = \frac{\varphi(N_1)\Delta\varphi(N_2) - \varphi(N_2)\Delta\varphi(N_1)}{\Delta\varphi(N_2) - \Delta\varphi(N_1)}. \tag{3}$$

The results that are obtained with this extrapolation are listed in the table under φ_e. The values listed under φ_f are the results of fits to the scaling relation (1) for φ, assuming ν to be 4/3 in two dimensions and 0.88 in three dimensions. The values for the critical exponent ν were obtained by fits with the scaling relation (2) for $\Delta\varphi$.

The results for the critical exponent ν are consistent, within one or two standard deviations, with the values 4/3 and 0.88 for lattice percolation [2], and with the result 0.94 ± 0.2 reported by Elam *et al.* [8] for void percolation between equal size spheres. This can be seen either as a check on the present calculation, or as further evidence that this exponent is universal.

Concerning the percolation threshold, it appears that in two dimensions it is 0.159 ± 0.002, and in three dimensions 0.030 ± 0.002, independent of the ratio r_2/r_1. Compared to the sphere percolation threshold, the void percolation threshold is less sensitive to the distribution of sphere radii. This follows from the work of Lorenz *et al.* [21], who calculated the sphere percolation threshold, and found 0.6764 ± 0.0009 and 0.6860 ± 0.0012 for two different two-dimensional models. One of their models is the $r_1 = r_2$ system considered here. For the other model I have calculated that the percolation threshold is 0.159 ± 0.002 as well. The latter model uses a sphere radius distribution $p(r) = \text{const}$ for r between 0 and a maximum $r_{\max}$.

It is interesting to note that Roberts and Schwartz [6] calculated the percolation threshold for a realistic bead pack. Their result was 0.030 ± 0.004. Although this number is based on a single bead pack, and should not therefore be interpreted strictly, it does indicate that the void percolation threshold is rather insensitive to the structure of the material.

Let us suppose for a moment that the void percolation threshold is indeed universal, and let us return to the problem of fluid flow through a porous medium. Bryant and Blunt [15] calculated the permeability of a random bead pack, using the Voronoi tessellation to map the void space onto a network. They found a good agreement with experimental data for Fontainebleau sandstone [28], whereas a simple Kozeny-Carman equation [29]

$$k = \frac{\varphi^3 D^2}{180(1 - \varphi)^2}$$

did not give good results for porosities below 10%. Here, k is the permeability (in units m^2) and D is the average diameter of the sand grains (in units m). However, since the pore space does not percolate below 3%, we can heuristically modify the Kozeny-Carman equation as follows:

$$k = \frac{(\varphi - \varphi_c)^3 D^2}{180(1 - \varphi)^2}, \tag{4}$$

where $\varphi_c = 0.03$. From Fig. 1 it follows that this equation is a considerable improvement for low porosities. A similar improvement can be obtained for the electrical conductivity in porous media, which is most easily checked for the simple models introduced in Ref. [6]. (For a discussion on experimental evidence for a nonzero φ_c, see also Ref. [30].)

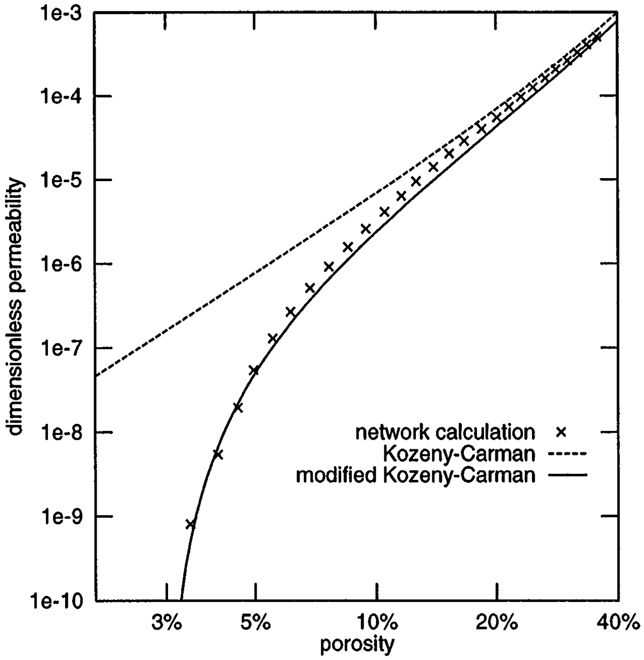

FIG. 1. The dimensionless permeability k/D^2 of a bead pack as a function of porosity. The network calculation is shown to coincide with experiments in Ref. [15], and is matched very well by a simple modification of the well known Kozeny-Carman equation; see Eq. (4).

In summary, I have shown that the void space in any packing of spheres can be mapped onto a network. This technique can be used for different purposes. In particular, I have used it here to calculate the percolation threshold of the pore space in sphere packings with spheres of different sizes. Since this percolation threshold is remarkably constant, it is an indication that it is a universal characteristic for uncorrelated sphere systems. The relevance of such a conclusion is demonstrated in the example presented of the permeability of sandstones as a function of porosity.

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