# Transport properties of disordered continuum systems

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We show that random-walk simulations are particularly well suited to the description of transport in continuum systems. This approach is illustrated with calculations on consolidated multisize granular materials where our results are in excellent agreement with experimental data on sintered binary composites. We also present the first detailed calculations on anisotropic packings. Here, our calculations are in good agreement with the results of electrical measurements on brine-saturated spherical rubber grains under uniaxial pressure.

## I. INTRODUCTION

The transport of electrical current and viscous fluids through the pore space of disordered continuum systems is a subject of wide interest.[1-3] Examples of the porous media involved in such processes are reservoir rocks, ceramics, and catalytic beds. In the design of composites it is important to estimate the transport properties of systems with varying constituent concentrations. In the case of two-component materials there exist well-established analytic methods when the concentration of one of the constituents is small[1] or when the system is near a percolation threshold.[2] Unfortunately, the cases of greatest practical interest are almost always between these two limits. In addition, we note that while most naturally occurring composite materials are characterized by a distribution of grain sizes, experimental and theoretical work on well-characterized synthetic materials has focused, almost entirely, on the properties of systems with a single grain size.[4,5] More recently, however, there have been detailed experimental studies on sintered granular composites with binary-grain-size distributions.[6,7] In addition, electrical measurements have been made on anisotropic, pressure-generated composites.[8] Clearly, there is a need for the development of more general theoretical methods in this area.

Several authors have suggested that Einstein's relation between the conductivity $\sigma$ and the diffusion constant $D$ might provide a useful approach to this class of problems.[9,10] In the present paper, we show that random-walk simulations can, indeed, be used to describe several features of disordered composites. In particular, we consider (1) electrical conduction, (2) fluid permeability, and (3) nuclear magnetic relaxation (NMR) in mixed-grain-size sintered bead packs, and (4) electrical conduction in anisotropic granular composites. For the conductivity $\sigma$ and the permeability $k$ we obtain good agreement with experimental data on fused binary mixtures of glass beads. In further accord with the experiments,[6] our calculations of $\sigma$, $k$, and the NMR spectrum indicate that, in many respects, the behavior of these quantities is not particularly sensitive to the details of the grain-size distribution. Finally, our calculations of the transverse and axial electrical conductivity agree with measurements on anisotropic granular composites.

While electrical conduction and NMR can be directly modeled by diffusion simulations, we emphasize that there is no analog of the Einstein relation for the permeability. Thus our estimates of $k$ are based on the calculated values of $\sigma$ and the length parameter $\Lambda$ introduced by Johnson *et al.*[11] This estimate is of interest because both $\sigma$ and $\Lambda$ are determined from the solutions of the Laplace equation and are not, in any fundamental way, connected to the Stokes equation that describes viscous fluid flow. In this connection we note that the concept of the $\Lambda$ parameter can easily be extended to anisotropic systems and that measurements of the permeability in such systems would be of particular interest. As is the case in monosize packings,[12] our calculations suggest that NMR can also be expected to provide a useful permeability indicator in multisize composites. Here, again, there is a need for detailed experimental data on both isotropic and anisotropic composites.

## II. CALCULATIONS AND COMPARISON WITH EXPERIMENT

### A. Electrical conductivity

Our analysis is based on the grain-consolidation (GC) model in which the porosity of an initial grain pack is reduced by allowing the grains to grow uniformly.[5] This algorithm yields results that are in qualitative accord with the observed behavior of reservoir sandstones and are in quantitative agreement with experimental data on fused monosized bead packs. We consider here the application of the GC model to systems with monosize, uniform, and binary-size distributions. The Visscher-Bolsterli[13] algorithm is employed to generate the initial granular packings. Briefly, this procedure consists of dropping one sphere at a time selected from any desired size distribution onto an area in the $xy$ plane. Periodic boundary conditions are employed in the $x$ and $y$ directions. A sphere comes to rest either when it hits the floor or when it comes to a stable resting position in contact with three other spheres. In the present paper we will be concerned with three packings, each of which is comprised of

 

roughly 10 000 grains. (Systems of this size, cubes roughly 21 grains on a side, are necessary to obtain estimates of $\sigma$ that are free of boundary effects.) They are (1) all spheres of radius 100 $\mu$m, (2) spheres with radii uniformly distributed between 50 and 150 $\mu$m, and (3) a binary packing consisting of spheres of radii 88 and 298 $\mu$m with the smaller and larger spheres occupying, respectively, 30% and 70% of the available volume. (The parameters for the binary distribution were chosen to match those of the systems studied experimentally in Ref. 6.) The mean sphere radius for all of the three distributions is 100 $\mu$m. The initial porosities of the sphere packs were $\phi=0.40$ (monosize), $\phi=0.38$ (uniform), and $\phi=0.30$ (binary). Figure 1 shows a two-dimensional cross section through the uniform distribution. Note that, despite the fact that grains with large and small radii occur in equal numbers, the visual distribution is shifted towards the blue (i.e., larger) grains. This shift reflects the fact that it is much more likely that a random plane will intersect a large grain and illustrates how difficult it can be to obtain reliable grain-size information from image cross sections. Clearly, a fully three-dimensional analysis is required to describe the transport properties of such systems. Once the original packings were in place, the simplest GC algorithm, in which the radius of each grain was increased by the same amount, was used to generate a sequence of consolidated systems with lower porosities. (Clearly, there are a number of reasonable ways in which the growth rate for grains with different radii might be specified.) The connectivity of the pore space is maintained down to a percolation threshold which typically occurs at a porosity less than 5%.

To begin our discussion of transport in multisize packings, we consider the evaluation of the electrical conductivity. In previous work on disordered monosize packings, the pore space of the system was represented as a network formed from the edges of the Voronoi polyhedra.[5] While this method can be applied to any monosize sphere pack, it fails when the grain radii are not all equal because the edges of the Voronoi polyhedra are no longer

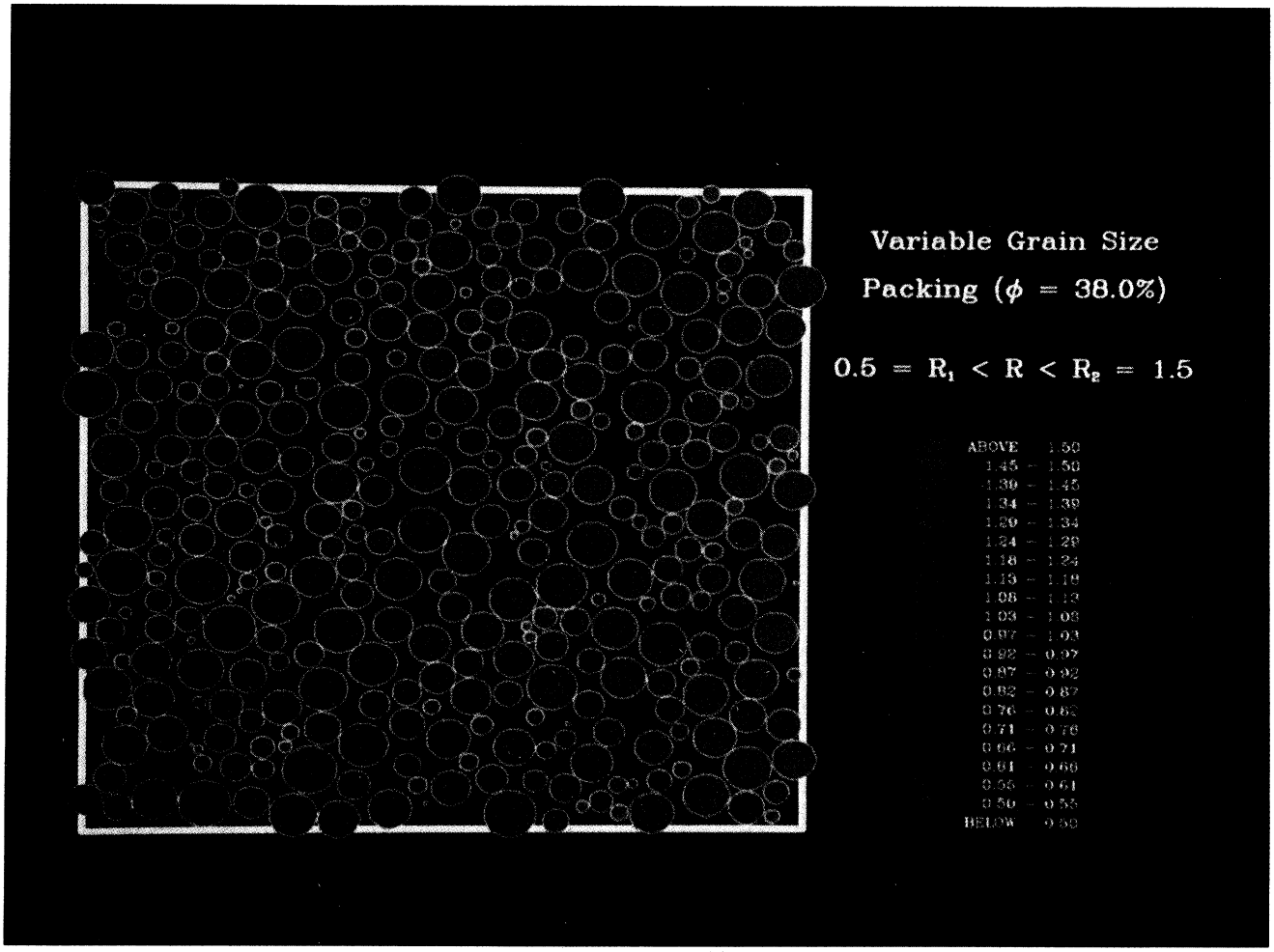


FIG. 1. Two-dimensional horizontal slice through the packing with a uniform distribution of sphere radii. The white border represents the box in the $xy$ plane within which the spheres are dropped. The length of the box edge is taken to be 40 times the average sphere radius.

related to the physically relevant pore-throat-pore network. Indeed, most theoretical work on mixed-grain-size composites is limited to setting bounds on their physical properties rather than dealing with explicit calculations.[14] We emphasize that a direct solution of Laplace's equation in such large systems is out of the question. [Since we are dealing with a model that is roughly 20 grains on a side, a fine mesh with of order $(2000)^3$ points would be needed to evaluate the electrostatic potential with reasonable accuracy; such a large network is well beyond the scope of relaxation, random-walk, or conjugate-gradient methods.] Accordingly, we have abandoned the notion of obtaining a complete solution of the electrostatics problem and have developed, instead, a method of calculating just $\sigma$. The key ideas are (1) that Einstein's relation,

$$\sigma \propto D\phi \ , \tag{1}$$

provides a link between $\sigma$ and the diffusion coefficient $D$; and (2) that the evaluation of $D$ can be achieved by Monte Carlo simulation, even in relatively large systems. The essential point is that in this approach one does *not* keep track of the potential at each of a large number of mesh points; the penalty, of course, is that the calculation yields only $\sigma$ and *not* the associated electric fields. (An analogous situation exists in the description of viscous-fingering interfaces at infinite viscosity ratio; here the results of the gradient-governed growth model, which requires a complete solution of the Laplace equation for the pressure field, can be duplicated by the more efficient diffusion-limited aggregation algorithm.[15]) We estimate $D$ numerically by simulating a random walk with what are referred to as *blind* boundary conditions at the pore-grain interface.[10] Random starting locations for the walker are specified using a Monte Carlo algorithm. Only starting locations within the pore space are retained and provide a measure of the porosity. With a step size chosen to be roughly one 100th of an average grain diameter, the walker steps randomly within the pore space in one of six directions $(\pm x, \pm y, \pm z)$ at every time increment. A step which would take the walker into a grain is not carried out (i.e., the walker is returned to the attempt position); however, the clock is allowed to advance by one time step. The mean-square distance traveled by the walkers is monitored as a function of time to determine $D$. Physically, we expect that a typical walker would have to go through several links in the pore-throat-pore network (i.e., travel a distance of order several grain diameters) to properly simulate electrical conduction. In practice this may require up to 300 000 time steps in low-porosity samples.[16] We have considered the effects of varying the step size and have employed several thousand independent walkers to insure statistical accuracy. We have confirmed that, for the ordered simple-cubic GC model, our diffusion algorithm yields values of the formation factor $F(\phi)$ that are in excellent agreement with those determined by finite-difference methods.[5] ($F$ is defined as the ratio $F \equiv \sigma_f/\sigma$, where $\sigma_f$ is the conductivity of the pore fluid; in the present context, $\sigma_f$ is just the free space limit of $D$.) The error bars on $F$, defined by the usual statistical measures, are about $\pm 10\%$. In Fig. 2 we compare the calculated values of $F$ for the three packings described above. Interestingly, we see that the different grain-size distributions lead to very similar $F$ vs $\phi$ relations. The implication here is that, in some average sense, the tortuosity of the pore space must be independent of the details of the original packing, at least within the range of parameters considered here. In Fig. 3 our calculations on the binary packing are compared with the experimental results of Guyon *et al.*[6] The level of agreement between theory and experiment is seen to be quite satisfactory.

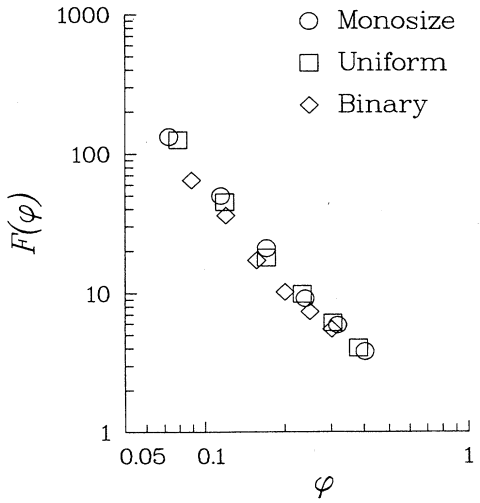


FIG. 2. Calculated electrical formation factors are compared for the three packings.

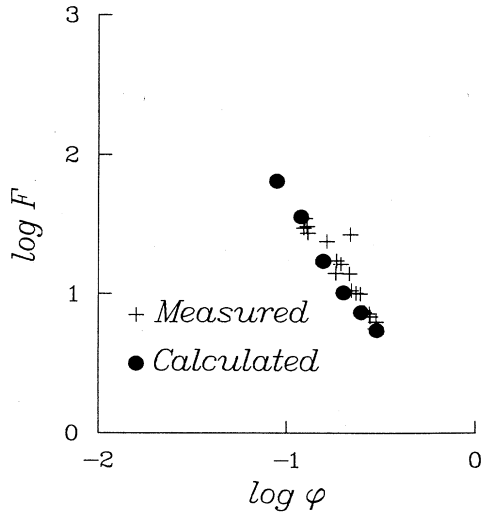


FIG. 3. Calculated electrical formation factors for the binary packing are compared with the experimental results of Guyon *et al.* (Ref. 6).

The multisize granular composites, heretofore described are, on the average, isotropic. The method we have described, however, can easily be applied to anisotropic systems (e.g., catalytic beds, clay sediments, and shale lenses). To illustrate the feasibility of such calculations, a model system can be generated by beginning with the original monosized packing and uniformly compressing the $z$ coordinate axis by a factor of $\alpha$ (Fig. 4). This transformation takes the original grains into oblate spheroids. Clearly, in such a system the flow of electrical current along the vertical $z$ axis will be significantly more difficult than within the horizontal plane. We emphasize that, to our knowledge, the conductivity of this system *cannot* be calculated by a simple rescaling of the results for the original isotropic composite. Once again, however, the physics is faithfully represented by following the trajectories of random walkers. In Fig. 5 the vertical and horizontal formation factors are plotted as a function of the compression factor $\alpha$. Interestingly, the value of $F_{xy}$ decreases slightly as the grains change shape. This reflects the fact that the particular algorithm used to generate this system allows for less restricted motion in the horizontal plane as the grains are elongated. From an experimental viewpoint, a more easily realized anisotropic composite can be generated by the application of uniaxial pressure to a system of compressible spherical grains. McLachlan *et al.*[8] have made electrical measurements on such systems, beginning with a binary distribution of grain radii. Unfortunately, it is difficult to get any precise information about the shapes of either the distorted grains or the interstitial pores. Accordingly, we suggest modeling this system by a two-stage extension of the GC process: (1) Beginning with an isotropic, unconsolidated sphere pack with the appropriate distribution of grain radii, the $z$ (pressure) axis is compressed by an amount $\alpha$, and (2) the resulting spheroidal grains are then consolidated by allowing growth along the $x$, $y$, and $z$ axes that restores the volume lost in the original compression. Thus a sphere of radius $R$, centered at $x_0,y_0,z_0$ is replaced by the spheroid

$$\alpha^{2/3}(x-x_0)^2+\alpha^{2/3}(y-y_0)^2+\alpha^{-4/3}(z-\alpha z_0)^2=R^2 . \quad (2)$$

While this transformation is certainly *ad hoc*, it provides a simple one-parameter family of anisotropic systems (i.e., there is a direct relation between $\alpha$ and the porosity $\phi$) and it realistically allows for consolidation along all three principal directions. In Fig. 6 calculations based on the random-walk method are compared with the data

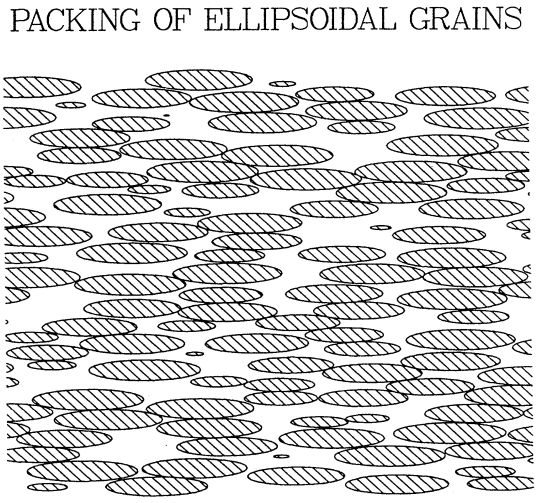


FIG. 4. A vertical slice through an unconsolidated packing of spheroids generated by a $z$ axis shrinking with $\alpha=0.2$.

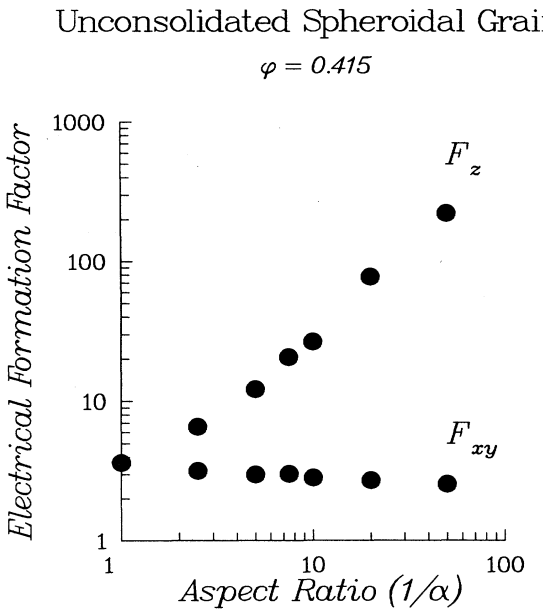


FIG. 5. Calculated horizontal and vertical formation factors for unconsolidated packings of the kind shown in Fig. 4.

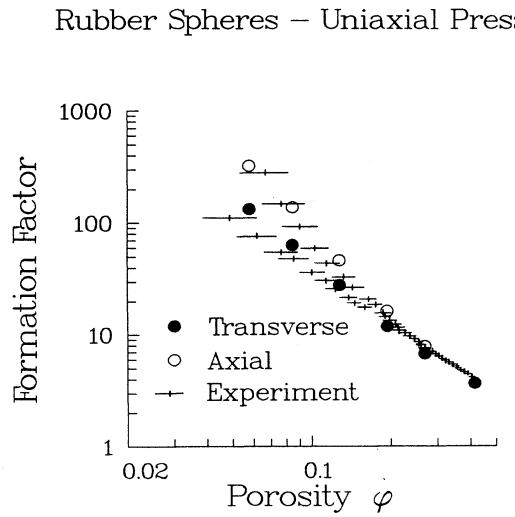


FIG. 6. Calculated horizontal (transverse) and vertical (axial) formation factors are compared with the experimental results of McLachlan *et al.* (Ref. 8).

presented in Ref. 8 and the agreement is seen to be quite satisfactory.

### B. dc permeability

Let us return to our discussion of the multisize composites. The formation factor is a *dimensionless* transport coefficient. By contrast, the permeability $k$ has the dimensions of area. Physically the value of $k$ may be thought of as the cross-sectional area of the effective pore channel for flow of a viscous fluid. What are the different length scales that characterize the granular composites of interest here? The simplest is the ratio $V_p/S$ of the pore volume-to-surface area. In general, however, $V_p/S$ includes contributions from dead ends and isolated regions of the pore space, and its relation to fluid permeability is, at best, indirect. Recently, it has been shown that a length directly relevant to transport in porous media is given by a parameter $\Lambda$ which may be viewed as a dynamically weighted version of $V_p/S$.[11] Within the framework of the uniform-growth GC model, $\Lambda$ may be calculated as

$$\frac{2}{\Lambda} = -\frac{S}{V_p}\frac{d\ln F}{d\ln\phi} . \tag{3}$$

The logarithmic derivative in this equation is easily calculated by making a least-squares quadratic fit to our calculated values of $F$. $V_p/S$ can be computed by counting the number of intersections of the pore-grain interface per unit length $I_L$ of randomly oriented straight-line segments drawn through the porous medium and using the standard stereological identity:[17] $\phi/(2I_L)=V_p/S$. In Fig. 7 we compare the calculated values of $S/V_p$ for the three packings. The three packings yield different values of the $S/V_p$ ratio even though the mean sphere radius for all three distributions is the same. Once the value of $\Lambda$ is known, the permeability can be estimated from the relation[11]

$$k \approx \frac{\Lambda^2}{4F} . \tag{4}$$

This approximation has been shown to work well in monosized granular composites[18] and is conjectured to hold for a wide class of porous media. In Fig. 8 we compare the calculated permeabilities for the binary-grain-size composites with the experimental values of Guyon *et al.*[6] Here again the level of agreement is excellent.

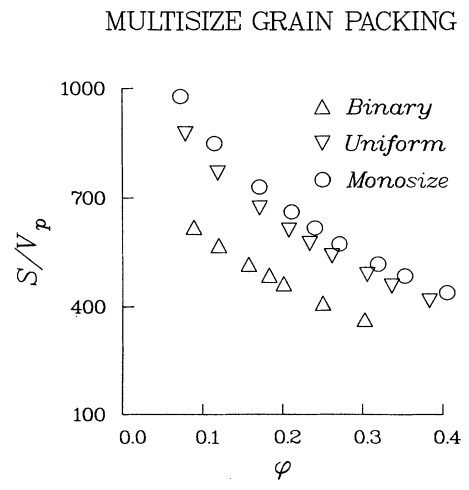


FIG. 7. Surface-to-pore-volume ratio calculated for three disordered packings. $S/V_p$ is given in inverse centimeters.

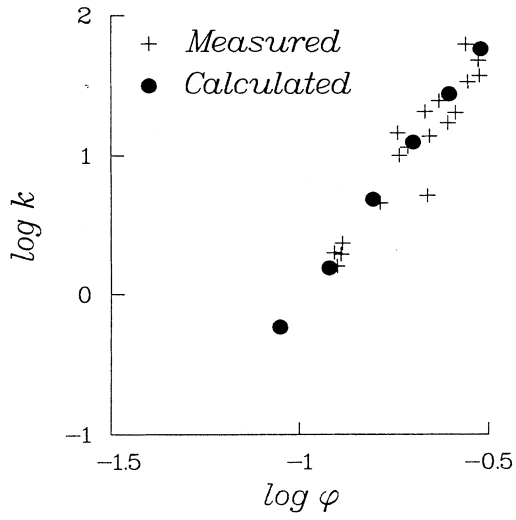


FIG. 8. Calculated permeabilities for binary packings are compared with the experimental results of Guyon *et al.* (Ref. 6). The values of $k$ are given in Darcies [$D=(\mu m)^2$].

### C. Magnetic resonance

We have also studied the relation between permeability and the NMR response of multisize granular systems. The lifetime $T_1$ in these systems can also be calculated by random-walk techniques.[12] The enhanced decay rate at the pore-grain interface is modeled by allowing the spin associated with each walker to decay at the grain boundary with probability $\gamma$. In the weak-killing regime ($\gamma\rightarrow 0$) the NMR relaxation time depends only on the $S/V_p$ ratio and the surface relaxation parameter, viz., $T_1 \sim V_p/(S\gamma)$. In the strong-killing limit ($\gamma\rightarrow 1$), the proton undergoes instantaneous relaxation at the pore-grain interface and the lifetime is controlled by the pore geometry and the diffusion coefficient of the water molecules. Calculations on the three isotropic packings are summarized in Fig. 9. These results cover a wide range of killing strengths ($\gamma=0\rightarrow\gamma=0.001$) and show that, for a given value of $\gamma$, there is an excellent correlation when the values of $k$ are cross plotted against $\phi^4 T_1^2$. (Here, again, we find that the calculations do not indicate a

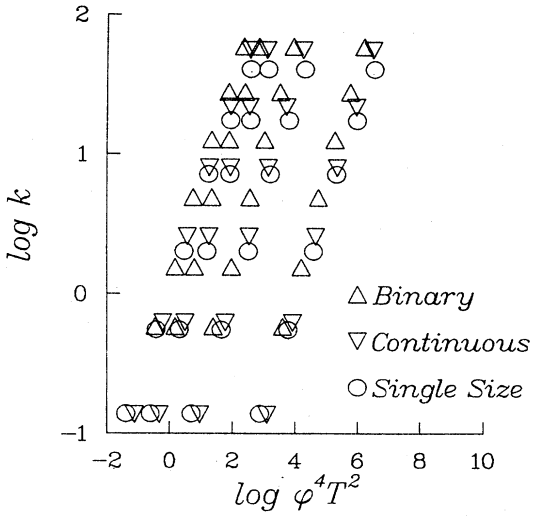


FIG. 9. Calculated NMR lifetimes and porosities are cross plotted against the estimated permeabilities for the three disordered packings. Proceeding from left to right, the four sets of data correspond to $\gamma=0$, $\gamma=0.1$, $\gamma=0.01$, and $\gamma=0.001$.

strong dependence on the grain-size distribution.) This correlation holds in both the strong- and weak-killing regimes and indicates that NMR provides a measure of the characteristic length scale relevant to the permeability of the granular composites. To our knowledge, there has not been a careful experimental study of the relation between NMR lifetimes and permeability in multisize granular composites. Such a study would be of great interest.

## III. CONCLUSIONS

We have shown that random-walk diffusion simulations can be used to describe the pore-space transport properties of complex granular composites. This approach can be applied to large model systems (typically, 10 000 grains) and yields results that are in good agreement with experimental data on sintered binary composites and anisotropic systems generated by uniaxial pressure. Regarding the dc fluid permeability, we find that estimates based on the $\Lambda$ parameter[11] are in excellent agreement with experiment. Our calculations also indicate that the permeability in multisize packings can be estimated from NMR $T_1$ measurements. We see a clear need for more experimental work on transport in anisotropic composites and on NMR in a variety of complex systems.

## ACKNOWLEDGMENTS

We thank W. Visscher and M. Bolsterli for providing a copy of their packing code. We are grateful to P.-z. Wong for stimulating discussions at the outset of this work. Conversations with E. Guyon, A. Kerstein, T. Plona, and D. Wilkinson are also appreciated.

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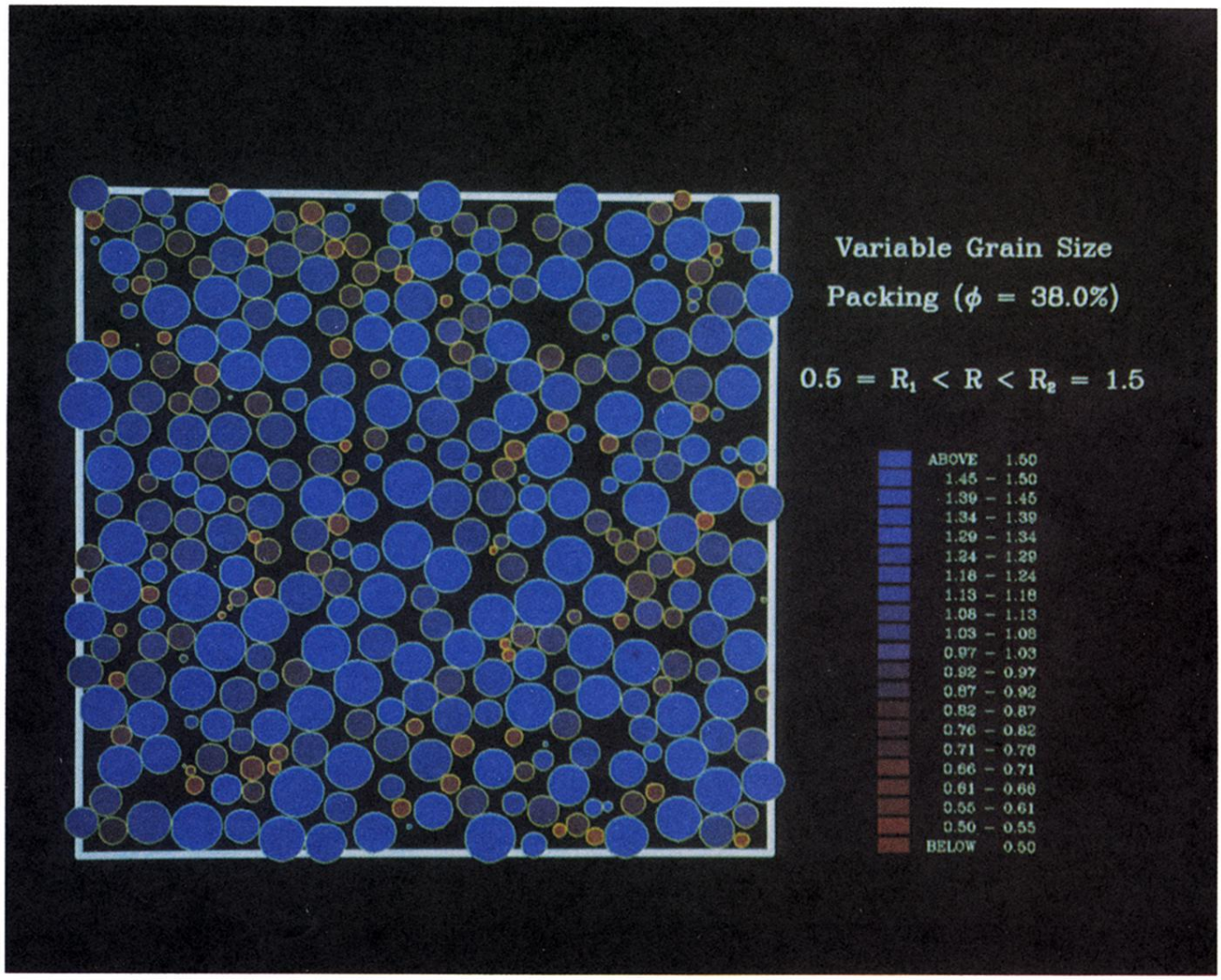


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