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N-63-4-3

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Effective Diffusion Coefficient in Porous Media *

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Recent calculations [S. Prager, AFOSR-2803 (June 1962)] of upper bounds for the effective diffusion coefficient (or conductivity) in porous media, in terms of certain statistical parameters of the random geometry, are reformulated so as to apply specifically to a bed of spherical particles. The calculations are simplified by considering an idealized bed in which centers are randomly situated without restricting the spheres to nonoverlapping locations. The result, applicable to randomly overlapping spheres of either uniform or nonuniform sizes, gives the upper bound for the effective diffusion coefficient as $\phi D_o/[1 - \frac{1}{2}\ln\phi]$, where D_o is the actual diffusion coefficient in a fluid which fills the void regions of the bed and ϕ is the void fraction. This result is compared with experimental results by various investigators for nonoverlapping spheres and also with the best upper bound that can be calculated without taking the statistics of a particular random geometry into account [Z. Hashin and S. Shtrikman, J. Appl. Phys. 33, 3125 (1962)].

1. INTRODUCTION

Attempts at estimating the extent to which the apparent diffusion coefficient is lowered when diffusion occurs in the open regions of a porous medium, and analogous calculations related to the thermal or electrical conductivity of inhomogeneous substances, are at least as old as the writings of Maxwell.[1] The purpose of the present work is to show how previous theoretical estimates can be improved by the utilization of statistical information about the random geometry of the medium.

Maxwell's formula[1] gives the electrical conductivity of a medium which contains a dilute suspension of spheres; as applied to nonconducting spheres the result, expressed in the terminology of our diffusion problem, is

$$D_e/D_o = \phi / [1 + \frac{1}{2}(1 - \phi)] \tag{1}$$

where ϕ is the volume fraction not occupied by spheres, D_o is the diffusion coefficient in the open space, and D_e is the effective diffusion coefficient defined as the ratio of average flux to average concentration gradient. It has recently been shown by Hashin and Shtrikman[2] that the right side of this equation, originally derived for $\phi \longrightarrow 1$, is an upper bound for D_e/D_o in an isotropic medium for <u>any</u> value of ϕ even when the solid portions of the medium are not spheres. Moreover these authors showed that this bound is the closest that can be obtained without providing additional statistical specification of the medium.

A method for introducing the required statistics has recently been presented by Prager[3] in terms of a variational formulation of the diffusion problem. His results are applicable to a very general class of isotropic porous media; however, the statistical data required for

such applications are not yet available. Therefore, in the present work, the variational approach is reformulated so as to apply specifically to a bed of spheres. It will be seen that the appropriate statistical specification can then be greatly simplified.

2. EFFECTIVE DIFFUSION COEFFICIENT

The bound on D_e/D_o, which is formulated in reference 3 in terms of a trial concentration fluctuation c', is equivalent to the following inequality in terms of a trial concentration c:

$$\frac{D_e}{D_o} < \frac{\langle g(\mathbf{r})\,[\nabla c(\mathbf{r})]^2\rangle}{\langle \nabla c\rangle^2}\,, \tag{2}$$

where $g(\mathbf{r})$ is a random function of the position vector $\mathbf{r}$, defined to have the value zero in the solid regions and unity in the void regions of the porous medium. The angular brackets denote an average taken over a volume V which is large in comparison to the scale of the inhomogeneties of the medium. For example, the "porosity" or void fraction ϕ is given by

$$\phi = \langle g(\mathbf{r})\rangle \equiv (1/V)\int g(\mathbf{r})\,d\mathbf{r}\,. \tag{3}$$

2.1 Trial Function for a Bed of Spheres

The trial concentration gradient which is now used in Eq. (2) involves a sum of contributions from each sphere center, the ith center being located at the position $\mathbf{r}_i$. To this sum is added a constant vector $\mathbf{A}$ in the direction of the average concentration gradient $\langle\nabla c\rangle$. Thus

$$\nabla c(\mathbf{r}) = \mathbf{A} + m\sum_i \nabla f(\boldsymbol{\rho}_i) \tag{4a}$$

where $\boldsymbol{\rho}_i \equiv \mathbf{r} - \mathbf{r}_i$ and, for spheres of radius a

$$f(\rho) = \begin{cases} A \cdot \rho / \rho^3, & \rho > a \\ A \cdot \rho / a^3, & \rho < a. \end{cases} \tag{4b}$$

This form of the contribution from each center is suggested by the solution of the diffusion problem in which the obstruction is a single isolated sphere;[1] its use here insures that the upper bound for D_e becomes exact as ϕ approaches unity.

The scalar multiplier m in Eq. (4a) is to be adjusted so as to minimize the right side of Eq. (2) when substitution is made for ∇c from (4). The result of this substitution, after some reduction involving use of Eq. (3), can be written as

$$\frac{D_e}{D_o} < \frac{\phi A^2 + m^2 \left\langle g(\mathbf{r}) \left[\sum_i \nabla f(\rho_i)\right]^2 \right\rangle}{(1 + (4/3)\pi\, n\, m)^2} \tag{5}$$

where n is the average density of sphere centers.

The optimum value of m, obtained by differentiating the right side of Eq. (5) with respect to m, is

$$m = \frac{4\pi n \phi A^2}{3 \left\langle g(\mathbf{r}) \left[\sum_i \nabla f(\rho_i)\right]^2 \right\rangle} .$$

Expanding the squared sum in the denominator and substituting the resulting expression for m into Eq. (5) gives

$$D_e / D_o < \phi / q \tag{6a}$$

where

$$q = 1 + \frac{16\, \pi^2\, n^2\, \phi\, A^2 / 9}{\sum_i \left\langle g(\mathbf{r}) [\nabla f(\rho_i)]^2 \right\rangle + \sum_i \sum_{\substack{j \\ i \neq j}} \left\langle g(\mathbf{r}) \nabla f(\rho_i) \cdot \nabla f(\rho_j) \right\rangle} \tag{6b}$$

The parameter q is related to a "tortuosity factor" which has been discussed by Carman[4] and others.

2.2 Simplification of the Random Geometry

It is in the evaluation of the summations over sphere centers and over pairs of centers, which appear in Eq. (6b), that the statistical properties of the bed of spheres must be considered. In this connection, one naturally thinks of a bed in which each center is at least one diameter from its neighbors, but the evaluation of the pertinent sums is then far from simple. However, it is possible, at least conceptually, to produce a bed of spheres for which the calculations are greatly simplified; this is achieved by removing the constraint on the locations of centers.[5]

Thus, if centers are distributed at random, regardless of interpenetration of spheres, then the coordinates $\underset{\sim}{\rho}_i$ and $\underset{\sim}{\rho}_j$ of the members of an ij pair of centers in Eq. (6b) are completely uncorrelated and it is seen from the form, Eq. (4b), of $f(\underset{\sim}{\rho}_i)$ and $f(\underset{\sim}{\rho}_j)$ that the double sum in (6b) vanishes.

The single sum in Eq. (6b) is also readily evaluated when the spheres are allowed to overlap; for then the probability that a random point is in a void region, even though the point is known to be in the vicinity of the ith center, is simply ϕ for all $\underset{\sim}{\rho}_i > a$. Thus, when Eq. (4b) is used for $f(\underset{\sim}{\rho}_i)$, the single summation over, say, N spheres can be expressed as

$$\sum_{i=1}^{N} \left\langle g(\underset{\sim}{r}) \left[\nabla f(\underset{\sim}{\rho}_i)\right]^2 \right\rangle = n\phi \int_{\rho > a} \left[\frac{\underset{\sim}{A}}{\rho^3} - \frac{3(\underset{\sim}{A}\cdot\underset{\sim}{\rho})\underset{\sim}{\rho}}{\rho^5} \right]^2 d\underset{\sim}{\rho} = \frac{8\pi n\phi A^2}{3a^3}. \quad (7)$$

To eliminate n and a from the final result, we note that

$$\phi = \exp(-4\pi a^3 n/3); \quad (8)$$

this expression for the void fraction of a bed of randomly overlapping spheres is derived in the Appendix along with certain other interesting statistical properties of this kind of porous medium.

Substitution of Eq. (7) in (6b) and then using (8) gives

$$q_1 = 1 - \frac{1}{2}\ln\phi \tag{9a}$$

2.3 Nonuniform Spheres

Although Eq. (9a) was derived for a bed of uniform spheres, it is interesting to note that the same result is obtained when the bed contains overlapping spheres of several sizes. The generalized derivation is a straightforward repetition of the procedure used above for uniform spheres; we need only mention here the form of the trial function and the expression for the void fraction.

The trial function which replaces Eq. (4) is

$$\nabla c(\mathbf{r}) = \mathbf{A} + m_1 \sum_i \nabla f_1(\boldsymbol{\rho}_i) + m_2 \sum_i \nabla f_2(\boldsymbol{\rho}_i) + \cdots \tag{10a}$$

where

$$f_j(\boldsymbol{\rho}) \equiv \begin{Bmatrix} \mathbf{A} \cdot \boldsymbol{\rho}/\rho^3, & \rho > a_j \\ \mathbf{A} \cdot \boldsymbol{\rho}/a_j^3, & \rho < a_j \end{Bmatrix} \quad ; \; j = 1, 2, \cdots . \tag{10b}$$

Thus there is an adjustable multiplier m_j for each different sphere radius a_j.

The required expression for the void fraction, calculated by the same method as is described for uniform spheres in the Appendix, is

$$\phi = \exp\left[-(4\pi/3)\,(n_1 a_1^3 + n_2 a_2^3 + \cdots)\right], \tag{11}$$

where n_1, n_2, --- are the respective densities of sphere centers for the several sizes.

3. DISCUSSION OF RESULTS

The result given by Eq. (9a) may be compared with the corresponding expression for q from Maxwell's formula, Eq. (1):

$$q_m = 1 + \frac{1}{2}(1 - \phi). \tag{9b}$$

We note, for example, that for dilute beds ($\phi \longrightarrow 1$) the two expressions are identical to first order in $(1 - \phi)$. A graphical comparison of (9a) and (9b) is shown in Fig. 1.

The values q_1 and q_m may be regarded as estimates q of the true value q* defined such that $D_e/D_o \equiv \phi/q^*$. Then, from (6a), these estimates are rigorous lower bounds for q* and the previously cited theorem of Hashin and Shtrikman[2] asserts that q_m is the greatest lower bound that can be derived without considering statistical descriptions of the medium other than the void fraction. That a higher bound is indeed obtained when additional statistics are introduced is illustrated by the graph of q_1 vs. ϕ, shown as the upper curve in Fig. 1.

It is, of course, expected that use of sufficient statistical information would provide bounds on q* which are sufficiently close to furnish useful predictions of experimental results. Although the kind of sphere bed for which Eq. (9a) provides a rigorous bound would be difficult if not impossible to produce in the laboratory, it is nevertheless interesting to compare calculated values of q_1 with measured values of q* as obtained from more readily fabricated sphere beds in which centers are separated by at least one diameter. Such measured values by various investigators have been tabulated by Carman.[4] These results were obtained for various kinds of porous media among which were beds of uniform spheres and also mixtures of two and three different sphere sizes; the data for the nonuniform as well as uniform sphere beds are plotted in Fig. 1. This comparison of experimental data for nonoverlapping spheres with the theoretical estimate for overlapping spheres (upper curve) cannot, of course, be regarded as a valid test of the latter; it does provide, however, a good indication that the kind of rigorous

bounds calculated here can indeed furnish useful estimates of effective diffusion coefficients or conductivities.

ACKNOWLEDGEMENTS

The considerable contribution to this work made by Professor S. Prager in many conversations with the author is gratefully acknowledged.

APPENDIX: VOID FRACTION AND TWO- AND THREE-POINT CORRELATIONS FOR A BED OF OVERLAPPING SPHERES.

To obtain an expression for the void fraction ϕ in terms of the density of sphere centers n and the sphere radius a, we first calculate the probability of placing N centers at random in a large finite volume V in such a way that a smaller volume v contains no centers. Since each random placement of a center is independent of the positions of the other centers, this probability is $[(V-v)/V]^N = [1 - (nv/N)]^N$. As N is made larger and larger, holding n and v fixed, the probability P_v that the volume v contains no centers becomes

$$P_v = \lim_{N\to\infty} \left(1 - \frac{nv}{N}\right)^N = e^{-nv}. \tag{A1}$$

Now ϕ can be regarded as the probability that a random point is not contained by any sphere in the bed, or, equivalently, as the probability that the portion of the bed which lies within a distance a from the random point contains no centers. Hence ϕ is given by Eq. (A1) with $v = 4\pi a^3/3$, which is the result given in Eq. (8).

It is interesting to note that Eq. (A1) also provides an expression for the two-point correlation function $S(r)$ defined as the probability that two points separated by a distance r both lie in void regions. This or closely related functions have been used in the previously-cited calculation of diffusion in porous media[3] and in calculations of x-ray scattering in random media[6] and of viscous flow of fluids through porous media.[7,8] It can be obtained for a bed of overlapping spheres by setting v in Eq. (A1) equal to $V_{\perp\perp}(r)$ as defined in reference 8. The result is

$$S(r) = \begin{cases} \exp\left[-\frac{4\pi a^3 n}{3}\left(1 + \frac{3r}{4a} - \frac{r^3}{16a^3}\right)\right], & r < 2a \\ \exp\left[-\frac{8\pi a^3 n}{3}\right] & ; \; r > 2a \end{cases} \tag{A2}$$

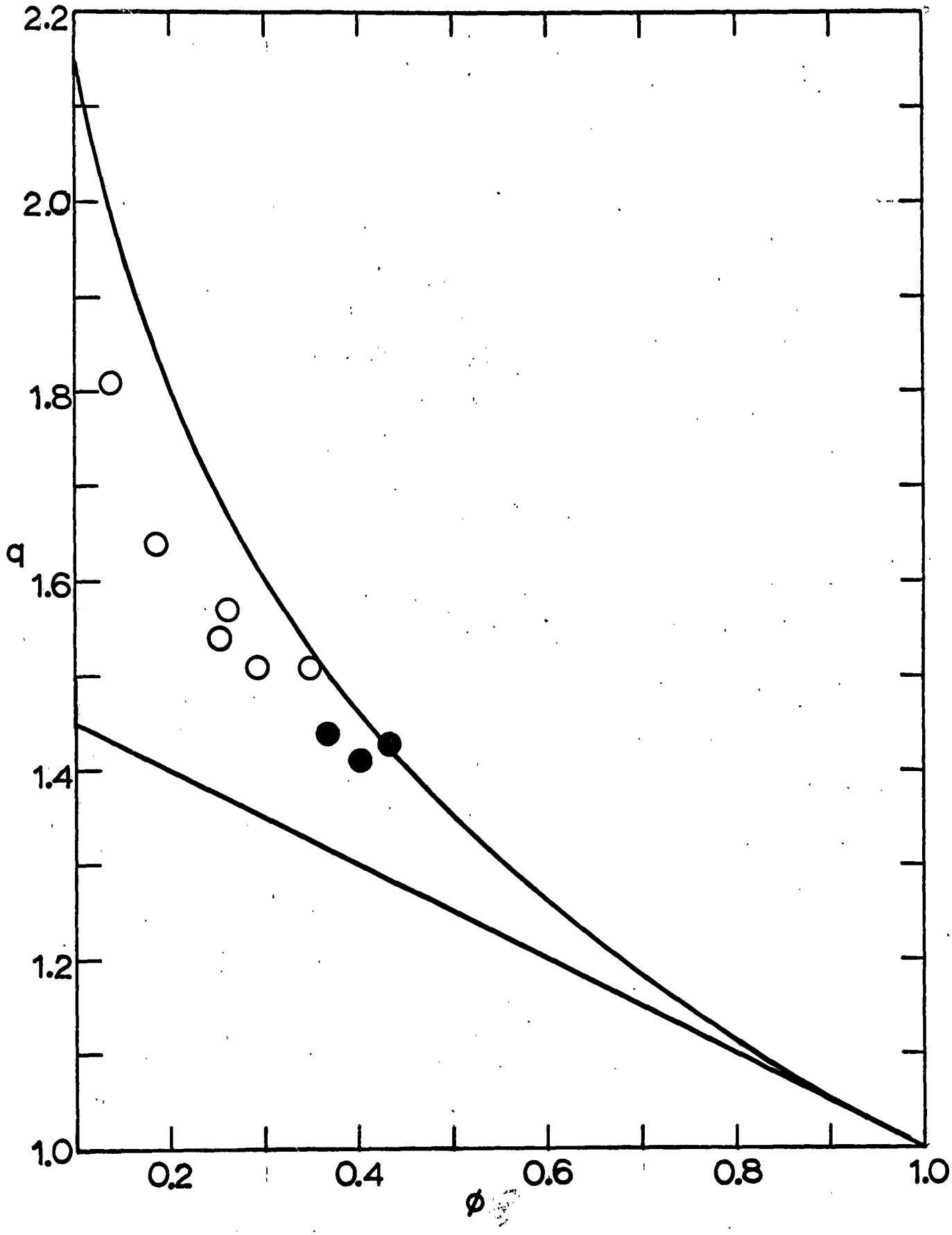
This form of the two-point correlation, since it is derived for a specified (albeit artificial) random geometry, may be preferable to the simpler exponential form discussed by Debye, Anderson, and Brumberger;[6] it is not certain whether there is any three-dimensional geometry which is consistent with the kind of randomness postulated by these authors.

The three-point correlation function $G(\mathbf{r}, \mathbf{r}')$ has also been used in previous calculations for porous media.[3,7,8] It is obtained by setting v in (A1) equal to $V_{\perp\perp}(\mathbf{r}, \mathbf{r}')$ as defined in reference 8. The latter quantity represents the volume enclosed by three spheres with centers at the vertices of a triangle with sides $\mathbf{r}$, $\mathbf{r}'$, and $\mathbf{r} - \mathbf{r}'$; the cumbersome expression for this volume, involving various forms for various kinds of $\mathbf{r}$, $\mathbf{r}'$ configurations, will not be repeated here.

FIGURE CAPTION

Fig. 1. Tortuosity parameter $q = \phi D_o / D_e$ vs. void fraction ϕ for a bed of overlapping spheres. Upper curve - eq. (9a), lower curve - eq. (9b). The plotted points represent experimental results for nonoverlapping spheres from reference 4: ● - bed of uniform spheres; O - mixtures of spheres of more than one size.

Both curves are theoretical lower bounds; the upper curve illustrates the improvement obtained by incorporating in the calculation a statistical description of the porous medium.



M. Weissberg Journal of Applied Physics Fig. 1

FOOTNOTES

* This work was done at the University of Minnesota under Air Force Office of Scientific Research Contract No. AF 49(638)-720 and under a Contract between the University and Union Carbide Nuclear Company.

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*** Operated by Union Carbide Nuclear Company for the U. S. Atomic Energy Commission.

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[5] The author is indebted to Professor W. F. Brown for this useful model.

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