Cross-property relations for momentum and diffusional transport in porous media

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Cross-property relations linking the fluid permeability k associated with viscous flow through a porous medium to effective diffusion properties of the medium have recently been derived. Torquato [Phys. Rev. Lett. **64**, 2644 (1990)] found that $k < D\phi_1\tau$, where τ is the "mean survival time" associated with steady-state diffusion of "reactants" in the fluid region of diffusion coefficient D and porosity ϕ_1 of a porous medium containing absorbing walls (i.e., trap boundaries). Subsequently, Avellaneda and Torquato [Phys. Fluids A **3**, 2529 (1991)] related k to the electrical formation factor F (inverse of the dimensionless effective electrical conductivity) and the principal (largest) diffusion relaxation time T_1 associated with the time-dependent trapping problem, namely, $k < DT_1/F$. In this study, we compute the aforementioned bounds, using an efficient first-passage-time algorithm, for grain-consolidation models of porous media and compare them to exact results for these models. We also conjecture a new relation connecting k to τ and F for a wide class of porous media, namely, $k < D\tau/F$, and show that it gives the sharpest permeability estimate among the existing bounds. The importance of this relation lies not only in its usefulness as an estimator of the permeability but that it involves the diffusional parameters τ and F which can be measured *in situ*.

I. INTRODUCTION

An intriguing fundamental as well as practical question in the study of heterogeneous materials is the following: Can different effective properties of the medium be *rigorously* linked to one another? Such cross-property relations become especially useful if one property is more easily measured than another property. In the context of transport in porous media, this question has been explored only very recently.[1–3]

The fluid permeability k of a porous medium, defined by Darcy's law,

$$\mathbf{U}(\mathbf{x}) = -\frac{k}{\mu}\nabla p_0(\mathbf{x}),\qquad(1)$$

governs the rate at which a viscous fluid flows through it. Here $\mathbf{U}(\mathbf{x})$ is the average fluid velocity, $\nabla p_0(\mathbf{x})$ is the applied pressure gradient, and μ is the dynamic viscosity. The permeability k, which has dimensions of (length),[2] depends upon the details of the pore geometry in a complex fashion, and, roughly speaking, may be regarded to be an effective cross-sectional area of pore "channels." Indirect measurements of the permeability are of great interest because it is often difficult to measure *in situ*. There are numerous relations which *approximately* relate k to other effective properties of the porous medium:[4–6] the most notable among them is an approximate relation due to Johnson *et al.*[6]

Torquato[1] derived the first rigorous relation connecting the permeability tensor to an effective diffusion parameter, namely, the mean survival time τ associated with steady-state diffusion of "reactants" in the fluid region of a porous medium containing perfectly absorbing pore walls (i.e., infinite surface rate constant κ). The scalar version of this expression, valid for arbitrary isotropic media, is given by

$$k < D\phi_1\tau,\qquad(2)$$

where D is the diffusion coefficient and ϕ_1 is the porosity. Relation (2) becomes an equality for transport interior to parallel tubes of arbitrary cross section (in the direction of the tubes). The bound (2) is relatively sharp for flow around dilute arrays of obstacles, e.g., for equi-sized spheres $k = 2D\phi_1\tau/3$. For a cubic array of narrow tubes it is less sharp: $k = D\phi_1\tau/3$. This last example is revealing in that it highlights the fact that the mean survival time τ can not distinguish between pore channels involving significant *momentum* transport from those involving little or no momentum transport. Moreover, for any *disconnected* pore space, k is zero while τ is nonzero, reflecting the fact that τ does not contain nontrivial topological information. Note that in the more general case of partially reflecting pore walls ($\kappa < \infty$), $\tau(\kappa) > \tau \equiv \tau(\infty)$, and hence one has the generally weaker inequality

$$k < D\phi_1\tau(\kappa).\qquad(3)$$

It is important to emphasize that τ can be obtained experimentally from nuclear magnetic resonance (NMR) measurements in fluid-saturated porous media.[7] This point is elaborated upon below.

More recently, Avellaneda and Torquato[3] derived the first rigorous relation connecting the permeability to the

effective electrical conductivity of the porous medium. For a porous medium with effective electrical conductivity σ_e containing a conducting fluid of conductivity σ_1 and an insulating solid phase, they found

$$k = \frac{L^2}{8F}, \qquad (4)$$

where F is the *formation factor* defined by

$$F = \frac{\sigma_1}{\sigma_e} \qquad (5)$$

and L is a length parameter which is a weighted sum over the *viscous relaxation times* Θ_n associated with the time-dependent Stokes equations (i.e., inversely proportional to the eigenvalues of the Stokes operator).[3] Relation (4) is exact. The parameter L, which interestingly reflects both information on momentum and electrical transport, was bounded from above in terms of the principal (largest) viscous relaxation time Θ_1:[3]

$$k < \frac{\nu \Theta_1}{F}, \qquad (6)$$

where ν is the kinematic viscosity. Avellaneda and Torquato also showed that

$$\nu \Theta_1 < D T_1, \qquad (7)$$

where T_1 is the principal (largest) *diffusion* relaxation time (see Sec. II) and hence, in light of (5), found

$$k < \frac{D T_1}{F}. \qquad (8)$$

In principle, T_1 can be obtained from NMR experiments. Thus, the permeability is related to purely diffusional parameters, i.e., T_1 and F, which are more easily measured than the viscous relaxation time Θ_1.

Let us compare bound (2) to bound (8). It was shown[3] that for flow through arrays of circular tubes of radius a the upper bound (8) gives

$$k < \frac{a^2 \phi_1}{5.784}, \qquad (9)$$

in contrast to (2), which is exact for this microgeometry. Moreover, for porous media characterized by a wide range of pore sizes, T_1 is substantially larger than τ (see Ref. 2) and relation (2) is expected to provide a better estimate of the permeability than (8). On the other hand, for porous media with a small and finite range of pore sizes and significant tortuosity, relation (8) should yield a sharper estimate of k than (2), especially at low porosities. This follows for two basic reasons: First, it is rigorously true that $F^{-1} < \phi_1$. Significant tortuosity results in an inverse formation factor that is considerably smaller than the porosity, especially at low porosities. Indeed, it is noteworthy that in contrast to formula (2), which is nonzero when the pore space is disconnected, formula (8) is identically zero, as it should be since $F^{-1} = 0$. Second, although it is rigor-

ously true that $T_1 \gg \tau$, it has been argued that T_1 will be of order of τ provided that there is a small and finite range of pore sizes.[2]

There are virtually no calculations of the relaxation time T_1 for nontrivial models of porous media. One of the aims of this paper will be to compute T_1 for grain-consolidation models and thus evaluate the bound (8) on the fluid permeability for such models. The bound (8) is then compared to bound (2) and another bound

$$k < \frac{D\tau}{F}, \qquad (10)$$

relating permeability, mean survival time, and formation factor, which we conjecture here to hold for a wide class of porous media. Relation (10), which is seen to be a hybridization of expressions (2) and (8), is shown to provide the sharpest upper bound on the permeability for this class of media. Relation (10) is not only appealing because it appears to provide a relatively sharp bound on k but because τ and F can be measured *in situ*: the former from an NMR measurement and the latter from an electrical resistivity measurement. Relation (10), which is sharper than either of the aforementioned bounds, is seen to be a hybridization of expressions (2) and (8).

In Sec. II we describe the basic equations for the time-dependent and steady-state diffusion problems and discuss the connection with NMR measurements. In Sec. III we calculate the principal relaxation time T_1 for grain-consolidation models for a wide range of porosities. For selected values of the porosity, we also determine the mean survival time τ for these models. In Sec. IV we compare the bounds (2) and (8) to exact results for the permeability k for the same models. We also propose the cross-property relation (10) and show that the bound is satisfied for a host of porous media. Finally, in Sec. V we make some concluding remarks.

II. BASIC EQUATIONS FOR THE RELAXATION AND MEAN SURVIVAL PROBLEMS

The random porous medium is a portion of space $\mathscr{V}(\omega) \in \mathbb{R}^3$ (where the realization ω is taken from a probability space Ω) of volume V, which is composed of two regions: the void (pore) region $\mathscr{V}_1(\omega)$ through which fluid is transported of volume fraction (porosity) ϕ_1, and a solid-phase region $\mathscr{V}_2(\omega)$ of volume fraction ϕ_2. Let V_i be the volume fraction of region $\mathscr{V}_i$, $V = V_1 + V_2$ be the total system volume, $\partial \mathscr{V}(\omega)$ be the surface between $\mathscr{V}_1$ and $\mathscr{V}_2$, and S be the total surface area of the interface $\partial \mathscr{V}$. The characteristic function of the pore region is defined by

$$I(\mathbf{r}, \omega) = \begin{cases} 1, & \mathbf{r} \in \mathscr{V}_1(\omega), \\ 0, & \mathbf{r} \in \mathscr{V}_2(\omega). \end{cases} \qquad (11)$$

The characteristic function of the pore-solid interface is defined by

$$M(\mathbf{r}, \omega) = |\nabla I(\mathbf{r}, \omega)|. \qquad (12)$$

For statistically homogeneous, but possibly anisotropic, media, the ensemble averages of (11) and (12) yield

$$\phi_1 = \langle I \rangle = \lim_{V_1, V \to \infty} \frac{V_1}{V}, \tag{13}$$

$$\sigma = \langle M \rangle = \lim_{S, V \to \infty} \frac{S}{V}, \tag{14}$$

which are, respectively, the porosity and specific surface. Here angular brackets denote ensemble averaging.

A. Time-dependent relaxation problem

The relaxation times associated with the decay of physical quantities such as the concentration field or nuclear magnetization density are related closely to the characteristic length scales of the pore of the fluid region. Let $c(\mathbf{r},t)$ generally denote the physical quantity of interest at local position $\mathbf{r}$ and time t, obeying the time-dependent diffusion equation

$$\frac{\partial c}{\partial t} = D \Delta c + c_0 \delta(t) \quad \text{in } \nu_1 \tag{15}$$

$$D \frac{\partial c}{\partial n} + \kappa c = 0 \quad \text{on } \partial \nu, \tag{16}$$

in the *finite* but *large* pore region ν_1. Here κ is the surface rate constant, Δ is the Laplacian operator, $\mathbf{n}$ is the unit outward normal from the pore region, c_0 is the initial constant field, and $\delta(t)$ is the Dirac delta function.[8]

The solution of (15) and (16) can be expressed as an expansion in orthonormal eigenfunctions $\{\Psi_n\}$:

$$\frac{c(\mathbf{r},t)}{c_0} = \sum_{n=1}^{\infty} a_n e^{-t/T_n} \Psi_n(\mathbf{r}), \tag{17}$$

where

$$\Delta \Psi_n = -\lambda_n \Psi_n \quad \text{in } \nu_1,$$

$$D \frac{\partial \Psi_n}{\partial n} + \kappa \Psi_n = 0 \quad \text{on } \partial \nu. \tag{18}$$

The diffusion relaxation times T_n are related to the eigenvalues λ_n by the simple relation

$$T_n = \frac{1}{D \lambda_n}. \tag{19}$$

At long times, the smallest eigenvalue λ_1 or principal relaxation time T_1 dominates. The initial condition and the normal mode expansion (17) give

$$\sum_{n=1}^{\infty} a_n \Psi_n(\mathbf{r}) = 1. \tag{20}$$

The eigenfunctions $\{\Psi_n\}$ are orthonormal such that

$$\frac{1}{V_1} \int_{\nu_1} \Psi_m(\mathbf{r}) \Psi_n(\mathbf{r}) d\mathbf{r} = \delta_{mn}, \tag{21}$$

and therefore the eigenfunction coefficients are given by

$$a_n = \frac{1}{V_1} \int_{\nu_1} \Psi_n(\mathbf{r}) d\mathbf{r}. \tag{22}$$

It is to be recalled that

$$V_1 = \phi_1 V \tag{23}$$

is the *total pore volume*. We also have, because the set $\{\Psi_n\}$ is complete, that

$$\sum_{n=1}^{\infty} a_n^2 = 1. \tag{24}$$

The survival probability $S(t)$ in terms of $c(\mathbf{r},t)$ is given by the relation

$$S(t) = \frac{1}{V_1} \int_{\nu_1} \frac{c(\mathbf{r},t)}{c_0} d\mathbf{r}. \tag{25}$$

This quantity gives the fraction of Brownian particles which survive until time t. Substitution of (17) into (25) gives

$$S(t) = \sum_{n=1}^{\infty} a_n^2 e^{-t/T_n}. \tag{26}$$

This relation will prove to be very useful to us in the subsequent section.

Ultimately, we will pass to the limit $V_1 \to \infty$, $V \to \infty$. In this limit, ergodicity enables us to equate ensemble and volume averages of some stochastic function $f(\mathbf{r})$ so that

$$\langle f \rangle = \lim_{V \to \infty} \frac{1}{V} \int f(\mathbf{r}) d\mathbf{r}.$$

Equations (17), (18) and (21) become, respectively,

$$\frac{1}{\phi_1} \langle \Psi_m(\mathbf{r}) \Psi_n(\mathbf{r}) \rangle = \delta_{mn}, \tag{27}$$

$$a_n = \frac{1}{\phi_1} \langle \Psi_n(\mathbf{r}) \rangle, \tag{28}$$

and

$$S(t) = \frac{1}{\phi_1} \left\langle \frac{c(\mathbf{r},t)}{c_0} \right\rangle. \tag{29}$$

B. Steady-state survival problem

A different but related diffusion problem is the one associated with steady-state diffusion of "reactants" among static, partially absorbing traps with a prescribed rate of production of the reactants. The average or mean survival time τ of a Brownian particle is given by[9]

$$\tau = \frac{\langle u \rangle}{\phi_1 D}, \tag{30}$$

where the scaled field u solves the equations

$$\Delta u = -1 \quad \text{in } \nu_1, \tag{31}$$

$$D \frac{\partial u}{\partial n} + \kappa u = 0 \quad \text{on } \partial V. \tag{32}$$

The mean survival time τ depends not only on D but on the surface rate constant κ.

We note that τ is related to the survival probability $S(t)$:

$$\tau = \int_0^\infty S(t)\,dt. \tag{33}$$

This relation is easily proven using the results of Ref. 2.

C. Relationship between relaxation and survival problems

Torquato and Avellaneda[2] showed that the relaxation times and the mean survival time are related to one another through the relation

$$\tau = \sum_{n=1}^\infty a_n^2 T_n, \tag{34}$$

which states that τ is a weighted sum over the relaxation times. Using this expression, Torquato and Avellaneda[2] easily proved that

$$\tau < T_1, \tag{35}$$

and thus related the mean survival time τ to the principal diffusion relaxation time T_1. This relation will also be useful to us later.

D. Connection to NMR measurements

It is important to emphasize that the problems described above have a direct connection to NMR measurements in fluid-saturated porous media.[7] The characteristic times involved in the decay of nuclear magnetism are related to the pore size because of enhanced relaxation at the pore-solid interface. The equations governing the decay of the magnetization density $m(\mathbf{r},t)$ are precisely Eqs. (15) and (16) with $c(\mathbf{r},t)$ and c_0 replaced by $m(\mathbf{r},t)$ and m_0, respectively. The dimensionless volume-integrated magnetization $M(t)/M_0$ ($M_0 = m_0 V_1$) is simply what we have referred to as the survival probability $S(t)$ given by relation (25), i.e.,

$$S(t) = \frac{M(t)}{M_0}. \tag{36}$$

The net magnetization $M(t)$ is usually the quantity of principal interest in an NMR experiment.

III. CALCULATION OF THE PRINCIPAL RELAXATION TIME T_1 OR SMALLEST EIGENVALUE λ_1 FOR GRAIN-CONSOLIDATED MODEL

A. Periodic grain-consolidated models

Consider a periodic lattice of spheres such as simple cubic (SC), body-centered cubic (BCC), or face-centered cubic (FCC). The grain consolidation (GC) model[10] is a trivial extension of these sphere lattices in that it allows the sphere radii to increase beyond the point of touching. The overlapping spheres then form a consolidated medium whose solid volume fraction ϕ_2 may increase up to unity, completely filling all space (or, equivalently, whose porosity may decrease down to zero). Thus in the GC model, the entire volume fraction range may be spanned, i.e., $0 < \phi_2 < 1$ or $0 < \phi_1 < 1$. The feature of overlapping particles beyond touching enables one to achieve two microstruc-
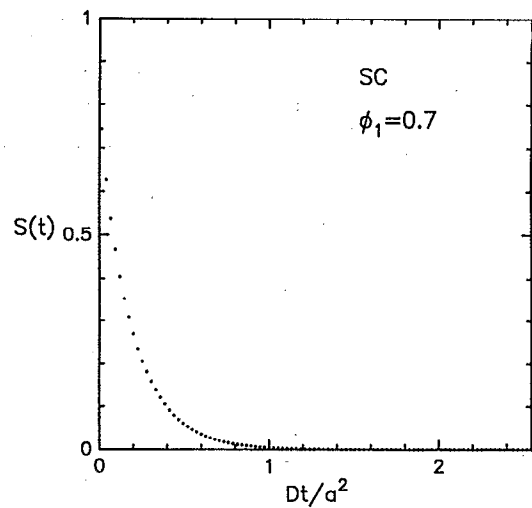

FIG. 1. The survival probability $S(t)$ vs the dimensionless time Dt/a^2 for the grain-consolidation model in the case of a simple-cubic (SC) lattice at a porosity $\phi_1 = 0.7$. The sphere radius is denoted by a. Note that $S(t)$ is equal to the dimensionless net magnetization $M(t)/M_0$ [cf. (36)].

tural aspects of realistic porous media that are absent in classical *unconsolidated* periodic arrays: (1) very low porosities (or very high solid volume fractions) and (2) bicontinuous phases. For a SC lattice, for example, the spheres touch at $\phi_1 = 1 - \pi/6 \approx 0.476$. Below this porosity the grains are consolidated but the pore space remains interconnected until a threshold is reached at $\phi_1^c \approx 0.0349$.

B. Calculation procedure

The principal relaxation time T_1 or smallest eigenvalue λ_1 has not been computed for the GC model for arbitrary porosity ϕ_1. For simplicity, we consider perfectly absorbing traps ($\kappa = \infty$) only. This is accomplished by determining the survival probability $S(t)$ [or, equivalently, the dimensionless net magnetization $M(t)/M_0$, cf. (36)] for large time t. According to relation (26), for large t, the survival probability has the asymptotic form

$$S(t) \sim e^{-t/T_1} \tag{37}$$

or, alternatively,

$$\ln S(t) \sim t/T_1. \tag{38}$$

Thus, the inverse of the slope of $\ln S(t)$ vs t yields T_1 for large t.

The survival probability $S(t)$ is determined using the efficient first-passage time algorithm of Torquato and Kim[11] used to compute the mean survival time τ. For a particular volume fraction, we employ a very large number of Brownian particles (up to 10^8) and record the fraction of them that survive up to time t. As an example, Fig. 1 shows a plot of $S(t)$ vs t for a SC lattice of spheres of radius a at a porosity $\phi_1 = 0.7$. For large t, we obtain T_1 from relation (38).

One of the objectives of this study is to compare the survival time bound (2) to the relaxation time bound (8). Felderhof[12] obtained τ exactly for unconsolidated lattices.

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TABLE I. Dimensionless relaxation time DT_1/a^2, and dimensionless mean survival time $D\tau/a^2$, for the grain-consolidation model in the case of simple-cubic lattice, as function of porosity ϕ_1. Results for T_1 are our simulation data. Results for τ for $\phi_1 \geq 0.5$ are obtained from Felderhof[a] and for $\phi_1 < 0.5$ are the simulation data of the present study.

ϕ_1	DT_1/a^2	$D\tau/a^2$
0.1	0.0193	0.0111
0.2	0.0274	0.0171
0.3	0.0405	0.0260
0.4	0.0574	0.0389
0.5	0.0821	0.0576
0.6	0.125	0.0910
0.7	0.198	0.161
0.8	0.387	0.338
0.9	1.127	1.041
0.99	21.432	21.131
0.997	84.474	83.479

[a]See Ref. 12.

For consolidated cases (low porosities), τ was computed and plotted by Kostek *et al.*[13] but for such low porosities it is difficult to accurately read their figure. Accordingly, we will calculate and tabulate here τ for the consolidated cases using the efficient first-passage-time algorithm.[11]

There are several ways that we can check our numerical determinations of the principal relaxation time T_1. First, in the dilute-sphere limit, one can compute T_1 exactly[14] according to the relation

$$T_1 = \frac{a^2}{3D\phi_2}[1 - 1.76\phi_2^{1/3} + O(\phi_2^{2/3})], \quad \phi_2 \ll 1. \quad (39)$$

This limit represents a severe test on the simulation technique because the Brownian particles can wander a substantial amount of time in the large void space before they are trapped. Second, the integral of $S(t)$ over time is the mean survival time τ [cf. (35)]. This calculation of τ can be compared to Felderhof's exact calculation for unconsolidated cubic lattices[12] and to our simulation data for the consolidated cases obtained here. Third, according to (35) the relaxation time T_1 must bound τ from above.

C. RESULTS

Tables I–III summarize our numerical determinations of T_1 for the GC models in the cases of SC, BCC, and FCC lattices, respectively. Included in the tables are correspond-

TABLE II. Dimensionless relaxation time DT_1/a^2, and dimensionless mean survival time $D\tau/a^2$, for the grain-consolidation model in the case of face-centered-cubic lattice, as function of porosity ϕ_1. Results for T_1 are our simulation data. Results for τ for $\phi_1 \geq 0.3$ are obtained from Felderhof[a] and for $\phi_1 = 0.1$ is the simulation datum of the present study.

ϕ_1	DT_1/a^2	$D\tau/a^2$
0.1	0.0134	0.00578
0.3	0.0277	0.0115
0.5	0.0534	0.0356
0.7	0.154	0.131
0.9	1.054	0.986

[a]See Ref. 12.

TABLE III. Dimensionless relaxation time DT_1/a^2, and dimensionless mean survival time $D\tau/a^2$, for the grain-consolidation model in the case of body-centered-cubic lattice, as function of porosity ϕ_1. Results for T_1 are our simulation data. Results for τ for $\phi_1 \geq 0.3$ are obtained from Felderhof[a] and for $\phi_1 = 0.1$ is the simulation datum of the present study.

ϕ_1	DT_1/a^2	$D\tau/a^2$
0.1	0.00345	0.00209
0.3	0.0147	0.0112
0.4	0.0249	0.0187
0.5	0.0451	0.0348
0.7	0.148	0.130
0.9	1.072	0.986

[a]See Ref. 12.

ing exact data for the mean survival time τ. Data for τ for unconsolidated and consolidated porosities are obtained from Felderhof[12] and the present study, respectively. For small sphere concentrations (high porosities), the data for the principal relaxation time T_1 are seen to be in excellent agreement with the results derived from the exact asymptotic expression (39). The integral of the survival probability (equal to τ) was found to be in very good agreement with data for τ. Finally, it is seen from the tables that T_1 and τ satisfy the bound (35). These three checks attest to the accuracy of our data for the relaxation time T_1. Figure 2 depicts the dimensionless time DT_1/a^2 versus porosity for the three GC lattices.

IV. COMPARISON OF RIGOROUS PERMEABILITY BOUNDS AND A NEW RELATION CONNECTING k TO τ AND F

Using the results of the previous section and data for the formation factor,[10] we compare the survival time bound (2) to the relaxation time bound (8) for the GC models. It is convenient to restate these bounds here:
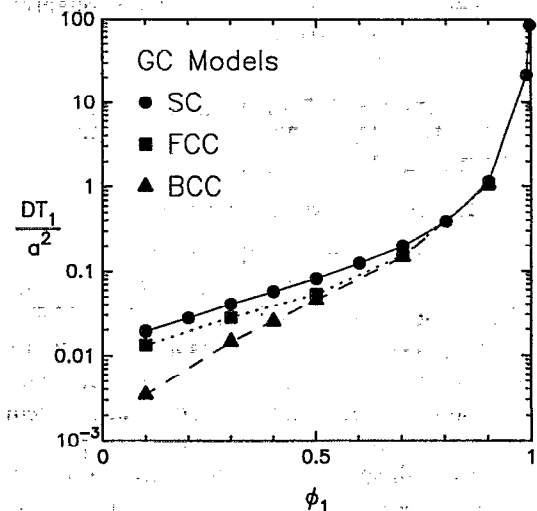
$$k \leq D\phi_1\tau, \quad (40)$$

FIG. 2. The dimensionless principal relaxation time DT_1/a^2 vs porosity ϕ_1 for the GC models in the case of a simple-cubic (SC) and face-centered-cubic (FCC) lattices. The sphere radius is denoted by a.
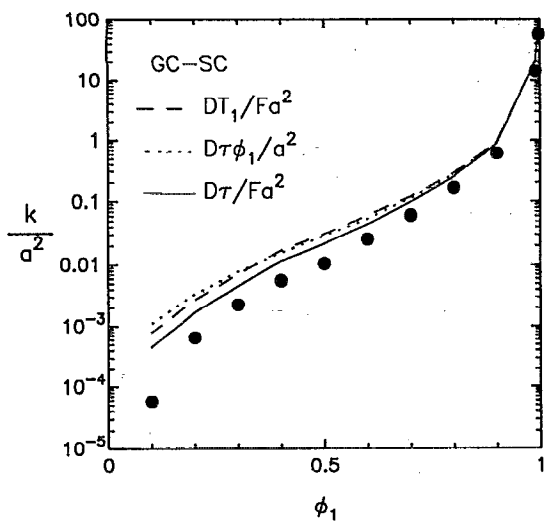
FIG. 3. The dimensionless permeability k/a^2 vs porosity ϕ_1 for the GC model in the case of a SC lattice. The black circles are the permeability data of Refs. 15 and 16, dashed line is the upper bound (41), dotted line is the upper bound (40), and the solid line is the relation (43). The sphere radius is denoted by a.

$$k < \frac{DT_1}{F}. \qquad (41)$$

Figures 3–5 compare these bounds to the exact data of k/a^2 obtained from Sangani and Acrivos[15] for the unconsolidated porosities and from Larson and Higdon[16] for the consolidated porosities. For a wide range of porosities, provided that ϕ_1 is not small, the survival time bound (39) is sharper than the relaxation-time bound (41). For low porosities, however, the converse is true. Thus, even though $\tau < T_1$, F^{-1} becomes appreciably smaller than the porosity ϕ_1 at small porosities, consistent with expectations given in the Introduction. Both bounds are sharp at high porosities but become progressively worse as the porosity is decreased.
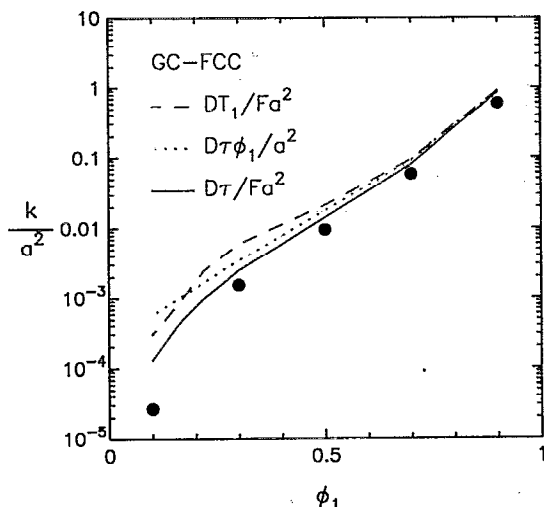

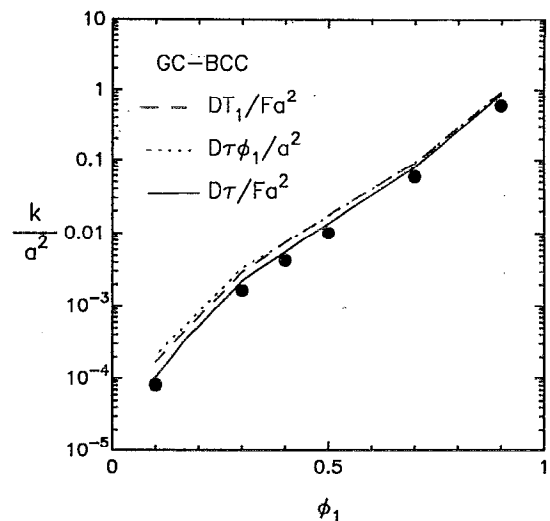FIG. 4. As in Fig. 3, except for the GC model in the case of a FCC lattice.

FIG. 5. As in Fig. 3, except for the GC model in the case of a BCC lattice.

As noted earlier, bound (41) will be a substantially poorer estimator of the permeability than bound (40) for porous media characterized by a wide range of pore sizes, because $T_1 \gg \tau$ in such instances. An example of such a porous medium is a solid phase composed of a Poisson distribution of spheres in a large but finite box.[2] Thus, the GC models present bound (42) in a favorable light because the range of pore sizes is limited by the lattice spacing.

Let us examine a little more closely the observation that both bounds (40) and (41) give poor estimates of k at low porosities. It is convenient to restate the exact relation[3] for the permeability involving the length parameter L:

$$k = \frac{L^2}{8F}. \qquad (42)$$

The appearance of F reflects tortuosity information about the pore topology. In the absence of tortuosity, e.g., flow in parallel tubes, F^{-1} is simply equal to the porosity ϕ_1. For general topologies, $F^{-1} \leqslant \phi_1$. The parameter L^2, roughly speaking, reflects information about the effective minimum "throat area" for the "dynamically connected" part of the pore region. For flow in a bundle of parallel, circular tubes of radius a, $L^2 = a^2$. Generally, L^2 depends upon the dynamically connected pore topology in a complex fashion. Bound (40) appreciably overestimates k at low porosities because ϕ_1 is appreciably greater than F^{-1} and τD overestimates $L^2/8$, for reasons already noted in the Introduction. Similarly, although bound (41) correctly reflects tortuosity information in that it contains the correct factor of F^{-1}, the quantity DT_1 grossly overestimates the effective minimum throat area associated with the dynamically connected pore topology, i.e., $DT_1 \gg L^2/8$ at small ϕ_1. On physical grounds, one expects that $D\tau$ would provide a considerably sharper upper bound on $L^2/8$.

We therefore conjecture that the fluid permeability k for a wide class of porous media is bounded from above in terms of the mean survival time τ and formation factor F according to the relation
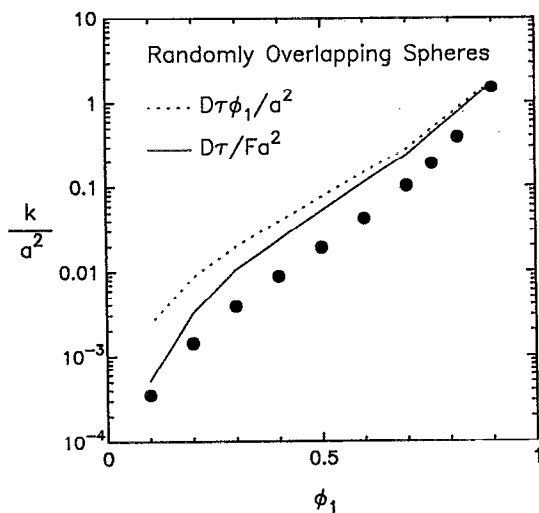
FIG. 6. The dimensionless permeability k/a^2 vs porosity ϕ_1 for randomly overlapping spheres of radius a. The black circles are the permeability data of Ref. 17, dotted line is the upper bound (40), and the solid line is the relation (43). Data for τ and F are obtained from Refs. 18 and 19, respectively. The sphere radius is denoted by a. The bound (41) involving the relaxation time T_1 is infinitely large for this model because of rare fluctuations characterized by infinitely large pores (Ref. 2) and hence is not shown.

$$k \leqslant \frac{D\tau}{F} . \tag{43}$$

This conjecture is motivated by several observations. First, for transport around dilute periodic arrays of spheres, the exact relations

$$\tau \sim \frac{a^2}{3D\phi_2}(1 - 1.76\phi_2^{1/3}), \tag{44}$$

$$F \sim 1 - \tfrac{3}{2}\phi_2, \tag{45}$$

$$k \sim \frac{2a^2}{9\phi_2}(1 - 1.76\phi_2^{1/3}), \tag{46}$$

have been derived. Therefore, since

$$\frac{D\tau}{F} \sim \frac{a^2}{3\phi_2}(1 - 1.76\phi_2^{1/3}), \tag{47}$$

the inequality (43) is obeyed. Second, for transport around dilute arrays of randomly arranged spheres, we have the exact results

$$k \sim \frac{2a^2}{9\phi_2}\left(1 - \frac{3}{\sqrt{2}}\phi_2^{1/2}\right), \tag{48}$$

$$\frac{D\tau}{F} \sim \frac{a^2}{3\phi_2}(1 - \sqrt{3}\phi_2^{1/2}). \tag{49}$$

The inequality (43) is again satisfied. Third, the bound is satisfied for all porosities in the GC models (see Figs. 3–5). Fourth, the bound (43) is satisfied for transport around fully penetrable spheres (i.e., Poisson distributed spheres). This is demonstrated in Fig. 6, where bound (43) is compared to bound (40) and simulation data[17] for this model. Here the data for survival time τ and formation factor F

are obtained from Refs. 18 and 19, respectively. Fifth, the bound (43) is obeyed for all of the two-dimensional models studied recently by Kostek et al.,[13] namely, the "tortuosity models" and "Koch curve models." Thus, there is considerable evidence to support the existence of bound (43) for a wide class of porous media. Identification of this class of media still must be determined, however (see discussion in Sec. V).

It is clear that because $F^{-1} \leqslant \phi_1$ and $\tau \leqslant T_1$, then the relation (43) for the permeability will always be below or equal to either bound (40) or (41). At low to moderate volume porosities, the bound (43) is seen to be substantially sharper than either bounds (40) or (41). Indeed, in the BCC case (cf. Fig. 5), relation (43) provides a relatively accurate estimate of the permeability.

V. CONCLUSIONS AND DISCUSSION

We have devised a methodology to compute the principal relaxation time T_1 in fluid-saturated porous media using first-passage-time techniques. The procedure has been specifically applied to determine T_1 for three grain-consolidation (GC) models. These results combined with data for the formation factor F enabled us to compute upper bound (41) for these geometries and to compare it to cross-property relations (40) and (43) and to "exact" permeability data. In all cases, relation (43) provided the best estimate of k and always lay above the permeability data. For moderate to large porosities, the survival-time bound (40) was found to be sharper than (41). However, for small ϕ_1, the converse is true. The GC models cast bound (41) in a favorable light because the range of pore sizes is limited by the lattice spacing. For porous media characterized by a wide range of pore sizes, such as randomly overlapping spheres, $T_1 \gg \tau$ and therefore bound (41) is a very poor estimator of the permeability (cf. Fig. 6).

In contrast to relation (43), expression (41) is a rigorous upper bound for any isotropic porous medium. The precise class of microgeometries for which (43) is a rigorous upper bound on k should be identified in future work. Insight into this question can be obtained by constructing models that violate the bound (43). For example, consider a porous medium comprised of a bundle of parallel circular tubes of radius R_T and porosity ϕ_T and isolated spheres of radius R_S and porosity ϕ_S, such that the total porosity $\phi_1 = \phi_S + \phi_T$.[20] Fluid is contained in both the tubes and spheres but can only flow in the tubes. For this highly idealized model, it is easy to compute all of the properties in (43) exactly, i.e.,

$$k = \frac{R_T^2 \phi T}{8}, \tag{50}$$

$$\frac{D\tau}{F} = \frac{\phi_T}{\phi_1}\left(\frac{R_T^2 \phi_T}{8} + \frac{R_S^2 \phi_S}{15}\right). \tag{51}$$

Thus, (43) is violated when $R_S/R_T \leqslant (15/8)^{1/2} \approx 1.369$. We conclude that (43) can be violated for porous media containing isolated pores and dead-end regions whose size

is on the order of or smaller than the *effective dynamic "channel" length L* which appears in the exact expression (42). Although such counterexamples are not common in practice, they clearly serve to offer insight into the wide class of porous media that indeed satisfy the bound.

In a future study we intend to examine the aforementioned cross-property relations for other model microstructures. There we will also compare them to the useful approximate relation

$$k \approx \frac{\Lambda^2}{8F},$$ (52)

obtained by Johnson, Koplik, and Schwartz.[6] Here Λ^2 is a dynamically weighted ratio V_1/S (pore volume to surface area) involving the electric field. The formula (52) provides a good estimate of k for a variety of media[6,21] and is usually superior to the well-known Kozeny–Carmen relation

$$k \approx \frac{\phi_1 (V_1/S)^2}{2},$$ (53)

which just involves the simple length scale V_1/S. We note in passing that in contrast to relations (40), (41), and (43), the formula (52) captures the correct critical behavior at the threshold where the pore space of the GC models become disconnected.[13,22] On the other hand, quantities such as the mean survival time τ appearing in both relations (40) and (43) or the principal relaxation time T_1 appearing in (41) are easier to measure than the parameter Λ in (52). Ease of measurement is a practically important point. If the quantities involved in an indirect measurement of the permeability are difficult to measure, then the cross-property relation loses its practical appeal even if it is an accurate expression. This explains why to this day the simple Kozeny–Carmen relation (53) is still employed by practicing scientists and engineers in spite of the fact that it is sometimes not very accurate.

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