Relationship between Permeability and Diffusion-Controlled Trapping Constant of Porous Media

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For anisotropic porous media of arbitrary topology, it is shown that there exists a rigorous relation between the fluid permeability tensor **k** and the diffusion-controlled trapping constant γ, namely, $\mathbf{k} \le \gamma^{-1}\mathbf{I}$. It is demonstrated that the equality is achieved for a certain class of microstructures and that the bound can be relatively sharp for other media. The important fundamental as well as practical implications of this relation are discussed.

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In the study of porous and composite media, expressions which relate one effective property of the medium to a different property have been long sought.[1-3] Two important properties of porous media which have received considerable attention are the trapping constant γ (associated with diffusion-controlled processes among static traps) and the fluid-permeability tensor **k** (see Refs. 3–7 and references therein).

In this Letter, a new expression rigorously relating the seemingly disparate properties **k** and γ of anisotropic porous media of general topology is proven. This is the first time that the permeability tensor **k** has been *rigorously* linked to another effective property for media of arbitrary topology. Specifically, it is shown that (1) $\mathbf{k} \le \gamma^{-1}\mathbf{I}$ (where **I** is the identity tensor); (2) the equality sign is achieved for a certain class of microstructures; and (3) the bound on one of the properties, given the other, can be relatively sharp for geometries which do not achieve the equality sign. The fundamental as well as practical implications of this relation are subsequently described.

Before discussing the relation between **k** and γ, it is first necessary to precisely define the effective properties. Consider the trapping problem first. Let $\mathcal{V}_1$ and $\mathcal{V}_2$ represent the trap-free and trap regions, respectively, and $\partial\mathcal{V}$ denote the surface between $\mathcal{V}_1$ and $\mathcal{V}_2$. Let ϕ_i denote the volume fraction of region $\mathcal{V}_i$. The reactant diffuses (with scalar diffusion coefficient D) in $\mathcal{V}_1$ but is instantly absorbed on contact with any trap. At steady state, the rate of production of the reactant (per unit trap-free volume) σ is exactly compensated by its removal by the traps. For *statistically anisotropic* media, it has been rigorously shown, using the method of homogenization,[5] that $\sigma = \gamma D C_0$, where C_0 is an average concentration field (per unit body volume),

$$\gamma^{-1} = \langle u \rangle , \tag{1}$$

and

$$\Delta u = -1 \text{ in } \mathcal{V}_1 , \quad u = 0 \text{ on } \partial\mathcal{V} . \tag{2}$$

The angular brackets of (1) denote an ensemble average. u is zero in $\mathcal{V}_2$. Note that the trapping constant γ is a scalar quantity even for statistically *anisotropic* media.[8] The trapping constant γ defined by (1) has dimensions of $(\text{length})^{-2}$. Using this definition of the trapping constant, $\gamma\phi_1 D$ is the *trapping rate* and, hence, $(\gamma\phi_1 D)^{-1}$ is the average *survival time* of a Brownian particle.[9]

For the case of slow viscous flow through *statistically anisotropic* porous media, Darcy's law $\mathbf{U} = \mu^{-1}\mathbf{k}\cdot\nabla p_0$ (where **U** is the average flow velocity, ∇p_0 is the applied pressure gradient, and μ is the viscosity) has been derived,[6] where the symmetric, second-rank fluid-permeability tensor is given by

$$\mathbf{k} = \langle \mathbf{w} \rangle , \tag{3}$$

and

$$\Delta \mathbf{w} = \nabla \boldsymbol{\pi} - \mathbf{I} \text{ in } \mathcal{V}_1 , \quad \nabla\cdot\mathbf{w} = 0 \text{ in } \mathcal{V}_1 , \quad \mathbf{w} = 0 \text{ on } \partial\mathcal{V} . \tag{4}$$

Here $\mathcal{V}_1$ and $\partial\mathcal{V}$ denote the fluid region and pore-solid interface, respectively; $\mathbf{w} = [w_{ij}]$ is the ith component of the velocity field due to a unit pressure gradient in the jth direction, equal to the null tensor in $\mathcal{V}_2$, and $\boldsymbol{\pi}$ is the associated scaled vector pressure field.[6] Both **w** and $\boldsymbol{\pi}$ are stationary random fields. The scaled tensor velocity field **w** is generally not symmetric. Note that **k** has the same dimensions as γ^{-1}, namely, $(\text{length})^2$. Forming the scalar product of **w** with the left- and right-hand sides of the first line of Eqs. (4) (momentum equation), and ensemble averaging, yields the following equivalent energy representation of the fluid-permeability tensor $\mathbf{k} = [k_{ij}]$:

$$k_{ij} = \left\langle \frac{\partial w_{li}}{\partial x_k} \frac{\partial w_{lj}}{\partial x_k} \right\rangle . \tag{5}$$

In deriving (5), one must integrate by parts the aforementioned averages[6] and use Gauss' divergence theorem. The resulting surface integrals will vanish because of the stationarity of $\mathbf{w}$ and $\boldsymbol{\pi}$. Note that (5) implies that the permeability tensor is both positive semidefinite and symmetric.

Proposition.— Given a statistically anisotropic porous medium of arbitrary topology having a fluid region or a trap-free region $\mathcal{V}_1$ of porosity ϕ_1, then

$$\mathbf{k} \le \gamma^{-1}\mathbf{I}\,; \tag{6}$$

i.e., the symmetric tensor which results by subtracting the fluid-permeability tensor $\mathbf{k}$ from the rotationally invariant inverse trapping-constant tensor $\gamma^{-1}\mathbf{I}$ is *positive semidefinite.*

The proof of the proposition is now sketched (details shall be given elsewhere[10]). First, introduce the auxiliary stationary and symmetric tensor field $\mathbf{v}$ defined by

$$\mathbf{v} = \mathbf{u} - \mathbf{w}\,, \tag{7}$$

where

$$\mathbf{u} = u\mathbf{I}\,. \tag{8}$$

Combination of (2), (4), (7), and (8) yields the governing equations for $\mathbf{v}$:

$$\begin{aligned} &\Delta\mathbf{v} = -\nabla\boldsymbol{\pi} \text{ in } \mathcal{V}_1\,,\\ &\nabla\cdot\mathbf{v} = \nabla\cdot\mathbf{u} \text{ in } \mathcal{V}_1\,,\\ &\mathbf{v} = 0 \text{ on } \partial\mathcal{V}\,. \end{aligned} \tag{9}$$

Forming the scalar product of $\mathbf{v}$ with the left- and right-hand sides of the first line of Eqs. (9), averaging, and integrating by parts, gives

$$\left\langle \frac{\partial v_{li}}{\partial x_k}\frac{\partial v_{lj}}{\partial x_k}\right\rangle = -\left\langle \pi_j \frac{\partial v_{li}}{\partial x_l}\right\rangle. \tag{10}$$

Utilizing the divergence condition of (9), the relation above becomes

$$\begin{aligned}\left\langle \frac{\partial v_{li}}{\partial x_k}\frac{\partial v_{lj}}{\partial x_k}\right\rangle &= -\left\langle \pi_j \frac{\partial u_{li}}{\partial x_l}\right\rangle\\ &= \left\langle u_{li}\frac{\partial \pi_j}{\partial x_l}\right\rangle. \end{aligned} \tag{11}$$

The second line of (11) follows by integrating the right-hand side of the first line by parts. Forming the scalar product of $\mathbf{u}$ with the left- and right-hand sides of the momentum equation in (4), ensemble averaging, and integrating by parts, gives

$$\begin{aligned}\left\langle u_{li}\frac{\partial \pi_j}{\partial x_l}\right\rangle &= \langle u_{ij}\rangle - \langle w_{ij}\rangle\\ &= \gamma^{-1}\delta_{ij} - k_{ij}\,. \end{aligned} \tag{12}$$

The second line of (12) follows from the definitions (3) and (8). Combination of (11) and (12) finally gives

$$\langle v_{ij}\rangle = \left\langle \frac{\partial v_{li}}{\partial x_k}\frac{\partial v_{lj}}{\partial x_k}\right\rangle = \gamma^{-1}\mathbf{I} - \mathbf{k}\,, \tag{13}$$

which states that $\langle\mathbf{v}\rangle$, given by (7), is positive semidefinite and thus proves proposition (6).

How sharp is the bound of proposition (6)? Are there microgeometries which achieve the equality sign of proposition (6)? Consider the second query first and assume, without loss of generality, that the coordinate frame is aligned with the principal axes of the medium. The equality sign is achieved whenever a principal component of (13) is zero. Thus, it is achieved for transport in *parallel channels* (in the x_3 direction) of constant cross section dispersed throughout a solid or trap region with porosity ϕ_1. For example, for identical channels of arbitrary cross-sectional shape in three dimensions, it is easily shown that one exactly has

$$k_{33} = \gamma^{-1} = \phi_1^3/cs^2\,, \tag{14}$$

where c is a shape-dependent constant (e.g., $c=2$ for circles, $c=\frac{5}{3}$ for equilateral triangles, and $c=1.78$ for squares), and s is the specific surface (interface area per unit volume). The part of (14) relating k_{33} to ϕ_1 and s is the well-known Kozeny equation which for flow in real *isotropic* porous media is a useful empirical relation ($c=5$ models many porous media well).[1] To my knowledge, however, relation (14) is new in the context of the trapping problem primarily because previous investigators usually considered modeling a dispersed or disconnected trap phase. Note that since there is no flow in the other principal directions for this anisotropic geometry, i.e., $k_{11}^{-1} = k_{22}^{-1} = \infty$, the bound of (6) is clearly satisfied for these diagonal elements. The observation that there are microstructures which achieve the equality sign of (6) is new and has important implications for stimulating flow through porous media. This point shall be elaborated upon shortly.

Let us now consider the question regarding the sharpness of the bound proposition (6) for media that do not achieve the equality sign. For general microstructures, this is a difficult question to answer since there are relatively few "exact" results for the permeability tensor and trapping constant for well-defined models. The preponderance of such exact results exist for macroscopically isotropic media in which proposition (6) simplifies as

$$k \le \gamma^{-1}\,. \tag{15}$$

Here k is defined by $\mathbf{k} = k\mathbf{I}$. Clearly, there are microstructures for which the bound (15) is not sharp. For example, for any microstructure with a completely disconnected pore space, k is zero while γ is nonzero, so that $k\gamma = 0$. Less trivially, for any cubic array of narrow tubes, it is easy to see that $k = \gamma^{-1}/3$. For the case of flow and diffusion exterior to isotropic distributions of spheres, the bound (15) is substantially sharper. For example, for a dilute bed of spheres, $k = 2\gamma^{-1}/3$. Existing analytical results for random distributions of spheres[11] and for periodic arrays of spheres[12] demonstrate that bound (15) is relatively sharp for low to moderate values of ϕ_2. For high values of ϕ_2, bound (15) is not sharp, at least in the case of periodic arrays for which we have exact results. However, in the special case of transport in beds of particles, a more restrictive bound[13] [closely related to (15)] can be obtained which is sharper than the best available "direct" variational bounds on either k or γ.[5-7] Given exact data for the trapping constant γ of random porous media composed of spheres with a variable degree of penetrability and a polydispersivity in size recently obtained using Brownian-motion simulation techniques,[14-17] one can now use these data in conjunction with result (15) to bound the fluid permeability for such models.

The relationship between the permeability tensor **k** and the trapping constant γ is much deeper than anyone previously thought. The fact that proposition (6) exists suggests that techniques used to solve the scalar trapping-constant problem may be employed, with some modification, to solve for the tensor fluid-permeability problem. Indeed, for the aforementioned parallel-channel geometries, the trapping problem is isomorphic to the flow problem (in the direction of the channels). For such microstructures, the mean-square displacement of a *diffusion* tracer before trapping yields not only γ but k_{33} and hence the diffusion tracer is equivalent to a "momentum" tracer. The inequality of proposition (6) suggests that a momentum tracer may still exist to yield **k** for general microstructures but would not be identical to the diffusion tracer in the trapping problem. The formulation of the permeability problem in terms of a tracer of momentum would represent not only an important breakthrough theoretically but computationally, especially in light of the recent dramatic improvement in the computational speed in obtaining γ using Brownian-motion simulation techniques.[16]

Finally, it is useful to comment on the relationship between the present work and the recent experimental correlation which relates the permeability to the nuclear-magnetic-resonance (NMR) relaxation time of porous media.[18] In the latter problem, the magnetic moment per unit volume **M** satisfies a time-dependent diffusion equation with a more complicated boundary condition than that of (2). However, for very large *bulk* relaxation times and in the "strong-killing limit," the magnetic problem becomes a diffusion-controlled process. Thus, under such conditions the magnetic problem and the one described by (2) are very similar except for the fact that the former is a *time-dependent* process and the latter is a *steady-state* process. Nonetheless, it may prove fruitful to reexamine the correlation of the permeability and the NMR response of a porous medium in light of proposition (6) (or some variant of it) since a rigorous explanation of such correlations may follow.

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[8] It is important to distinguish between *macroscopic* anisotropy and *statistical* anisotropy for two-phase media composed of isotropic phases. Macroscopic anisotropy refers to anisotropy with respect to the macroscopic properties of the system, e.g., fluid-permeability tensor. By statistical anisotropy we mean that the n-point correlation functions that statistically characterize the microstructure (see Refs. 5-7) do not remain invariant under rotation. Although macroscopic anisotropy always implies statistical anisotropy, the converse is not necessarily true. For example, a cubic array of spheres (statistically anisotropic) is described by a scalar permeability; a porous medium composed of oriented cylinders of finite aspect ratio (statistically anisotropic), although described by a permeability tensor, possesses a scalar trapping constant.

[9] See P. M. Richards and S. Torquato, J. Chem. Phys. **87**, 4612 (1987), for an explanation of the relationships between the various definitions of the trapping rate (or rate constant) that have arisen in the literature.

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[13] For isotropic porous media composed of distributions of particles, previous results (Refs. 11 and 12) indicate that the more restrictive inequality $k/k_0 \leq \gamma_0/\gamma$ holds, where k_0 and γ_0 are the dilute-limit ($\phi_2 \ll 1$) values of k and γ, respectively (e.g., for equisized spheres of radius R, $k_0 = 2R^2/9\phi_2$ and $\gamma_0 = 3\phi_2/R^2$). This sharper bound will be derived in a future paper.

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