Optimal Bounds on the Trapping Constant and Permeability of Porous Media

S. Torquato* and D. C. Pham

Department of Chemistry and Materials Institute, Princeton University, Princeton, New Jersey 08544, USA

(Received 5 January 2004; published 23 June 2004)

We derive exact expressions for so-called "void" bounds on the trapping constant γ and fluid permeability k for coated-sphere and coated-cylinder models of porous media. We find that in some cases the bounds are optimal. In these instances, exact expressions are obtained for the relevant length scale that arises in the void bounds, which depends on a two-point correlation function that characterizes the porous medium. This is the first time that model microstructures have been found that exactly realize bounds on either the trapping constant or fluid permeability.

DOI: 10.1103/PhysRevLett.92.255505 PACS numbers: 47.55.Mh, 66.10.–x

The study of the effective properties of heterogeneous materials, such as composite and porous media, has a rich history [1,2] and is a continuing source of theoretically challenging questions [3–9]. Except for a few special microstructures [6–8], exact predictions of the properties are impossible because they depend on an infinite set of microstructural correlation functions [8]. Rigorous upper and lower property bounds [6–8,10,11] are useful because often one of the bounds can provide a useful property estimate [8]. Moreover, it is highly desirable to determine optimal bounds and the microstructures that attain them. The best known bounds in the cases of the effective conductivity and bulk modulus of two-phase media are the Hashin-Shtrikman bounds [10]. These are optimal bounds, given the phase volume fractions, because they are realizable by, among other geometries [6–8], certain coated-sphere and coated-cylinder assemblages.

Two important effective properties of fluid-saturated porous media are the trapping constant γ [8,12,13] and scalar fluid permeability k [3,8,9,14,15]. Bounds on γ [8,16–19] and k [8,20–23] have been derived and computed. However, microstructures that exactly realize any of these bounds have yet to be identified. The difficulty in identifying optimal microstructures lies in the fact that γ and k (unlike the conductivity and elastic moduli) are length-scale dependent properties and known bounds on them depend nontrivially on two-point and higher-order correlation functions [8]. For example, the so-called *void* bounds on γ and k [8,19,23] depend on a two-point correlation function $S_2(r)$ (defined below) and have been evaluated for various particle models for the trapping constant [8,19,24] and fluid permeability [8,20,21,23].

In this Letter, we exactly evaluate the void bounds on the trapping constant γ and fluid permeability k for the coated-sphere and coated-cylinder models of porous media. Interestingly, we show that in some cases the void bounds are optimal because they coincide with the corresponding exact solutions of γ and k for these particular coated-inclusion porous-media models. In these cases, we obtain exact expressions for the relevant length scale that arises in the void bounds, which depends on $S_2(r)$.

Each realization of the porous medium occupies a region of d-dimensional space $\mathcal{V}$ of volume V that is partitioned into two disjoint regions: a pore space $\mathcal{V}_P$ of porosity ϕ_P and a solid space $\mathcal{V}_S$ of volume fraction $\phi_S = 1 - \phi_P$. The pore-space *indicator function* $I^{(P)}(\mathbf{x})$ is equal to unity when $\mathbf{x}$ is in $\mathcal{V}_P$ and zero otherwise. $\mathcal{M}(\mathbf{x}) = |\nabla I^{(P)}(\mathbf{x})|$ is the indicator function for the *interface* $\partial\mathcal{V}$ between $\mathcal{V}_P$ and $\mathcal{V}_S$. For homogeneous media, the ensemble averages of these indicator functions are the porosity $\phi_P = \langle I^{(P)}(\mathbf{x})\rangle$ and the specific surface $s = \langle \mathcal{M}(\mathbf{x})\rangle$ (interfacial area per unit volume).

Before evaluating the bounds, we first define the effective properties γ and k and the coated-sphere model. In the trapping problem [8], a reactant diffuses in the pore space $\mathcal{V}_P$ (i.e., trap-free region) with scalar diffusion coefficient D but is instantly absorbed when it makes contact with the interface $\partial\mathcal{V}$ (i.e., diffusion-controlled reaction). At steady state, the rate of production of the reactant G (per unit trap-free volume) is exactly compensated by its removal by the traps. Two-scale homogenization theory [18] shows that γ for an ergodic medium obeys the first-order rate equation $G = \gamma DC$, where

$$\gamma^{-1} = \langle u \rangle = \lim_{V\to\infty} \frac{1}{V}\int_{\mathcal{V}} u(\mathbf{x})d\mathbf{x}, \tag{1}$$

C is the average concentration, and $u(\mathbf{x})$ is the scaled concentration field that solves

$$\nabla^2 u(\mathbf{x}) = -1, \qquad \mathbf{x} \in \mathcal{V}_P, \tag{2}$$

$$u(\mathbf{x}) = 0, \qquad \mathbf{x} \in \partial\mathcal{V}. \tag{3}$$

For any d, γ has units of inverse of length squared [8].

Rubinstein and Torquato [18] have formulated a variational principle in terms of the trial function $v(\mathbf{x})$ that leads to the following lower bound on γ for ergodic media:

$$\gamma \geq \frac{1}{\langle \nabla v(\mathbf{x}) \cdot \nabla v(\mathbf{x}) I^{(P)}(\mathbf{x})\rangle}, \tag{4}$$

where $v(\mathbf{x})$ is required to satisfy the Poisson equation

$$\nabla^2 v(\mathbf{x}) = -1, \qquad \mathbf{x} \in \mathcal{V}_P. \tag{5}$$

Torquato and Rubinstein [19] constructed a so-called void trial field in three dimensions. The generalization of this trial field for any $d \geq 2$ [8] is given by

$$v(\mathbf{x}) = \frac{1}{\phi_S} \int_{\mathcal{V}} g(\mathbf{x} - \mathbf{y})[\mathcal{I}^{(P)}(\mathbf{y}) - \phi_P] d\mathbf{y}, \tag{6}$$

where

$$g(\mathbf{r}) = \begin{cases} \frac{1}{2\pi} \ln(\frac{1}{r}), & d = 2 \\ \frac{1}{(d-2)\Omega(d)} \frac{1}{r^{d-2}}, & d \geq 3 \end{cases} \tag{7}$$

is the d-dimensional Green's function for the Laplace operator [8], $\Omega(d) = 2\pi^{d/2}/\Gamma(d/2)$ is the total solid angle contained in a d-dimensional sphere, ϕ_S is trap volume fraction, and $r \equiv |\mathbf{r}|$. Substitution of (6) into (4) yields the two-point void lower bound on γ as

$$\gamma \geq \frac{\phi_S^2}{\ell_P^2}, \tag{8}$$

where ℓ_P is a pore length scale defined by

$$\ell_P^2 = \begin{cases} -\int_0^\infty [S_2(r) - \phi_P^2] r \ln r dr, & d = 2 \\ \frac{1}{(d-2)} \int_0^\infty [S_2(r) - \phi_P^2] r dr, & d \geq 3, \end{cases} \tag{9}$$

and $S_2(\mathbf{r}) = \langle \mathcal{I}^{(\mathcal{P})}(\mathbf{x}) \mathcal{I}^{(\mathcal{P})}(\mathbf{x}+\mathbf{r}) \rangle$ is a two-point correlation function, equal to the probability of finding the end points of the displacement vector $\mathbf{r}$ in the pore space [8].

Using homogenization theory, Rubinstein and Torquato [23] derived the conditions under which the slow flow of an incompressible viscous fluid through macroscopically anisotropic random porous medium is described by Darcy's law $\mathbf{U} = -\mu^{-1}\mathbf{k} \cdot \nabla p_0$, where $\mathbf{U}$ is the average fluid velocity, ∇p_0 is the applied pressure gradient, μ is the dynamic viscosity, and $\mathbf{k}$ is the fluid permeability tensor. For the special case of macroscopically isotropic media, the scalar fluid permeability $k = \mathrm{Tr}(\mathbf{k})/d$ (where Tr denotes the trace) is given by

$$k = \langle \mathbf{w} \cdot \mathbf{e} \rangle = \lim_{V \to \infty} \frac{1}{V} \int_{\mathcal{V}} \mathbf{w}(\mathbf{x}) d\mathbf{x}, \tag{10}$$

where $\mathbf{e}$ is a unit vector, and $\mathbf{w}$ and Π are, respectively, a scaled velocity and scaled pressure that satisfy the scaled Stokes equations

$$\nabla^2 \mathbf{w} = \nabla \Pi - \mathbf{e} \quad \text{in} \quad \mathcal{V}_P, \tag{11}$$

$$\nabla \cdot \mathbf{w} = 0 \quad \text{in} \quad \mathcal{V}_P, \tag{12}$$

$$\mathbf{w} = \mathbf{0} \quad \text{on} \quad \partial \mathcal{V}. \tag{13}$$

For any d, k has units of length squared [8].

Prager [20] was the first to derive a two-point void upper bound on the permeability using a variational principle. Subsequently, Berryman and Milton [21] corrected a normalization constraint in the Prager variational principle using a volume-average approach. Rubinstein and Torquato [23] formulated new upper and lower bound variational principles employing an ensemble-average approach and also derived the void upper bound.

For our purposes, the Rubinstein-Torquato variational principle for the upper bound is the most natural. It states that for ergodic media the trial function $\mathbf{q}(\mathbf{x})$ enables one to obtain the following upper bound on k:

$$k \leq \langle \mathbf{q}(\mathbf{x}) : \nabla \mathbf{q}(\mathbf{x}) \mathcal{I}^{(P)}(\mathbf{x}) \rangle, \tag{14}$$

where $\mathbf{q(x)}$ is required to satisfy the momentum equation

$$\nabla \times \nabla^2(\mathbf{q} + \mathbf{e}) = \mathbf{0}, \qquad \mathbf{x} \in \mathcal{V}_P. \tag{15}$$

Rubinstein and Torquato [23] constructed a void trial field in three dimensions. The generalization of this trial field to any dimension $d \geq 3$ is given by [8]

$$\mathbf{q}(\mathbf{x}) = \frac{1}{\phi_S} \int_{\mathcal{V}} \mathbf{\Psi}(\mathbf{x} - \mathbf{y}) \cdot \mathbf{e}[\mathcal{I}^{(P)}(\mathbf{y}) - \phi_P] d\mathbf{y}, \tag{16}$$

where

$$\mathbf{\Psi}(\mathbf{r}) = \frac{d}{(d^2 - 3)\Omega(d) r^{d-2}} [\mathbf{I} + \mathbf{nn}], \qquad d \geq 3, \tag{17}$$

is the d-dimensional Green's function $\mathbf{\Psi}$ (second-order tensor) associated with the velocity for Stokes flow, $\mathbf{n} = \mathbf{r}/r$, and ϕ_S is the volume fraction of the obstacles. Substitution of trial field (16) into (14) yields the two-point void upper bound on k [8] as

$$k \leq \frac{(d+1)(d-2)}{d^2 - 3} \frac{\ell_P^2}{\phi_S^2}, \qquad d \geq 3, \tag{18}$$

where ℓ_P is the length scale defined by (9), which is precisely the same as the one that arises in the void lower bound on the trapping constant γ for $d \geq 3$.

The coated-sphere model [10] consists of composite spheres that are composed of a spherical core of phase 2 (inclusion) and radius R_I, surrounded by a concentric shell of phase 1 (matrix) and outer radius R_M. The ratio $(R_I/R_M)^d$ is fixed and equal to the inclusion volume fraction ϕ_2. The composite spheres fill all space, implying that there is a distribution in their sizes ranging to the infinitesimally small (see Fig. 1), but there are restrictions on this distribution. Without loss of generality, we assume that the composite spheres possess an infinite number of discrete sizes. Let ρ_k be the number density of the kth type of composite sphere of radius R_{M_k} and let R_{I_k} denote the corresponding inclusion radius. Since the composite spheres fill all of space, it follows that ρ_k must diverge to infinity as R_{M_k} approaches zero and the specific surface s must also diverge (see Ref. [25] for details). Let us introduce the following nth moment of R_I:

$$\langle R_I^n \rangle = \frac{1}{\rho} \sum_{k=1}^{\infty} \rho_k R_{I_k}^n, \tag{19}$$

where ρ is a characteristic density and $n \geq 3$.

We first evaluate the void lower bound on γ for the three-dimensional coated-sphere model. To begin, we take the connected matrix phase $\mathcal{V}_1$ to be the traps and

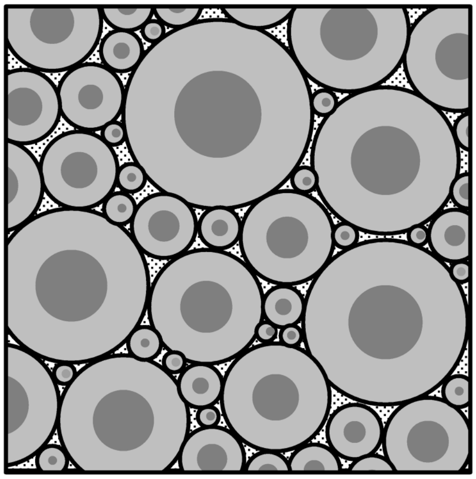

FIG. 1. Schematic of the coated-sphere model microstructure.

the disconnected inclusion phase $\mathcal{V}_2$ to be the pore space. Therefore, the porosity is given by $\phi_P = \phi_2$. Using the void trial field (6) for $v(\mathbf{x})$, we can obtain from (4) the following lower bound on γ:

$$\gamma \geq \left[\lim_{V\to\infty} \frac{1}{V} \int_{\mathcal{V}} \nabla v \cdot \nabla v \, I^{(2)}(\mathbf{x}) d\mathbf{x} \right]^{-1}, \tag{20}$$

where we have equated ensemble averages with volume averages via the ergodic hypothesis. The key volume integrals can be evaluated following Pham [26], but such details will be given elsewhere [25]. We find that the void lower bound is exactly given by

$$\gamma \geq \frac{15\langle R_I^3 \rangle}{\phi_P \langle R_I^5 \rangle}. \tag{21}$$

Comparison of (21) to the general bound (8) reveals that the square of the pore length scale ℓ_P for this coated-sphere model in three dimensions is exactly given by

$$\ell_P^2 = \int_0^\infty [S_2(r) - \phi_P^2] r dr = \frac{\phi_P \phi_S^2}{15} \frac{\langle R_I^5 \rangle}{\langle R_I^3 \rangle}. \tag{22}$$

Now we show that bound (21) coincides with the exact solution for this particular coated-sphere model. Specifically, the exact solution of the boundary-value problem (2) and (3) for diffusion inside a spherical inclusion S_I of radius R_I is given by [8] $u = (R_I^2 - r^2)/6$ for $0 \leq r \leq R_I$. Hence, using definition (1), we find that γ, for *nonoverlapping* sphere models with a *general size distribution* (not just the coated-sphere model) is exactly given by

$$\gamma = \left[\lim_{V\to\infty} \frac{1}{V} \sum_{S_I \in \mathcal{V}_2} \int_0^{R_I} \frac{1}{6} (R_I^2 - r^2) 4\pi r^2 dr \right]^{-1} = \frac{15\langle R_I^3 \rangle}{\phi_P \langle R_I^5 \rangle}. \tag{23}$$

We see that the void bound (21) coincides with the exact solution (23) for the coated-sphere model, and hence the bound is exactly realizable when the inclusions comprise the pore space. One might conclude that the void bound is optimal among all microstructures, but such a statement cannot be made unless one attaches special conditions. Recall that, unlike the effective conductivity or elastic moduli, γ and k are length-scale dependent properties. Thus, any statement about optimality must fix not only the porosity but the relevant length scales. The correct statement is the following: The void bound is optimal among all microstructures that share the same porosity ϕ_P and pore length scale ℓ_P defined by relation (9). One can always adjust the pore length scale (22) of the coated-sphere model at some porosity ϕ_P to be equal to ℓ_P for any microstructure with the same porosity [27].

Next we take the connected matrix phase $\mathcal{V}_1$ to be the pore space and the disconnected inclusion phase $\mathcal{V}_2$ to be the traps so that $\phi_P = \phi_1$. Using the trial field (6) for $v(\mathbf{x})$, we obtain the void lower bound for the model as

$$\frac{\gamma}{\gamma_s} \geq \left(1 + \frac{1}{5}\phi_S^{1/3} - \phi_S - \frac{1}{5}\phi_S^2 \right)^{-1}, \tag{24}$$

where $\gamma_s = 3\phi_S \langle R_I^3 \rangle / \langle R_I^5 \rangle$. The exact solution in this case is not known.

The procedure above can be repeated with the two-dimensional coated-cylinder model. For diffusion inside circular inclusions, we obtain the void lower bound as

$$\gamma \geq \frac{8\langle R_I^2 \rangle}{\phi_P \langle R_I^4 \rangle}, \tag{25}$$

which coincides with the exact result, and thus is an optimal bound in the sense described above. Comparison of this result to the general bound (8) yields the following exact expression for the square of the pore length scale ℓ_P for the coated-cylinder model:

$$\ell_P^2 = -\int_0^\infty [S_2(r) - \phi_P^2] r \ln r dr = \frac{\phi_P \phi_S^2}{8} \frac{\langle R_I^4 \rangle}{\langle R_I^2 \rangle}. \tag{26}$$

For diffusion exterior to the circular inclusions, we obtain the void lower bound as

$$\frac{\gamma}{\gamma_s} \geq \left(-\ln\phi_S - \frac{3}{2} + 2\phi_S - \frac{1}{2}\phi_S^2 \right)^{-1}, \tag{27}$$

where $\gamma_s = 4\langle R_I^2 \rangle \phi_S / \langle R_I^4 \rangle$.

Consider fluid flow along (inside or outside) bundles of parallel cylindrical circular tubes corresponding to the coated-cylinder model. The velocity field reduces to an axial component only, and the Stokes equation reduces to a simple Poisson equation identical to that of the 2D trapping problem. Hence, we have exactly the same solution for the axial component of velocity as for the concentration field in the trapping problem, leading to the exact result that $k = \gamma^{-1}$ [8]. Exploiting this observation and using the previous results, we simply summarize the appropriate results below for k.

In particular, for axial flow inside the cylindrical tubes (Poiseuille flow), the void upper bound is $k \leq \ell_P^2/\phi_S^2$ or

$$k \leq \frac{\phi_P \langle R_I^4 \rangle}{8\langle R_I^2 \rangle}; \tag{28}$$

i.e., ℓ_P^2 is given by (26). This bound coincides with the exact result [8] and, thus, is an optimal bound.

A well-known empirical estimate for the permeability is the Kozeny-Carmen relation $k = \phi_P^3/(cs^2)$ [8,11], where c is an adjustable parameter and s is the specific surface. However, for the coated-inclusion model, we saw earlier that the specific surface s diverges to infinity and therefore the Kozeny-Carmen relation incorrectly predicts a vanishing permeability. This emphasizes the well-established fact that the permeability cannot generally be represented by a simple length scale, such as the specific surface [3,8,15]. Note that the permeabilities of real porous media with high tortuosities will lie well below the optimal void upper bound.

For flow exterior to the cylindrical tubes, we obtain the void upper bound as

$$\frac{k}{k_s} \leq -\ln\phi_S - \frac{3}{2} + 2\phi_S - \frac{1}{2}\phi_S^2, \tag{29}$$

where $k_s = \langle R_I^4 \rangle / (4\phi_s \langle R_I^2 \rangle)$. For flow exterior to spherical obstacles, we exploit the fact that the void upper bound (18) on k is trivially related to the void lower bound (8). Thus, we deduce the upper bound on k for flow exterior to spherical inclusions in the coated-sphere model from the corresponding bound (24) on γ:

$$k/k_s \leq 1 + \tfrac{1}{5}\phi_S^{1/3} - \phi_S - \tfrac{1}{5}\phi_S^2, \tag{30}$$

where $k_s = 2\langle R_I^5 \rangle / (9\phi_S \langle R_I^3 \rangle)$.

To summarize, we have exactly evaluated the two-point void bounds (8) and (18) on γ and k, respectively, for the coated-inclusion models of porous media. In certain instances, the void bounds are optimal among all microstructures that share the same porosity ϕ_P and pore length scale ℓ_P as the coated-sphere model. In contrast to bounds on the effective conductivity and elastic moduli of composite media, this is the first time that model microstructures have been found that exactly realize bounds on either the trapping constant or permeability. In future studies, it will be of interest to investigate what the optimal microstructures are that correspond to the improved two-point "interfacial-surface" bounds on both γ and k, which also incorporate surface correlation functions [8].

The work was completed during D. C. P.'s visit to Princeton University, where he was supported by the Fulbright Foundation. S. T. was supported by the NSF MRSEC Grant DMR - 0213706 at Princeton University and by AFOSR under Grant No. F49620-03-1-0406.

*Corresponding author.
Electronic address: torquato@princeton.edu

[1] J. C. Maxwell, *Treatise on Electricity and Magnetism* (Clarendon, Oxford, 1873).
[2] A. Einstein, Ann. Phys. (Berlin) **19**, 289 (1906).
[3] D. L. Johnson, J. Koplik, and L. M. Schwartz, Phys. Rev. Lett. **57**, 2564 (1986).
[4] S. Feng, B. I. Halperin, and P. N. Sen, Phys. Rev. B **35**, 197 (1987).
[5] S. Torquato, Phys. Rev. Lett. **64**, 2644 (1990).
[6] A. V. Cherkaev, *Variational Methods for Structural Optimization* (Springer-Verlag, New York, 2000).
[7] G. W. Milton, *The Theory of Composites* (Cambridge University, Cambridge, 2002).
[8] S. Torquato, *Random Heterogeneous Materials: Microstructure and Macroscopic Properties* (Springer-Verlag, New York, 2002).
[9] M. Sahimi, *Heterogeneous Materials I: Linear Transport and Optical Properties* (Springer-Verlag, New York, 2003).
[10] Z. Hashin and S. Shtrikman, J. Appl. Phys. **33**, 3125 (1962); J. Mech. Phys. Solids **4**, 286 (1963).
[11] M. J. Beran, *Statistical Continuum Theories* (Wiley, New York, 1968).
[12] D. J. Wilkinson, D. L. Johnson, and L. M. Schwartz, Phys. Rev. B **44**, 4960 (1991).
[13] S. Torquato and M. Avellaneda, J. Chem. Phys. **95**, 6477 (1991).
[14] P. Sheng and M.-Y. Zhou, Phys. Rev. Lett. **61**, 1591 (1988).
[15] M. Avellaneda and S. Torquato, Phys. Fluids A **3**, 2529 (1991).
[16] S. Prager, Chem. Eng. Sci. **18**, 227 (1963).
[17] M. Doi, J. Phys. Soc. Jpn. **40**, 567 (1976).
[18] J. Rubinstein and S. Torquato, J. Chem. Phys. **88**, 6372 (1988).
[19] S. Torquato and J. Rubinstein, J. Chem. Phys. **90**, 1644 (1989).
[20] S. Prager, Phys. Fluids **4**, 1477 (1961).
[21] J. G. Berryman and G. W. Milton, J. Chem. Phys. **83**, 754 (1985).
[22] S. Torquato and J. D. Beasley, Phys. Fluids **30**, 633 (1987).
[23] J. Rubinstein and S. Torquato, J. Fluid Mech. **206**, 25 (1989).
[24] K. Z. Markov, Proc. R. Soc. London, Ser. A **459**, 1035 (2003).
[25] D. C. Pham and S. Torquato (to be published).
[26] D. C. Pham, Acta Mech. **121**, 177 (1997); Mech. Mater. **27**, 249 (1998).
[27] Let us define another squared length scale $L_P^2 = \langle R_I^5 \rangle / \langle R_I^3 \rangle$ for a general nonoverlapping sphere model [cf. (23)]. In what follows, superscripts g and c are appended to quantities associated with the general sphere model and coated-sphere model, respectively. The use of expressions (8), (21), and (23) reveals the following interrelations between these two models: at fixed ϕ_P, if $L_P^{(g)} = L_P^{(c)}$, then $\gamma^{(g)} = \gamma^{(c)}$ and $\ell_P^{(g)} \geq \ell_P^{(c)}$, and if $\ell_P^{(g)} = \ell_P^{(c)}$, then $\gamma^{(g)} \geq \gamma^{(c)}$ and $L_P^{(g)} \leq L_P^{(c)}$.