Rigorous link between fluid permeability, electrical conductivity, and relaxation times for transport in porous media

M. Avellaneda and S. Torquato[a)]
Courant Institute of Mathematical Sciences, New York University, 251 Mercer Street, New York, New York 10012

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A rigorous expression is derived that relates exactly the static fluid permeability k for flow through porous media to the electrical formation factor F (inverse of the dimensionless effective conductivity) and an effective length parameter L, i.e., $k = L^2/8F$. This length parameter involves a certain average of the eigenvalues of the Stokes operator and reflects information about electrical and momentum transport. From the exact relation for k, a rigorous upper bound follows in terms of the principal viscous relation time Θ_1 (proportional to the inverse of the smallest eigenvalue): $k \leqslant \nu\Theta_1/F$, where ν is the kinematic viscosity. It is also demonstrated that $\nu\Theta_1 \leqslant DT_1$, where T_1 is the diffusion relaxation time for the analogous scalar diffusion problem and D is the diffusion coefficient. Therefore, one also has the alternative bound $k \leqslant DT_1/F$. The latter expression relates the fluid permeability on the one hand to purely diffusional parameters on the other. Finally, using the exact relation for the permeability, a derivation of the approximate relation $k \simeq \Lambda^2/8F$ postulated by Johnson *et al.* [Phys. Rev. Lett. **57**, 2564 (1986)] is given.

I. INTRODUCTION

The slow flow of viscous fluids through porous media is of importance in diverse technological areas such as oil recovery, hydrology, filtration, and reaction in zeolites. A key macroscopic property of porous media is the fluid permeability k, which is described by the so-called Darcy law[1]

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

where $\mathbf{U}(\mathbf{x})$ is the average fluid velocity, $\nabla p_0(\mathbf{x})$ is the applied pressure gradient, and μ is the dynamic viscosity. The permeability, which has dimensions of (length)^2, depends upon the details of the pore geometry in a complex fashion. Physically it may be interpreted as an effective cross-sectional area of pore "channels."

Many attempts have been made to relate the permeability to the pore geometry. The most notable empirical relation is the Kozeny–Carmen equation[1]

$$k = \phi_1^3/c\sigma^2, \tag{2}$$

where ϕ_1 is the porosity, σ is the specific surface (interfacial surface per unit volume), and c is an empirical constant ($c = 5$ models many porous media well). Relation (2) is exact for flow in an array of parallel tubes of arbitrary cross-sectional area with c a shape-dependent constant. For example, for circular tubes of radius a, Eq. (2) gives

$$k = a^2\phi_1/8. \tag{3}$$

Various theoretical approaches have been taken to predict k. One approach idealizes the microgeometry by flow around spheres centered on the points of a periodic lattice.[2] For random porous media, effective-medium theories[3] and rigorous bounding techniques[4,5] have been employed.

Recently there has been a resurgence of interest in relating k to different measurable transport properties of the porous medium. Empirical relations used in the past[1] have linked the permeability k to the electrical formation factor F, which is related to the effective electrical conductivity σ_e of a porous medium containing a conducting fluid of conductivity σ_1 and an insulating solid phase by

$$F = \sigma_1/\sigma_e. \tag{4}$$

Thompson[6] was the first to propose the relation

$$k \propto l_c^2/F, \tag{5}$$

where l_c is the length scale obtained in mercury-intrusion experiments on porous rocks. More recently, Johnson *et al.*[7] proposed the following interesting approximate relation involving the electrical conductivity:

$$k \simeq \Lambda^2/8F, \tag{6}$$

where

$$\frac{\Lambda}{2} = \frac{\int|\mathbf{E}(\mathbf{r})|^2\,dV_1}{\int|\mathbf{E}(\mathbf{r})|^2\,dS}. \tag{7}$$

Here the $\mathbf{E}(\mathbf{r})$ is the local electric field, dV_1 denotes an integration over the pore volume, and dS denotes an integration over the pore-solid surface. The parameter Λ is a weighted pore volume-to-surface ratio that provides a measure of the dynamically connected part of the pore region. It arises rigorously in the dynamic frequency-dependent permeability[8,9] in the high-frequency limit. Relation (6) yields the exact result (3) in the case of flow through parallel tubes ($\Lambda = a$ and $F^{-1} = \phi_1$ in this case) and provides good estimates of k for a variety of porous media.

Nuclear magnetic resonance (NMR) relaxtion times of porous media have been experimentally found to provide estimates of k.[10,11] Since the nuclear magnetization is governed by a diffusion equation (see Appendix A), then such correlations relate, in an empirical way, the permeability on

[a)] Permanent address: Department of Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, North Carolina 27695-7910.

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the one hand to the diffusion parameters on the other, as does (6). Unfortunately, these correlations are not rigorous.

Torquato[12] derived the first rigorous expression linking the permeability to a diffusion parameter, namely, the mean survival time τ associated with the steady-state diffusion of "reactants" in a fluid with diffusion coefficient D with perfectly absorbing pore walls (see Appendix A). For porous media with scalar permeability, his expression is given by

$$k \leqslant D\phi_1\tau. \tag{8}$$

Relation (8) becomes an equality for transport interior to parallel tubes of arbitrary cross section; for a cubic array of narrow tubes $k = D\phi_1\tau/3$ and for a dilute distribution of spheres $k = 2D\phi_1\tau/3$. For porous media with low porosity and significant tortuosity, the bound (8) is not sharp because the mean survival time τ, unlike the permeability, is relatively insensitive to the presence of narrow "throats." The result (8) motivated Wilkinson *et al.*[13] very recently to reexamine the problem of NMR relaxation in fluid-saturated porous media by focusing attention on τ instead of the NMR relaxation times. Torquato and Avellaneda[14] have recently obtained, among other results, rigorous lower bounds on τ.

In this paper we provide what are, to our knowledge, the first rigorous expressions that link the static permeability to the effective electrical conductivity for arbitrary porous media. The central results we obtain can be summarized by stating three relations derived in the subsequent sections. The first of these relations is

$$k = L^2/8F, \tag{9}$$

where L is a parameter having dimensions of length, given by

$$L^2 = 8\nu\left(\frac{\sum_{n=1}^{\infty} b_n^2 \Theta_n}{\sum_{n=1}^{\infty} b_n^2}\right). \tag{10}$$

The numbers b_n, $n = 1,2,3,\ldots$, are the eigenfunction expansion coefficients for a nondimensional electric field $\mathbf{E}$ in the fluid relative to the basis of the eigenfunctions of the Stokes operator [defined by (34)], Θ_n are the viscous relaxation times (which are inversely proportional to the eigenvalues), and ν is the kinematic viscosity. We emphasize that relation (9) is exact and involves the length parameter L, which is shown to contain information about both electrical and momentum transport. For a certain universality class, we are able to show in Sec. V that the parameter L can be estimated in terms of the Λ parameter of Ref. 7.

Using (9) and (10), we show that the permeability k is bounded from above according to the relation

$$k \leqslant \nu\Theta_1/F, \tag{11}$$

where Θ_1 is the principal (largest) viscous relaxation time. It is also demonstrated here that $\nu\Theta_1 \leqslant DT_1$, where T_1 is the principal *diffusion* relaxation time (see Sec. IV and Appendix A), and hence combination of this result with (11) yields

$$k \leqslant DT_1/F. \tag{12}$$

In principle, T_1 can be obtained from NMR experiments. Thus, the fluid permeability is related to purely diffusional parameters, i.e., T_1 and F. How sharp are the bounds (11) and (12)? To answer this question, let us focus on the bound (12) and compare it to the mean survival bound (8) derived by Torquato.[11] In Appendix B, it is shown that for flow through arrays of circular tubes of radius a the upper bound (11) is

$$k \leqslant a^2\phi_1/5.784, \tag{13}$$

in contrast to (8), 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 and hence relation (8) is expected to provide a better estimate of the permeability than (12). On the other hand, for porous media with a small and finite range of pore sizes and significant tortuosity, relation (12) should yield a sharper estimate of k than (8), especially at low porosities. This follows for two basic reasons. First, it is rigorously true that $F^{-1} \leqslant \phi_1$ (see, for example, Ref. 15 and references therein). 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 (8), which is nonzero when the pore space is disconnected, formula (12) is identically zero, as it should be, since $F^{-1} = 0$. Second, although it is rigorously true that $T_1 \geqslant \tau$, the authors[14] have shown that T_1 will be of the order of τ provided that there is a small and finite range of pore sizes.

The essential purpose of this paper is to present the derivation of the above results. Our permeability relations are computed here for flow through arrays of parallel tubes, and give reasonable agreement in comparison with exact values. The application of the results of this paper to more realistic microgeometries will be examined in a future work.

II. MATHEMATICAL PRELIMINARIES

A. Basic equations

The random porous medium is a portion of space $\mathscr{V}(\omega) \in \mathbf{R}^3$ (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 flows of volume fraction (porosity) ϕ_1, and a solid-phase region $\mathscr{V}_2(\omega)$ of the volume fraction ϕ_2. Let V_i be the volume 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

$$I(\mathbf{r},\omega) = \begin{cases} 1, & \mathbf{r} \in \mathscr{V}_1(\omega), \\ 0, & \mathbf{r} \in \mathscr{V}_2(\omega). \end{cases} \tag{14}$$

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

$$M(\mathbf{r},\omega) = |\nabla I(\mathbf{r},\omega)|. \tag{15}$$

For statistically homogeneous, but possibly anisotropic, media, the ensemble averages of (14) and (15) yield

$$\phi_1 = \langle I \rangle = \lim_{V_1, V \to \infty} (V_1/V), \tag{16}$$

$$\sigma = \langle M \rangle = \lim_{S, V \to \infty} (S/V), \tag{17}$$

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

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B. Relation between electrical conductance and viscous relaxation

Consider the unsteady Stokes equations for the fluid velocity vector field $\mathbf{v}(\mathbf{r},t)$ at position $\mathbf{r}$ and time t in $\mathscr{V}_1$:

$$\frac{\partial \mathbf{v}}{\partial t} = -\nabla\left(\frac{p}{\rho}\right) + \nu\,\Delta \mathbf{v} + v_0 \mathbf{e}\delta(t), \quad \text{in} \quad \mathscr{V}_1, \tag{18}$$

$$\nabla\cdot\mathbf{v} = 0, \quad \text{in} \quad \mathscr{V}_1, \tag{19}$$

$$\mathbf{v} = 0, \quad \text{on} \quad \partial\mathscr{V}. \tag{20}$$

Here $p(\mathbf{r},t)$ is the pressure, ρ is the constant fluid density, ν is the kinematic viscosity, v_0 is a constant, $\mathbf{e}$ is an arbitrary unit vector, and $\delta(t)$ is the Dirac delta function. The solution of (18)–(20) can be expressed as a sum of normal modes as follows:

$$\frac{\mathbf{v}(\mathbf{r},t)}{v_0} = \sum_{n=1}^{\infty} b_n e^{-t/\Theta_n}\Psi_n(\mathbf{r}), \tag{21}$$

where the vector eigenfunctions Ψ_n satisfy

$$\Delta\Psi_n + \nabla Q_n = -\epsilon_n \Psi_n \quad \text{in} \quad \mathscr{V}_1, \tag{22}$$

$$\nabla\cdot\Psi_n = 0, \quad \text{in} \quad \mathscr{V}_1, \tag{23}$$

$$\Psi_n = 0, \quad \text{on} \quad \partial\mathscr{V}, \tag{24}$$

$$\Theta_n = 1/\nu\epsilon_n. \tag{25}$$

Here the Θ_n are viscous relaxation times and so the nth eigenvalue ϵ_n has dimensions of (length)$^{-2}$. The functions Q_n in (22) are the corresponding pressures. The eigenfunctions Ψ_n are orthonormal, in the sense that

$$\frac{1}{V_1}\int_{\mathscr{V}_1} \Psi_m(\mathbf{r})\cdot\Psi_n(\mathbf{r})d\mathbf{r} = \delta_{mn}, \tag{26}$$

where δ_{mn} is the Kronecker delta, and the eigenfunction expansion coefficients are given by

$$b_n = \frac{1}{V_1}\int_{\mathscr{V}_1} \mathbf{e}\cdot\Psi_n(\mathbf{r})d\mathbf{r}. \tag{27}$$

Here V_1 denotes the total pore volume. It is important to recall that the set of orthonormal eigenfunctions Ψ_n is complete in the closed subspace of square integrable, divergence-free fields having zero normal component on $\partial\mathscr{V}$.[16] According to the classical Hodge decomposition,[17] we can express the constant unit vector $\mathbf{e}$ as the sum of a solenoidal field with vanishing normal component on the pore–surface interface, and the gradient of a potential, as follows:

$$\mathbf{e} = \mathbf{E} + \nabla\phi. \tag{28}$$

Here $\mathbf{E}$ is a dimensionless field satisfying

$$\nabla\cdot\mathbf{E} = 0, \quad \text{in} \quad \mathscr{V}_1, \tag{29}$$

$$\mathbf{E}\cdot\mathbf{n} = 0, \quad \text{on} \quad \partial\mathscr{V}_1, \tag{30}$$

where $\mathbf{n}$ is the unit outward normal from the pore region. Relation (28) implies that

$$\nabla\times\mathbf{E} = 0, \quad \text{in} \quad \mathscr{V}_1. \tag{31}$$

We observe that the field $\mathbf{E}$ then solves the corresponding electrical conduction problem for a porous medium filled with a conducting fluid of conductivity σ_1 and having an insulating solid phase. Hence, $\mathbf{E}$ can be physically interpreted as a scaled electric field, i.e., the actual electric field divided by the modulus of the ensemble-averaged electric field. The field $\mathbf{E}$ is related to the scaled effective conductivity of the porous medium σ_e/σ_1 by the well-known energy representation formula

$$\sigma_e/\sigma_1 = F^{-1} = \langle\mathbf{E}\cdot\mathbf{E}\rangle. \tag{32}$$

Here F denotes the formation factor that is the commonly employed designation for σ_1/σ_e and angular brackets denote ensemble averaging. For statistically homogeneous media, ergodicity enables us to equate ensemble averages with volume averages, so that, for an arbitrary stochastic function $f(\mathbf{r})$ that is defined in $\mathscr{V}_1$,

$$\langle f\rangle = \lim_{V\to\infty}\frac{1}{V}\int_{\mathscr{V}_1} f(\mathbf{r})d\mathbf{r}. \tag{33}$$

Substitution of (28) into (27) yields, after integration by parts,

$$b_n = \frac{1}{V_1}\int_{\mathscr{V}_1}\mathbf{E}(\mathbf{r})\cdot\Psi_n\,d\mathbf{r} = \frac{1}{\phi_1}\langle\mathbf{E}\cdot\Psi_n\rangle. \tag{34}$$

Therefore the coefficients $\{b_n\}$ coincide with the coefficients of the normal mode expansion of the dimensionless field $\mathbf{E}$ in the orthonormal set of solenoidal eigenfunctions $\{\Psi_n\}$. Since the Ψ_n are complete in the aforementioned subspace, we have

$$\sum_{n=1}^{\infty} b_n\Psi_n = \mathbf{E} \tag{35}$$

and

$$\sum_{n=1}^{\infty} b_n^2 = \frac{1}{\phi_1}\langle\mathbf{E}\cdot\mathbf{E}\rangle = \frac{1}{\phi_1}\frac{\sigma_e}{\sigma_1} = \frac{1}{F\phi_1}. \tag{36}$$

Relation (36) will provide valuable to us in the subsequent section. The product $F\phi_1$ is referred to as the "tortuosity."

The arguments in this subsection show that *the response of the Stokes fluid to the external force* $\mathbf{e}$ *is identical to the response obtained if* $\mathbf{e}$ *is replaced by* $\mathbf{E}$, *the dimensionless electric field*. The reason for this is that, in steady state, the gradient of the potential, $\nabla\phi$, in the Hodge decomposition of $\mathbf{e}$ corresponds to a pressure fluctuation that does not affect the velocity field.

C. Steady-state equations defining the fluid permeability

The isotropic fluid permeability k arising in Darcy's law $\mathbf{U} = -\mu^{-1}k\nabla p_0$ can be expressed in terms of a certain scaled velocity field for periodic media[18] and random media.[5] The permeability is given by the formula

$$k = \langle\mathbf{w}\cdot\mathbf{e}\rangle, \tag{37}$$

where the vector velocity field $\mathbf{w}$ satisfies

$$\Delta\mathbf{w} = \nabla\pi - \mathbf{e}, \quad \text{in} \quad \mathscr{V}_1, \tag{38}$$

$$\nabla\cdot\mathbf{w} = 0, \quad \text{in} \quad \mathscr{V}_1, \tag{39}$$

$$\mathbf{w} = 0, \quad \text{on} \quad \partial\mathscr{V}. \tag{40}$$

The fields $\mathbf{w}$ and π are defined to be zero in the solid region $\mathscr{V}_2$.

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III. RIGOROUS LINK BETWEEN FLUID PERMEABILITY, FORMATION FACTOR, AND VISCOUS RELAXATION TIMES

Here we show that the fluid permeability k is related to certain averages of the relaxation times Θ_n. We also demonstrate that k is bounded from above and below in terms of the principal (largest) relaxation time Θ_1. These statements are given and proven in the form of two propositions.

Proposition 1: For porous media of arbitrary topology with scalar permeability at porosity ϕ_1, the following expression holds:

$$k = \nu\phi_1 \sum_{n=1}^{\infty} b_n^2 \Theta_n = \frac{\nu}{F}\left(\frac{\sum_{n=1}^{\infty} b_n^2\Theta_n}{\sum_{n=1}^{\infty} b_n^2}\right) = L^2/8F, \tag{41}$$

where F is the formation factor, Θ_n are the viscous relaxation times, and b_n are the eigenfunction expansion coefficients given by (34).

Proof: First we take the Laplace transform in time of (18)–(20) and find

$$s\hat{\mathbf{v}} = -\nabla(\hat{p}/\rho) + \nu\,\Delta\hat{\mathbf{v}} + v_0\mathbf{e}, \tag{42}$$

$$\nabla\cdot\hat{\mathbf{v}} = 0, \tag{43}$$

$$\hat{\mathbf{v}} = 0, \tag{44}$$

where

$$\hat{\mathbf{v}}(\mathbf{r},s) = \int_0^{\infty} \mathbf{v}(\mathbf{r},t)e^{-st}\,dt. \tag{45}$$

Setting $s=0$ in Eqs. (42) and (43) yields

$$\nu\,\Delta\hat{\mathbf{v}}(\mathbf{r},0) = \nabla[\hat{p}(r,0)/\rho] - v_0\mathbf{e}, \tag{46}$$

$$\nabla\cdot\hat{\mathbf{v}}(\mathbf{r},0) = 0, \tag{47}$$

$$\hat{\mathbf{v}}(\mathbf{r},0) = 0. \tag{48}$$

Letting

$$\mathbf{w}(\mathbf{r}) = \nu\hat{\mathbf{v}}(\mathbf{r},0)/v_0, \quad \pi(\mathbf{r}) = \hat{p}(\mathbf{r},0)/\rho v_0 \tag{49}$$

in (46)–(48) yields the canonical equations (38)–(40), which determine the fluid permeability. Therefore the solution of (38)–(40) can be expressed in terms of the eigenfunctions $\{\Psi_n\}$ that solve (22)–(24) by Laplace transforming the normal mode solution (21):

$$\frac{\hat{\mathbf{v}}(\mathbf{r},s)}{v_0} = \sum_{n=1}^{\infty} b_n \Psi_n(\mathbf{r})\frac{1}{1/\Theta_n + s}. \tag{50}$$

Setting $s=0$ in (50) and employing (45) gives

$$\mathbf{w}(\mathbf{r}) = \nu \sum_{n=1}^{\infty} b_n \Psi_n(\mathbf{r})\Theta_n. \tag{51}$$

Forming the scalar product of the scaled electric field $\mathbf{E}$ with (51), ensemble averaging, and using (34)–(36) along with the identity

$$\langle \mathbf{w}\cdot\mathbf{e}\rangle = \langle \mathbf{w}\cdot\mathbf{E}\rangle, \tag{52}$$

yields

$$k = \nu\phi_1 \sum_{n=1}^{\infty} b_n^2\Theta_n = \frac{\nu}{F}\,\frac{\sum_{n=1}^{\infty} b_n^2\Theta_n}{\sum_{n=1}^{\infty} b_n^2} = L^2/8F, \tag{53}$$

according to the definition of the parameter L. This proves the proposition.

Remark 1: Relation (41) applies not only to statistically isotropic media but to anisotropic porous media as well, with the obvious modifications.

Remark 2: For subsequent results, it will be useful to introduce a Laplace-variable-dependent fluid permeability, defined as

$$k(s) = \nu\langle \hat{\mathbf{v}}(\mathbf{r},s)\cdot\mathbf{e}\rangle/v_0. \tag{54}$$

Notice that $k(0)\equiv k$ is just the standard steady state or static permeability defined by (37). Substitution of (50) into (54) yields

$$k(s) = \nu\phi_1 \sum_{n=1}^{\infty} \frac{b_n^2}{1/\Theta_n + s}. \tag{55}$$

If a porous medium saturated with a viscous fluid is subjected to an oscillatory pressure gradient $\nabla p_0(\omega)$ (where ω is the frequency), then the induced averaged velocity $\mathbf{U}(\omega)$ will also be oscillatory and proportional to the pressure gradient according to $\mathbf{U}(\omega) = -\tilde{k}(\omega)\nabla p_0(\omega)/\mu$. Here $\tilde{k}(\omega)$ is the so-called *dynamic permeability*[8,9] and it can be related to the Laplace-variable-dependent permeability defined by (54) according to the relation

$$\tilde{k}(\omega) = k(s = -i\omega). \tag{56}$$

Proposition 2: For porous media of arbitrary topology with scalar permeability at porosity ϕ_1, the fluid permeability k is bounded from above according to

$$k \leqslant \nu\Theta_1/F, \tag{57}$$

and from below according to

$$k \geqslant \nu\phi_1 b_1^2\Theta_1, \tag{58}$$

where F is the formation factor and b_1 is the first eigenfunction coefficient given by (34).

Proof: Since the eigenvalues ϵ are positive and $\epsilon_1 \leqslant \epsilon_n$ $(\Theta_1 \geqslant \Theta_n)$ for $n \neq 1$, then

$$\sum_{n=1}^{\infty} b_n^2\Theta_n \leqslant \sum_{n=1}^{\infty} b_n^2\Theta_1. \tag{59}$$

This result, in combination with (36) and Proposition 1 gives the upper bound

$$k \leqslant \nu\Theta_1/F. \tag{60}$$

Furthermore, Proposition 1 combined with inequality

$$\sum_{n=1}^{\infty} b_n^2\Theta_n \geqslant b_1^2\Theta_1, \tag{61}$$

gives

$$k \geqslant \nu\phi_1 b_1^2\Theta_1. \tag{62}$$

Proposition 3: For porous media of arbitrary topology with scalar permeability, the fluid permeability k is bounded

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from above as follows:

$$k < DT_1/F, \tag{63}$$

where D is the diffusion coefficient of the fluid and T_1 is the principal relaxation time for diffusion-controlled processes among static, perfectly absorbing traps.

Proof: This follows immediately from Proposition 2 and Proposition 4 (discussed in the next section), which states that $\nu\Theta_1 < DT_1$.

Remark 3: The diffusion-controlled trapping problem is described in detail in Appendix A.

Remark 4: The calculations made in this section assume implicitly that the spectrum of the Stokes operator in V_1 is discrete—a hypothesis that is justified if the pore volume $\mathscr{V}_1$ is finite or if the microstructure is periodic. However, the reader will easily verify that Proposition 1 is valid also for arbitrary statistically homogeneous porous media, with the series in (41) replaced by integrals over the density of states. Also notice that the upper bounds (57) and (63) are valid for general random porous media. On the other hand, the lower bound (58) makes sense only for microstructures corresponding to a discrete spectrum $\{\Theta_n\}$, $n \geqslant 0$.

IV. RIGOROUS LINK BETWEEN VISCOUS AND DIFFUSION RELAXATION TIMES

Measurement of the viscous relaxation time Θ_1 can be used to determine information about the diffusion relaxation time T_1, and vice versa. Here T_1 is the principal relaxation time for diffusion of reactants among static traps (see Appendix A for details). In fact, we shall demonstrate that an inequality between Θ_1 and T_1 holds for all porous microgeometries. Thus, an upper bound, or estimate, on the relaxation time T_1, obtainable, in principle, from NMR relaxation experiments,[10,11] can be used to bound the viscous relaxation time from above.

Proposition 4: For any porous medium, the following inequality holds between Θ_1 and T_1:

$$\nu\Theta_1 < DT_1. \tag{64}$$

Proof: To prove the inequality (64), recall that

$$\Theta_1 = 1/\nu\epsilon_1 \quad \text{and} \quad T_1 = 1/D\lambda_1, \tag{65}$$

where ϵ_1 and λ_1 are, respectively, the fundamental eigenvalues for the Stokes equation and the Laplace equation in $\mathscr{V}_1$. *We shall prove (64) by showing that, for all porous microgeometries, we have $\epsilon_1 \geqslant \lambda_1$.*

For this, we recall the classical Rayleigh–Ritz variational principle,[19] according to which

$$\epsilon_1 = \min_{\substack{\nabla\cdot\mathbf{v}(\mathbf{r})=0 \\ \mathbf{v}(\mathbf{r})=0 \ \text{on}\ \partial\mathscr{V}_1}} \frac{\int_{\mathscr{V}_1} |\nabla\mathbf{v}(\mathbf{r})|^2\, d\mathbf{r}}{\int_{\mathscr{V}_1} |\mathbf{v}(\mathbf{r})|^2\, d\mathbf{r}}. \tag{66}$$

The eigenfunction $\Psi_1(\mathbf{r})$, associated with the principal eigenvalue ϵ_1, minimizes the Rayleigh quotient in (66). The constraint $\nabla\cdot\mathbf{v}(\mathbf{r}) = 0$ in this variational principle is necessary to guarantee incompressibility. If this constraint is dropped, then the minimum possible value that can be achieved by the quotient $\int_{\mathscr{V}_1} |\nabla\mathbf{v}|^2\, d\mathbf{r} / \int_{\mathscr{V}_1} |\mathbf{v}|^2\, d\mathbf{r}$ cannot increase, and hence

$$\epsilon_1 \geqslant \min_{\mathbf{v}(\mathbf{r})=0 \ \text{on}\ \partial\mathscr{V}_1} \frac{\int_{\mathscr{V}_1} |\nabla\mathbf{v}(\mathbf{r})|^2\, d\mathbf{r}}{\int_{\mathscr{V}_1} |\mathbf{v}(\mathbf{r})|^2\, d\mathbf{r}}, \tag{67}$$

where the minimum is now taken over the *larger* class of trial fields consisting of vector-valued functions $\mathbf{v}(\mathbf{r})$ vanishing on $\partial\mathscr{V}_1$, but not necessarily satisfying the incompressibility condition. Let $\mathbf{v}_{\min}(\mathbf{r})$ denote a minimizer of the right-hand side of (67), such that $\int_{\mathscr{V}_1} |\mathbf{v}_{\min}(\mathbf{r})|^2\, d\mathbf{r} \neq 0$. Such a function necessarily satisfies the equations

$$\begin{aligned} &\Delta\mathbf{v}_{\min}(r) + \tilde{\lambda}\mathbf{v}_{\min}(\mathbf{r}) = 0, \quad \text{in } \mathscr{V}_1, \\ &\mathbf{v}_{\min}(\mathbf{r}) = 0, \quad \text{on } \partial\mathscr{V}, \end{aligned} \tag{68}$$

where $\tilde{\lambda}$ is a suitable Lagrange multiplier. If $v^{(1)}(\mathbf{r})$, $v^{(2)}(\mathbf{r})$, $v^{(3)}(\mathbf{r})$ denote the components of $\mathbf{v}_{\min}(\mathbf{r})$ in a fixed coordinate frame, we have, from (68),

$$\begin{aligned} &\Delta v^{(i)}(\mathbf{r}) + \tilde{\lambda} v^{(i)}(\mathbf{r}) = 0, \quad \text{in } \mathscr{V}_1, \\ &v^{(i)}(\mathbf{r}) = 0, \quad \text{on } \partial\mathscr{V}_1, \end{aligned} \tag{69}$$

for $i = 1,2,3$. This means that $\tilde{\lambda}$ is necessarily an eigenvalue of the Laplacian on $\mathscr{V}_1$ and $v^{(i)}(\mathbf{r})$ are eigenfunctions with the same eigenvalue, $\tilde{\lambda}$. Multiplying both sides of Eq. (69) by $v^{(i)}(\mathbf{r})$ and integrating both sides of the equation yields

$$\int_{\mathscr{V}_1} |\nabla v^{(i)}(\mathbf{r})|^2\, d\mathbf{r} = \tilde{\lambda} \int_{\mathscr{V}_1} |v^{(i)}(\mathbf{r})|^2\, d\mathbf{r}. \tag{70}$$

Summing over $i = 1,2,3$, we conclude that

$$\tilde{\lambda} = \frac{\int_{\mathscr{V}_1} |\nabla\mathbf{v}_{\min}(\mathbf{r})|^2\, d\mathbf{r}}{\int_{\mathscr{V}_1} |\mathbf{v}_{\min}(\mathbf{r})|^2\, d\mathbf{r}}, \tag{71}$$

and hence, from (67), that ϵ_1 satisfies

$$\epsilon_1 \geqslant \tilde{\lambda}. \tag{72}$$

Recalling that λ_1 is the *smallest* eigenvalue of the Laplacian, we have

$$\tilde{\lambda} \geqslant \lambda_1 \tag{73}$$

and hence

$$\epsilon_1 \geqslant \lambda_1. \tag{74}$$

Using the expressions for the viscous and diffusion relaxation times given in (65), we obtain the inequality (64), as claimed.

Remark 1: A further inspection of (69) and (73) shows that $\tilde{\lambda} = \lambda_1$ and that a vector-valued function that minimizes the right-hand side of (67) is necessarily of the form

$$\mathbf{v}_{\min}(\mathbf{r}) = \psi_1(\mathbf{r})\mathbf{v}_0, \tag{75}$$

where $\psi_1(\mathbf{r})$ is the first eigenfunction of the Laplacian (notice that the first eigenvalue λ_1 is nondegenerate[19]), and $\mathbf{v}_0$ is a constant, nonzero vector.

Remark 2: For transport interior to parallel channels of arbitrary cross section, (64) becomes an equality, i.e., $\nu\Theta = DT_1$ for the same reasons that the Torquato bound (8) relating k to the mean survival time τ becomes an equality, i.e., since the pressure gradient is constant.

V. A DERIVATION OF THE EMPIRICAL FORMULA (6) INVOLVING THE Λ PARAMETER

In this section we evaluate the effective length L, defined by the formula

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$$L^2 = \frac{8\nu \Sigma_n b_n^2 \Theta_n}{\Sigma_n b_n^2}, \qquad (76)$$

in terms of the so-called Λ parameter, or electrically weighted volume-to-surface ratio, given by

$$\Lambda = \frac{2\int |\mathbf{E}(\mathbf{r})|^2 \, dV_1}{\int |\mathbf{E}(\mathbf{r})|^2 \, dS}, \qquad (77)$$

thereby showing that our formula $k = L^2/8F$ reduces to $k \approx \Lambda^2/8F$ under reasonable assumptions.

The fundamental interest in the Johnson–Koplik–Schwartz empirical formula (6) resides in the fact that Λ can be measured by performing high-frequency experiments in the porous medium consisting of imposing an oscillatory pressure gradient and measuring the dynamic fluid response. In fact, it can be shown, following a boundary-layer analysis suggested by Sheng and Zhou[9] (see Appendix D), that the following exact relation holds for the dynamic permeability in the high-frequency limit:

$$\lim_{\omega \to +\infty} [\omega^{3/2} \operatorname{Re} \tilde{k}(\omega)] = \nu^{3/2}\sqrt{2}/\Lambda F. \qquad (78)$$

This result provides a dynamical characterization of the Λ parameter (77), and the Johnson–Koplik–Schwartz formula (6) can be viewed as the result of attempting to use the high-frequency information on $\tilde{k}(\omega)$ to obtain information on $\tilde{k}(0)$.

We will argue here that the asymptotic result (78) provides a relation between the length scales L and Λ, implying that we have

$$L = C\Lambda, \qquad (79)$$

where C is a numerical constant on the order of unity, for a wide class of porous materials. Thus, from (79) and our basic identity $k = L^2/8F$, we obtain a relation that agrees well with the empirical formula (6).

Our argument is based on the observation that (78) provides a dispersion relation between the coefficients b_n^2 and the relaxation times Θ_n, as $n \to \infty$, which can be stated as

$$\lim_{\Theta \to 0} \frac{1}{\sqrt{\Theta}} \left(\frac{\Sigma_{\Theta_n < \Theta} b_n^2}{\Sigma_n b_n^2} \right) = \frac{4\nu^{1/2}}{\pi\Lambda}. \qquad (80)$$

In order to derive this formula and analyze its consequences, it is convenient to introduce the *cumulative distribution of relaxation times*,

$$G(\Theta) = \frac{\Sigma_{\Theta_n \leqslant \Theta} b_n^2}{\Sigma_n b_n^2}, \qquad (81)$$

which is a nondecreasing, right-continuous function on the real axis, such that

$$G(\Theta) = 0, \quad \text{for } \Theta \leqslant 0$$

and (82)

$$G(\Theta) = 1, \quad \text{for } \Theta \geqslant \Theta_1.$$

The frequency-dependent permeability defined in (56) can be conveniently expressed in terms of $G(\Theta)$ as the Stieltjes integral

$$\tilde{k}(\omega) = \frac{\nu}{F} \int \frac{\Theta \, dG(\Theta)}{1 - i\omega\Theta}; \qquad (83)$$

in particular, we have

$$\operatorname{Re} \tilde{k}(\omega) = \frac{\nu}{F} \int \frac{\Theta \, dG(\Theta)}{1 + \omega^2\Theta^2} \qquad (84)$$

and

$$\operatorname{Im} \tilde{k}(\omega) = \frac{\nu}{F} \int \frac{\Theta^2 \omega \, dG(\Theta)}{1 + \omega^2\Theta^2}. \qquad (85)$$

The fundamental result characterizing the real part of the dynamical permeability in the high-frequency limit is equivalent, using (84), to

$$\lim_{\omega \to \infty} \omega^{3/2} \int \frac{\Theta \, dG(\Theta)}{1 + \omega^2\Theta^2} = \frac{\nu^{1/2}\sqrt{2}}{\Lambda}. \qquad (86)$$

In Appendix C, it is shown, by analyzing the properties of the Stieltjes integral in (84), that (84) implies the scaling relation

$$G(\Theta) = (4\nu^{1/2}/\pi\Lambda)\Theta^{1/2} + o(\Theta^{1/2}) \qquad (87)$$

for $\Theta \ll 1$, which agrees with the claim (80). The importance of this result, underscored in Refs. 9 and 10, is that the shape of $G(\Theta)$ near $\Theta = 0$ is universal, i.e., geometry independent for a wide class of porous media, and is characterized solely in terms of the parameter Λ. Accordingly, defining the *effective relaxation time*

$$\Theta_0 \doteq \Lambda^2/8\nu, \qquad (88)$$

we can write the cumulative relaxation time distribution in scaled form,

$$G(\Theta) = H(\Theta/\Theta_0), \qquad (89)$$

where $H(x)$, $0 \leqslant x < \Theta_1/\Theta_0$ is the probability distribution function of a nondimensional random variable on the positive real axis, satisfying

$$H(x) = (\sqrt{2}/\pi)x^{1/2} + o(x^{1/2}), \quad x \ll 1. \qquad (90)$$

Using expressions (89) and (84) with $\omega = 0$, we obtain

$$\begin{aligned} k &= \frac{\nu}{F} \left(\frac{\Sigma b_n^2 \Theta_n}{\Sigma b_n^2} \right) \\ &= \frac{\nu}{F} \int_0^\infty \Theta \, dG(\Theta) \\ &= \frac{\nu\Theta_0}{F} \left(\int_0^\infty x \, dH(x) \right) \\ &= \frac{\Lambda^2}{8F} \left(\int_0^\infty x \, dH(x) \right). \end{aligned} \qquad (91)$$

In particular, we obtain the following relation between L and Λ:

$$L^2 = \Lambda^2 \left(\int_0^\infty x \, dH(x) \right). \qquad (92)$$

The numerical factor $\int_0^\infty x \, dH(x)$ depends on the microgeometry of the porous medium. According to the universal scaling relations (78), (80), and (87) and the nondimensional form (90), the fluctuations in the numerical ratio L/Λ from one porous material to another must be due to

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differences in the shapes of the corresponding functions $G(\Theta)$ at large values of Θ [or, equivalently, of $H(x)$ for large x]. The complete form of the function $H(x)$ for a given porous medium is very difficult to calculate. In a first approximation, we can obtain information about the variations of L/Λ by considering a class of ideal porous media formed of arrays of parallel tubes of circular or rectangular cross sections. For circular cylinders, we have $L/\Lambda = 1$; this corresponds to taking $G(\Theta) = G_t(\Theta)$ in (91), where $G_t(\Theta)$ is defined in Appendix B, Eq. (B12). For rectangular cross sections, with dimensions a, b, with $c = b/a$, we have

$$\frac{L^2}{\Lambda^2} = \frac{512}{\pi^6} \sum_{m,n\ \text{odd}} \frac{(1+c)^2}{m^2 n^2 (c^2 m^2 + n^2)}. \tag{93}$$

This relation, derived in Appendix B, shows that L/Λ is, strictly speaking, a geometrical constant that depends on the specific microgeometry under consideration. As the aspect ratio varies from $c = 1$, corresponding to a square cross section, to $c = \infty$, for an infinitely elongated cross section, we find that the ratio L^2/Λ^2 varies in the range (cf. Appendix B)

$$0.66 < L^2/\Lambda^2 < 1.112. \tag{94}$$

One can argue in this approximation that for porous rocks the aspect ratios of the channels will be polydispersed, and hence that the ratio L^2/Λ^2 will lie somewhere between the bounds. The range of the ratio L/Λ indicated by the inequalities in (94) lends support to the idea according to which, after averaging over a distribution of pore aspect ratios, we have $L/\Lambda \approx 1$. This simple argument neglects, of course, the influence of the tortuosity of the porous medium microstructure on the L parameter. A more detailed study of the L parameter requires a better understanding of the geometric distribution $H(x)$ associated with a random porous medium. The recent results of Sheng and Zhou[9] on the universality properties of the dynamic permeability $\tilde{k}(\omega)$ suggest, in fact, that the entire distribution $H(x)$ should exhibit universal properties justifying the $L \approx \Lambda$ approximation. This question will be taken up in a forthcoming work.

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APPENDIX A: RIGOROUS LINK BETWEEN FREQUENCY-DEPENDENT FLUID PERMEABILITY AND MEAN SURVIVAL TIME

1. Diffusion relaxation times

The relaxation times associated with the decay of diffusional quantities such as concentration field and nuclear magnetization are intimately related to the characteristic length scales of the pore region. Let $c(\mathbf{r},t)$ generally denote the physical quantity of interest at position $\mathbf{r}$ and time t, which obeys the following equations:

$$\frac{\partial c}{\partial t} = D\,\Delta c + c_0\delta(t), \quad \text{in } \mathscr{V}_1, \tag{A1}$$

$$c = 0, \quad \text{on } \partial\mathscr{V}_1, \tag{A2}$$

where D is the diffusion coefficient and c_0 is a constant. The boundary condition (A2) implies an infinite surface reaction rate, i.e., the process is diffusion controlled. From a Brownian motion viewpoint, a Brownian particle "survives" provided it does not reach the interface $\partial\mathscr{V}$, at which point the Brownian motion ceases. Torquato and Avellaneda[14] considered the more general case where the surface reaction rate is finite, but for present purposes we limit our discussion to the diffusion-controlled limit. Note that in the NMR context, the field c plays the role of the nuclear magnetization.[10,11,13]

The solution of (A1) and (A2) can be given as an expansion in orthonormal eigenfunctions $\{\psi_n\}$:

$$\frac{c(\mathbf{r},t)}{c_0} = \sum_{n=1}^{\infty} a_n e^{-t/T_n}\psi_n(\mathbf{r}), \tag{A3}$$

where

$$\Delta\psi_n = -\lambda_n\psi_n, \quad \text{in } \mathscr{V}_1, \tag{A4}$$

$$\psi_n = 0, \quad \text{on } \partial\mathscr{V}_1, \tag{A5}$$

with conditions analogous to (26). Here a_n, $n = 1,2,3,\ldots$, represent the eigenfunction coefficients of the function $I(r,\omega)$ in (14) and the T_n are the diffusion relaxation times, where

$$T_n = 1/D\lambda_n. \tag{A6}$$

2. Mean survival time

A different but related diffusion problem is the *steady-state* diffusion of reactants (Brownian particles) among static traps, in which the production rate of the reactants per unit pore volume is $G(\mathbf{x})$. The *trapping constant* γ is defined through an analogous "Darcy's law" given by $G(\mathbf{x}) = \gamma D\overline{C}(\mathbf{x})$, where $\overline{C}(\mathbf{x})$ is a mean concentration field. This problem for statistically homogeneous media in the diffusion-controlled limit was investigated by Rubinstein and Torquato[20] using the method of homogenization. They demonstrated that the trapping constant is given by

$$\gamma = \langle u\rangle^{-1}, \tag{A7}$$

where the scaled concentration field $u(\mathbf{r})$ solves

$$\Delta u = -1, \quad \text{in } \mathscr{V}_1, \tag{A8}$$

$$u = 0, \quad \text{on } \partial\mathscr{V}. \tag{A9}$$

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The trapping constant (having dimensions of inverse length squared) is trivially related to the *mean survival time* τ of a Brownian particle by

$$\tau = 1/\gamma\phi_1 D, \tag{A10}$$

and thus application of (A9) gives

$$\tau = \langle u\rangle / D\phi_1. \tag{A11}$$

The authors[14] also considered the survival problem for the general case of finite reaction rate. Among other results, they introduced a *frequency-dependent* mean survival time, which is defined by

$$\tau(s) = \langle \hat{c}(\mathbf{r},s)\rangle / c_0\phi_1, \tag{A12}$$

where $\hat{c}(\mathbf{r},s)$ is the Laplace transform of field, which solves, in the diffusion-controlled limit, i.e., it solves

$$s\hat{c}(\mathbf{r},s) = D\,\Delta\hat{c}(\mathbf{r},s) + c_0, \quad \text{in } \mathscr{V}_1, \tag{A13}$$

$$\hat{c} = 0, \quad \text{on } \partial\mathscr{V}. \tag{A14}$$

Relation (A12) implies the existence of a frequency-dependent mean survival time. Note that $\tau(0) \equiv \tau$ is just the standard static survival time.

APPENDIX B: TRANSPORT INTERIOR TO PARALLEL TUBES

1. Circular cross section

Consider the Eqs. (18)–(20) for unsteady flow in a circular cylindrical tube of radius a:

$$\frac{\partial v}{\partial t} = \nu\left(\frac{\partial^2 v}{\partial r^2} + \frac{1}{r}\frac{\partial v}{\partial r}\right) + v_0\delta(t), \quad 0 \leqslant r \leqslant a, \tag{B1}$$

$$v(a,t) = 0, \tag{B2}$$

where $v(r,t)$ is the axial component of the velocity and r is the radial coordinate measured with respect to the center of the tube. The solution of (B1) and (B2) is given by

$$\frac{v}{v_0} = \sum b_n e^{-t/\Theta_n}\Psi_n(r), \tag{B3}$$

where

$$b_n = 2/a\sqrt{\epsilon_n}, \tag{B4}$$

$$\Psi_n = J_0(r\sqrt{\epsilon_n})/J_1(a\sqrt{\epsilon_n}), \tag{B5}$$

$$J_0(a\sqrt{\epsilon_n}) = 0, \tag{B6}$$

$$\sum_{n=1}^{\infty} b_n\Psi_n(r) = 1, \tag{B7}$$

$$\sum_{n=1}^{\infty} b_n^2 = 1, \tag{B8}$$

$$\Theta_n = 1/\nu\epsilon_n. \tag{B9}$$

Here J_0 and J_1 are, respectively, the zeroth-order and first-order Bessel functions.

For arrays of parallel tubes at porosity ϕ_1, the static permeability is given by

$$k = (a^2/8)\phi_1, \tag{B10}$$

so that $L = a = \Lambda$. Notice that the eigenvalues ϵ_n and relaxation times Θ_n, $n = 1,2,3,\ldots$, are related to the zeros z_n, $n = 1,2,3,\ldots$, of the Bessel function J_0, by the formulas

$$\epsilon_n = z_n^2/a^2, \quad \Theta_n = a^2/\nu z_n^2. \tag{B11}$$

We deduce from this that the relaxation-time distribution $G(\Theta)$ defined in (81) is, for an array of parallel tubes with circular cross-section, given by

$$G_t(\Theta) = \sum_{z_n^2 > a^2/\nu\Theta}\left(\frac{4}{z_n^2}\right). \tag{B12}$$

The first zero of $J_0(z)$ occurs at $z_0 \simeq 2.405$ and thus

$$\epsilon_n = 5.784/a^2, \tag{B13}$$

$$\nu\Theta_1 = 0.1729a^2, \tag{B14}$$

$$\nu b_1^2\Theta_1 = 0.1196a^2. \tag{B15}$$

Application of Proposition 2 [Eq. (57)] for an array of tubes gives

$$0.1196a^2\phi_1 \leqslant k = 0.125a^2\phi_1 \leqslant 0.1729a^2\phi_1, \tag{B16}$$

which shows that the bounds on $k = 0.125a^2\phi_1$ are reasonably sharp. Therefore, the static permeability k can be reasonably estimated in terms of the principal relaxation time Θ_1, as given by Proposition 2, provided that the porous medium is characterized by a finite range of pore sizes.

As previously discussed, the flow and diffusion problems are isomorphic for transport interior to parallel tubes. Therefore, we have

$$\tau = k = (a^2/8)\phi_1, \tag{B17}$$

$$DT_n = \nu\Theta_n, \tag{B18}$$

where the relaxation times Θ_n are determined from (B6).

2. Rectangular cross sections

For an array of parallel tubes with rectangular cross sections, the quantities of interest can be computed using Fourier series. Accordingly, if a and b denote the dimensions of the cross section, we have

$$\Psi_{m,n}(x,y) = 2\sin(m\pi x/a)\sin(n\pi y/b), \tag{B19}$$

$$b_{m,n} = 8/\pi^2 mn, \tag{B20}$$

$$\epsilon_{m,n} = \pi^2(m^2/a^2 + n^2/b^2), \tag{B21}$$

and

$$\Theta_{m,n} = [\nu\pi^2(m^2/a^2 + n^2/b^2)]^{-1}, \tag{B22}$$

where m, n are odd, positive integers. The parameter L corresponding to an array of rectangular tubes with dimensions a and b is given, from (B20), (B22), by

$$L^2 = \frac{512}{\pi^6}\sum_{m,n\ \mathrm{odd}}\frac{1}{m^2n^2(m^2/a^2 + n^2/b^2)}. \tag{B23}$$

On the other hand, the Λ parameter for this geometry coincides with the (usual) volume to surface ratio, since the electric field is uniform, so that

$$\Lambda = \frac{2V}{S} = \frac{2ab}{2a + 2b} = \frac{ab}{a + b}. \tag{B24}$$

Introducing the aspect ratio $c = b/a$, we have

$$\frac{L^2}{\Lambda^2} = \frac{512}{\pi^6}\sum_{m,n\ \mathrm{odd}}\frac{(1+c)^2}{m^2n^2(c^2m^2 + n^2)}, \tag{B25}$$

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which shows that the ratio L/Λ is not, strictly speaking, geometry independent. For a square cross section ($c=1$) we have, with $\Lambda = a/2$,

$$\frac{L_1^2}{\Lambda^2} = \frac{2048}{\pi^6} \sum_{m,n \text{ odd}} \frac{1}{m^2 n^2 (m^2+n^2)}, \qquad \text{(B26)}$$

while for an infinitely long cross section (flow between two parallel surfaces) we obtain, with $c=\infty$, $\Lambda = a$,

$$\frac{L_\infty^2}{\Lambda^2} = \frac{L_\infty^2}{a^2} = \frac{2}{3} \simeq 0.66. \qquad \text{(B27)}$$

The numerical value of L_1^2/Λ^2 can be evaluated with two significant decimal digits by summing the first four terms of the series in (B26), yielding

$$L_1^2/\Lambda^2 \simeq 1.112. \qquad \text{(B28)}$$

Finally, we compare the bounds of Proposition 2 with exact results in both cases. Accordingly, for the square cross section,

$$k_1 \cong (1.112)\phi_1\Lambda_1^2/8 \cong (0.139)\phi_1\Lambda_1^2 \qquad \text{(B29)}$$

represents the exact result. The corresponding upper bound (57) is

$$k_1 \leqslant (0.203)\phi_1\Lambda_1^2, \qquad \text{(B30)}$$

while the lower bound (58) is

$$k_1 \geqslant (0.133)\phi_1\Lambda_1^2, \qquad \text{(B31)}$$

where $\Lambda_1 = a/2$. For the slablike cross section, the exact result is

$$k_\infty = a^2\phi_1/12 \cong (0.083)\phi_1 a^2, \qquad \text{(B32)}$$

and the upper and lower bounds are, respectively,

$$k_\infty \leqslant (0.101)\phi_1 a^2 \qquad \text{(B33)}$$

and

$$k_\infty \geqslant (0.067)\phi_1 a^2. \qquad \text{(B34)}$$

For the purposes of Sec. V and for comparison with (B12), we note that the general relaxation time distribution for arrays of tubes with rectangular cross sections is

$$G_{a,b}(\Theta) = \sum_{m^2/a^2 + n^2/b^2 > 4\Lambda^2/\pi^2 \nu\Theta} \left(\frac{64}{\pi^4 m^2 n^2}\right). \qquad \text{(B35)}$$

APPENDIX C: SCALING PROPERTIES OF THE STIELTJES TRANSFORM

Define the *Stieltjes transform* of a probability distribution $G(\Theta)$, $0 < \Theta < \infty$ by the formula

$$S(\omega) = \int_0^\infty \frac{\Theta}{1+\Theta^2\omega^2}\, dG(\Theta). \qquad \text{(C1)}$$

In this section we show, based on classical Tauberian theorems,[21] that the scaling properties of $S(\omega)$ for $\omega \gg 1$ and of $G(\Theta)$ for $\Theta \ll 1$ are related in a simple way. In fact, we have the following.

Proposition: Let $0 < \alpha < 1$. *Then if*

$$\lim_{\omega \to +\infty} [\omega^{1+\alpha} S(\omega)] = C_1, \qquad \text{(C2)}$$

then

$$\lim_{\Theta \to 0} [\Theta^{-\alpha} G(\Theta)] = \frac{C_1 \cos[\alpha\pi/2]}{[\pi\alpha/2]}. \qquad \text{(C3)}$$

For applications to porous media, for which the asymptotic formula (78) holds, we shall take $\alpha = \frac{1}{2}$. Then, this proposition provides a justification for Eq. (87) in Sec. V.

Proof of the Proposition: Since

$$\int_{-\infty}^{+\infty} e^{-i\omega t - |t|/\Theta}\, dt = \frac{2\Theta}{1+\Theta^2\omega^2}, \qquad \text{(C4)}$$

we have

$$2S(\omega) = \int_{-\infty}^{+\infty} e^{-i\omega t}\, dt \left(\int_0^\infty e^{-|t|/\Theta}\, dG(\Theta)\right), \qquad \text{(C5)}$$

and $2S(\omega)$ can be viewed as the Fourier transform of the function

$$g(t) = \int_0^{+\infty} e^{-|t|/\Theta}\, dG(\Theta). \qquad \text{(C6)}$$

Our assumption on $S(\omega)$, given in (C2), states that the Fourier transform of $g(t)$ decays like $\omega^{-(1+\alpha)}$ as $\omega \to \infty$. Therefore, by a standard Abelian theorem for the Fourier transform, we have

$$g(t) = g(0) + C_2 t^\alpha + o(t^\alpha)$$
$$= 1 + C_2 t^\alpha + o(t^\alpha), \qquad \text{(C7)}$$

as $t \to 0$, where C_2 is a numerical constant. This equation can, in turn, be rewritten as

$$\int_0^\infty \left(\frac{1-e^{-t/\Theta}}{t}\right) dG(\Theta) \sim \frac{C_2}{t^{1-\alpha}}, \qquad \text{(C8)}$$

for $t \ll 1$. Introducing the auxiliary distribution function $\tilde{G}(s) = 1 - G(1/s)$, we have, from (C8),

$$\int_0^\infty \left(\frac{1-e^{-st}}{t}\right) d\tilde{G}(s) \sim \frac{C_2}{t^{1-\alpha}}, \qquad \text{(C9)}$$

for $t \ll 1$. Performing integration by parts, on the left-hand side of (C9), we obtain

$$\int_0^\infty e^{-st}[1-\tilde{G}(s)]\, ds \sim \frac{C_2}{t^{1-\alpha}}, \quad t \to 0. \qquad \text{(C10)}$$

We apply next the Tauberian theorem[21] to conclude that

$$1 - \tilde{G}(s) \sim C_3 s^{-\alpha}, \quad s \to \infty, \qquad \text{(C11)}$$

where C_3 is a constant depending on α and C_2. Recalling the definition of $\tilde{G}(s)$ we conclude that

$$G(\Theta) \sim C_3 \Theta^\alpha, \quad \Theta \to 0, \qquad \text{(C12)}$$

which proves the claim, insofar as the exponent in (C3) is concerned. To evaluate explicitly the constant C_3, we substitute the function $C_3\Theta^\alpha$ in the place of $G(\Theta)$ in (C1) and apply (C2). The conclusion is that

$$\lim_{\omega \to \infty} C_3 \int \frac{\omega^{1+\alpha}\Theta\, d\Theta^\alpha}{1+\omega^2\Theta^2} = C_1, \qquad \text{(C13)}$$

so that

$$C_3 \cdot \alpha \int_0^\infty \frac{\Theta^\alpha\, d\Theta}{1+\Theta^2} = C_1. \qquad \text{(C14)}$$

The integral in this last formula can be readily computed using contour integration, leading to the final answer

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$$C_3 = \frac{C_1 \cos[\alpha\pi/2]}{[\alpha\pi/2]}. \quad \text{(C15)}$$

This proves the proposition.

Taking $\alpha = \frac{1}{2}$ in (C3) we obtain, using the asymptotic relation (86), the asymptotic formula for the relaxation time distribution

$$G(\Theta) \sim (4\nu^{1/2}/\pi\Lambda)\Theta^{1/2}. \quad \text{(C16)}$$

APPENDIX D: HIGH-FREQUENCY LIMIT OF THE DYNAMIC PERMEABILITY AND THE Λ PARAMETER

Here we derive the asymptotic relation (78), i.e.,

$$\lim_{\omega\to\infty} \omega^{3/2}\,\mathrm{Re}\,\tilde{k}(\omega) = \nu^{3/2}\sqrt{2}/F\Lambda, \quad \text{(D1)}$$

where

$$\Lambda = \frac{2\int_{V_1} |\mathbf{E}(\mathbf{r})|^2\,dV}{\int_{\partial V_1} |\mathbf{E}(\mathbf{r})|^2\,dS}. \quad \text{(D2)}$$

The proof of (D1) and (D2) that we give follows the boundary-layer calculation suggested by Sheng and Zhou in Ref. 9, with the important difference that we incorporate in the boundary-layer expansion of the Stokes velocity terms up to order $\omega^{-3/2}$. The necessity of considering terms beyond the leading-order term (which is of order ω^{-1}) was overlooked in Ref. 9, leading to a value of the "Λ parameter" that is different from the Johnson–Koplik–Schwartz weighted volume-to-surface ratio [compare (D2) with Eq. (30) in Ref. 9]. We believe that the asymptotic analysis given hereafter clarifies this discrepancy.

We assume, as in Sheng and Zhou[9] that the pore-surface $\partial\mathscr{V}_1$ is a smooth, twice-differentiable surface.[22] According to Ref. 9 [also see (56)] the dynamic permeability $\tilde{k}(\omega)$ is given by

$$\tilde{k}(\omega) = \langle \mathbf{w}\cdot\mathbf{e}\rangle, \quad \text{(D3)}$$

where $\mathbf{w}$ is the solution of the Stokes boundary-value problem

$$\Delta\mathbf{w} + i(\omega/\nu)\mathbf{w} = \nabla p + \mathbf{e},$$
$$\nabla\cdot\mathbf{w} = 0, \quad \text{in } \mathscr{V}_1, \quad \text{(D4)}$$
$$\mathbf{w} = 0, \quad \text{on } \partial\mathscr{V}_1.$$

We introduce the small parameter $\epsilon = (\nu/\omega)^{1/2}$ (with dimensions of length) and rewrite the Stokes equation in (D4) as

$$\epsilon^2\,\Delta\mathbf{w} + i\mathbf{w} = \epsilon^2(\nabla p + \mathbf{e}). \quad \text{(D5)}$$

We wish to study the behavior of Re $\mathbf{w}$ as $\epsilon\to 0$. For this, observe that the fundamental solution of the equation

$$\Delta G(\mathbf{r}) + (i/\epsilon^2)G(\mathbf{r}) = \delta(\mathbf{r}), \quad \text{(D6)}$$

in three-space, where $\delta(\mathbf{r})$ is the Dirac delta function, satisfies

$$G(\mathbf{r}) = (1/4\pi|\mathbf{r}|)e^{-\sqrt{i}|\mathbf{r}|/\epsilon}, \quad \text{(D7)}$$

with $\sqrt{i} = (1+i)/\sqrt{2}$. A standard argument then shows that, for each positive length l, the solution of (D5), $\mathbf{w}(\mathbf{r})$, converges to zero exponentially as $\epsilon\to 0$ for $|\mathbf{r}|\geqslant l$. More precisely, we have the estimate $|\mathbf{w}(\mathbf{r})| \leqslant c_1 e^{-c_2/\epsilon}$ *uniformly for all* $\mathbf{r}$ *that lie at a distance* l *or more from* $\partial\mathscr{V}_1$, where c_1 and c_2 are positive constants depending on l but not on ϵ. Therefore, the leading contribution to the integral

$$\int_{\mathscr{V}_1} \mathbf{w}(\mathbf{r})\cdot\mathbf{e}\,dV \quad \text{(D8)}$$

comes from a boundary layer of width l near $\partial\mathscr{V}_1$, l being an arbitrary, finite length. The smoothness of $\partial\mathscr{V}_1$ assumed here implies that the pore surface has bounded curvature. Therefore, we can partition the boundary layer for small enough l into a union of "slablike" regions that project simply onto portions of the pore surface $\partial\mathscr{V}_1$ and cover completely the boundary layer. In each such region we can introduce a local coordinate system and study Eq. (D5). In a system of normal coordinates,[23] an elementary slablike region is described by the inequalities

$$-a < x < a, \quad -b < y < b, \quad 0 < z < l, \quad \text{(D9)}$$

where x, y represent (curvilinear) coordinates on the pore surface $\partial\mathscr{V}_1$, and z denotes the distance from the point $\mathbf{r}(x,y,z)$ to ∂V_1. In these coordinates, the Euclidean length element satisfies

$$ds^2 = g_{11}\,dx^2 + 2g_{12}\,dx\,dy + g_{22}\,dy^2 + dz^2, \quad \text{(D10)}$$

where g_{ij} are functions of (x,y,z). The equations for the velocity $\mathbf{w} = (w_x, w_y, w_z)$ in the coordinate system (x,y,z) are

$$\epsilon^2\Delta_g\mathbf{w} + \epsilon^2\frac{1}{\sqrt{g}}\frac{\partial}{\partial z}\left(\sqrt{g}\frac{\partial\mathbf{w}}{\partial z}\right) + i\mathbf{w} = \epsilon^2\begin{bmatrix} \nabla_g p + \begin{pmatrix} e_x \\ e_g \end{pmatrix} \\ \dfrac{\partial p}{\partial z} + e_z \end{bmatrix} \quad \text{(D11)}$$

and

$$\nabla_g\cdot\begin{pmatrix} w_{0x} \\ w_{0y} \end{pmatrix} + \frac{\partial w_{0z}}{\partial z} = 0, \quad \text{(D12)}$$

where the operators ∇_g and Δ_g are given, respectively, by

$$\nabla_g = \begin{bmatrix} g^{11} & g^{12} \\ g^{12} & g^{22} \end{bmatrix}\begin{bmatrix} \dfrac{\partial}{\partial x} \\ \dfrac{\partial}{\partial y} \end{bmatrix}, \quad \text{(D13)}$$

$$\Delta_g = \frac{1}{\sqrt{g}}\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}\right)\sqrt{g}\begin{bmatrix} g^{11} & g^{12} \\ g^{12} & g^{22} \end{bmatrix}\begin{bmatrix} \dfrac{\partial}{\partial x} \\ \dfrac{\partial}{\partial y} \end{bmatrix}. \quad \text{(D14)}$$

Here $\{g^{ij}\}$ denotes the inverse of the matrix $\{g^{ij}\}$ defined in (D10) and $g = \det(g_{ij}) = g_{11}g_{12} - g_{22}^2$. Note that in this coordinate system we have

$$dV = \sqrt{g}\,dx\,dy\,dz$$

and (D15)

$$dS = \sqrt{g}\,dx\,dy \quad (\text{for } z = 0).$$

To study the limit as $\epsilon\to 0$ of the Stokes velocity $\mathbf{w}$, we introduce the "stretched" variable

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$$\zeta = z/\epsilon. \quad \text{(D16)}$$

The equations satisfied by the velocity $\mathbf{w} = \mathbf{w}_\epsilon$ become

$$\epsilon^2 \Delta_g^{(\epsilon)} \mathbf{w}^{(\epsilon)} + \frac{1}{\sqrt{g^{(\epsilon)}}} \frac{\partial}{\partial \zeta}\left(\sqrt{g^{(\epsilon)}} \frac{\partial \mathbf{w}^{(\epsilon)}}{\partial \zeta}\right) + i\mathbf{w}^{(\epsilon)} = \epsilon^2 \begin{bmatrix} \nabla_g^{(\epsilon)} p^{(\epsilon)} + \begin{pmatrix} e_x \\ e_y \end{pmatrix} \\ \dfrac{1}{\epsilon}\dfrac{\partial p^{(\epsilon)}}{\partial \zeta} + e_z \end{bmatrix} \quad \text{(D17)}$$

and

$$\nabla_g^{(\epsilon)} \cdot \begin{bmatrix} \omega_x^{(\epsilon)} \\ \omega_y^{(\epsilon)} \end{bmatrix} + \frac{1}{\epsilon}\frac{\partial \omega_z^{(\epsilon)}}{\partial \zeta} = 0, \quad \text{(D18)}$$

in the domain

$$-a < x < a, \quad -b < y < b, \quad 0 < z < l/\epsilon, \quad \text{(D19)}$$

with the no-slip boundary condition

$$\mathbf{w}^{(\epsilon)} = 0 \quad \text{for } \zeta = 0. \quad \text{(D20)}$$

Superscripts (ϵ) are used to indicate the dependence of various quantities on the parameter ϵ. To calculate the limit of $\mathbf{w}^{(\epsilon)}$ as $\epsilon \to 0$, we use the ansatz

$$\mathbf{w}^{(\epsilon)} = \epsilon^2 \mathbf{w}_0(x,y,\zeta) + \epsilon^3 \mathbf{w}_1(x,y,\zeta) + \cdots,$$
$$p^{(\epsilon)} = p_0(x,y,\zeta) + \epsilon p_1(x,y,\zeta) + \cdots, \quad \text{(D21)}$$

substituting these expressions in (D17) and (D18) and equating powers of ϵ. This leads to a hierarchy of equations that can be solved explicitly. To leading order, we find that

$$\frac{\partial p_0}{\partial \zeta} = 0, \quad \frac{\partial w_{0z}}{\partial \zeta} = 0 \quad \text{(D22)}$$

and

$$\frac{\partial^2 \mathbf{w}_0}{\partial \zeta^2} + i\mathbf{w}_0 = \begin{bmatrix} \nabla_g^{(0)} p_0 + \begin{pmatrix} e_x \\ e_y \end{pmatrix} \\ \dfrac{\partial p_1}{\partial \zeta} + e_z \end{bmatrix}, \quad \text{(D23)}$$

where $\nabla_t^{(0)}$ denotes the operator ∇_g with $z = 0$ in the coefficients g^{ij}. We conclude from these equations that

$$p_0 = p_0(x,y) \quad \text{(D24)}$$

and that

$$w_{0z}(x,y,\zeta) = 0.$$

This, in turn, leads to

$$\frac{\partial p_1}{\partial \zeta} + e_z = 0,$$

which determines the function $p_1(x,y,\zeta)$ up to a function of x and y. Solving (D21) for w_{0x} and w_{0y} yields

$$\begin{bmatrix} w_{0x}(x,y,\zeta) \\ w_{0y}(x,y,\zeta) \end{bmatrix} = \frac{1}{i}\left[\nabla_g^{(0)} p + \begin{pmatrix} e_x \\ e_y \end{pmatrix}\right](1 - e^{-\sqrt{i}\zeta}). \quad \text{(D25)}$$

The first-order term in the expansion for the pressure $p_0(x,y)$ can be identified by recalling the well-known fact that the pressure gradient $\nabla p(x,y,z) + \mathbf{e}$ approaches, as $\omega \to \infty$ or $\epsilon \to 0$, the scaled electric field $\mathbf{E}$. From this it follows that $\nabla_g^{(0)} p + \binom{e_x}{e_y}$ coincides with the electric field on the pore surface, i.e.,

$$\mathbf{E}(x,y,0) = \begin{bmatrix} \nabla_g^{(0)} p + \binom{e_x}{e_y} \\ 0 \end{bmatrix}. \quad \text{(D26)}$$

Hence the (normalized) leading-order term in the expansion of $\mathbf{w}$ is

$$\mathbf{w}_0(x,y,\zeta) = (1/i)\mathbf{E}(x,y,0)(1 - e^{-\sqrt{i}\zeta}). \quad \text{(D27)}$$

This expression was derived by Sheng and Zhou in Ref. 9 by the same method. The real part of $\mathbf{w}_0$ is given by

$$\text{Re}\, \mathbf{w}_0(x,y,\zeta) = \mathbf{E}(x,y,0) e^{-\zeta/\sqrt{2}} \sin(\zeta/\sqrt{2}). \quad \text{(D28)}$$

Is it sufficient to take the leading-order term $\text{Re}\, \mathbf{w}_0(x,y,\zeta)$ to evaluate $\text{Re}\, \tilde{k}(\omega)$ as $\omega \to \infty$? The answer to this question is no, because the domain of integration has dimension l/ϵ in the ζ direction, so that terms of order ϵ (corresponding to $\mathbf{w}_1$) can yield finite contributions to the volume integral, unless they decay rapidly as $\zeta \to \infty$. Due to the exponential decay of the tangential components of $\text{Re}\, \mathbf{w}_1$ (this can easily be verified) it is sufficient to consider only the higher-order correction arising from $w_{1z}(x,y,\zeta)$. Using the incompressibility condition (D18) we obtain

$$\text{Re}\, w_{1z}(x,y,\zeta) = -(\nabla_g^{(0)} \cdot \mathbf{E})(x,y) \times \int_0^\zeta e^{-\sigma/\sqrt{2}} \sin\left(\frac{\sigma}{\sqrt{2}}\right) d\sigma, \quad \text{(D29)}$$

where $(\nabla_g^{(0)} \cdot \mathbf{E})(x,y)$ represents the *surface divergence* of the electric field $\mathbf{E}$ on $\partial\mathscr{V}_1$. In general, this quantity is nonzero, and then $\text{Re}\, w_{1z}(x,y,\zeta)$ converges to a finite limit as $\zeta \to \infty$. To calculate the contribution to $\text{Re}\langle \mathbf{w}_\epsilon \cdot \mathbf{e}\rangle$ arising from the "slab" under consideration we set

$$\mathbf{w}_\epsilon(x,y,z) \cong \begin{bmatrix} \epsilon^2 w_{0x}(x,y,z/\epsilon) \\ \epsilon^2 w_{0y}(x,y,z/\epsilon) \\ \epsilon^3 w_{1z}(x,y,z/\epsilon) \end{bmatrix}, \quad \text{(D30)}$$

so that

$$\text{Re}\, \mathbf{w}_\epsilon(x,y,z) \cong \epsilon^2 \mathbf{E}(x,y,0) e^{-z/\epsilon\sqrt{2}} \sin(z/\epsilon\sqrt{2}) - \epsilon^3 (\nabla_g^{(0)} \cdot \mathbf{E})(x,y)\boldsymbol{\eta} \int_{z/\epsilon}^0 e^{-\sigma/\sqrt{2}} \sin(\sigma/\sqrt{2}) d\sigma, \quad \text{(D31)}$$

where

$$\boldsymbol{\eta} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

represents that normal to $\partial\mathscr{V}_1$. Let us consider an arbitrary field

$$F_\epsilon(x,y,z) = \mathbf{F}_0(x,y) + \epsilon \mathbf{F}_1(x,y,\zeta) + o(\epsilon). \quad \text{(D32)}$$

Using (D31), we have

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$$\int_0^l \int_{-b}^{+b} \int_{-a}^{a} \mathrm{Re}\, \mathbf{w}_\epsilon \cdot \mathbf{F}_\epsilon \, dV = \epsilon^3 \int_0^{l/\epsilon} \int_{-b}^{+b} \int_{-a}^{+a} \mathbf{E}(x,y,0) \cdot \mathbf{F}_0(x,y) e^{-\xi/\sqrt{2}} \sin\left(\frac{\xi}{\sqrt{2}}\right) dS^{(\epsilon)} \, d\xi$$

$$- \epsilon^3 \int_0^l \int_{-b}^{+b} \int_{-a}^{+a} [\nabla_g^{(0)} \cdot \mathbf{E}(x,y)] F_{0z}(x,y) \int_0^{z/\epsilon} e^{-\sigma/\sqrt{2}} \sin\left(\frac{\sigma}{\sqrt{2}}\right) dV + o(\epsilon^3). \quad \text{(D33)}$$

According to (D3), we are interested in $F_\epsilon(x,y,z) = \mathbf{e}$, where $\mathbf{e}$ is the applied pressure drop. Substitution of this value in (D33) yields

$$\lim_{\epsilon \downarrow 0} \epsilon^{-3} \int_0^l \int_{-b}^{+b} \int_{-a}^{+a} \mathrm{Re}\, \mathbf{w}_\epsilon(x,y,z) \cdot \mathbf{e} \, dx\, dy\, dz$$

$$= \frac{1}{\sqrt{2}} \int_{-b}^{b} \int_{-a}^{+a} \mathbf{E}(x,y,0) \cdot \mathbf{e} \, dS^{(0)}$$

$$- \frac{1}{\sqrt{2}} \int_0^l \int_{-b}^{+b} \int_{-a}^{+a} [\nabla_g \cdot \mathbf{E}(x,y)] \mathbf{e}_z \, dV. \quad \text{(D34)}$$

The second term in this equation does not reduce, apparently, to a boundary integral. A more explicit calculation of this limit can be made using the fact that $\mathbf{e} = \mathbf{E} + \nabla \phi$, where ϕ is a scalar. A simple way of eliminating the volume integral contribution to (D33) is to replace $\mathbf{e}$ by $\mathbf{E}$ in (D3)—which is legitimate since $\langle \mathbf{w} \cdot \nabla \phi \rangle = 0$. Accordingly, if we set $\mathbf{F}_\epsilon(x,y,z) = \mathbf{E}(x,y,\epsilon\zeta)$ in (D34) we observe that, to leading order, $\mathbf{E}_0(x,y) = \mathbf{E}(x,y,0)$ is *tangential*, i.e., $E_{0z} = 0$, and hence the volume integral correction in (D34) vanishes. Thus, using (D33), we conclude that

$$\lim_{\epsilon \downarrow 0} \epsilon^{-3} \int_0^l \int_{-b}^{+b} \int_{-a}^{+a} \mathrm{Re}\, \mathbf{w}_\epsilon(x,y,z) \cdot \mathbf{E}(x,y,z) dx\, dy\, dz$$

$$= \frac{1}{\sqrt{2}} \int_{-b}^{+b} \int_{-a}^{+a} |\mathbf{E}(x,y)|^2 \, dS^{(0)}(x,y), \quad \text{(D35)}$$

where $dS^0(x,y) = \sqrt{g^{(0)}} dx\, dy$ is the surface element on $\partial \mathscr{V}_1$. We can now sum all the contributions to (D3) arising from elementary slablike regions in the boundary layer. Recalling that $\epsilon = \sqrt{\nu/\omega}$, we conclude that

$$\lim_{\omega \to \infty} \omega^{3/2} \mathrm{Re} \langle \mathbf{w} \cdot \mathbf{e}_0 \rangle$$

$$= \lim_{\omega \to \infty} \omega^{3/2} \mathrm{Re} \langle \mathbf{w} \cdot \mathbf{E} \rangle$$

$$\mathbf{E} = \frac{\nu^{3/2}}{\sqrt{2}} \frac{1}{V} \int_{\partial \mathscr{V}_1} |\mathbf{E}(\mathbf{r})|^2 \, dS. \quad \text{(D36)}$$

Finally, using the definition (D3) for the Λ parameter and the formula

$$\frac{1}{F} = \frac{1}{V} \int_{\mathscr{V}_1} |\mathbf{E}(\mathbf{r})|^2 \, dV, \quad \text{(D37)}$$

we conclude that $\lim_{\omega \to \infty} \omega^{3/2} \mathrm{Re}\, \tilde{k}(\omega) = \nu^{3/2} \sqrt{2}/\Lambda F$, as claimed.

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