New Pore-Size Parameter Characterizing Transport in Porous Media

David Linton Johnson, Joel Koplik, and Lawrence M. Schwartz
Schlumberger-Doll Research, Ridgefield, Connecticut 06877
(Received 12 June 1986)

We introduce a well-defined geometrical parameter, Λ, related to *dynamically connected* pore sizes in composite materials. Λ describes the effects of an internal boundary layer on a variety of processes including electrical surface conduction, high-frequency viscous damping of acoustic waves, and healing length effects in fourth sound. We argue that Λ is also related to the dc permeability to flow of a viscous fluid.

PACS numbers: 73.25.+i, 47.60.+i, 62.90.+k, 67.40.Hf

Fluid-saturated porous media arise in contexts as different as polymer gels, catalytic beds, and sedimentary rocks. These systems exhibit a wide range of unusual phenomena and are, in some respects, different from either liquids or solids. While recent authors have devoted considerable attention to porous media, our understanding of the basic physics of these composite materials is still at a fairly primitive stage. It would be particularly valuable to have a manageable set of *geometrical* parameters in terms of which the transport properties of porous media could be described. Obvious candidates are the porosity (the dimensionless pore volume) and the ratio of pore volume to surface area (a characteristic pore size), but these parameters are influenced by isolated sections of the pore space that do *not* contribute to either electrical or fluid flow. In this Letter we introduce a new length parameter, Λ, which is an intrinsic measure of interconnected pore size and is directly related to transport. In discussing a range of experiments influenced by surface effects involving the pore-grain interface, previous authors[1-6] have relied on *ad hoc* "effective radii" or "effective surface areas." We show that the parameter Λ (1) has a precise definition in terms of the solution of the potential flow problem and is readily calculated in a variety of physical models, (2) leads to a unified description of seemingly unrelated phenomena (the value of Λ deduced from one experiment can be used to *predict* the results of another), and (3) may provide a long-sought link between electrical conductivity and the dc permeability to flow of a viscous fluid.

Consider electrical conduction in an insulating porous medium saturated with fluid of conductivity $\sigma(\mathbf{r})$. Suppose that such a cube, with edges of length L, is placed between bus bars across which there is a potential difference $\Delta\psi$. The microscopic potential $\psi(\mathbf{r})$ obeys the identity

$$\nabla\cdot[\psi(\mathbf{r})\sigma(\mathbf{r})\nabla\psi(\mathbf{r})]=\sigma(\mathbf{r})\,|\nabla\psi(\mathbf{r})|^2.$$

On integration over the volume of the pore space,[7] the effective conductivity is exactly related to $\sigma(\mathbf{r})$ and $\psi(\mathbf{r})$ by

$$\sigma_{\text{eff}}=|\Delta\psi|^{-2}L^{-1}\int\sigma(\mathbf{r})\,|\nabla\psi(\mathbf{r})|^2dV.$$

In a case of particular importance, the conductivity of the pore fluid is uniform [i.e., $\sigma(\mathbf{r})\to\sigma_f$, $\psi(\mathbf{r})\to\psi_0(\mathbf{r})$] and it is conventional to introduce the formation factor $F\equiv\sigma_f\sigma_{\text{eff}}^{-1}$. Let the microscopic conductivity be perturbed to $\sigma(\mathbf{r})=\sigma_f+\delta\sigma(\mathbf{r})$. There is a corresponding change, $\psi(\mathbf{r})\to\psi_0(\mathbf{r})+\delta\psi(\mathbf{r})$, in the microscopic potential, but, because $\delta\psi(\mathbf{r})$ vanishes on the bus bars, there is no first-order contribution to σ_{eff} from terms explicitly containing $\delta\psi$. [We have

$$\sigma_{\text{eff}}=F^{-1}\sigma_f+|\Delta\psi|^{-2}L^{-1}\int\delta\sigma(\mathbf{r})\,|\nabla\psi_0|^2dV+O(\delta\sigma^2),$$

the first two terms being analogous to the Born approximation in scattering theory.] Consider perturbations of the form $\delta\sigma(\mathbf{r})=f(\varepsilon)$ in which ε is a local coordinate measured from the pore wall into the conducting region. We assume that the range of f is very small compared to the sizes of the pores, so that locally the walls appear to be flat on a length scale comparable to the range of f. $\Sigma_s\equiv\int f(\varepsilon)\,d\varepsilon$ is the interfacial conductivity and it follows that

$$\sigma_{\text{eff}}=F^{-1}\{\sigma_f+2\Sigma_s/\Lambda\}+O(\Sigma_s^2),\tag{1}$$

where the quantity Λ has dimensions of length and is rigorously given by

$$\frac{2}{\Lambda}=\frac{\int|\nabla\psi_0(\mathbf{r})|^2dS}{\int|\nabla\psi_0(\mathbf{r})|^2dV_p}.\tag{2}$$

Integration in the numerator of (2) is over the walls of the pore-grain interface; that in the denominator is over the pore volume. Thus, one accounts for the leading effects of surface conduction by means of a perturbation theory in which the relevant parameter, $2/\Lambda$, is an effective surface-to-pore-volume ratio wherein each area or volume element is weighted according to the local value of the field $\mathbf{E}_0$, which would exist in the *absence* of the surface mechanism. This weighting *eliminates* contributions from the isolated regions of the pore space that do not contribute to transport. Λ is a parameter characteristic of the *geometry* of the porous medium; a determination of Λ from one experiment is immediately transferable to another.

How does one calculate Λ? Any model system for which a theory of bulk conduction exists automatically yields Λ simply by the carrying out of the indicated in-

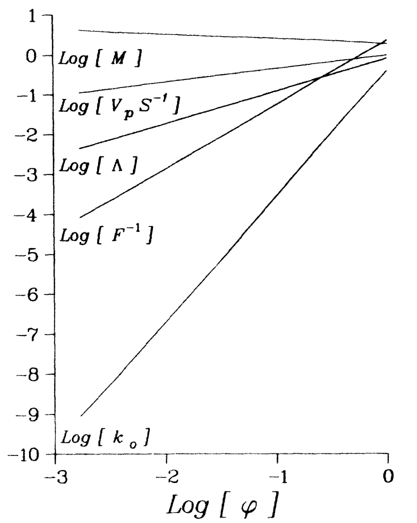

FIG. 1. Variations in M, V_p/S, F, Λ, and k_0 for shrinking-tubes model plotted against the porosity. Λ and V_p/S are normalized to c_0, F is the formation factor times $c_0^2 l^{-2}$ (where l is the tube length), and k_0 is the permeability multiplied by $l^2 c_0^{-4}$.

tegration in (2). An example is the "shrinking tubes" model[8] in which the pore space is pictured as a simple cubic array of tubes whose initial radii, $\{r\}$, are specified in terms of a distribution $P(r)$, and the porosity is then reduced by random shrinking of the tubes by a factor x. In Fig. 1 results are shown for the specific choice $P(r) = c_0^{-1}\exp(-r/c_0)$ and $x = 0.5$. Note that Λ decreases more rapidly as a function of porosity than the pore volume-to-surface ratio. A second class of models includes those in which the porosity decreases by uniform growth of the insulating phase into the pore space. The growth of the solid phase can be viewed either as a change in F due to a change in ϕ *or*, equivalently, as a surface layer perturbation. From (1) we have

$$\frac{2}{\Lambda} = \frac{d\ln F}{d\ln\phi}\frac{S}{V_p} \equiv m(\phi)\frac{S}{V_p}, \tag{3}$$

where ϕ is the porosity. (Note that this relation between Λ and the ratio of pore volume-to-surface area is *not* satisfied by the shrinking-tubes model because there the mechanism by which porosity decreases is quite different.) As long as there is no clustering, the high-porosity behavior of this model is independent of the arrangement of the sphere centers. For suspensions $(0.40 < \phi < 1.00)$, it is known experimentally[9] that $m(\phi) \approx 1.5$. It then follows that $\Lambda = 2\phi d/9(1-\phi)$ where d is the grain diameter. Values of Λ calculated from Eq. (3) are presented in Table I along with the relevant experimental values discussed below.

We now summarize some of the experimental situations in which Λ appears.

(1) Shaly sands.—The most direct realization of (2) occurs in the electrical conductivity of sandstones in which the (insulating) grains are coated with appreciable amounts of clay minerals.[1,2] Dry clay minerals usually contain charged impurities which are balanced by counter ions bound to their external surfaces. However, once the pore space is saturated with brine, the hydrated counter ions become mobile within a layer (whose thickness, h, depends on the brine salinity but is typically less than 40 Å) surrounding the clay particles. Surface conduction due to the counter ions then proceeds in parallel with the ionic conductivity associated with the brine. As typical pore sizes are greater than 1000 Å, the first requirement for the validity of (1) is easily fulfilled. Empirically, one finds that for "large enough" pore-fluid conductivity, there is a linear relationship which is commonly written as[1,2]

$$\sigma_{\text{eff}} = F^{-1}\{\sigma_f + BQ_v\}. \tag{4}$$

Here Q_v is the density of counter ions per unit pore volume and B is the equivalent conductance per ion, assumed to be the same as that of the bulk fluid. Equations (1) and (4) are identical if $2/\Lambda$ is replaced by S/V_p because $Q_v = n_s(S/V_p)$ where n_s is the surface charge density of the clay mineral and $\Sigma_s = n_s B$. If the pore fluid conductivity, σ_f, is reduced below BQ_v then σ_{eff}

TABLE I. Measured and calculated values of Λ and predicted permeability ratio M (see text).

Technique	ϕ	Grain diameter (μm)	$\frac{2\phi d}{9(1-\phi)}$ (μm)	Λ (Expt.) (μm)	k_0 (μm)^2	$\frac{8Fk_0}{\Lambda^2}$
First sound[a]	0.43	75	12.6	12.4	7	1.36
First sound[a]	0.41	110	17.0	17.9	12	1.44
First and second sound[a]	0.41	500	77.2	53.2	190	2.54
Second sound[b]	0.35	200	24	19	⋯	⋯
Fourth sound[c]	0.82	5.00×10^{-2}	5.06×10^{-2}	1.30×10^{-2}	⋯	⋯
Fourth sound[c]	0.60	9.0×10^{-3}	3.0×10^{-3}	2.4×10^{-3}	⋯	⋯

[a]Reference 5.
[b]Reference 4.
[c]Reference 3.

departs from the linear prediction of (4) (Ref. 1). It has been argued that this is due either to the breakdown of the assumption $h/\Lambda \ll 1$ (which seems unlikely), to a change in the surface ionic mobility (i.e., a change in B), or to the importance of the neglected diffusion current at low salinities.[2] Alternatively, we suggest that the decrease in $\sigma_{\rm eff}$ simply reflects the fact that (1) is valid only when $2\Sigma_s/\Lambda \ll \sigma_f$. To investigate this possibility we performed numerical calculations on a grain consolidation model in which the grains were coated with a uniform layer of thickness h and conductivity σ_l, and the conductivity of the pore fluid, σ_f, was varied. (This model begins, in the high-porosity limit, with a simple cubic array of identical spheres; the porosity is decreased by growth of the grains beyond the point where they overlap and form a continuous solid phase.[10]) Note that the numerical results plotted in Fig. 2 are in excellent agreement with the predictions of Eq. (1) for $\sigma_f \gtrsim \sigma_l$, but they depart significantly for $\sigma_l \ll \sigma_f$. This departure is due entirely to the different *geometrical path lengths* associated with surface and bulk conductivity in porous media.

(2) Dynamic permeability.—Suppose that a rigid porous solid is saturated with a Newtonian fluid of viscosity η and density ρ and subjected to a small-amplitude oscillatory pressure gradient at frequency ω. The rate at which fluid flows through a unit area of the sample is $\dot{Q} = -[\tilde{k}(\omega)/\eta]\nabla P$, where $\tilde{k}(\omega)$ is the dynamic permeability. As the frequency increases to the point where the viscous skin depth, $\delta = (2\eta/\rho\omega)^{1/2}$, becomes small compared to the pore dimensions, the microscopic fluid-flow pattern crosses over to potential flow except within a boundary layer of thickness δ at the pore walls

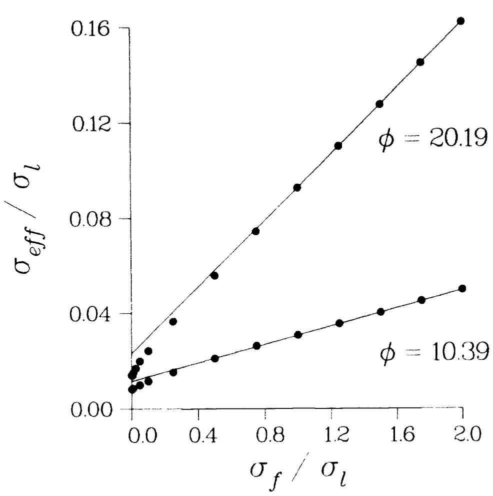

FIG. 2. Calculated conductivity, $\sigma_{\rm eff}$, as a function of pore fluid conductivity, σ_f for the grain consolidation model. The grain surface has been coated with a layer of conductivity σ_l and thickness $h = 0.015a$ (where a is the cube edge). The dots are the results of numerical calculations and the solid curves are based on Eqs. (1) and (3).

and it has been shown that[11]

$$\lim_{\omega\to\infty} \tilde{k}(\omega) = \frac{i\eta}{F\rho\omega}\left[1 - \left(\frac{i\eta}{\rho\omega}\right)^{1/2}\frac{2}{\Lambda}\right]. \tag{5}$$

We emphasize that this result, which follows from a solution to the Navier-Stokes equation, involves parameters (F and Λ) which derive from a solution to Maxwell's equations. For porous media saturated with superfluid ^{4}He, Eq. (5) leads to a prediction for the temperature and frequency dependence of the attenuation and dispersion of first and second sound. In particular, values of Λ [r in the notation of Ref. 4 and $(8/\delta)(ka/P)^{1/2}$ in that of Ref. 5] have been measured and are in good agreement with the calculated values (Table I). If one considers the acoustic properties of porous media more generally by relaxing the assumption of a rigid frame, the notion of dynamic permeability can be incorporated into the Biot theory.[12] The high-frequency attenuation of all three modes, fast compressional, slow-compressional, and shear, are proportional to δ/Λ, where δ is the viscous skin depth of the pore fluid, and we have another class of experiments for which Λ is transferable.

(3) Healing-length effects in fourth sound.—Consider He II confined to a superleak whose pores are so small that not only is the normal fluid clamped by its viscosity, but the healing length, ξ_H (the distance from the interface over which the superfluid density departs from its bulk value), may be comparable to the pore sizes.[13] Assuming the validity of two-fluid hydrodynamics, let us write for the variation of the superfluid density near the walls $\rho_s(\mathbf{r}) = \rho_s^{(0)}[1 - g(\varepsilon)]$, where $\rho_s^{(0)}$ is the bulk superfluid density and $\xi_H \equiv \int_0^\infty g(\varepsilon)\,d\varepsilon$. This hydrodynamic problem maps directly onto the canonical electrical problem and, to first order in ξ_H/Λ, the speed of fourth sound is

$$v_4^2 = \frac{1 - 2\xi_H/\Lambda}{F\phi}\frac{\rho_s^0}{\rho}c_1^2(1+\zeta), \tag{6}$$

where c_1 is the speed of first sound (assumed constant in the healing-length region) and ζ is a parameter whose value is less than 0.01 for all temperatures at saturated vapor pressure. This result is equivalent to the equation used by Tam and Ahlers[3] to interpret their fourth-sound data in packed-powder superleaks using ξ_H calculated from a theory using neutron-scattering and thermodynamic data. Values of Λ ($2a/f_1$ in their notation) for two superleaks are given in Table I and compared against the theoretical values. While the geometry of packed-powder superleaks does not correspond to a random distribution of particles because of clustering effects, the calculated values are nevertheless close to those measured.

We now wish to speculate on a relationship between Λ and the dc permeability $k_0 = \tilde{k}(\omega = 0)$. In a system of winding, nonintersecting tubes of radius R we have $k_0 = R^2/8F$ (Ref. 6). However, in a real porous medium the appropriate value of R is not obvious.[14] Historically, there have been attempts to correlate k_0 with the total pore-surface area which have met with limited success largely because the total surface area includes parts of the pore space in which little flow occurs.[6] One may expect Λ to be more closely related to k_0 because it is a measure of *dynamically connected* porosity. Returning to the intersecting-tube model (for which $\Lambda = R$, exactly), we are led to the conjecture $M \equiv 8Fk_0/\Lambda^2 \approx 1$ for a variety of porous media. The limited amount of experimental data available shows that M takes on values in the range 1.4 to 2.5 (Table I). While there is no rigorous reason why M should be constant, numerical simulations on the shrinking-tubes model indicate that, over a range of porosity in which k_0 varies by eight decades, the variation in M is within a factor of 2. (See Fig. 1.) We note also that for this model, the Kozeny-Carman relationship,[6] $k_0 \sim F^{-1}(V_p/S)^2$, fails utterly.

Finally, suppose that the pore-grain interface is a fractal.[15] To be specific, consider the healing-length effect; since Λ^{-1} is an effective surface area (normalized to a Euclidean volume), it scales with the size of the yardstick, ξ_H, viz., $\Lambda^{-1} \propto \xi_H^{2-d_\Lambda}$ where d_Λ is noninteger. The generalization of Eq. (6) is then open to experimental investigation with use of the known temperature dependence of $\xi_H(T)$.

We are grateful for several stimulating discussions with A. Libchaber, B. I. Halperin, and especially J. Banavar, who pointed out a serious inconsistency in an earlier version of the theory.

[1]M. H. Waxman and L. J. M. Smits, Trans. Soc. Pet. Eng. **243**, 107 (1968).

[2]W. C. Chew and P. N. Sen, J. Chem. Phys. **77**, 2042 (1982), and **77**, 4683 (1982); C. Clavier, G. Coates, and J. Dumanoir, SPEJ Soc. Pet. Eng. J. **24**, 153 (1984).

[3]W. Y. Tam and G. Ahlers, Phys. Lett. **92A**, 445 (1982).

[4]D. Singer, F. Pasierb, and H. Kojima, Phys. Rev. B **30**, 2909 (1984).

[5]S. R. Baker, Ph.D. thesis, Department of Physics, University of California, Los Angeles, 1985 (unpublished); S. R. Baker and I. Rudnick, IEEE Trans. Ultrason. Ferroelect. Freq. Control **33**, 118 (1986); and in *Proceedings of the 1985 IEEE Ultrasonics Symposium, San Francisco, 1985* (IEEE, New York, 1986).

[6]A. E. Scheidegger, *Physics of Flow Through Porous Media* (University of Toronto Press, Toronto, 1974), 3rd ed.; see also D. Wilkinson, Phys. Fluids **28**, 1015 (1985).

[7]This derivation is identical to that of (2.2) in D. J. Bergman, Phys. Rep. **43**, 377 (1978).

[8]P.-z. Wong, J. Koplik, and J. P. Tomanic, Phys. Rev. B **30**, 6606 (1984).

[9]R. E. De La Rue and C. W. Tobias, J. Electrochem. Soc. **106**, 827 (1959).

[10]J. N. Roberts and L. M. Schwartz, Phys. Rev. B **31**, 5990 (1985).

[11]D. L. Johnson, J. Koplik, and R. Dashen, to be published.

[12]D. L. Johnson, in "Frontiers of Physical Acoustics," International School of Physics "Enrico Fermi," Course XCIII, edited by D. Sette and A. Palma (North-Holland, Amsterdam, to be published).

[13]S. J. Putterman, *Superfluid Hydrodynamics* (North-Holland, Amsterdam, 1974); I. Rudnick, in *New Directions in Physical Acoustics,* International School of Physics "Enrico Fermi," Course LXIII, edited by D. Sette (North-Holland, Amsterdam, 1976), p. 112.

[14]A. J. Katz and A. H. Thompson (unpublished) have recently related R to l_c, the critical pore size for a percolating path.

[15]D. Avnir, D. Farin, and P. Pfeiffer, Nature (London) **308**, 261 (1984); A. J. Katz and A. H. Thompson, Phys. Rev. Lett. **54**, 1325 (1985); P.-z. Wong, J. Howard, and J.-S. Lin, Phys. Rev. Lett. **57**, 637 (1986).