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# Characteristic pore sizes and transport in porous media

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Analytic calculations of Λ, a pore-size parameter which characterizes surface effects on transport in porous media, are carried out using two distinct approximations: (1) effective-medium theory and (2) percolation ideas recently applied by Katz and Thompson to the permeability of sedimentary rocks. Our calculations suggest that Λ may be determined by mercury injection experiments. We also study the phenomenon of electrical surface conduction using both approximations.

Porous media abound in nature and are increasingly finding applications in such diverse fields as physics, chemistry, biology, and geology. Examples include polymer gels, catalytic beds, biological cells, and sedimentary rocks. How does one characterize transport in porous media? For electrical conduction, the answer is straightforward. The conductivity $\sigma$ in a porous medium where the pores are conducting and the solid is insulating, is a quantity that takes into account the volume fraction of the conducting phase ($\phi$) and the tortuous paths that the electrical current has to take in the complex geometry of the porous medium. A uniform scale transformation of the porous medium, where, for example, all the pores (conducting regions) and all the grains (insulating regions) are increased (or decreased) in size by a constant scale factor does *not* alter the electrical conductivity. The situation is not this simple for fluid transport. In this case, the analog of the electrical conductivity is the permeability $k$, defined by the Darcy equation (the fluid-transport analog of Ohm's law): $\mathbf{v}=(-k/\eta)\nabla p$, where $\mathbf{v}$ is the fluid flow velocity in the porous medium, $\eta$ is the fluid viscosity, and $\nabla p$ is the gradient in the pressure across the sample. The permeability has units of length squared and thus depends not only on the porosity and tortuosity (as does the electrical conductivity) but also on the absolute length scales of the pores that govern fluid transport.

Two recent papers[1,2] have addressed the problem of how one identifies the relevant length scale characterizing fluid transport in porous media. In an elegant formulation, Katz and Thompson[1] (KT) have shown both theoretically and experimentally that when the porous medium (made of insulating solid) is characterized by a broad distribution of pore sizes (e.g., log-normal) there exists a simple relationship between the permeability and conductivity, viz.,

$$k=c_1 l_c^2/F \ , \tag{1}$$

where $F$, a dimensionless constant called the formation factor, relates the conductivity of the sample $\sigma$ to that of the pore fluid, $\sigma_f$, viz., $F=(\sigma_f/\sigma)$, and $c_1$ is a constant that KT estimate to be $4.4\times10^{-3}$ and $l_c$ is a characteristic length that KT relate to the threshold pressure in a mercury injection experiment. $l_c$ is well defined only when the porous medium can be modeled as a distribution of cylindrical pores on a lattice. On the other hand, Johnson, Koplik, and Schwartz[2] (JKS) have introduced a geometrical pore-size parameter Λ, which is always well defined for any porous medium and which describes the effects of an internal boundary layer on a variety of processes such as electrical surface conduction, high-frequency viscous damping of acoustic waves, and healing-length effects in fourth sound. [The precise definition of Λ appears in (4a) and (4b), below.] Unlike such standard pore-size indicators as the pore-volume-to-surface-area ratio, Λ is a measure of *dynamically* connected pore sizes and so it is reasonable to expect that it may be related to permeability, at least approximately, because dead-end and isolated pores are irrelevant to the value of Λ. Based on plausible physical arguments, and backed by detailed computer simulations on random materials, JKS show that

$$k=c_2\frac{\Lambda^2}{8F} \ , \tag{2}$$

where $c_2$ is a constant of order 1; $c_2\equiv1$ for an array of nonintersecting tubes canted at an arbitrary angle. The limited amount of available experimental data on real porous media indicates that $c_2$ is indeed of order unity. There is no fundamental reason why (2) should hold—Λ (below) and $F$ are defined in terms of the solution to a potential flow problem, whereas $k$ is determined from the solution to Poiseuille flow—but it has all the right ingredients in terms of well-defined independently measurable quantities: Equation (2) includes a dynamically connected pore-size parameter Λ, and it includes tortuosity effects through $F$.

The question we wish to address in the present Rapid Communication is this: For the broad distributions of tube radii for which the KT analysis can be presumed to have approximate validity, can one establish a relation between $l_c$ and Λ which makes Eqs. (1) and (2) consistent? We show that within the framework of the KT derivation of Eq. (1), Λ can be calculated as well; the constant $c_2$ can be evaluated and is indeed of order unity. Our result implies not only that Λ can be determined from a measurement of permeability, but also that it may be determined by a mercury injection experiment. Obviously one would like to know the value of Λ in cases for which the surface conductivity $\Sigma_s$ (below) is not known.

As stated earlier, the KT analysis was specifically designed for a broad distribution of pore sizes. To complement the KT analysis for a more normal (not unusually broad) pore-size distribution, we consider the effective-medium theory which is known to give an accurate solution to the random-lattice problem even when the distribution is quite broad; it becomes exact in the limit of a narrow distribution. We show how $\Lambda$ can be calculated using effective-medium theory and again show that $c_2$ is of order unity for a uniform distribution of pore sizes.

Thus, we have established, both for extremely broad distributions of tube radii as well as for more "normal" ones, that $\Lambda$, which is always well defined, is also related to permeability via Eq. (2). Finally, to establish connection with the shaley-sand conductivity problem to which we alluded, we carry out analytic calculations, using both the KT approximation and effective-medium theory, of the conductivity of a porous medium having a layer of constant surface conductance as the conductivity of the pore fluid $\sigma_f$ is varied.

The KT analysis[1] is based on ideas introduced by Ambegaokar, Halperin, and Langer[3] (AHL) and refined by Shante and Kirkpatrick[4] (SK) to deal with electrical transport in a random system with a broad distribution of conductances. We assume such a wide distribution of pore sizes. A cylindrical pore geometry of diameter $d$ and length $l$ is assumed. To study the robustness of $c_1$ and $c_2$, two simple cases may be considered. Following KT, we may take $d=l$ or, alternatively, $l$ may be held fixed and $d$ varied independent of $l$. To calculate $\Lambda$, we carry out the KT analysis, but include an additional surface conductivity whose value is $\Sigma_s$.

$l=l_0$ (constant): The effective electrical conductance $g_e(d)$ and the hydraulic conductance $g_h(d)$ of a pore of diameter $d$ are given by

$$g_e(d)=\frac{\pi d^2}{4l_0}\sigma_f+\frac{\pi d\Sigma_s}{l_0} , \tag{3a}$$

and

$$g_h(d)=\frac{\pi d^4}{128 l_0 \eta} , \tag{3b}$$

where $\eta$ is the fluid viscosity and $\Sigma_s$ is the surface conductivity of the pore walls. Following JKS,[2] $\Lambda$ may be determined by computing the electrical conductivity of the porous medium $\sigma$ in the limit where the bulk conduction due to $\sigma_f$ dominates that due to the surface conduction $\Sigma_s$:

$$\sigma=F^{-1}\left(\sigma_f+\frac{2\Sigma_s}{\Lambda}\right)+O(\Sigma_s^2) . \tag{4a}$$

$F$ is as defined previously; it is determined experimentally from a plot of $\sigma$ vs $\sigma_f$ in the region of high salinity where the data approach a straight line. $\Lambda$ is an effective pore radius given exactly by

$$\frac{2}{\Lambda}=\frac{\int |E_0|^2 dS}{\int |E_0|^2 dV_p} , \tag{4b}$$

in which $E_0$ is the microscopic electric field when $\Sigma_s\equiv 0$. The integration of the numerator is taken over the pore-wall surface; that of the denominator is taken over the pore volume. Equations (4a) and (4b) predict that a plot of $\sigma$ vs $\sigma_f$ holding $\Sigma_s$ fixed will tend to a straight line for large enough $\sigma_f$, whose slope and intercept are determined from the solution to Poisson's equation in the *absence* of a surface mechanism.

The effective permeability (hydraulic conductivity) and $\sigma$ can be computed quite readily. We illustrate the calculation by showing how $\sigma$ may be obtained. Following SK,[4] $\sigma$ may be obtained as a variational bound by maximizing $\sigma_1$ given by

$$\sigma_1=\frac{T}{l_0}g_e(d)[p(d)-p(d_c)]^t , \tag{5}$$

with respect to $d$. $g_e(d)$ for this case is given in Eq. (3a). $T$ is a constant which depends on the lattice structure; the *same* constant appears for the hydraulic conductivity calculation as well and therefore drops out when the ratio of the permeability to the conductivity is taken. $p(d)$ is the probability that there exists a pore of size greater than $d$. $d_c[\equiv l_c$ in Eq. (1)] is the diameter of the smallest pore (weakest link) in a percolation network of the largest pores in the porous medium and $t\simeq 1.9$ is the percolation conductivity exponent. Physically, Eq. (5) arises on replacing all pores of size greater than $d$ by pores of size $d$ and all pores of size less than $d$ by size 0. Hence $\sigma_1$ in Eq. (5) is necessarily less than the true $\sigma$ and the best estimate of $\sigma$ is obtained on maximizing the expression in Eq. (5) with respect to $d$. Setting the derivative of $\sigma$ with respect to $d$ equal to zero and making the KT linearization approximation[1] $[d_c t p''(d_c)/p'(d_c)\ll 1$, where $p'$ and $p''$ are first and second derivatives of $p(d)$ with respect to $d$], we find that $d_m$, the value of $d$ that maximizes (5) is given by

$$d_m=\frac{d_c[1-2z(1+t)+\sqrt{1+4z^2(1+t)^2+4z}\,]}{2+t} , \tag{6}$$

with

$$z=\frac{\Sigma_s}{\sigma_f d_c} .$$

$\sigma$ is then obtained by evaluating $\sigma_1$ [given by Eq. (5)] at $d=d_m$ [defined by Eq. (6)]. A linearization of $\sigma$, about $z=0$, is used in conjunction with Eq. (4) to obtain $\Lambda$:

$$\Lambda=\frac{d_c}{t+2} . \tag{7}$$

A similar analysis for the permeability may also be carried out, finally yielding

$$c_1=2\frac{(2+t)^{2+t}}{(4+t)^{4+t}}$$

and

$$c_2=16\frac{(2+t)^{4+t}}{(4+t)^{4+t}} . \tag{8}$$

For $t=1.9$, $c_1\simeq 1.14\times 10^{-2}$ and $c_2\simeq 1.39$.

$l=d$: The calculational procedure is identical to the one sketched above and the results are

$$\Lambda=\frac{d_c}{2(1+t)}=\frac{l_c}{2(1+t)} ,$$
$$c_1=\frac{27}{32}\frac{(1+t)^{1+t}}{(3+t)^{3+t}} , \tag{9}$$

and

$$c_2 = 27\frac{(1+t)^{3+t}}{(3+t)^{3+t}} .$$

For $t=1.9$, $c_1 \simeq 7.68\times 10^{-3}$ and $c_2 \simeq 2.07$.

It should be noted that our result for $c_1$ for the case $l=d$, is different from that obtained by KT. The reason for this difference is that whereas we maximize $\sigma_1$ in Eq. (5) and assume that the electrical conductivity is proportional to this maximum value, KT divide this maximum value not by $l_0$ but by $d_m$ (and in the case of the hydraulic conductivity by the corresponding $d_m$) to get the effective conductivity. Such a calculation leads to

$$\Lambda = \frac{l_c}{2(1+2t)} ,$$

$$c_1 = \frac{9}{32}\frac{(1+t)^t}{(3+t)^{2+t}} , \tag{10}$$

and

$$c_2 = \frac{9(1+2t)^2(1+t)^t}{(3+t)^{2+t}} .$$

Again, with $t=1.9$, $c_1 \simeq 4.32\times 10^{-3}$ (as given by KT) and $c_2 \simeq 3.19$.

The previous analysis is valid only when there is a wide distribution of sizes in a porous medium. In many situations, this may not be realized and we now proceed to an effective-medium theory[5] calculation of $\Lambda$ and $c_2$ for such cases. For simplicity and to be specific, let us focus on a network consisting of a simple cubic array of tubes of fixed length $l_0$ and varying radii $r_i$ between 0 and $r_0$. The electrical and the hydraulic conductance of a tube of radius $r$ is, as before, given by Eq. (3) with $d=2r$. Within the framework of effective-medium theory, the conductivity $\sigma$ and the permeability $k$ are obtained by solving

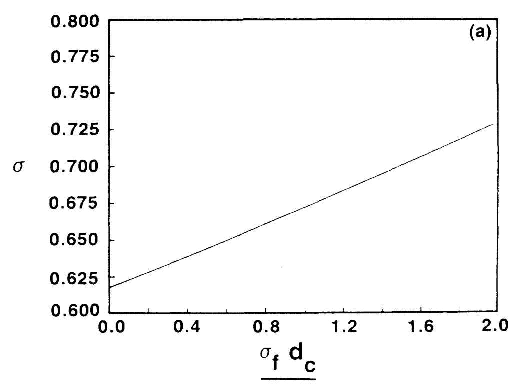
$$\frac{1}{r_0}\int_0^{r_0} dr \frac{\sigma - g_e(r)/l_0}{2\sigma + g_e(r)/l_0} = 0 \tag{11}$$

and

$$\frac{1}{r_0}\int_0^{r_0} dr \frac{k/\eta - g_h(r)/l_0}{2k/\eta + g_h(r)/l_0} = 0 . \tag{12}$$

The integrals are readily evaluated in closed form. We merely summarize the results. As before, $\sigma$ is expanded in a power series in $\Sigma$ to obtain the leading order correction and hence $\Lambda$. Evaluating the permeability from Eq. (12) enables us to calculate $c_2$. We find that $\Lambda = 0.508 r_0$ for the simple example and that $c_2 = 1.46$, a number which is again of order unity. The value of $\Lambda$ is substantially different from a characteristic tube radius derived from an average surface to volume ratio, i.e., $2r_0/3$. Therefore, even though the distribution of tube radii is narrow enough for the validity of the effective mass approximation to hold, it is not so narrow that one can neglect the fluctuation of $E_0$ in Eq. (4b) altogether. The value of $\Lambda$ and $c_2$ derived from effective-medium theory are in excellent agreement with numerical simulations carried out by Koplik[6] for the same distribution.

We now turn to the shaley-sandstone conductivity problem.[7] As discussed in JKS,[2] clay minerals containing charged impurities balanced by counter ions bound to their external surface cling to the walls of the insulating grains. When such a rock is saturated with even mildly salty water, the hydrated counter ions become mobile in a very thin layer surrounding the clay particles. This provides a surface conduction mechanism in addition to the usual bulk electrical conduction analogous to Eq. (3). For large values of $\sigma_f$, Eq. (4a) will hold, but when $\sigma_f \leq \Sigma_s/\Lambda$ a plot of $\sigma$ vs $\sigma_f$ will, in general, depart from the linear relation implied by (4a). Using each of the two approximations described above, it is straightforward to calculate the dependence of $\sigma$ as a function of $\sigma_f$ for a constant $\Sigma_s$. The resulting plots in Figs. 1(a) and 1(b) show little curvature, implying, somewhat surprisingly, that within each of the two widely differing approximations—one appropriate to a relatively narrow distribution of radii, the other appropriate to a very broad distribution—the geometrical path lengths associated with surface and bulk conductivity are nearly the same *for random lattices.* We note that the effective-medium approximation has previously been shown[5] to give an accurate description of transport in random lattices having narrow to mediumly broad distributions of pore sizes, whereas the AHL formalism has been shown[3] to give an accurate description of systems having



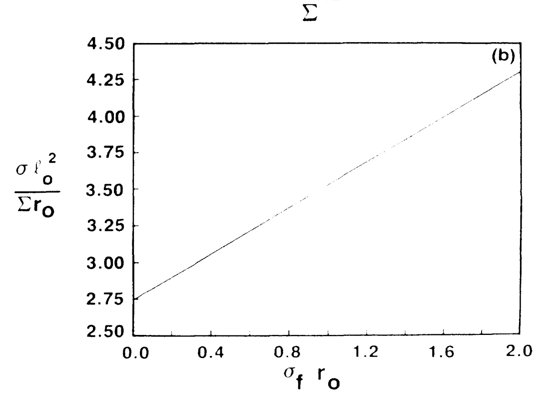




FIG. 1. Variation of $\sigma$ as $\sigma_f$ is changed. A constant surface conductivity $\Sigma_s$ is assumed. Both the figures assume that the tube length is a constant. (a) The KT scheme: plot of $\sigma$ (to within a multiplicative constant that depends on the actual distribution of pore sizes) vs $\sigma_f d_c/\Sigma_s$. (b) Effective-medium theory: plot of $\sigma l_0^2/\Sigma_s r_0$ vs $r_0\sigma_f/\Sigma_s$. A uniform distribution in tube radii between 0 and $r_0$ is assumed.

medium to very broad distributions. We conclude that random lattices will always tend to give a linear dependence of $\sigma$ on $\sigma_f$ throughout the entire range, unless the distribution is pathological. By contrast, it is noteworthy that the numerical simulations described in JKS,[2] for the grain consolidation model exhibit appreciable curvature for low values of $\sigma_f$. 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. This, then, points up a qualitative difference between random lattices and other geometries for porous media. We note that sedimentary rocks containing appreciable amounts of charged clay minerals (i.e., appreciable values of $\Sigma_s$) also exhibit substantial curvature at low salinities.[7] At present it is not known whether $\Sigma_s$, in these "shaley sands" may sensibly be considered to be independent of salinity, i.e., whether it is constant as $\sigma_f$ varies. Nonetheless, for all geometries thus far considered, Eq. (2) holds with $c_2 \simeq 1-3$, which implies that transport can be characterized by a single effective pore size $\Lambda$.

In summary, we have studied transport in random lattice models of porous media using two distinct schemes, one suitable for a broad distribution of pore sizes and the other applicable when the distribution is not unusually broad. In the former case, we established a connection between $\Lambda$ and a threshold length scale that can be determined using a mercury injection experiment. In all the cases studied $\Lambda$, which is defined in terms of surface effects on potential flow, was shown to be suitable candidate for the unique length scale that characterizes Poiseuille flow in porous media.

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