which has been attained for liquid diffusivity measurements with the wedge interferometer by Duda et al. (1969). The only significant disadvantages of the technique are the fact that it is probably more difficult to carry out an experiment with this apparatus than with the equipment utilized in previous investigations and the fact that accurate diffusivity data must be available. However, such data can be generated from appropriately conducted free diffusion experiments by using the wedge interferometer.

ACKNOWLEDGMENT

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

NOTATION

d = wedge thickness
D = binary mutual diffusion coefficient
L = membrane thickness
n = refractive index
n_A = mass flux of alcohol with respect to a fixed reference frame
n_W = mass flux of water with respect to a fixed reference frame
n_z = refractive index along a fringe at position z
n_2 = refractive index of solution used for reference free-diffusion experiment
n_∞ = refractive index of flowing solution
q = quantity defined by Equation (8)
X = quantity defined by Equation (14)
y = distance variable parallel to membrane
y_z, y_1, y_2, y_∞ = fringe positions defined in Figure 3
Y = quantity defined by Equation (13)
z = distance variable normal to membrane
z_o = reference position in diffusion field

Greek Letters

λ = wavelength of monochromatic light
ν = integer
ρ = total mass density of binary liquid phase solution
ϕ = distance of reference line from wedge axis
ω_A = mass fraction of alcohol
ω_W = mass fraction of water
ω_{WO} = mass fraction of water at z_o

LITERATURE CITED

Bollenbeck, P. H., and W. F. Ramirez, "Use of a Rayleigh Interferometer for Membrane Transport Studies," *Ind. Eng. Chem. Fundamentals*, **13**, 385 (1974).

Duda, J. L., W. L. Sigelko, and J. S. Vrentas, "Binary Diffusion Studies with a Wedge Interferometer," *J. Phys. Chem.*, **73**, 141 (1969).

Forgacs, C., J. Leibovitz, R. N. O'Brien, and K. S. Spiegler, "Interferometric Study of Concentration Profiles in Solutions near Membrane Surfaces," *Electrochimica Acta*, **20**, 555 (1975).

Hammond, B. R., and R. H. Stokes, "Diffusion in Binary Liquid Mixtures. Part 1.—Diffusion Coefficients in the Systems Ethanol + Water at 25°," *Trans. Faraday Soc.*, **49**, 890 (1953).

Min, S., "Phenomenological Studies of Membrane Transport with a Wedge Interferometer," Ph.D. thesis, The Pennsylvania State University, University Park (1975).

Perry, J. H., *Chemical Engineers' Handbook*, 3 ed., p. 188, McGraw-Hill, New York (1950).

Smith, K. A., C. K. Colton, E. W. Merrill, and L. B. Evans, "Convective Transport in a Batch Dialyzer: Determination of True Membrane Permeability from a Single Measurement," *Chem. Eng. Progr. Symposium Ser., No. 84*, **64**, 45 (1968).

Washburn, E. W., *International Critical Tables*, Vol. VII, p. 67, McGraw-Hill, New York (1930).

Manuscript received August 1, 1975; revision received November 4, and accepted November 5, 1975.

Prediction of Transport Processes Within Porous Media: Diffusive Transport Processes Within Anisotropic or Isotropic Swarms of Nonspherical Particles

The effects of particle shape and orientation upon diffusive transport processes occurring within unconsolidated porous media are investigated analytically. By means of a generalization of an earlier presented geometric model, diffusivities are predicted for both anisotropic systems (represented by swarms of aligned oblate or prolate spheroids) and isotropic systems (represented by swarms of randomly orientated spheroids). Theoretical predictions are compared with experimental data reported in the literature.

G. NEALE
and
W. K. NADER

Chemical Engineering Department
The University of Alberta
Edmonton, Canada

Correspondence concerning this paper should be addressed to W. K. Nader.

SCOPE

The principal objectives of this work are to gain insight into and to predict the effects which particle shape and orientation have on diffusive transport processes (notably molecular diffusion, ionic diffusion, and electric conduction) occurring within unconsolidated porous media.

In practice, many porous media are anisotropic, being composed of preferentially orientated particles far removed in shape from the spherical geometry, for example, sand beds consisting of flattish or elongated particles. A fair representation of such anisotropic systems may be provided by a homogeneous swarm of aligned particles possessing the shape of oblate or prolate spheroids, respectively. The spheroid appears to be the most advantageous generalized geometry for this study because spheroids approximate a vast range of physically important shapes (ranging between such extremes as thin circular disks and slender circular cylinders) and because the mathematical model based upon the spheroid lends itself to a rigorous mathematical treatment.

This analysis seeks to achieve the above-mentioned objectives by generalizing the geometric model proposed earlier for spheres (Neale and Nader, 1973, 1974) and extended recently to the case of cylinders (Neale and Masliyah, 1975) to the case of aligned spheroids. Also considered is the case of isotropic systems composed of spheroids orientated randomly without preferred orientation.

CONCLUSIONS AND SIGNIFICANCE

A new geometric model for studying transport processes within isotropic porous media composed of spherical particles was recently proposed (Neale and Nader, 1973, 1974). This model proved particularly useful as it produced successful predictions not only for diffusive transport processes but also for creeping fluid flow.

However, not all unconsolidated porous media can be represented, even approximately, by a swarm of spherical particles. Indeed, the constituent particles of many porous media are distinctly nonspherical, often being flattish or elongated in shape. Such systems are markedly anisotropic when the particles are similarly orientated but may well be isotropic when they are orientated randomly according to a uniform distribution.

The model proposed previously for spheres cannot be expected to provide satisfactory predictions for porous media composed of distinctly nonspherical particles. That model has therefore been generalized to accommodate particles having the shape of spheroids (ellipsoids of revolution); spheroids possessing various eccentricities serve as fair representations of a vast spectrum of convex particle shapes, ranging between such extremes as those of thin circular disks (flakes) and thin circular cylinders (rods, fibers). Based upon this generalized model, a theory has been developed which permits the quantitative study of diffusive transport processes occurring within the interstices of a broad class of anisotropic unconsolidated porous media. Predictions are presented here for the effective diffusivity (electric conductivity) of anisotropic systems composed of aligned oblate spheroids [Equations (20) and (21), Figure 3] or aligned prolate spheroids [Equations (24) and (25), Figure 4], and for isotropic systems composed of randomly orientated spheroids [Equation (31) and Figures 5 and 6]. The numerical values predicted by the theory are in good agreement with the rather sparse experimental data available in the literature (Figure 7).

The theory developed here should find useful application in the numerous areas where anisotropic porous media are encountered in practice. Notable examples of anisotropic media include many catalyst beds, filter cakes, sewage sediments, river beds, petroleum reservoir rock formations and, among others, the drilling muds and mud cakes used in the drilling of oil wells. Moreover, the analysis presented here indicates that anisotropic porous media are amenable to mathematical modeling, and this may encourage further research into this practically important, but hitherto rather neglected, field.

ANISOTROPIC POROUS MEDIA

One considers an isotropic porous medium to behave as a macroscopically quasihomogeneous mass. Therefore, diffusion within an anisotropic porous medium is governed by the generalized form of Fick's law:

$$\mathbf{q} = -\mathbf{D}\,\mathrm{grad}(c) \qquad (1)^*$$

where $\mathbf{q}$ denotes the diffusive flux vector, c the concentration of the diffusing species, and $\mathbf{D}$ the symmetric, second-order diffusivity tensor. In a Cartesian frame of reference $[x, y, z]$, the matrix associated with the diffusivity tensor has the form (Rice et al., 1970):

$$\begin{bmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{xy} & D_{yy} & D_{yz} \\ D_{xz} & D_{yz} & D_{zz} \end{bmatrix} \qquad (2)$$

When the Cartesian frame of reference is space rotated so that the axes become collinear with the mutually orthogonal characteristic directions of the above matrix, that is, collinear with the principal axes of the anisotropic porous medium, the matrix becomes diagonal:

$$\begin{bmatrix} D_x & 0 & 0 \\ 0 & D_y & 0 \\ 0 & 0 & D_z \end{bmatrix} \qquad (3)$$

where $D_x \equiv D_{xx}$, $D_y \equiv D_{yy}$ and $D_z \equiv D_{zz}$ denote the observed macroscopic diffusivities in the principal x, y, and z directions, respectively.

Porous Media Composed of Aligned Spheroids

Having discussed the nature of the tensor $\mathbf{D}$, we can return to the original problem of interest, namely, the study of diffusion (electrical conduction) through a homogeneous swarm of aligned spheroids.

An oblate (or prolate) spheroid is generated when an ellipse is rotated about its minor (or major) axis and may be visualized as a sphere which has undergone a flattening (or elongating) deformation. Figure 1*a* depicts a homo-

* Equations analogous to (1) to (5) describe electric conduction through liquid saturated porous media composed of nonconducting particles upon replacing q by i (the current density), D by K (the electric conductivity), and c by V (the electric potential). In fact, the whole succeeding analysis remains valid for electric conduction provided surface conductance effects (Dukhin and Derjaguin, 1974; Levine et al., 1975) may be disregarded. The analysis is not valid for hydrodynamic flow.

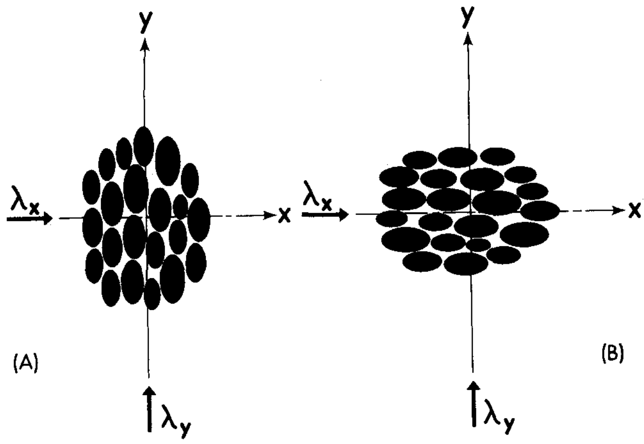

Fig. 1. Homogeneous swarm of aligned spheroids: *(a)* oblate spheroids, *(b)* prolate spheroids.

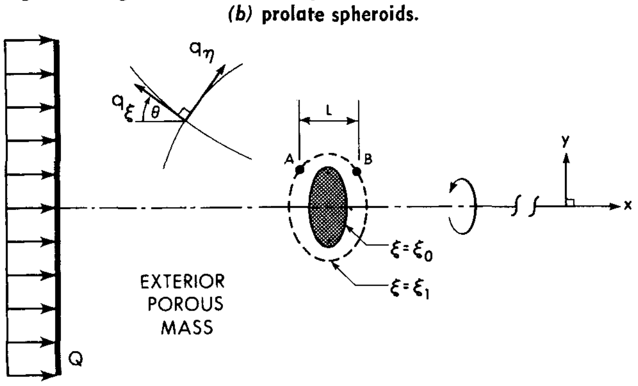

Fig. 2. Proposed model for homogeneous swarm of aligned oblate spheroids. (The case of axially symmetric diffusion is shown here.)

geneous swarm of impermeable oblate spheroidal particles possessing an arbitrary size distribution, each having identical shape as specified by the eccentricity e [e = length of minor axis/length of major axis], aligned such that the axis of revolution of each spheroid is collinear with the x direction (Figure 1*b* depicts the dual system of aligned prolate spheroids). In these systems, the x direction represents the preferred direction of symmetry of the entire system. In either case it follows necessarily that

$$D_z = D_y \tag{4}$$

and the diffusivity matrix assumes the simpler form

$$\begin{bmatrix} D_x & 0 & 0 \\ 0 & D_y & 0 \\ 0 & 0 & D_y \end{bmatrix} \tag{5}$$

In fact, the diffusivity in any direction parallel with the yz plane must be equal to D_y. Hence, in order to extract complete information concerning diffusion through such an anisotropic system, the determination of both D_x and D_y will suffice. In the preferred Cartesian frame of reference, the diffusive flux vector is given by $[q_x, q_y, q_z] = [-D_xG_x, -D_yG_y, -D_zG_z]$ by using the components of grad(c) = $[G_x, G_y, G_z]$.

Proposed Model for Aligned Spheroids

According to the earlier published geometric model for a homogeneous swarm of spherical particles having porosity ϵ (Neale and Nader, 1973, 1974), one selects any typical reference particle and surrounds it with a concentric spherical shell of pore space having an outer diameter such that the porosity of the unit cell (comprising reference particle and shell) is equal to that of the original particle swarm. This unit cell is considered to be embedded within a homogeneous porous mass of porosity equal to ϵ. One imposes a uniform field upon the entire system and studies the circumstances caused by this field.

The suggested two-region matching principle of modeling was to solve the requisite differential equations within both the unit cell and the exterior porous mass, requiring that these two solutions comply with realistic boundary conditions and uniformity conditions at the boundaries.

It was then shown that for diffusive transport processes, the macroscopic field within the exterior porous mass remains everywhere undisturbed (Neale and Nader, 1973). For the hydrodynamic problem of creeping liquid flow, the macroscopic flow field within the exterior porous mass was found to be slightly disturbed in the vicinity of the unit cell (Neale and Nader, 1974).

Another, actually more demanding, one-region principle of modeling requires that the macroscopic field within the exterior porous mass must everywhere remain undisturbed and that the solution of the single differential equation within the unit cell must properly match with the macroscopic field at the outer boundary of the unit cell. According to the above remark, the two principles of modeling yield identical results when applied to diffusive transport processes.

The modeling procedure for aligned spheroids is entirely analogous to that summarized above for spheres. Thus, for the system of oblate spheroids depicted in Figure 1*a*, one selects any typical reference spheroid and postulates that this particle, together with its associated pore space (most logically represented in the theory by a confocal spheroidal shell), sees the remainder of the system as a homogeneous exterior porous mass of porosity equal to that of the original system; this modeled system is illustrated in Figure 2. For the system of prolate spheroids depicted in Figure 1*b*, a corresponding model is employed but is not separately illustrated here.

We propose to solve the modeled system depicted in Figure 2 for the three distinct cases corresponding to a uniform diffusive field Q imposed separately upon the system in each of the three principal directions, x (illustrated in Figure 2), y, and z. By the above remark, either of the two basic principles of modeling may be employed. The detailed development following the two-region matching principle is presented elsewhere (Neale, 1972). In this work, we shall employ the more demanding one-region principle of modeling, as it actually affords a much simpler mathematical treatment.

THEORY

Solution for Aligned Oblate Spheroids

The equation governing steady state diffusion (electrical conduction) within the shell of pore space is Laplace's equation:

$$\nabla^2 c = 0 \tag{6}$$

We seek the solution of the boundary value problem specified by Equation (6) together with realistic, compatible, and sufficient boundary conditions, using oblate spheroidal coordinates $[\xi, \eta, \phi]$ (Moon and Spencer, 1961).* Denoting by θ the angle between the direction of q_ξ and the $-x$ direction (see Figure 2), we can formulate the boundary conditions

$$\text{as} \quad \xi \to \xi_o, \quad q_\xi \to 0 \tag{7}$$

$$\text{as} \quad \xi \to \xi_1, \quad q_\xi \to -Q\cos\theta \tag{8}$$

---

* Cartesian coordinates $[x, y, z]$ are related to oblate spheroidal coordinates by

$$x = a \sinh\xi \sin\eta$$
$$y = a \cosh\xi \cos\eta \cos\phi$$
$$z = a \cosh\xi \cos\eta \sin\phi$$

where $\xi \geq 0$; $-\pi/2 \leq \eta \leq \pi/2$; $0 \leq \phi < 2\pi$. The quantity a denotes the distance between the trajectory of the focus [0, a, 0] and the geometric center [0, 0, 0] of the spheroid. Surfaces of constant ξ comprise a family of confocal oblate spheroids.

where q_ξ, the flux component normal to surfaces of constant ξ, is given by the appropriate form of Fick's law, $\mathbf{q} = -D\,\text{grad}(c)$; namely

$$q_\xi = -D\frac{1}{m_\xi}\frac{\partial c}{\partial \xi}$$

where $m_\xi = a\sqrt{\sinh^2\xi + \sin^2\eta}$.

From fundamental geometry of the oblate spheroid, it can be shown that

$$\cos\theta = -\cosh\xi\,\sin\eta/\sqrt{\sinh^2\xi + \sin^2\eta} \qquad (9)$$

or

$$\cos\theta = -\sinh\xi\,\cos\eta\,\cos\phi/\sqrt{\sinh^2\xi + \sin^2\eta} \qquad (10)$$

for flow in the x direction and the y direction, respectively.

General solutions of Equation (6) for diffusion parallel to the x direction (axial symmetry case) and for diffusion perpendicular to the x direction may be extracted from fundamental series solutions developed by Lamb (1932). The particular solutions which satisfy Equations (6) to (10) may be verified to be as follows:

For diffusion in x direction

$$c = c_o - (aQ/D)\,\frac{g(\xi_o) - f(\xi)}{g(\xi_o) - g(\xi_1)}\sinh\xi\,\sin\eta \qquad (11)$$

$$q_\xi = (aQ/m_\xi)\,\frac{g(\xi_o) - g(\xi)}{g(\xi_o) - g(\xi_1)}\cosh\xi\,\sin\eta \qquad (12)$$

where c_o is the constant, reference concentration in the plane $\eta = 0$.

For diffusion in y direction

$$c = c_o - (aQ/D)\,\frac{h(\xi_o) - g(\xi)}{h(\xi_o) - h(\xi_1)}\cosh\xi\,\cos\eta\,\cos\phi \qquad (13)$$

$$q_\xi = (aQ/m_\xi)\,\frac{h(\xi_o) - h(\xi)}{h(\xi_o) - h(\xi_1)}\sinh\xi\,\cos\eta\,\cos\phi \qquad (14)$$

where here c_o is the constant concentration in the plane $\phi = \pi/2$. The solution for diffusion in the z direction is given by Equations (13) and (14) upon replacing each $\cos\phi$ by $\sin\phi$. The functions $f(\xi)$, $g(\xi)$, and $h(\xi)$ possess the following forms:

$$f(\xi) = \frac{1}{\sinh\xi} - \cot^{-1}(\sinh\xi) \qquad (15)$$

$$g(\xi) = \frac{\sinh\xi}{\cosh^2\xi} - \cot^{-1}(\sinh\xi) \qquad (16)$$

$$h(\xi) = 2f(\xi) - g(\xi) \qquad (17)$$

According to the basic modeling principles enunciated above, the drop in concentration between any pair of points A and B, each located on the cell surface $\xi = \xi_1$ as well as on the same flux line (Figure 2), must be given not only by Equations (11) or (13) but also by the appropriate macroscopic form of Fick's law; that is

$$Q = D_x\,(c_A - c_B)/L \qquad (18)$$

for diffusion in the x direction (where $L = 2a\,\sinh\xi_1\,\sin\eta$ denotes the rectilinear distance between A and B) and

$$Q = D_y\,(c_A - c_B)/L \qquad (19)$$

for diffusion in the y direction (where now $L = 2a\,\cosh\xi_1\,\cos\eta\,\cos\phi$).

Evaluation of D_x from Equation (18) with (11), and D_y from (19) with (13), yields the sought predictions:

$$\lambda_x = D_x/D = \frac{g(\xi_o) - g(\xi_1)}{g(\xi_o) - f(\xi_1)} \qquad (20)$$

$$\lambda_y = D_y/D = \frac{h(\xi_o) - h(\xi_1)}{h(\xi_o) - g(\xi_1)} \qquad (21)$$

where λ is termed the diffusivity factor (Neale and Nader 1973) or the diffusibility (van Brakel, 1975). The appropriate value of ξ_o is uniquely specified in terms of the eccentricity e by

$$\xi_o = \tanh^{-1}e \qquad (22)$$

The coordinate description of the outer envelope of the unit cell, $\xi = \xi_1$, is obtained according to the requirement that the void fraction of the unit cell be equal to the macroscopic void fraction ϵ of the original system of spheroids. Thus, it follows that ξ_1, ξ_o, and ϵ must be related by

$$\sinh^3\xi_1 + \sinh\xi_1 - \frac{\cosh^2\xi_o\,\sinh\xi_o}{1-\epsilon} = 0 \qquad (23)$$

Equations (20) to (23) together provide explicit predictions for λ_x and λ_y for systems of aligned oblate spheroids (unfortunately, closed form expressions in terms only of e and ϵ could not be derived).

Solution for Aligned Prolate Spheroids

Rather than retracing the process of solution using prolate spheroidal coordinates, one can proceed more directly by making avail of the preceding results for oblate spheroids together with a standard mathematical transformation (Lamb, 1932). Thus, Equations (11) to (23) become valid for aligned prolate spheroids upon replacing every a by $-ia$, every $\sinh\xi$ by $i\cosh\xi$, and every $\cosh\xi$ by $i\sinh\xi$ (where $i^2 = -1$). In this manner, we obtain

$$\lambda_x = D_x/D = \frac{G(\xi_o) - G(\xi_1)}{G(\xi_o) - F(\xi_1)} \qquad (24)$$

$$\lambda_y = D_y/D = \frac{H(\xi_o) - H(\xi_1)}{H(\xi_o) - G(\xi_1)} \qquad (25)$$

where

$$F(\xi) = \frac{1}{\cosh\xi} - \coth^{-1}(\cosh\xi) \qquad (26)$$

$$G(\xi) = \frac{\cosh\xi}{\sinh^2\xi} - \coth^{-1}(\cosh\xi) \qquad (27)$$

$$H(\xi) = 2F(\xi) - G(\xi) \qquad (28)$$

$$\cosh^3\xi_1 - \cosh\xi_1 - \frac{\sinh^2\xi_o\,\cosh\xi_o}{1-\epsilon} = 0 \qquad (29)$$

with ξ_o being defined by Equation (22).

Proposed Solution for Isotropic Swarm of Randomly Orientated Spheroids

Sedimented media composed of nonspherical particles are generally anisotropic, since the particles would usually have settled with some preferred orientation. In contrast, systems of nonspherical particles in which the particles display no preferred orientation (that is, are randomly orientated), such as suspensions, will be inherently isotropic. Such isotropic systems ought to be represented by a swarm of randomly oriented, rather than aligned, oblate or prolate spheroids.

The solution for a system of randomly orientated spheroids may be constructed by a superposition of the three principal solutions for the aligned case (Rice et al., 1970). Since $1/\lambda$ is a direct measure of the resistance of a porous medium to diffusion (or electrical conduction),

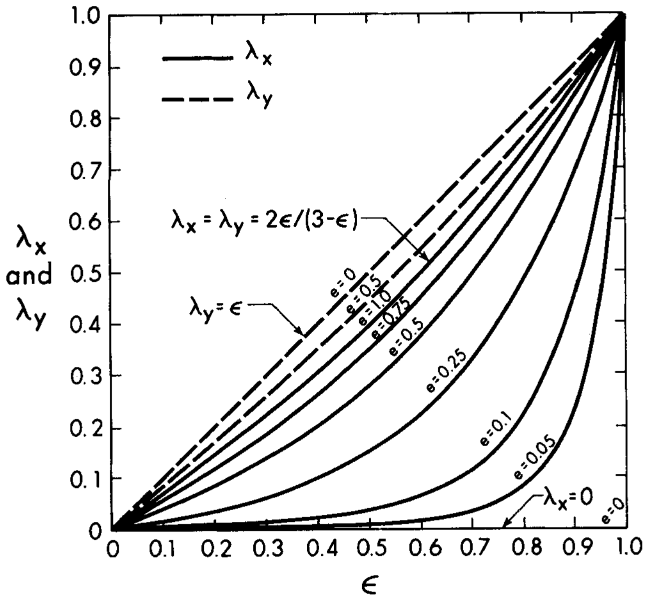

Fig. 3. Predicted dependence of λ_x and λ_y on ϵ for aligned oblate spheroids.

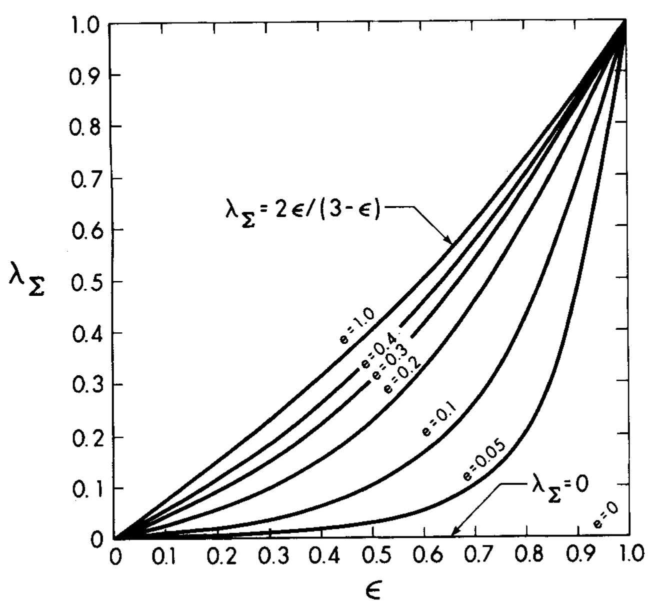

Fig. 5. Predicted dependence of λ_Σ on ϵ for randomly orientated oblate spheroids.

the following estimate may be made for the diffusivity (conductivity) factor λ_Σ of a system of randomly orientated spheroids:

$$\frac{1}{\lambda_\Sigma} = \frac{1}{3}\frac{1}{\lambda_x} + \frac{1}{3}\frac{1}{\lambda_y} + \frac{1}{3}\frac{1}{\lambda_z} \tag{30}$$

Thus

$$\frac{1}{\lambda_\Sigma} = \frac{1}{3}\frac{1}{\lambda_x} + \frac{2}{3}\frac{1}{\lambda_y} \tag{31}$$

since $\lambda_z = \lambda_y$, where λ_x and λ_y are defined by Equations (20) and (21) for oblate spheroids and by (24) and (25) for prolate spheroids.

COMPUTED RESULTS

Aligned Oblate Spheroids

Figure 3 presents the $\lambda_x = \lambda_x(\epsilon)$ and $\lambda_y = \lambda_y(\epsilon)$ relationships predicted by Equations (20) and (21) for several representative systems of aligned oblate spheroids. For any specific eccentricity e, it may be observed that $\lambda_x \leqq \lambda_y$; also, that λ_x is far more affected by eccentricity than is λ_y.

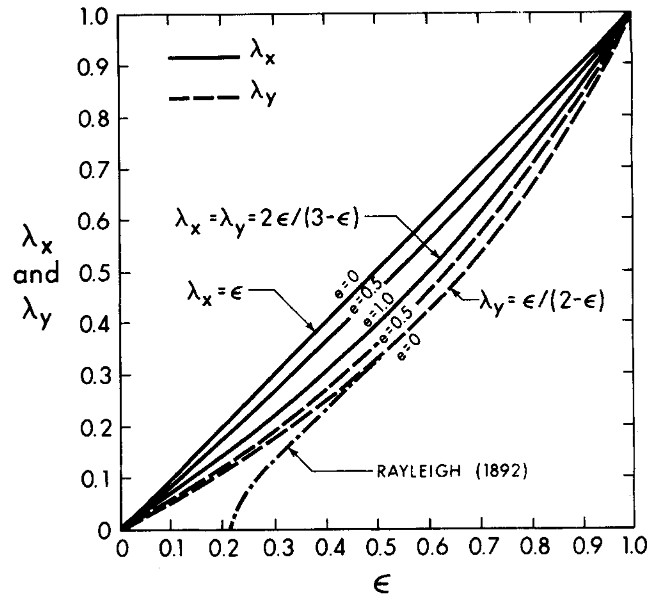

Fig. 4. Predicted dependence of λ_x and λ_y on ϵ for aligned prolate spheroids.

This is especially evident for $e < 0.5$, that is, for flattish particles.

For the particular case defined by $e = 1.0$, the oblate spheroids are spherical, and the predictions offered here are in accord with those developed specifically for spheres (Neale and Nader, 1973), namely

$$\lambda_x = \lambda_y = 2\epsilon/(3-\epsilon) \tag{32}$$

For the specific case $e \to 0$, that is, for an aligned swarm of very thin circular disks, the present predictions are

$$\lambda_x \to 0 \tag{33}$$

$$\lambda_y \to \epsilon \tag{34}$$

This representation of a porous medium constitutes a plate type of model.

Aligned Prolate Spheroids

Figure 4 presents the $\lambda_x = \lambda_x(\epsilon)$ and $\lambda_y = \lambda_y(\epsilon)$ relationships predicted by Equations (24) and (25) for representative systems of aligned prolate spheroids. For any specific eccentricity e, it may be observed that $\lambda_x \geqq \lambda_y$; however, in contrast to the preceding case for oblate spheroids, λ_x is only slightly more dependent upon e than is λ_y.

The predictions for $e = 1.0$, that is, for spheres, are once again given by Equation (32). However, for $e \to 0$, that is, for an aligned swarm of very thin circular cylinders, the predictions are as follows:

$$\lambda_x \to \epsilon \tag{35}$$

$$\lambda_y \to \epsilon/(2-\epsilon) \tag{36}$$

This representation of a porous medium constitutes a coaxial cylinder type of model.

Equation (35) actually constitutes the exact solution for diffusion parallel to very long aligned cylinders. Moreover, Equation (36) constitutes a truncation of Lord Rayleigh's (1892) exact solution for conduction perpendicular to monosized circular cylinders arranged in a square pattern, namely

$$\lambda_y = \frac{\epsilon - 0.31(1-\epsilon)^4 - \ldots}{2 - \epsilon - 0.31(1-\epsilon)^4 - \ldots} \quad [\text{for } \epsilon > 0.2146] \tag{37}$$

The prediction (37) is displayed in Figure 4. It must be

TABLE 1. PREDICTIONS FOR RANDOMLY ORIENTATED SPHEROIDS (AFTER FRICKE, 1924)

	A	
e	Oblate	Prolate
1.0	2.000	2.000
0.9	1.994	1.995
0.8	1.974	1.979
0.7	1.931	1.950
0.6	1.854	1.909
0.5	1.730	1.854
0.4	1.541	1.786
0.3	1.271	1.707
0.2	0.911	1.623
0.1	0.474	1.545
0.0	0.000	1.500

emphasized that Rayleigh's classic solution was derived for a system of coaxial, monosized circular cylinders arranged in a square pattern, for which 0.2146 represents the minimum attainable porosity [note that Equation (37) predicts that $\lambda_y \to 0$ in the limit $\epsilon \to 0.2146$]. However, for aligned cylinders possessing a sufficiently wide distribution of size, arbitrarily low values of the porosity can be realized.

It is appropriate to mention here that knowledge of the ratio λ_x/λ_y for a porous medium provides a direct measure of the extent of its anisotropy. The presented results have additional significance in that anisotropic porous media may now be quantitatively constructed in the laboratory from disklike or rodlike particles (approximating oblate or prolate spheroids, respectively), an estimate of the required eccentricity of these particles being obtained by inspection of Figure 3 (for disks) or Figure 4 (for rods).

Randomly Orientated Oblate Spheroids

Figure 5 displays the $\lambda_\Sigma = \lambda_\Sigma(\epsilon)$ relationship predicted by Equation (31) for several representative systems of randomly orientated oblate spheroids. It is obvious that λ_Σ is strongly affected by the eccentricity.

The solution for $e = 1.0$ (spheres) follows immediately from Equations (31) and (32); namely

$$\lambda_\Sigma = 2\epsilon/(3 - \epsilon) \qquad (38)$$

a result which is to be anticipated since spheres do not possess a preferred axis of orientation.

The solution for $e \to 0$ (thin circular disks) follows directly from Equations (31), (33), and (34); thus

$$\lambda_\Sigma \to 0 \qquad (39)$$

which is to be expected from physical considerations.

Randomly Orientated Prolate Spheroids

Figure 6 displays the $\lambda_\Sigma = \lambda_\Sigma(\epsilon)$ relationship for systems of randomly orientated prolate spheroids of various eccentricities. The dependency of λ_Σ on eccentricity is surprisingly mild compared with that for oblate spheroids.

For $e = 1.0$ (spheres), the prediction for λ_Σ is given again by Equation (38), as required.

The solution for $e \to 0$ (thin circular cylinders) follows from Equations (31) with (35) and (36), but cannot be anticipated:

$$\lambda_\Sigma \to 3\epsilon/(5 - 2\epsilon) \qquad (40)$$

PREVIOUS WORK

No work appears to have been reported to date concerning diffusive transport processes within an anisotropic system composed of aligned spheroids. However, Fricke (1924) did extend Maxwell's classic theory (concerning electric conduction through a dispersion of spheres) to the case of randomly orientated spheroids. From considerations of the potential of a single spheroid in space, he developed the following formula for a low concentration dispersion of nonconducting spheroids within a conducting medium:

$$\lambda_\Sigma = A\epsilon/(A + 1 - \epsilon) \quad \text{for} \quad \epsilon \simeq 1.0 \qquad (41)$$

the parameter A being a function of eccentricity alone. Some specific values of A for different shapes, as computed from Fricke's complicated formulas, are presented in Table 1 for reference. Fricke himself was of the opinion that his predictions were rather high, considerably so for oblate spheroids.

The predictions offered here agree identically with those of Fricke in the limit as $\epsilon \to 0$. This is to be expected, since each theory then considers a single spheroid in unbounded space. Furthermore, total agreement of the predictions is observed for the extreme values of the eccentricity, for both $e = 0$ (spheres) and $e \to 1$ (thin circular disks for oblate spheroids, and long circular cylinders for prolate spheroids).

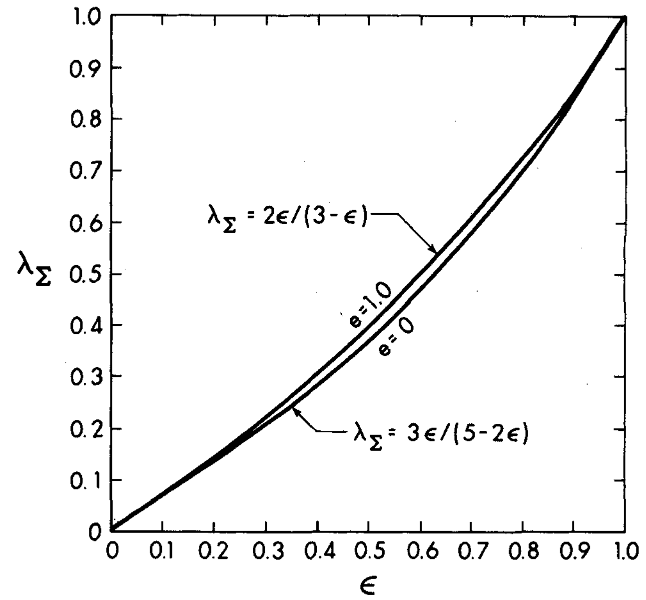

Fig. 6. Predicted dependence of λ_Σ on ϵ for randomly orientated prolate spheroids.

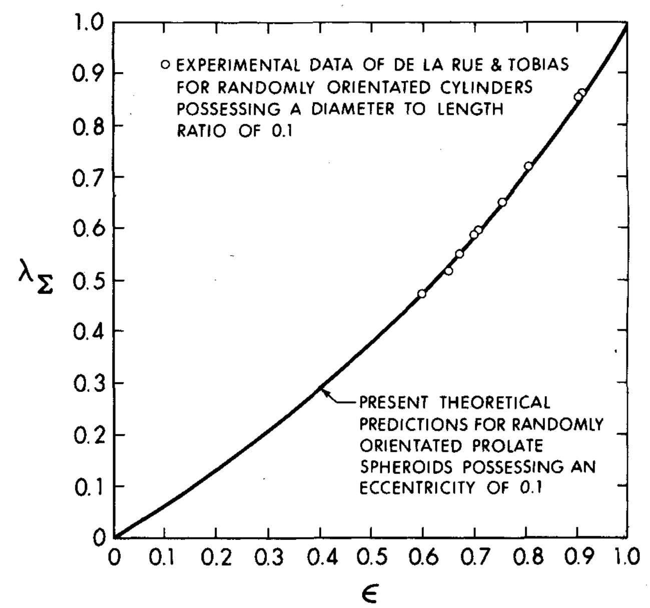

Fig. 7. Predicted results for randomly orientated prolate spheroids: comparison with experimental data.

Figure 7 displays the experimental electric conductivity data of De la Rue and Tobias (1959) for a dispersion of randomly orientated cylinders possessing a diameter to length ratio of 0.1. Now, such cylinders are well approximated by prolate spheroids possessing an eccentricity of 0.1. The results predicted by Equation (31) for randomly orientated prolate spheroids of $e = 0.1$ can be seen to conform closely with the presented data, lending support to the realistic nature of the proposed geometric model. Unfortunately, no comparable experimental data on anisotropic particulate systems appears to be available in the literature at the present time.

SUMMARY

The presented results demonstrate that the proposed geometric model offers a satisfactory representation not only of an isotropic swarm of spherical particles but also of an important class of anisotropic porous media, namely, those composed of aligned disklike or rodlike particles (represented in the theory by oblate spheroids or prolate spheroids, respectively).

It has been demonstrated that swarms of aligned spheroidal particles possessing an eccentricity of less than 0.5 are markedly anisotropic, although this is much more in evidence with oblate than with prolate spheroids. The predictions for λ_x and λ_y should prove to be useful in those areas in which diffusivity (electrical conductivity measurements are made on unconsolidated anisotropic porous media.

A study has also been made of diffusion (electrical conduction) through isotropic porous media composed of randomly orientated disklike or rodlike particles. Such systems are often encountered when one deals with particulate suspensions. The diffusivity (conductivity) factor λ_Σ of such systems has been shown to be strongly influenced by the shape (eccentricity) for disklike particles, but surprisingly weakly influenced by the shape (eccentricity) for rodlike particles.

It must be reiterated that the theory presented here is valid for electrical conduction only when the contribution to the electric current due to surface conductance is negligible. Surface conductance is a direct consequence of the separation of electric charge which usually takes place when a solid surface comes into contact with an electrolyte (Dukhin and Derjaguin, 1974; Levine et al., 1975). Generally speaking, the effects of surface conductance can be neglected when we deal with concentrated electrolytes, but not when we deal with weak electrolytes (for example, plain water).

ACKNOWLEDGMENT

The authors are indebted to the National Research Council of Canada for continuing financial support.

NOTATION

a = distance between trajectory of focus and geometric center of spheroid
c = concentration of diffusing species
D = absolute diffusivity of diffusing species in free fluid
D_i = observed macroscopic diffusivity in principal directions of porous medium ($i = x, y, z$)
e = eccentricity of spheroid (= length of minor axis/length of major axis)
$f(\xi)$, $g(\xi)$, $h(\xi)$ = functions of ξ, defined in Equations (15) to (17)
$F(\xi)$, $G(\xi)$, $H(\xi)$ = functions of ξ, defined in Equations (26) to (28)
$\mathbf{q}$ = diffusive flux vector
Q = magnitude of uniform mainstream diffusive flux
$[x, y, z]$ = Cartesian coordinates
ϵ = porosity of porous medium
λ = diffusivity (conductivity) factor, defined in Equations (20) and (21)
$[\xi, \eta, \phi]$ = spheroidal coordinates

Subscripts

o = reference spheroid
1 = outer surface of unit cell
x, y, z = properties of anisotropic porous medium in the principal directions, x, y, z, respectively
ξ, η, ϕ = directions orthogonal to surfaces of constant ξ, η, ϕ, respectively
Σ = randomly orientated nonspherical particles

LITERATURE CITED

De la Rue, R. E., and C. W. Tobias, "On the Conductivity of Dispersions," *J. Electrochem. Soc.*, **106**, 827 (1959).

Dukhin, S. S., and B. V. Derjaguin, *Surface and Colloid Science*, E. Matijevic, ed., Vol. 7, Wiley, New York (1974).

Fricke, H., "A Mathematical Treatment of the Electric Conductivity and Capacity of Disperse Systems," *Phys. Rev.*, **24**, 575 (1924).

Lamb, H., *Hydrodynamics*, 6 ed., Ch. 5, Cambridge Univ. Press, England (1932).

Levine, S., J. Marriott, G. Neale, and N. Epstein, "Theory of Electrokinetic Flow in Fine Cylindrical Capillaries at High Zeta-Potentials," *J. Colloid Interface Sci.*, **52**, 136 (1975).

Moon, P., and D. E. Spencer, *Field Theory for Engineers*, Van Nostrand, New York (1961).

Neale, G., "Prediction of Transport Phenomena occurring within Unconsolidated Porous Media," Ph.D. thesis, University of Alberta, Canada (1972).

———, and W. Nader, "Prediction of Transport Processes within Porous Media: Diffusive Flow Processes within an Homogeneous Swarm of Spherical Particles," *AIChE J.*, **19**, 112 (1973).

————, Prediction of Transport Processes within Porous Media: Creeping Flow Relative to a Fixed Swarm of Spherical Particles," *ibid.*, **20**, 530 (1974).

Neale, G., and J. H. Masliyah, "Flow Perpendicular to Mats of Randomly Arranged Cylindrical Fibers," *ibid.*, **21**, 805 (1975).

Rayleigh, Lord, "On the Influence of Obstacles Arranged in Rectangular Order Upon the Properties of a Medium," *Phil. Mag.*, **34**, 481 (1892).

Rice, P. A., D. J. Fontugne, R. G. Latini, and A. J. Barduhn, "Anisotropic Permeability in Porous Media," *Ind. Eng. Chem.*, **62**, 23 (1970).

van Brakel, J., "Pore Space Models for Transport Phenomena in Porous Media: Review and Evaluation with Special Emphasis on Capillary Liquid Transport," *Powder Technol.*, **11**, 205 (1975).

Manuscript received August 11, 1975; revision received October 15, and accepted October 17, 1975.