Prediction of Transport Processes within Porous Media: Diffusive Flow Processes within an Homogeneous Swarm of Spherical Particles

A geometric model for an homogeneous and isotropic porous medium composed of spherical particles is proposed. This model requires a minimum of geometric simplifications and lends itself to the study of hydrodynamic as well as diffusive flow processes, permitting in each application a mathematically rigorous and fully predictive analysis leading to mathematical representations of the respective flow parameters.

This particular investigation seeks to evaluate, and to provide physical insight into, diffusive flow processes occurring within an homogeneous swarm of spherical particles.

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SCOPE

Broadly speaking, the principal transport processes encountered within porous media may be classified as diffusive flow processes, including molecular (ionic) diffusion, electric conduction, and thermal conduction, or a hydrodynamic flow process which is momentum transport.

In engineering practice these elementary transport processes usually occur simultaneously, for example, evaporation of liquids, free convection, forced convection, electrolysis, etc. However, in order to be able to make meaningful predictions concerning such complex phenomena within porous media, a fuller understanding must first be developed for the elementary transport processes (listed above) when individually occurring therein.

Several models have been proposed and presented in the literature for the study of specific transport processes occurring within specific porous media. However, there does not appear to be available any single model which has been used to successfully predict diffusive as well as hydrodynamic flow processes when occurring within even the simplest homogeneous and isotropic porous medium, namely, within a randomly packed bed of spherical particles.* This is disappointing because geometric models are introduced solely to simulate the complicated pore structure of the medium in question, and ideally their success should not depend upon which particular transport process is being studied.

A considerable number of attempts aimed at predicting transport processes within isotropic porous media have been based upon the reasonably well developed theories when occurring in capillaries. However, all capillary models are inherently anisotropic in constitution and, without exception, their ultimate predictions incorporate at least one adjustable parameter which must be determined by experiment.

The principal objective of this analysis is therefore to develop for a homogeneous and isotropic porous medium (composed of spherical particles) one productive model to study several transport processes, in particular interstitial diffusion, interstitial electric conduction, heat conduction and fluid flow.

CONCLUSIONS AND SIGNIFICANCE

The principal significance of this work lies in the development of a versatile and productive geometric model for homogeneous and isotropic porous media (composed of spherical particles). This model is not restricted to the study of any one particular transport process. It may be applied with equal success to diffusion, electric conduction, and fluid flow, providing valuable physical insight and permitting a totally rigorous mathematical analysis (leading to *predictive* formulae which permit the evaluation of the respective flow parameters) in each application. The fluid flow case must be considered separately on account of its mathematical complexity.

The diffusivity factor [defined by Equation (2)] of an homogeneous swarm of impermeable spheres of porosity ϵ is calculated to be $\Lambda_D = 2\epsilon/(3 - \epsilon)$ independent of the size distribution of the spheres which constitute the swarm. For dielectric spheres, the electric conductivity factor

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* An homogeneous and isotropic swarm of spheres is of outstanding interest because it can be described by a minimum number of parameters, namely, the porosity and the particle size distribution. However, it should be mentioned that other representations of an isotropic porous medium are possible and sometimes preferable; for example, a homogeneous and isotropic porous medium may be represented by a swarm of randomly orientated oblate or prolate spheroids.

[Equation (23)] is shown to be given by a similar expression $\Lambda_K = 2\epsilon/(3-\epsilon)$, again independent of the size distribution of the spheres. These predictions are in satisfactory agreement with experimental data throughout the entire range of porosity, as demonstrated by laboratory experiment and by comparison with experimental data reported in the literature.

The equivalence of the derivation of the predictions for diffusion and for electric conduction suggests a fundamental similarity between these two important transport processes. However, this should not be misinterpreted as an implication that all diffusive flow processes occurring within porous media are necessarily similar to simple diffusion. This is demonstrated explicitly by the application of the proposed model to the problem of thermal conduction; here it is necessary to account for the thermal conductivity within the spheres and for a thermal film coefficient at the surface of the spheres. Consequently, when using the same geometric model of the porous medium to assess the thermal conductivity factor [Eequation (35)], a formula [Equation (51)] results which is far more involved than the two formulae quoted above.

The geometric model proposed here and developed for diffusive transport processes occurring individually should find further application among chemical engineers engaged in the study of several transport processes occurring simultaneously in porous media (for instance, forced and free convection, evaporation, etc.).

PROPOSED MODEL FOR AN HOMOGENEOUS AND ISOTROPIC SWARM OF SPHERICAL PARTICLES

Figure 1 depicts an unbounded, homogeneous, and isotropic swarm of impermeable spheres possessing a porosity ϵ and an arbitrary size distribution. Choosing any reference sphere (of radius R) within the swarm it is postulated that this sphere, together with its associated pore space (here represented by a concentric shell of outer radius S), sees the remainder of the system as an homogeneous and isotropic exterior porous mass of porosity ϵ; this modeled system is illustrated in Figure 2.†

The outer radius of the shell must be specified such that the porosity of the unit cell (comprising the reference sphere and the concentric shell) is identical to that of the original system. This necessitates that

$$S/R = (1-\epsilon)^{-1/3} \qquad 0 \leqq \epsilon < 1, \qquad (1)$$

thereby ensuring that the uniform porosity ϵ is not locally disturbed by the modeling procedure. An inherent advantage of the proposed model is that the macroscopically homogeneous and isotropic characteristics of the original system remain unaltered.

In essence, the technique of solution will be to solve the requisite differential equations within the unit cell and within the exterior porous mass and to connect these solutions at the separating interface by means of realistic boundary conditions and uniformity conditions.

STEADY STATE INTERSTITIAL DIFFUSION WITHIN ISOTROPIC POROUS MEDIA

The objective of this analysis is to develop a fuller understanding of molecular (ionic) diffusion occurring within the interstices of a homogeneous and isotropic porous medium composed of impermeable spherical particles possessing an arbitrary size distribution, in particular to evaluate the diffusivity factor Λ_D which is defined to be

$$\Lambda_D = \frac{\text{Effective diffusivity within the porous medium}}{\text{Absolute diffusivity in the unobstructed fluid}}$$

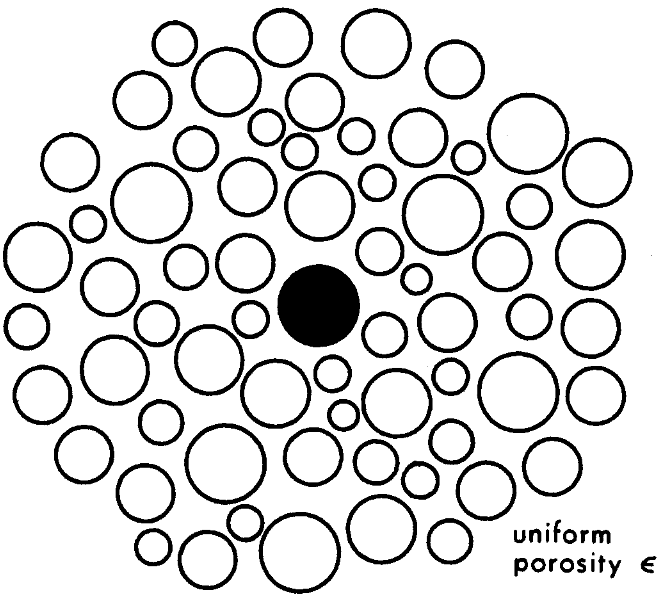

Fig. 1. An homogeneous and isotropic swarm of spheres (cross section through center of reference sphere).

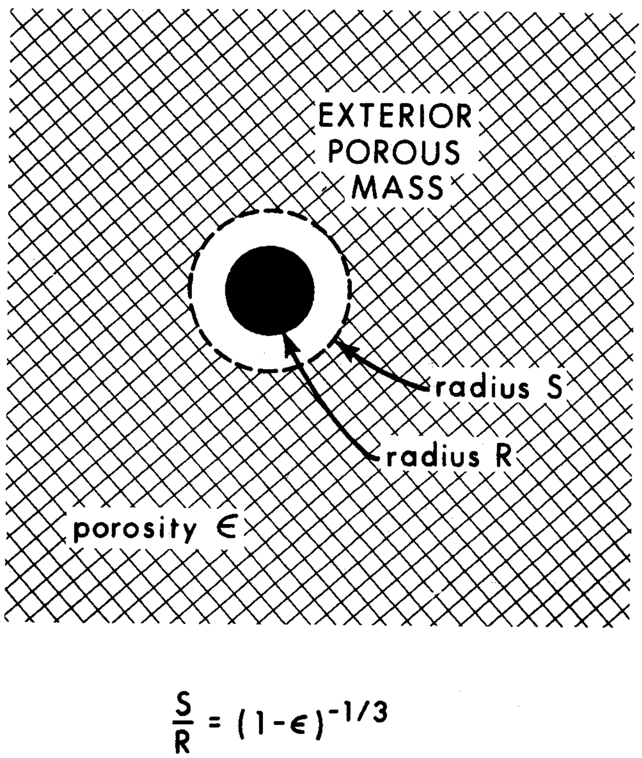

Fig. 2. The proposed model for an homogeneous and isotropic swarm of spheres (cross section through center of reference sphere).

† A geometric model, fundamentally equivalent to that introduced here for the modeling of porous media, has been employed by Hashin (1968) in the modeling of solid, heterogeneous media (polycrystalline aggregates and bimetallic composites in particular).

$$= \frac{D^*}{D^f} \quad (2)\ddagger$$

As a basis for further development, a uniform concentration gradient (in the $+x$-direction) will be considered imposed upon the macroscopically homogeneous and isotropic system (Figure 3), thereby inducing a uniform molecular (ionic) flux field $\underline{Q}^*$ defined by $\underline{Q}^* = [Q^*, 0, 0]$ in the Cartesian coordinates $[x, y, z]$.

MATHEMATICAL DESCRIPTION OF THE MODELED SYSTEM

The Partial Differential Equations

The validity of Fick's Law within the spherical shell and within the exterior porous mass will be acknowledged, namely,

$$\underline{q}^f = -D^f \nabla c^f \qquad R < r < S \qquad (3)$$

$$\underline{q}^* = -D^* \nabla c^* \qquad S < r < \infty \qquad (4)$$

For steady state diffusion, continuity demands that

$$\nabla \cdot \underline{q}^f = 0 \qquad R < r < S \qquad (5)$$

$$\nabla \cdot \underline{q}^* = 0 \qquad S < r < \infty \qquad (6)$$

Thus, since D^f and D^* are constants, Equations (3) and (4) reduce to

$$\nabla^2 c^f = 0 \qquad R < r < S \qquad 0 \leqq \theta < 2\pi \qquad -\pi \leqq \phi < +\pi \qquad (7)$$

$$\nabla^2 c^* = 0 \qquad S < r < \infty \qquad 0 \leqq \theta < 2\pi \qquad -\pi \leqq \phi < +\pi \qquad (8)$$

The Stipulated Boundary Conditions

In the steady state there can be no diffusive transport to or from the surface of the impermeable reference sphere, that is,

$$q_r^f(R^+, \theta, \phi) = 0 \qquad 0 \leqq \theta < 2\pi \qquad -\pi \leqq \phi < +\pi \qquad (9)$$

From considerations of continuity and equilibrium at the interface which separates the unit cell from the exterior porous mass, it follows that

$$q_r^f(S^-, \theta, \phi) = q_r^*(S^+, \theta, \phi) \qquad 0 \leqq \theta < 2\pi \qquad -\pi \leqq \phi < +\pi \qquad (10)$$

$$c^f(S^-, \theta, \phi) = c^*(S^+, \theta, \phi) \qquad 0 \leqq \theta < 2\pi \qquad -\pi \leqq \phi < +\pi \qquad (11)$$

Finally, the flux vector at any station sufficiently far removed from the unit cell must approach that of the undisturbed main stream; this implies that

$$\left.\begin{array}{l} q_r^*(r, \theta, \phi) \to -Q^* \cos\theta \\ q_\theta^*(r, \theta, \phi) \to Q^* \sin\theta \end{array}\right\} \text{as } r \to \infty$$

$$0 \leqq \theta < 2\pi \qquad -\pi \leqq \phi < +\pi \qquad (12)$$

Solution of the Boundary Value Problem for Molecular Diffusion

The formulated boundary value problem (differential equations and boundary conditions) exhibits complete symmetry with respect to ϕ; this symmetry must be reflected by the entire flow field. Consequently, there will be no ϕ-dependency in the solution of this boundary value problem, whence the variable ϕ may hereafter be suppressed.

General solutions of Equations (7) and (8), for axial symmetry, are

$$c^f(r, \theta) = \sum_n [A_n r^n + B_n r^{-n-1}] [P_n(\cos\theta) + C_n Q_n(\cos\theta)] \qquad R < r < S \qquad 0 \leqq \theta < 2\pi \qquad (13)$$

$$c^*(r, \theta) = \sum_n [A_n^* r^n + B_n^* r^{-n-1}] [P_n(\cos\theta) + C_n^* Q_n(\cos\theta)] \qquad S < r < \infty \qquad 0 \leqq \theta < 2\pi \qquad (14)$$

where A_n, B_n, C_n, A_n^*, B_n^* and C_n^* $(n = 0, 1, 2, \ldots)$ represent arbitrary constants, and P_n and Q_n denote Legendre functions of the first and the second kind respectively.

The particular solutions which satisfy the boundary conditions implicit in Equations (9) to (12), can then be shown to be

$$c^f(r, \theta) = A(RQ^*/D^*) [(r/R) + (1/2)(r/R)^{-2}] \cos\theta \qquad R < r < S \qquad 0 \leqq \theta < 2\pi, \qquad (15)$$

$$c^*(r, \theta) = (RQ^*/D^*) [(r/R) + (A^*/2)(r/R)^{-2}] \cos\theta \qquad S < r < \infty \qquad 0 \leqq \theta < 2\pi, \qquad (16)$$

where

$$A = \frac{3\Lambda_D}{(3\Lambda_D - \Lambda_D\epsilon + \epsilon)}, \qquad (17)$$

$$A^* = \frac{(3\Lambda_D - \Lambda_D\epsilon - 2\epsilon)}{(1 - \epsilon)(3\Lambda_D - \Lambda_D\epsilon + \epsilon)}. \qquad (18)$$

It will be demonstrated later that A^* must be zero if the modeled system is to remain uniformly representative of the original system.

Uniformity Considerations of the Modeled System

It will be recalled that the uniform porosity of the original homogeneous and isotropic swarm of spheres suffered no disturbance by the modeling procedure. It is desirable that the uniform mainstream flux, too, remains undisturbed by the modeling procedure. This necessitates that the macroscopic flux associated with the unit cell must be equal to that associated with the undisturbed mainstream. In particular, this implies that

$$\int_R^S q_\theta^f(r, \pi/2)\, 2\pi r\, dr = \pi S^2 Q^*, \qquad (19)$$

where

$$q_\theta^f(r, \pi/2) = -D^f (1/r) \left.\frac{\partial c^f}{\partial \theta}\right|_{@\ \theta = \pi/2} = \frac{3Q^* [1 + (1/2)(r/R)^{-3}]}{(3\Lambda_D - \Lambda_D\epsilon + \epsilon)}. \qquad (20)$$

Evaluating the integral and invoking Equation (1) yields the sought prediction

$$\Lambda_D = D^*/D^f = 2\epsilon/(3 - \epsilon) \qquad 0 \leqq \epsilon < 1. \qquad (21)$$

This formula predicts physically consistent values at both porosity extremes: thus as $\epsilon \to 0$, $\Lambda_D \to 0$, and as $\epsilon \to 1$, $\Lambda_D \to 1$ (Figure 5). Furthermore, it suggests that Λ_D is

‡ The superscript * will be employed to designate macroscopically averaged quantities pertaining specifically to a porous medium.

invariant with the size distribution for any homogeneous and isotropic swarm of impermeable spherical particles.

Disturbance Introduced by the Modeling Procedure

It is elucidating to compute the extent of any disturbance imposed upon the mainstream flow field during the modeling procedure. From Equations (18) and (21) it may be noted that, in fact, $A^* = 0$. In view of this it follows from Equation (16) that

$$\left.\begin{aligned} q_r^*(r,\theta) &= -D^*(\partial c^*/\partial r) = -Q^*\cos\theta \\ q_\theta^*(r,\theta) &= -D^*(1/r)(\partial c^*/\partial\theta) = Q^*\sin\theta \end{aligned}\right\} \quad \text{everywhere in} \begin{cases} S < r < \infty \\ 0 \leq \theta < 2\pi \\ -\pi \leq \phi < \pi \end{cases} \quad (22)$$

Thus, by comparing Equation (22) with Equation (12) it becomes clear that the flow field everywhere outside the unit cell is, indeed, totally undisturbed by the modeling procedure.

STEADY STATE INTERSTITIAL ELECTRIC CONDUCTION WITHIN ISOTROPIC POROUS MEDIA

This analysis seeks to develop a fuller understanding of electric conduction occurring within the interstices of an homogeneous and isotropic porous medium composed of impermeable, dielectric spherical particles possessing an arbitrary size distribution, in particular to evaluate the electric conductivity factor Λ_K which is defined to be:

$$\Lambda_K = \frac{\text{Effective conductivity within the porous medium}}{\text{Absolute conductivity in the unobstructed fluid}} = \frac{K^*}{K^f} \quad (23)$$

A uniform potential gradient (in the + x-direction) will be considered imposed upon the system (see Figure 3, but replace Q^* by I^*, and q^* by i^*), thereby inducing a uniform current flux $\underline{I}^*$ defined by $\underline{I}^* = [I^*, 0, 0]$ in the Cartesian coordinates $[x, y, z]$.

MATHEMATICAL DESCRIPTION OF THE MODELED SYSTEM

The partial Differential Equations

The validity of Ohm's Law within the spherical shell, and within the exterior porous mass will be acknowledged, namely,

$$\underline{i}^f = -K^f\nabla e^f \quad R < r < S \quad (24)$$

$$\underline{i}^* = -K^*\nabla e^* \quad S < r < \infty \quad (25)$$

For steady state conduction, continuity demands that

$$\nabla\cdot\underline{i}^f = 0 \quad R < r < S \quad (26)$$

$$\nabla\cdot\underline{i}^* = 0 \quad S < r < \infty \quad (27)$$

Thus, since K^f and K^* are constants, Equations (24) and (25) reduce to

$$\nabla^2 e^f = 0 \quad R < r < S \quad 0 \leq \theta < 2\pi \quad -\pi \leq \phi < +\pi \quad (28)$$

$$\nabla^2 e^* = 0 \quad S < r < \infty \quad 0 \leq \theta < 2\pi \quad -\pi \leq \phi < +\pi \quad (29)$$

The Stipulated Boundary Conditions

In the steady state no current can flow to or from the surface of the impermeable, dielectric reference sphere, that is,

$$i_r^f(R^+,\theta,\phi) = 0 \quad 0 \leq \theta < 2\pi \quad -\pi \leq \phi < +\pi \quad (30)$$

At the outer surface of the unit cell, considerations of continuity and equilibrium demand that

$$i_r^f(S^-,\theta,\phi) = i_r^*(S^+,\theta,\phi) \quad 0 \leq \theta < 2\pi \quad -\pi \leq \phi < +\pi \quad (31)$$

$$e^f(S^-,\theta,\phi) = e^*(S^+,\theta,\phi) \quad 0 \leq \theta < 2\pi \quad -\pi \leq \phi < +\pi \quad (32)$$

Finally, the disturbing effects of the modeling procedure must effectively be localized, that is,

$$\left.\begin{aligned} i_r^*(r,\theta,\phi) &\to -I^*\cos\theta \\ i_\theta^*(r,\theta,\phi) &\to I^*\sin\theta \end{aligned}\right\} \text{ as } r\to\infty \quad 0 \leq \theta < 2\pi \quad -\pi \leq \phi < +\pi \quad (33)$$

Solution of the Boundary Value Problem for Electric Conduction

It may be observed that the boundary value problem (differential equations and boundary conditions) representing the electric conduction problem [Equations (24) to (33)] is mathematically equivalent to that representing the diffusion problem [Equations (3) to (12)]. In consequence, the solutions for electric conduction must be identical to those derived for diffusion. Thus, by inspection of Equation (21), it follows that

$$\Lambda_K = 2\epsilon/(3-\epsilon) = \Lambda_D \quad 0 \leq \epsilon \leq 1 \quad (34)$$

However, the fact that the here presented problem of electric conduction and the problem of diffusion are entirely similar should not be allowed to create the impression that all diffusive transport processes are necessarily similar. The fallacy of such an unwarranted generalization is readily demonstrated by the application of the proposed geometric model to the problem of thermal conduction.

STEADY STATE THERMAL CONDUCTION THROUGH ISOTROPIC POROUS MEDIA

When considering steady state thermal conduction through a porous medium, it is not in order to presume that the matrix itself is thermally nonconductive. Consequently, when applying the proposed geometric model, allowance must be made for the conduction through the reference sphere as well as through the fluid in the spherical shell. In addition, provision ought to be made for heat transfer coefficients between the sphere and the fluid and between the exterior porous mass and the fluid in the

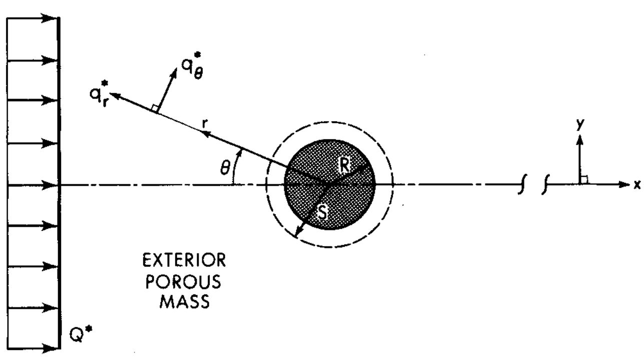

Fig. 3. Description of the modeled system for diffusion (conduction) through an homogeneous swarm of spheres (cross section through center of reference sphere).

spherical shell. Now, if h^s and h^* designate representative average values for the respective heat transfer coefficients and if we may assume that the effective zone in the fluid is thin, then we can express the physical conditions by the boundary conditions (44) and (46).

Analogous to the earlier given definitions we define a thermal conductivity factor Λ_k as follows:

$$\Lambda_k = \frac{\text{Effective thermal conductivity within the porous medium}}{\text{Absolute thermal conductivity in the unobstructed fluid}} = \frac{k^*}{k^f} \quad (35)$$

A uniform temperature gradient (in the $+x$-direction) will be considered imposed upon the system (Figure 3), thereby inducing a uniform thermal flux field $\underline{Q}^*$ defined by $\underline{Q}^* = [Q^*, 0, 0]$ in the Cartesian coordinates $[x, y, z]$.

MATHEMATICAL DESCRIPTION OF THE MODELED SYSTEM

The Partial Differential Equations

The validity of Fourier's Law will be acknowledged within the reference sphere, within the spherical shell and within the exterior porous mass, namely,

$$\underline{q}^s = -k^s \nabla t^s \qquad 0 \leq r < R \qquad (36)$$

$$\underline{q}^f = -k^f \nabla t^f \qquad R < r < S \qquad (37)$$

$$\underline{q}^* = -k^* \nabla t^* \qquad S < r < \infty \qquad (38)$$

Hence, in the steady state, Equations (36) to (38) reduce to

$$\nabla^2 t^s = 0 \quad 0 \leq r < R \qquad 0 \leq \theta < 2\pi \quad -\pi \leq \phi < +\pi \qquad (39)$$

$$\nabla^2 t^f = 0 \quad R < r < S \qquad 0 \leq \theta < 2\pi \quad -\pi \leq \phi < +\pi \qquad (40)$$

$$\nabla^2 t^* = 0 \quad S < r < \infty \qquad 0 \leq \theta < 2\pi \quad -\pi \leq \phi < +\pi \qquad (41)$$

since k^s, k^f and k^* are constants.

Stipulated Boundary Conditions

The thermal flux within the reference sphere must be finite; in particular it is necessary that

$$q_r^s(r, \theta, \phi) \rightarrow M < \infty, \quad \text{as} \quad r \rightarrow 0^+ \qquad 0 \leq \theta < 2\pi \quad -\pi \leq \phi < +\pi \qquad (42)$$

At the surface of the reference sphere, considerations of continuity require that

$$q_r^s(R^-, \theta, \phi) = q_r^f(R^+, \theta, \phi) \qquad 0 \leq \theta < 2\pi \quad -\pi \leq \phi < +\pi \qquad (43)$$

and, according to the above arguments

$$-q_r^s(R^-, \theta, \phi) = h^s[t^f(R^+, \theta, \phi) - t^s(R^-, \theta, \phi)] \qquad 0 \leq \theta < 2\pi \quad -\pi \leq \phi < +\pi \qquad (44)$$

At the outer surface of the unit cell, continuity demands that

$$q_r^f(S^-, \theta, \phi) = q_r^*(S^+, \theta, \phi) \qquad 0 \leq \theta < 2\pi \quad -\pi \leq \phi < +\pi \qquad (45)$$

and, by the above arguments,

$$q_r^*(S^+, \theta, \phi) = h^*[t^f(S^-, \theta, \phi) - t^*(S^+, \theta, \phi)] \qquad 0 \leq \theta < 2\pi \quad -\pi \leq \phi < +\pi \qquad (46)$$

Also, the disturbing effects of the modeling procedure must be localized, that is

$$\left.\begin{aligned} q_r^*(r, \theta, \phi) &\rightarrow -Q^* \cos\theta \\ q_\theta^*(r, \theta, \phi) &\rightarrow Q^* \sin\theta \end{aligned}\right\} \text{as} \quad r \rightarrow \infty \qquad 0 \leq \theta < 2\pi \quad -\pi \leq \phi < +\pi \qquad (47)$$

Solution of the Boundary Value Problem for Thermal Conduction

The solution of the boundary value problem for thermal conduction [Equations (36) to (47)] is considerably more involved than the solution of the boundary value problem for diffusion and for electric conduction [Equations (3) to (12)]. The sought prediction for $1/\Lambda_k$ can be shown to be

$$\frac{1}{\Lambda_k} = [k^f/h^*R](1-\epsilon)^{1/3} + \frac{2k^f + k^s + (k^f - k^s)(1-\epsilon) + k^s[k^f/h^sR](3-\epsilon)}{2k^f + k^s - 2(k^f - k^s)(1-\epsilon) + k^s[k^f/h^sR](2\epsilon)} \qquad (48)$$

On account of the isolation of the reference sphere imposed during the modeling procedure, Equation (48) can be expected to apply, as such, only to swarms of non-touching spheres. For systems in which the spheres form a connecting network, the thermal conductivity of the empty porous medium (that is, in vacuo) k^e ought to be added to k^* in order to arrive at the actual thermal conductivity of the system.

Invoking conventional averaging techniques, one might argue that

$$h^* = h^s/(1-\epsilon) \qquad (49)$$

Using this expression for h^*, and defining a mean Nusselt number by

$$Nu_m = h^sR/k^f \qquad (50)$$

one can rewrite Equation (48) exclusively in terms of dimensionless groups, thus

$$\frac{1}{\Lambda_k} = (1-\epsilon)^{4/3}/Nu_m + \frac{1 + 2[k^f/k^s] + \{[k^f/k^s] - 1\}(1-\epsilon) + (3-\epsilon)/Nu_m}{1 + 2[k^f/k^s] - 2\{[k^f/k^s] - 1\}(1-\epsilon) + (2\epsilon)/Nu_m} \qquad (51)$$

The mean Nusselt number can be expected [Schlichting (1968)] to depend upon the Prandtl number Pr, the Reynolds number Re and the Grashof number Gr as follows, namely,

$$Nu_m = Nu_m(Re, Pr) \qquad (52)$$

for forced convection, and

$$Nu_m = Nu_m(Gr, Pr) \qquad (53)$$

for free convection.

However, a far more exhaustive study of the proposed model of the porous medium would be required to produce predictions for (52) and for (53). Nevertheless, the Equation (51) does indicate the manner of involvement of the mean Nusselt number in the evaluation of Λ_k. Such an indication should prove beneficial in the interpretation of experimental results.

This digression into thermal conductivity has indeed served to demonstrate that not all diffusive transport processes occurring within porous media are necessarily similar to simple diffusion or to simple electric conduction.

COMPARISON OF PREDICTED VALUES WITH EXPERIMENTAL DATA

We recall that the boundary value problems for diffusion and for electric conduction within an homogeneous swarm of spheres are similar and that the solutions are equivalent. This implies that experimental verification of the predictions for diffusion [Equation (21)] is tantamount to verification for electric conduction [Equation (34)], and vice versa. Indeed, this equivalence has been experimentally confirmed by Schofield and Dakshinamurti (1948) and by Klinkenberg (1951), who actually measured Λ_D and Λ_K, for a wide range of porous media, obtaining agreement within the limits of experimental error.

Experimental Data for Electric Conduction

In this work verification of Equation (34) was sought using measurements of electric conductivity because such measurements are less prone to experimental error, and are less susceptible to convective disturbances, than are measurements of diffusion. Experiments were carried out within the porosity range $0.25 < \epsilon < 0.4$, using uniform mixtures of glass spheres contained within a plexiglass cell (Figure 4). Copper electrodes were placed at both ends of the cell and an acidified aqueous copper sulfate solution was employed as an electrolyte in order to effectively eliminate surface resistance phenomena at these electrodes (Nader, 1960). All measurements were made using audio frequency alternating current in order to suppress polarization at the electrodes. Effects due to packing discrepancies at the cell wall could be avoided by ensuring a minimum cell to particle diameter ratio of twenty-five to one (Wyllie and Gregory, 1953).

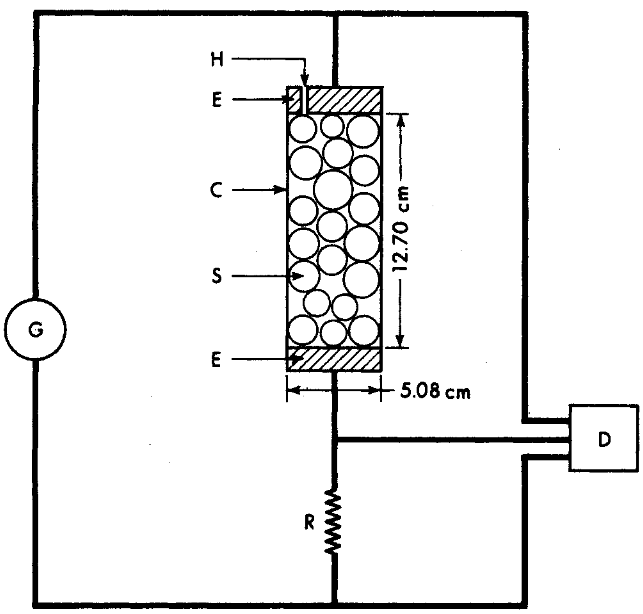

Fig. 4. Equipment used for the experimental determination of the electric conductivity factor of a pack of spheres: C. cylindrical plexiglass cell; E. solid copper electrodes; S. pack of glass spheres saturated with electrolyte; H. hole for liquid expansion; R. standard resistance, 100Ω; G. audio oscillator 1000Hz (General Radio Co. type 1311-A; and D. digital multifunction meter (Hewlett Packard, model 3450A).

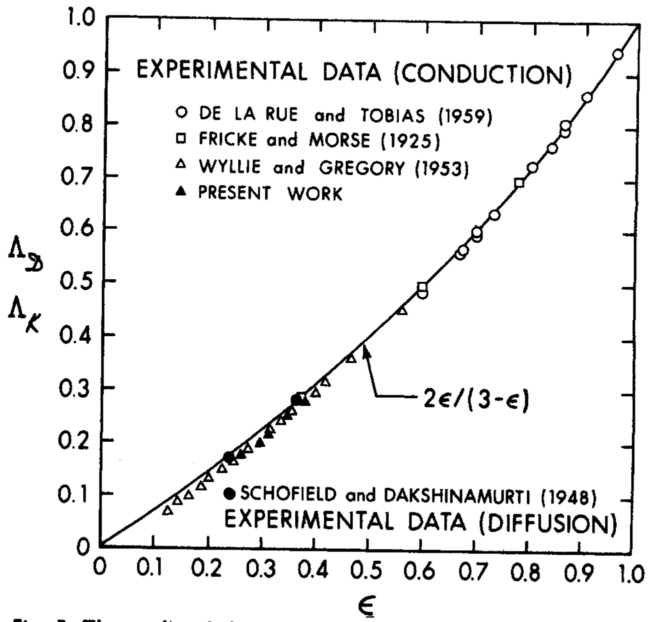

Fig. 5. The predicted dependence of Λ_D and Λ_K on ϵ for swarms of spheres, comparison with experimental data.

The electric resistance of the cell when filled with electrolyte alone was first measured, followed by a measurement of its resistance when packed with glass spheres and saturated with the same electrolyte; both measurements were taken at the same temperature. The ratio of these two resistances gives the electric conductivity factor Λ_K directly. Representative data obtained in this manner is tabulated below.

ϵ	Λ_K
0.261	0.174
0.296	0.198
0.309	0.214
0.348	0.248
0.380	0.278

This data is displayed also in Figure 5, together with the electric conductivity data of Fricke and Morse (1925), Wyllie and Gregory (1953), and De la Rue and Tobias (1959). The agreement of the predicted data [Equation (34)] and the experimental data can be seen to be satisfactory for packed beds ($\epsilon < 0.45$) and excellent for suspensions ($\epsilon > 0.45$).

Regarding the effect of size distributions in homogeneous swarms of spheres, the concensus of opinion is that Λ_K is invariant with this parameter; these experimental observations are also in accord with the conclusions of the presented analysis.

Experimental Data for Diffusion

Little experimental data has appeared in the literature concerning diffusion through porous media composed of spherical particles. However, Schofield and Dakshinamurti (1948) have reported ionic diffusivity measurements (using the K^+Br^--$NH_4^+NO_3^-$ system) for two different systems of packed glass spheres (compare Figure 5). This diffusivity data is particularly valuable because it affords a direct verification of Equation (21), as opposed to the indirect verification via electrical measurements. In consequence, confidence in Equation (34) for both diffusion and electric conduction is considerably enhanced.

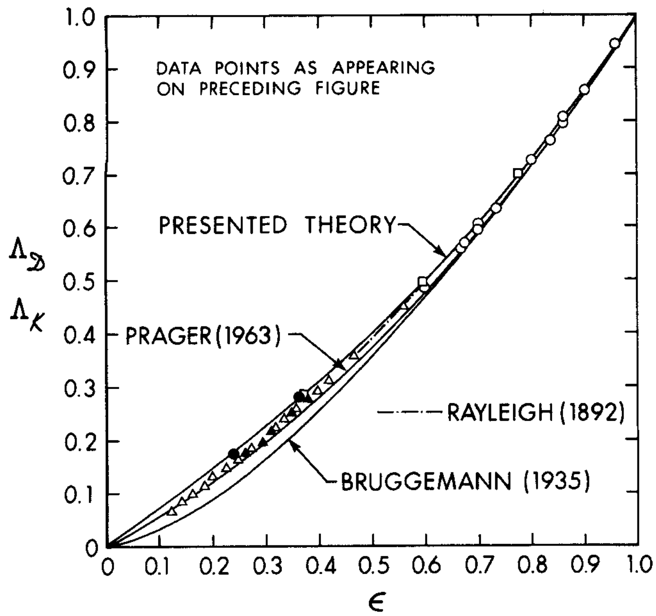

Fig. 6. The dependence of Λ_D and Λ_K on ϵ for swarms of spheres, comparison with previous work.

DISCUSSION OF PREVIOUS THEORETICAL WORK

Clerk Maxwell (1892) investigated the problem of electric conduction through a low concentration dispersion of impermeable conducting spheres of conductivity K^s, embedded within a conductive medium of conductivity K^f. From considerations of the potential of a single sphere in unbounded space he demonstrated that (ϵ designates here volume fraction of the continuous phase)

$$\Lambda_K \rightarrow \frac{2K^f + K^s - 2(K^f - K^s)(1-\epsilon)}{2K^f + K^s + (K^f - K^s)(1-\epsilon)} \quad \text{when} \quad \epsilon \rightarrow 1 \tag{54}$$

For dielectric spheres ($K^s = 0$), Equation (54) reduces to

$$\Lambda_K \rightarrow 2\epsilon/(3-\epsilon) \quad \text{when} \quad \epsilon \rightarrow 1 \tag{55}$$

This limit agrees with Equation (34) which has been derived for the entire porosity range, using the suggested model.

Equation (55) is consistent with Lord Rayleigh's (1892) exact solution for nonconductive monosized spheres arranged in a cubic array, namely,

$$\Lambda_K = \frac{2\epsilon - 0.3919(1-\epsilon)^{10/3} - \ldots}{3 - \epsilon - 0.3919(1-\epsilon)^{10/3} - \ldots} \quad 0.476 \leq \epsilon < 1 \tag{56}$$

the predictions of which are in very close agreement with those of the derived Equation (34), as shown in Figure 6.

Bruggemann (1935) examined the system in which one relatively large sphere is surrounded by a homogeneous swarm of much smaller spheres. Applying Maxwell's result, on the premise that the system is dilute with respect to the large sphere, he demonstrates that for dielectric spheres

$$\Lambda_K = \epsilon^{3/2} \tag{57}$$

However, for monosized spheres or for narrow size fractions the physical conditions necessary for justifying the Bruggemann approximation are not satisfied; this is reflected in the unsatisfactory overall agreement of his formula with experimental data (Figure 6).

Of particular interest is the work of Prager (1963) who applied the principle of minimum entropy generation to obtain bounds on the diffusivity factor for a homogeneous and isotropic suspension of solid particles of arbitrary shape. He showed that

$$\Lambda_D < \epsilon[1 - (1-\epsilon)/3] \tag{58}$$

while, for spheres in particular, he suggests that

$$\Lambda_D = \epsilon[1 - (1-\epsilon)/2] \tag{59}$$

This formula provides a good overall agreement with experimental data (Figure 6).

Not unrelated to the present work is the contribution by Hashin (1968) who employed a model similar to that proposed here for porous media to study the electrical and the thermal conductivity properties of solid heterogeneous media (polycrystalline aggregates, bimetallic composites in particular). Hashin proposes a universal result for electric and thermal conduction, equivalent to Maxwell's Equation (54) for electric conduction, namely,

$$\Lambda_K = \Lambda_k = \frac{2k^f + k^s - 2(k^f - k^s)(1-\epsilon)}{2k^f + k^s + (k^f - k^s)(1-\epsilon)} \tag{60}$$

However, when considering thermal conditions Hashin tacitly neglects the existence of any thermal film resistance between the constituent solid phases. Indeed, his result for thermal conduction follows directly from the derived Equation (48) for the case in which these resistances can be neglected (that is, for $h^s \rightarrow \infty$, $h^* \rightarrow \infty$).

SUMMARY: FURTHER APPLICATIONS OF THE PROPOSED GEOMETRIC MODEL*

The presented results demonstrate that the proposed model offers a satisfactory representation of, and provides valuable insight into, diffusive flow processes (interstitial diffusion, interstitial electric conduction, and thermal conduction) when occurring within an homogeneous and isotropic porous medium composed of spherical particles.

In view of the encouraging results reported here, the proposed geometric model has been further employed to study incompressible, creeping liquid flow through an homogeneous and isotropic porous medium composed of spherical particles and has been generalized (using aligned oblate or prolate spheroids) to serve as a geometric model for diffusive flow processes occurring within homogeneous and anisotropic porous media. Equally satisfactory results have been obtained in both instances.

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NOTATION

c = concentration
D = diffusivity
e = electric potential
Gr = Grashof number
h = heat transfer coefficient
$\underline{i}$ = electric flux reactor

* Notes relating to the Application of the Proposed Geometric Model of (Unconsolidated) Porous Media have been deposited as Document No. 01922 with National Auxiliary Publications Service (NAPS), c/o CCM Information Corp., 866 Third Ave., New York 10022 and may be obtained for $2.00 for microfiche or $5.00 for photocopies.

$\underline{I}$ = electric flux vector component
$\bar{I}$ = mainstream electric flux vector components
k = thermal conductivity
K = electric conductivity
Nu_m = mean Nusselt number
Pr = Prandtl number
$\underline{q}$ = diffusive (also thermal) flux vector
q = diffusive (also thermal) flux
$\underline{Q}$ = mainstream diffusive (also thermal) flux vector component
Q = mainstream diffusive (also thermal) flux
r = radial distance
R = radius of reference sphere
Re = Reynolds number
S = radius of unit cell
t = temperature

Greek Letters, Operator Symbols

ϵ = porosity
θ = polar angle
ϕ = azimuthal angle
Λ_D = molecular (ionic) diffusivity factor = D^*/D^f
Λ_k = thermal conductivity factor = k^*/k^f
Λ_K = electric conductivity factor = K^*/K^f
∇ = del (gradient) operator
∇^2 = Laplacian operator

Subscripts and Superscripts

r = radial vector component
θ = polar vector component
f = designates fluid which saturates the porous medium
s = designates impermeable sphere
$*$ = designates macroscopically averaged quantities pertaining specifically to a porous medium

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Dropwise and Filmwise Condensation of Water Vapor on Gold

A pure gold tube was found to give filmwise condensation in the absense of organic contamination in a flow situation simulating that found in seawater conversion plants. A sensitive test for the presence of organic contamination has been developed. The gold tube, promoted by paraffinic thio-silane or mercaptan, gave 100% excellent dropwise condensation. Overall heat transfer coefficients are reported for filmwise and dropwise condensation. The steamside heat transfer coefficient with dropwise condensation was estimated to be over 0.2 MW/m^2-°C (35,000 B.t.u./hr-ft^2-°F) at the 95% confidence level.

Gold plated tubes* gave 95% filmwise condensation after one week of operation in a clean, once-through system.

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SCOPE

Water vapor can condense as a continuous film or in discrete drops. The latter can result in greatly enhanced heat transfer. Noble metals such as gold have been reported as giving permanent dropwise condensation and gold plated tubes have been proposed for use in seawater conversion plants. Permanent dropwise condensation would also be very desirable for fundamental studies of the dropwise phenomena because variables such as promoter quality, life, thickness, and time dependence could

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