Similar results can be found for area and line integrals using the same approach as long as $l \ll L$. In particular, it is obvious that

$$\int_A f\nabla^n\langle\psi\rangle dA = \left(\int_A f dA\right)\nabla^n\langle\psi\rangle \tag{A.4}$$

and

$$\int_0^{s_b} f\nabla^n\langle\psi\rangle ds = \left(\int_0^{s_b} f ds\right)\nabla^n\langle\psi\rangle \tag{A.5}$$

if $A = 0(l^2)$ and $S_b = 0(l)$.

NOTATION

A_e = entrance and exit surface areas of volume V_f
A_i = interior surfaces of solid volume V_s inside V
d = microscopic length scale
e_s = unit tangent to curve s
e_1, e_2 = unit vectors in x and y directions, respectively
K = permeability
K_{ij} = permeability tensor
l = length scale of averaging volume V
L = length scale of boundary region
L_p = length scale of macroscopic process
L_{ijk} = tensor defined in text via an integral over A_e
M_{ij} = a linear transformation that maps $\langle v\rangle$ into v
n = unit outer normal
N_{ij} = tensor defined in text via an integral over A_e
m_j, r_j, & $\frac{\partial q_j}{\partial x_k}$ = vectors and tensors defined in text via line integrals
$P, \langle P\rangle$ = point and average pressure
s = arc length along curve going from 0 to s_b
$U, \hat{U}$ = characteristic velocity of fluid above and below boundary region
$v, \langle v\rangle$ = point and average velocity
V = averaging volume
V_f = total fluid volume within V
V_s = total solid volume within V
x = point in space

Greek Letters

α = dimensionless quantity that depends on the structure of the porous medium
β = void volume distribution function
δ_{ij} = Kronecker delta
ζ = equation of surface above the xz plane
Φ = porosity
ψ = a continuous tensor field
μ = fluid viscosity (Newtonian)

LITERATURE CITED

Beavers, G., and D. Joseph, "Boundary conditions at a naturally permeable wall," *J. Fluid, Mech.*, **30**, 197 (1967).
Beavers, G., E. Sparrow and R. Magnuson, "Experiments on coupled parallel flows in a channel and a bounding porous medium," *Trans. ASME, J. Basic Engineering*, **D92**, 843 (1970).
Beavers, G., E. Sparrow, and B. Masha, "Boundary condition at a porous surface which bounds a fluid flow," *AIChE J.*, **20**, No. 3, 596 (1974).
Fung, Y., *A First Course in Continuum Mechanics*, Prentice-Hall (1977).
Halmos, P., *Finite-Dimensional Vector Spaces*, D. Von Nostrand (1958).
Richardson, S., "A model for the boundary condition of a porous material," Part 2, *J. Fluid Mech.*, **49**, 327 (1971).
Saffman, P., "On the boundary condition at the surface of a porous material," *MIT Studies in Applied Math., L No. 2*, 93 (1971).
Slattery, J. C., "Flow of viscoelastic fluids through porous media," *AIChE J.*, **13**, 1066 (1967).
Taylor, G., "A model for the boundary condition of a porous material," Part 1, *J. Fluid Mech.*, **49**, 319 (1971).
Whitaker, S., "Advances in theory of fluid motion in porous media," *Flow Through Porous Media*, R. Nunge, Ed., Am. Chem. Soc. (1970).

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Effective Diffusion and Conduction in Two-Phase Media: a Unified Approach

A multiscale analysis based on two widely different length scales that exist in stagnant two-phase media is carried out to investigate diffusion and conduction in periodic and random systems. A variational form of the resulting unit cell equations allows one to demonstrate its equivalence to the cell equations of other independent approaches, thus unifying these widely different methods. The variational approach is also shown to facilitate numerical studies and to provide a link between random and periodic media by yielding an upper bound for the effective diffusivity in random media in terms of the periodic one.

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SCOPE

The need to describe transport phenomena in multiphase media with complex geometries in terms of simple "homogenized" equations with "effective" or "bulk" transport parameters have inspired a surfeit of widely different approaches to the problem for both periodic and random media. These approaches yield seemingly different methods for deriving the effective diffusivity or conductivity tensors. Perhaps because of the apparent divergence of these approaches, numerical studies and comparisons of theory with experimental data have been lacking. This paper aims to unify various approaches for periodic media and establish a relationship between the periodic and random model for heterogeneous media. Numerical studies are also performed with the most efficient numerical schemes and the results are compared to experimental data.

CONCLUSIONS AND SIGNIFICANCE

Three approaches to effective diffusity in periodic media are demonstrated to be equivalent. Of these three, the multiscale method is the most general and powerful since it allows local diffusivity/conductivity coefficients that are not piecewise constant and facilitates numerical studies for arbitrary particle geometries. One possible significant application of the first advantage is in Brownian movements of large solutes in porous media where the Einstein-Stokes relationship stipulates non-constant local diffusivities. The introduction of the variational form of the local equations also precipitates the versatile finite elements method for numerical studies. The extension of the multiscale analysis to random media and the derivation of an inequality between periodic and random effective diffusivities provide an important link between these two extreme views of the system.

The effective transport properties in periodic and random two-phase media are of considerable interest in a number of fields. Perhaps, because of this, theoretical derivations of the effective parameters have also appeared in many forms. The volume-averaging technique pioneered by Slattery (1972) and Whitaker (1973) has been applied to diffusion problems. Numerical values for the effective diffusivity in a two-dimensional periodic medium with square or rectangular particles have been derived by Ryan et al. (1980) using this approach.

An independent approach by Brenner (1980) for dispersion in strictly periodic media using a generalized moment analysis technique similar to the Taylor-Aris dispersion analysis (Aris, 1956) yields an independent set of unit cell equations. Numerical studies of Brenner's set of equations to obtain the effective diffusivity are not available even for the simplest case of pure diffusion in stagnant media.

Yet another independent school exists for the determination of thermal conductivity of periodic composite media consisting of spherical particles. Rayleigh (1892) was the first to use the dipoles (and higher-order multipoles) method to obtain the effective conductivity for a simple cubic array. His method has been extended (Runge, 1925; Meredith and Tobias, 1960) and modified (McPhedran et al., 1978; Perrins et al., 1979; Zuzovski and Brenner, 1977; Sangani and Acrivos, 1982) to obtain higher order approximations to the effective conductivity and/or to overcome mathematical difficulties in summing nonabsolutely convergent series. The mathematical approach of this particular school is referred to as the generalized functions approach. An alternative view of the problem is provided by Strieder and Aris (1973) who used variational methods to obtain an upper bound for the effective diffusivity in random media with overlapping spheres.

In an earlier paper (Chang, 1982), we presented a multiscale method based on the functional analysis approach developed by Bensoussan et al. (1978). Simple periodic geometries which allow analytical solutions of the local equations were considered and analytical expressions for the effective diffusivity and conductivity are obtained. Our numerical values were found to be consistent with those from the volume-averaging approach (Ryan et al., 1980) and with experimental data from random media even though the method is based on the assumption of a periodic medium. In this presentation, we demonstrate that, in the case of diffusion in periodic media, the unit cell equations of our multiscale approach are identical to those from volume-averaging (Ryan et al., 1980) and moment analysis (Brenner, 1980), thus unifying these three approaches. The agreement with moment analysis is especially gratifying since the two approaches are apparently completely different.

The multiscale technique is, however, not limited to diffusion problems. Effective conductivity values are obtained from a variational form of the unit cell equations for several two- and three-dimensional systems. The agreement of numerical results with those from the generalized function method (Perrins et al., 1979) also suggests the equivalence of these two methods. The numerical solutions of the unit cell equation are facilitated by the use of variation methods and numerical techniques such as Ritz's and finite elements methods. The finite elements method is especially powerful due to its ability to handle irregular particle geometries. In the last section of our presentation, the multiscale method is extended to random media. Using the variational form of the local equations and the periodic solutions as the trial functions, an upper bound for the random effective diffusivity is obtained in terms of the periodic effective diffusivity. This represents the first link between the two extreme views of two-phase media.

MULTISCALE APPROACH FOR PERIODIC MEDIA

We consider the following diffusion/conduction equation for periodic media

$$\frac{\partial u}{\partial t} = \nabla_x \cdot \alpha(\underline{x})\nabla_x u \tag{1}$$

where $\underline{x}$ are the spatial coordinates and α is the periodic diffusivity or conductivity. The spatial period of α is small compared to the macroscopic scales, *viz.*

$$\alpha(\underline{x}) = \alpha(\underline{x} + \epsilon\underline{x}_i^o) \quad i = 1,2,3$$

where $\epsilon\underline{x}_i^o$ are the latrice vectors of the unit cell and ϵ, which is the ratio of the short scale that is the period of α (or the characteristic length of the unit cell) to the global scale, is a small parameter.

We follow the formal multiscale expansion method (Nayfeh, 1973) for our analysis. This formal expansion method can be justified mathematically using functional analysis (Bensoussan et al., 1978). However, the rigorous proofs of convergence of the expansion series are omitted here and interested readers are referred to Bensoussan et al.'s book. In fact, the derivations from Eqs. 1 to 13 are reproduced from the same book for easy reference in later sections of this presentation and for completeness.

Defining a strained coordinate,

$$\underline{y} = \frac{1}{\epsilon}\underline{x} \tag{2}$$

Equation 1 is rewritten as

$$\frac{\partial u}{\partial t} = \nabla_x \cdot \alpha(\underline{y})\nabla_x u \tag{3}$$

Proceeding formally with the multiscale analysis by assuming an expansion of the form

$$u(t,\underline{x},\underline{y}) \sim u_o(t,\underline{x},\underline{y}) + \epsilon u_1(t,\underline{x},\underline{y}) + \epsilon^2 u_2(t,\underline{x},\underline{y}) \tag{4}$$

and replacing ∇_x by $\nabla_x + 1/\epsilon\nabla_y$ in Eq. 3 as stipulated by the analysis, one obtains, upon collecting terms of the same order,

$$L_1 u_o = 0 \tag{5a}$$

$$L_1 u_1 = -L_2 u_o \tag{5b}$$

$$L_1 u_2 = \frac{\partial u_o}{\partial t} - L_3 u_o - L_2 u_1 \tag{5c}$$

where

$$L_1 = \nabla_y \cdot \alpha(\underline{y})\nabla_y \tag{6a}$$

$$L_2 = \nabla_y \cdot \alpha(\underline{y})\nabla_x + \nabla_x \cdot \alpha(\underline{y})\nabla_y \tag{6b}$$

$$L_3 = \nabla_x \cdot \alpha(\underline{y})\nabla_x \tag{6c}$$

Equations 5a–c allow a recursive calculation of the various terms, u_i, in the expansion. However, a necessary condition for the expansion to be valid is that the various u_i's calculated from Eqs. 5 must be unique (up to an additive function of $\underline{x}$ and t) and periodic with respect to $\underline{y}$. The following theorem by Bensoussan et al. (1978) provides these conditions.

Theorem 1. Let $\alpha(\underline{y})$ be periodic in $\underline{y}$. Then $L_1 v(\underline{y}) = g(\underline{y})$ has a unique periodic solution (up to a constant) if

$$\int_Y g(\underline{y})dY = 0$$

where the integral is a volume integral over a unit cell, Y. Applying this theorem to Eq. 5a, one concludes that u_o is a constant with respect to $\underline{y}$, *viz.*

$$u_o = u_o(t,\underline{x}) \tag{7}$$

Substituting Eq. 7 into Eq. 5b, one obtains

$$L_1 u_1 = -\nabla_y \alpha \cdot \nabla_x u_o \tag{8}$$

which can be solved by defining the vector functions $\underline{\phi}(y)$ such that

$$L_1 \underline{\phi} = -\nabla_y \alpha \tag{9}$$

Then

$$u_1 = \underline{\phi} \cdot \nabla_x u_o + c(\underline{x},t) \tag{10}$$

Applying Theorem 1 to Eq. 5c, and substituting Eq. 10, one obtains the following macroscopic equation

$$\frac{\partial u_o}{\partial t} = \nabla_x \cdot \underline{A} \cdot \nabla_x u_o \tag{11}$$

where

$$\underline{A} = \langle \alpha \rangle \underline{I} + \langle \alpha \nabla_y \underline{\phi} \rangle \tag{12}$$

$$\langle \cdot \rangle = \frac{1}{|Y|} \int_Y \cdot \, dY \tag{13}$$

and $|Y|$ is the volume of the unit cell.

Equation 11 is the desired macroscopic equation and $\underline{A}$ the effective diffusivity/conductivity tensor which can be calculated if Eq. 9 is solved in a unit cell subjected to the periodic condition. Since ϵ is small $u_o(t,\underline{x})$ represents the leading order approximation to the exact solution u and u would converge to u_o as ϵ approaches zero. This approximate nature of the macroscopic equation, Eq. 11, to the exact local equation, Eq. 1, is the sacrifice one makes for the macroscopic description in Eq. 11. This is true of other approaches but the approximations take different forms. In the generalized function approach, the spherical particles are approximated by dipoles and higher-order multipoles. In moment analysis, the exact concentration distribution is characterized by the first three moments. In volume averaging, the various orders of magnitude arguments used to simplify the equations are again approximations. Consequently, it is extremely curious but gratifying that these different approaches yield identical unit cell equations as Eq. 9. This will be demonstrated in the next section.

For the layered structure depicted in Figure 1a where α is piecewise constant and takes on the value α_s on the solid (shaded region) and α_f in the fluid, analytical solutions to Eq. 9 is obtained (Chang, 1981),

$$A_{11} = \frac{1}{\psi/\alpha_f + (1-\psi)/\alpha_s} \tag{14a}$$

$$A_{22} = A_{33} = \psi\alpha_f + (1-\psi)\alpha_s \tag{14b}$$

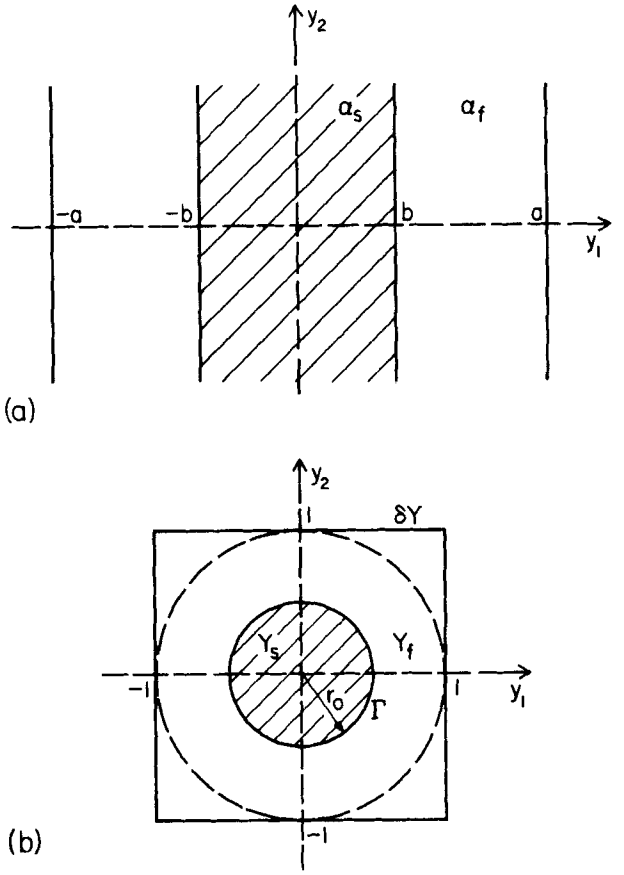

Figure 1. Unit cell for layered structure (a); unit cell for square structure and its approximation (b).

$$A_{ij} = 0 \quad i \neq j \tag{14c}$$

where ψ is the void volume fraction (porosity).

Similarly, if the two-dimensional square unit cell with a circular particle depicted in Figure 1b is approximated by a circle, analytical solutions for Eq. 9 can be obtained (Chang, 1982). Although the circular cell approximation is depicted to be contained in the original unit cell, the result is independent of the size of the circular (clindrical) cell. This approximation, while unjustified, has traditionally been used (Strieder and Aris, 1973; Tal and Sirignano, 1982). The effective conductivity tensor thus obtained is diagonal with identical elements, reflecting the isotropic nature of the unit cell,

$$A_{ii} = \frac{\psi\alpha_f + (2-\psi)\alpha_s}{\psi\beta + 2 - \psi} \tag{15}$$

where

$$\beta = \alpha_s/\alpha_f \tag{16}$$

This is exactly the result obtained by Rayleigh (1892) and other generized function approach for effective conductivity of a regular arrays of cylinders if their expression is truncated at the $0(c)$ term where c is the volume fraction $(1-\psi)$. Consequently, the circular (cylindrical) cell approximation corresponds to the "dilute" (high porosity) limit.

A similar spherical cell approximation can be made for three dimensional cubic unit cells and Eq. 9 can be again solved analytically to yield a diagonal $\underline{A}$ with identical elements,

$$A_{ii} = \frac{2\psi\alpha_f + \alpha_s(3-2\psi)}{\psi\beta + 3 - \psi} \tag{17}$$

The result is again the dilute limit of the generalized function approach for periodic media and also the dilute limit of randomly distributed spherical particle results using methods used by Batchelor (1972) and Jefferey (1973).

EQUIVALENCE OF DIFFERENT APPROACHES TO DIFFUSION PROBLEM

In this section, we demonstrate that the unit cell equations from the volume-averaging method (Ryan et al., 1980) and moment analysis (Brenner, 1980) are identical to Eqs. 9 and 12. First of all, one notes that Eq. 9 is valid for the entire unit cell, including both fluid and solid phases, and the volume average, $\langle\cdot\rangle$, in Eq. 12 is carried out in the entire cell, Y. In the analysis of both Ryan et al. (1980) and Brenner (1980), only the diffusion problem is considered ($\alpha_s = 0$) and volume integrals are over the fluid phase, Y_f, only. The fluid-solid interphase is denoted Γ and the unit-cell boundary ∂Y. These regions and boundaries are depicted in Figure 1b for the case of a circular particle in a square unit cell (simple array of cylinders).

In these notations, the unit cell equations from volume-averaging (Ryan et al., 1980) are,

$$\nabla_y^2 \underline{f} = 0 \quad Y_f \tag{18a}$$

$$\underline{n} \cdot \nabla_y \underline{f} = -\underline{n} \quad \Gamma \tag{18b}$$

$$\underline{\underline{A}}' = \alpha_f \left(\underline{\underline{I}} + \frac{1}{|Y_f|} \int_\Gamma \underline{n}\underline{f}\right) \tag{18c}$$

To demonstrate that Eqs. 18a–c are equivalent to Eqs. 9 and 12, we first prove that the solution of Eq. 9, ϕ_j (the jth element of $\underline{\phi}$), corresponds to the function that minimizes the following functional

$$F(v_j) = \left\langle \frac{\alpha}{2} \nabla_y v_j \cdot \nabla_y v_j - v_j \frac{\partial \alpha}{\partial y_j} \right\rangle \tag{19}$$

Consider the following trial function,

$$v_j = \phi_j + u_j \tag{20}$$

where u_j is a periodic variation on any periodic function.

Substituting Eq. 20 into Eq. 19,

$$F(v_j) = F_o(\phi_j) + F_1(\phi_j, u_j) + F_2(u_j) \tag{21}$$

where F_1 contains linear in u_j and F_2 contains higher order terms in u_j,

$$F_1 = \left\langle \alpha \nabla_y u_j \cdot \nabla_y \phi_j - u_j \frac{\partial \alpha}{\partial y_j} \right\rangle = \left\langle \nabla_y \cdot u_j \alpha \nabla_y \phi_j - u_j \nabla_y \cdot \alpha \nabla_y \phi_j - u_j \frac{\partial \alpha}{\partial y_j} \right\rangle \tag{22}$$

Using the divergence theorem on Eq. 22,

$$F_1 = \frac{1}{|Y|} \int_{\partial Y} \underline{n} \cdot u_j \alpha \nabla_y \phi_j - \left\langle u_j \left(\nabla_y \cdot \alpha \nabla_y \phi_j + \frac{\partial \alpha}{\partial y_j} \right) \right\rangle \tag{23}$$

Since $u_j \alpha \nabla_y \phi_j$ is periodic on the boundaries of the unit cell, the first term on the right hand side of Eq. 23 vanishes. The variation u_j is arbitrary, thus F_1 vanishes, indicating $F(v_j)$ exhibits an extremum at ϕ_j, if Eq. 9 holds everywhere in Y. Consequently, solving Eq. 9 is equivalent to finding the minimum to the functional in Eq. 19. (The extremum is a minimum since $F_2(u_j) = \langle \alpha/2 \nabla_y u_j \cdot \nabla_y u_j \rangle$ is positive-definite.)

We now modify Eq. 19 slightly by introducing the following identities

$$\left\langle v_j \frac{\partial \alpha}{\partial y_j} \right\rangle = \left\langle \frac{\partial \alpha v_j}{\partial y_j} \right\rangle - \left\langle \alpha \frac{\partial v_j}{\partial y_j} \right\rangle = - \left\langle \alpha \frac{\partial v_j}{\partial y_j} \right\rangle \tag{24}$$

where the divergence theorem and the periodicity of αv_j on ∂Y have been invoked. Substituting Eq. 24 into Eq. 19, one obtains the following functional,

$$F(v_j) = \left\langle \frac{\alpha}{2} \nabla_y v_j \cdot \nabla_y v_j + \alpha \frac{\partial v_j}{\partial y_j} \right\rangle \tag{25}$$

In subsequent analysis, we will use this variational form of the cell equation (Eq. 25) instead of Eq. 9.

In the case of diffusion ($\alpha_s = 0$), Eq. 25 simplifies to

$$F(v_j) = \alpha_f \psi \left\langle \frac{1}{2} \nabla_y v_j \cdot \nabla_y v_j + \frac{\partial v_j}{\partial y_j} \right\rangle_f \tag{26}$$

where

$$\langle\cdot\rangle_f = \frac{1}{|Y_f|} \int_{Y_f} \cdot \, dY \tag{27}$$

is the fluid-phase volume average.

Consequently, Eq. 22 becomes, after invoking Eq. 24,

$$F_2 = \alpha_f \psi \left[\langle \nabla_y \cdot u_j \nabla_y \phi_j \rangle_f - \langle u_j \nabla_y^2 \phi_j \rangle_f + \left\langle \frac{\partial u_j}{\partial y_j} \right\rangle_f \right] \tag{28}$$

Applying the divergence theorem to the first and third terms of Eq. 28, we now have contributions from two boundaries surrounding Y_f, ∂Y and Γ. The ∂Y terms vanish due to periodicity and one is left with

$$F_2 = \alpha_f \psi \left\{ - \langle u_j \nabla_y^2 \phi_j \rangle_f + \frac{1}{|Y_f|} \int_\Gamma \underline{n} \cdot [u_j \nabla_y \phi_j + \delta^j u_j] \right\} = 0 \tag{29}$$

where δ^j is a vector containing zeroes except the jth element which is unity. Since u_j is arbitrary, Eq. 29 is true if

$$\nabla_y^2 \underline{\phi} = 0 \quad Y_f \tag{30a}$$

$$\underline{n} \cdot \nabla_y \underline{\phi} = -\underline{n} \quad \Gamma \tag{30b}$$

which are simply Eqs. 18a and 18b. Finally, setting α_s to zero in Eq. 12, one obtains,

$$\underline{\underline{A}} = \alpha_f \psi [\underline{\underline{I}} + \langle \nabla_y \underline{\phi} \rangle_f] = \alpha_f \psi \left[\underline{\underline{I}} + \frac{1}{|Y_f|} \int_\Gamma \underline{n}\underline{\phi} \right] \tag{31}$$

where divergence theorem and periodicity condition on ∂Y is again invoked.

Comparing Eq. 31 with Eq. 18c, and realizing the equivalence of Eqs. 30a and b with Eqs. 18a and b, one concludes,

$$\psi \underline{\underline{A}}' = \underline{\underline{A}} \tag{32}$$

where the factor ψ is simply due to the choice of region over which volume integral is carried out. We have thus demonstrated the equivalence of the multiscale unit cell equations from volume averaging.

A moment analysis approach by Brenner (1980) yields the following cell equation for the case of diffusion without flow

$$\nabla_y^2 \underline{\hat{B}} = 0 \quad Y_f \tag{33a}$$

$$\underline{n} \cdot \nabla_y \underline{\hat{B}} = \underline{n} \quad \Gamma \tag{33b}$$

$$\underline{\underline{A}}'' = \alpha_f \langle \nabla_y B^T \cdot \nabla_y B \rangle_f \tag{33c}$$

where

$$\underline{\hat{B}} = \underline{B} + \underline{y} + \text{constant} \tag{34}$$

One immediately recognizes the correspondence between Eqs. 33a and b and Eqs. 18a and b. To equate $\underline{\underline{A}}''$ and $\underline{\underline{A}}'$, we substitute Eq. 34 into Eq. 33c and obtain

$$\underline{\underline{A}}'' = \alpha_f [\langle \nabla_y \hat{B} \cdot \nabla_y \hat{B} \rangle_f - 2 \langle \nabla_y \hat{B} \rangle_f + \underline{\underline{I}}] = \alpha_f \left[\langle \nabla_y \hat{B} \cdot \nabla_y \hat{B} \rangle_f - \frac{2}{Y_f} \int_\Gamma \underline{n}\underline{\hat{B}} + \underline{\underline{I}} \right] \tag{35}$$

where divergence theorem and periodicity of $\underline{\hat{B}}$ on ∂Y have been invoked.

To further simplify Eq. 35, we recall the following tensor identity;

$$\underline{\hat{B}} \nabla_y^2 \underline{\hat{B}} = \frac{1}{2} \nabla_y^2 \underline{\hat{B}}^2 - \nabla_y \underline{\hat{B}} \cdot \nabla_y \underline{\hat{B}} \tag{36}$$

Invoking Eq. 33a cancels the left hand side of Eq. 36, one obtains

$$\nabla_y \underline{\hat{B}} \cdot \nabla_y \underline{\hat{B}} = \frac{1}{2} \nabla_y^2 \underline{\hat{B}}^2 \tag{37}$$

Taking the fluid phase volume average of Eq. 37 and applying the divergence theorem and periodicity conditions to the right hand side, one obtains

$$\langle \nabla_y \underline{\hat{B}} \cdot \nabla_y \underline{\hat{B}} \rangle_f = \frac{1}{2|Y_f|} \int_\Gamma \nabla \underline{\hat{B}}^2 \cdot \underline{n}$$

$$= \frac{1}{|Y_f|} \int_\Gamma \underline{\hat{B}} \nabla \underline{\hat{B}} \cdot \underline{n} \tag{38}$$

Combining Eqs. 38, 33b and 35, one obtains

$$\underline{\underline{A}}'' = \alpha_f \left[\underline{\underline{I}} - \frac{1}{|Y_f|} \int_\Gamma n \underline{\hat{B}} \right] \tag{39}$$

Setting $\underline{\hat{B}} = -\underline{f}$, completes the proof of the equivalence between Eqs. 18 and 33. Consequently, the results from these widely different approaches are identical!

In spite of the equivalence of the unit cell equation for these three methods, the multiscale approach has definite advantages over the others. The multiscale results are mathematically justified (Bensoussan et al., 1978) whereas the mathematical validity of the theorem for the local volume average of a gradient (Slattery, 1972), which is a key step in the volume-averaging method, has recently been questioned by Veverka (1981). The moment analysis approach, on the other hand, is limited to diffusion problems whereas Eq. 25 is valid for conduction problems and even problems in which α is not piecewise constant. Furthermore, the generalized function approach, which will be compared in the next section, is limited to spherical particles while Eq. 25 is again valid for any geometry. This generality of Eq. 25 is discussed in the next section with the introduction of numerical methods which must be suitable for the variational form of Eq. 25.

NUMERICAL STUDIES

The only numerical studies of the unit cell equations in the literature are for diffusion in simple arrays of square particles using Eqs. 18 (Ryan et al., 1980), and the various studies on conduction in different arrays of cylinders and spheres using the generalized functions approach (McPhedran et al., 1978; Perrins et al., 1979; Sangani and Acrivos, 1982). The present study, in light of the results in the previous section, has three purposes. The advantage of the variational form of Eq. 25 is shown by appropriate numerical methods superior to the previous finite difference methods (Ryan et al., 1980). Secondly, a finite elements method is introduced, again utilizing the variational equation, for irregular particle geometries. Finally, numerical results are compared to those from the generalized function approach, which is only valid for spherical particles, for the final unification of all the different approaches and to experimental data for verification of the theory.

Let the function v_j in Eq. 25 be approximated by a truncated expansion in a complete set of trial functions $\{N_l\}$,

$$v_j = \bar{3}\underline{N} \cdot \underline{a} \tag{40}$$

Since N_l's are known, the task of finding the minimum of F with respect to v_j becomes minimizing with respect to a_l. Substituting Eq. 40 into 25 and differentiating with respect to a_l.

$$G_l \equiv \frac{\partial f}{\partial a_l} = \frac{\partial}{\partial a_l} \left\langle \frac{\alpha}{2} (\nabla_y \underline{N} \cdot \underline{a}) \cdot (\nabla_y \underline{N} \cdot \underline{a}) + \alpha \frac{\partial}{\partial y_j} (\underline{N} \cdot \underline{a}) \right\rangle$$

$$= \left\langle \alpha (a \cdot \nabla_y N) \cdot \nabla_y N_l + \alpha \frac{\partial N_l}{\partial y_j} \right\rangle = 0 \tag{41}$$

Equation 41 is a set of linear equations for and can be expressed as

$$\underline{\underline{K}} \underline{a} + \underline{P} = 0 \tag{42}$$

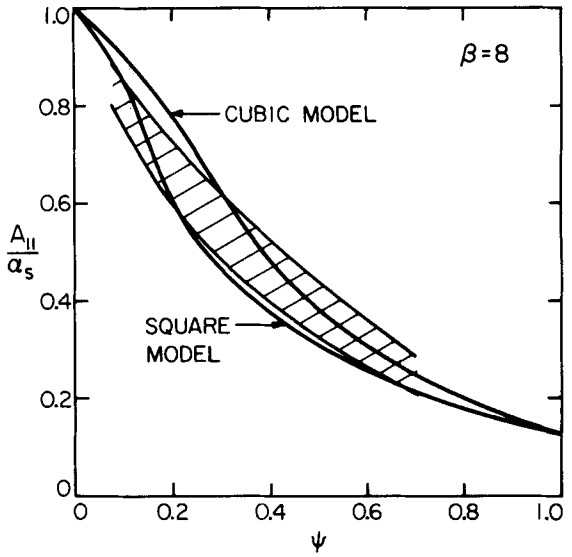

Figure 2. Comparison of numerical results for periodic square cylinders and cubes with conductivity data for random media ($\beta = 8$).

where

$$K_{lm} = \langle \alpha \nabla N_l \cdot \nabla N_m \rangle \tag{42a}$$

and

$$P_m + \left\langle \alpha \frac{\partial N_m}{\partial y_j} \right\rangle \tag{42b}$$

Thus, the optimal coefficients, $\underline{a}^*$, which minimizes F are simply

$$\underline{a}^* = -\underline{\underline{K}}^{-1} \underline{P} \tag{44}$$

which yields a truncated expansion for ϕ_j which can in turn be substituted into Eq. 12 to yield A_{ij}. If the trial functions are periodic orthonormal eigenfunctions in Y (such that the periodic conditions are satisfied), the above method is simply the Ritz's method. If the trial functions are defined only over a certain portion of Y (call an element), this is known as the finite elements method (Finlayson, 1980) and $\underline{\underline{K}}$ and $\underline{P}$ are obtained by summing over all elements.

Using the trial functions,

$$N_{lm} = \cos l\Pi y_1 \cos m\Pi y_2 \tag{45}$$

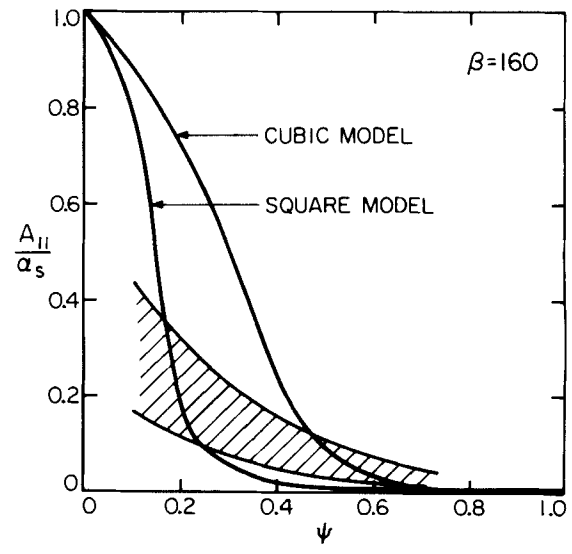

Figure 3. Comparison of numerical results for periodic square cylinders and cubes with conductivity data for random media ($\beta = 160$).

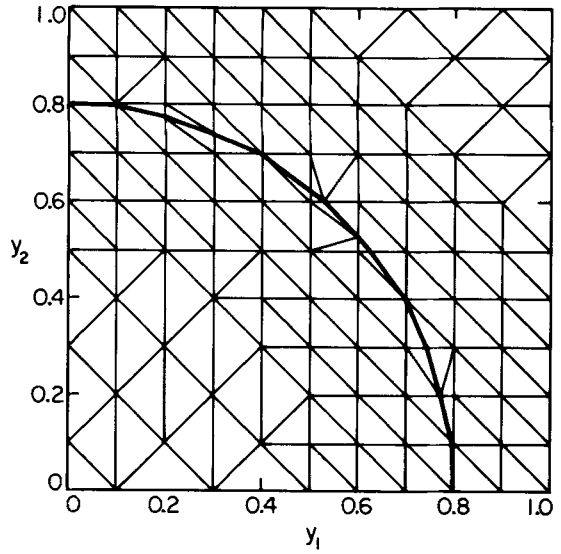

Figure 4. Elements and nodes used in the finite elements scheme (ψ = 0.503).

for square unit cells with square particles and the trial functions

$$N_{lmn} + \cos l\Pi y_1 \cos m\Pi y_2 \cos n\Pi y_3 \tag{46}$$

for cubic particles contained in cubic unit cells, the effective diffusivity and conductivity tensor are solved for both cases. The diffusivity result is numerically indistinguishable from the cylindrical and spherical cell approximations. Eqs. 15 and 17, which are presented in an earlier paper (Chang, 1982). The conductivity results, on the other hand, are higher than the cell approximations, Figures 2 and 3, for two different values of β. Overlapped on these curves for comparison are Krischen and Kröll's (1956) experimental data for nonperiodic media. There exist no experimental data on periodic arrays of square cylinders and cubes.

The finite elements method is especially useful for irregular particle geometries. We demonstrate this by treating the case of conduction in simple cylindrical arrays. Due to the symmetries of the geometry, only the first quadrant of Figure 1b needs to be considered and $\underline{\underline{A}}$ is again a diagonal matrix with identical elements. This region is divided into 162 triangular elements, Figure 4, for a particle of radius 0.8. For each void fraction, new elements are constructed such that the density is high near the solid-fluid

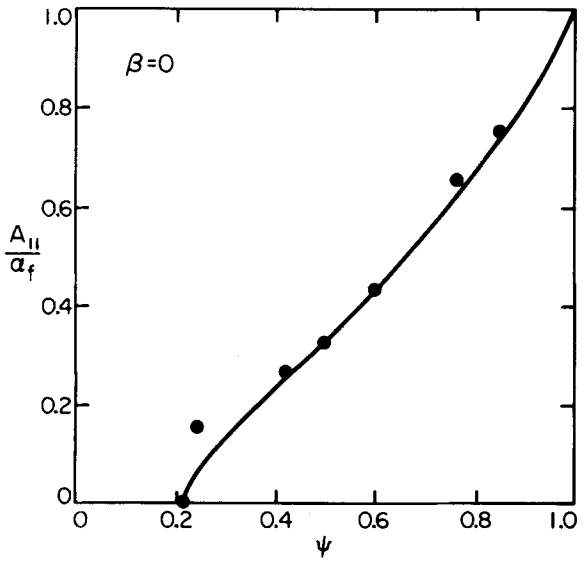

Figure 5. Numerical results for simple periodic arrays of cylinders (β = 0) and experimental data of Mashovets (1951).

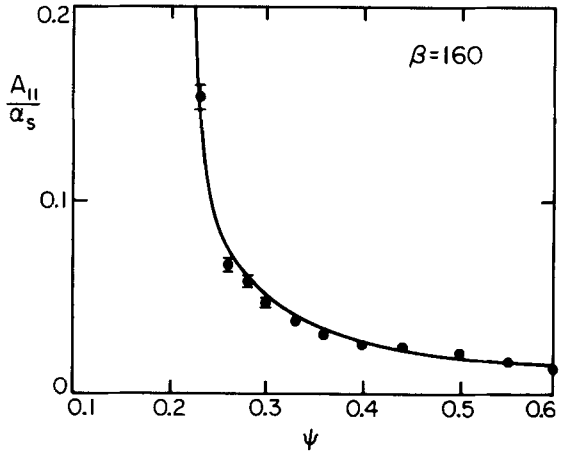

Figure 6. Numerical results for simple periodic arrays of cylinders (β = 160) and experimental data of Perrins et al. (1979).

interphase where ϕ_j exhibits the sharpest behaviors. The results are shown for $\beta = 0$ and $\beta = 160$ in Figures 5 and 6. These curves agree well with the experimental results of Mashovet (1951) and Perrins et al. (1979) for simple arrays of cylinders. The numerical values are also in complete agreement with those from the generalized function approach (Perrins et al., 1979). This finalizes the unification of four independent approaches for effective diffusion and conduction in periodic media.

RANDOM MEDIA

The multiscale analysis for periodic media can also be extended to random media. The conductivity, α, in Eq. 1 will now be replaced by α_r to indicate that it is now a stochastic function of y due to the randomness. The entire analysis from Eq. 2 to Eq. 6 are still valid upon substitution of α_r for α. We now let Ω be a large domain in the y-space and define the volume average to be

$$\langle\cdot\rangle_\Omega = \lim_{|\Omega|\to\infty} \frac{1}{|\Omega|} \int_\Omega \cdot\, d\Omega \tag{46}$$

For the expansion, Eq. 4, to be valid, u_i and its derivatives must be bounded in the infinitely large domain Ω. Since the u_i's are determined from Eqs. 6, the following theorem, analogous to Theorem 1, delineates a direct result of the validity of the expansion.

Theorem 2. If $L_1 v = g(\underline{y})$ where v and its derivatives are required to be bounded in Ω, $\langle g(\underline{y})\rangle_\Omega = 0$

Proof:

$$\int_\Omega L_1 v d\Omega = \int_{\partial\Omega} \underline{n} \cdot \alpha_r \nabla_y v \text{ (Divergence Theorem)}$$

Thus,

$$\lim_{|\Omega|\to\infty} \frac{1}{|\Omega|} \int_\Omega L_1 v d\Omega = \lim_{|\Omega|\to\infty} \frac{1}{|\Omega|} \int_{\partial\Omega} \underline{n} \cdot \alpha_r \nabla_y v$$

$$\sim 0(|\Omega|^{-1/3}) \qquad (\alpha_r \nabla_y v \text{ bounded})$$

$$= 0$$

Theorem 2 is, of course, analogous to Theorem 1; thus, all subsequent derivations (Eqs. 7–23) are identical except that the volume integrals are now carried out over the finite domain Ω. Consequently, the minimum of the functional in Eq. 19 is over the infinite domain with the stochastic α_r. We now derive an equation analogous to Eq. 25 by noting that

$$\left\langle v_j \frac{\partial \alpha_r}{\partial y_j} \right\rangle_\Omega = \lim_{|\Omega|\to\infty} \frac{1}{|\Omega|} \int_{\partial\Omega} \alpha_r v_j - \left\langle \alpha_r \frac{\partial v_j}{\partial y_j} \right\rangle_\Omega$$

$$= -\left\langle \alpha_r \frac{\partial v_j}{\partial y_j} \right\rangle_\Omega \tag{47}$$

since $\alpha_r v_j$ remains finite in Ω. Substituting into Eq. 19, one obtains the following functional

$$F_r(v_j) = \left\langle \frac{\alpha_r}{2} \nabla_y v_j \cdot \nabla_y v_j + \alpha_r \frac{\partial v_j}{\partial y_j} \right\rangle_\Omega \tag{48}$$

Let ϕ_j^r be the function that minimizes Eq. 48 and upon substitution of ϕ_j^r into F_r and invoking the analogous equation to Eq. 12, one obtains

$$F_r(\phi_j^r) = \left\langle \frac{\alpha_r}{2} \nabla_y \phi_j^r \cdot \nabla_y \phi_j^r \right\rangle_\Omega + A_{jj}^r - \langle \alpha \rangle_\Omega \tag{49}$$

Since the first term on the righthand side is positive-definite and $F_r(\phi_j^r)$ is the minimum of $F_r(v_j)$,

$$A_{jj}^r \langle F_r(\nabla_y v_j) + \langle \alpha \rangle_\Omega \tag{50}$$

where F_r is denoted as a function of $\nabla_y v_j$ rather than v_j as evidenced in Eq. 48. The choice of trial functions for $\nabla_y v_j$ will then set an upper bounds for A_{jj} of a random media. We choose the periodic solutions to Eq. 25, ϕ_j as the trial functions to investigate the relationship between the two media.

In particular, we choose the case of spheres (circles) in a cubic (square) unit cell from the periodic studies.
Let

$$\nabla_y \psi = \sum_k H(\underline{\rho}_k) \nabla_y \phi_j(\underline{\rho}_k) \tag{51a}$$

where

$$\underline{\rho}_k = \underline{y} - \underline{y}_k \tag{51b}$$

and $\underline{y}_k$ is the center of sphere (circle) k in the random media. The function $H(\underline{\rho}_k)$ is a Heaviside function which is zero outside the cube (square) with $\underline{y}_k$ as its center and unity within. Furthermore, if

$$\nabla_y v_j = \lambda \nabla_y \psi \tag{52}$$

one can further minimize the upper bound (*viz.*, the lowest upper bound for $\nabla\psi$) with respect to λ. Substituting Eq. 52 into Eq. 48, minimizing with respect to λ and substituting the resulting expression for λ into F_r, one concludes

$$A_{jj}^r < \langle \alpha \rangle_\Omega - \frac{1}{2} \frac{\left\langle \alpha_r \frac{\partial \psi}{\partial y_j} \right\rangle_\Omega^2}{\langle \alpha_r \nabla_y \psi \cdot \nabla_y \psi \rangle_\Omega} \tag{53}$$

Since the last term is positive-definite, a preliminary conclusion is that A_{jj} of a random media is always smaller than the volume-averaged α. We can, however, improve this result by considering the trial functions from periodic spheres (cylinders) in Eq. 51. We will restrict ourselves to the pure diffusion case ($\alpha_s = 0$).
From Eq. 51a,

$$\left\langle \alpha_r \sum_k \frac{\partial \phi_j(\underline{\rho}_k)}{\partial y_j} H(\underline{\rho}_k) \right\rangle_\Omega = \alpha_f \left\langle g(\underline{y}) \sum_k \frac{\partial \phi_j(\underline{\rho}_k)}{\partial y_j} H(\underline{\rho}_k) \right\rangle_\Omega \tag{54}$$

where

$$g(\underline{y}) = \begin{matrix} 1 \text{ in } \Omega_f \\ 0 \text{ in } \Omega_s \end{matrix} \tag{55}$$

If one considers the random media to be a random collection of freely overlapping spheres (circles) of radius a, the probability that a randomly selected point is in the void region is just the void fraction ψ (Strieder and Aris, 1970). Thus, Eq. 54 becomes

$$\alpha_f n \psi \int_{\Omega_a} H(\underline{\rho}) \frac{\partial \phi_j(\underline{\rho})}{\partial y_j} d\Omega_a = \alpha_f n \psi \int_{Y_f} \frac{\partial \phi_j(\underline{\rho})}{\partial y_j} dY_f \tag{56}$$

where $\Omega_a = \Omega / Y_s$ is the domain Ω with the sphere (circle) removed such that no sphere can be at a distance less than a from the point. The quantity n is the average density of center. Since $H(\rho)$ vanishes outside the unit cell Y, the volume integral can be simply taken over by $Y_f = Y/Y_s$. The quantity n is the average density of sphere centers. If corresponding periodic media are required to have the same average density,

$$n = \frac{1}{|Y|} \tag{57}$$

Combining Eqs. 54–57 and utilizing the fact that α vanishes inside the particle of the unit cell, one obtains

$$\left\langle \alpha_r \sum_k \frac{\partial \phi_j(\underline{\rho}_k)}{\partial y_j} H(\underline{\rho}_k) \right\rangle_\Omega = \psi \left\langle \alpha \frac{\partial \phi_j}{\partial \rho_j} \right\rangle \tag{58}$$

Note that the righthand side of Eq. 58 refers strictly to the periodic solution ϕ_j, and the integration is over a unit cell with periodic α. These are direct result of the choice of trial functions and the statistical properties of random media utilized in deriving Eq. 56.

Similarly, the following identity can also be shown (Strieder and Aris, 1970)

$$\left\langle \alpha_r \left[\sum_k \nabla_y \phi_j \right]^2 \right\rangle_\Omega = \alpha_f n \psi \int_{\Omega_a} H(\underline{\rho}) \nabla_y \phi_j(\underline{\rho}) \cdot \nabla_y \phi_j(\underline{\rho}) d\Omega_a + \alpha_f n^2 \psi \int_{\Omega_a} \int_{\Omega_a} \nabla_y \phi_j(\underline{\rho}_1) \cdot \nabla_y \phi_j(\underline{\rho}_2) H(\underline{\rho}_1) H(\underline{\rho}_2) d\underline{\rho}_1 d\underline{\rho}_2 \tag{59}$$

Invoking Eq. 57 and the definition of a Heaviside function, one obtains

$$\left\langle \alpha_r \left[\sum_k \nabla_y \phi_j \right]^2 \right\rangle_\Omega = \frac{\psi}{\alpha_f} [\alpha_f \langle \alpha (\nabla_y \phi_j(\underline{\rho}))^2 \rangle + \langle \alpha \nabla \phi_j \rangle^2] \tag{60}$$

We now return to the functional for periodic media, Eq. 25. Since ϕ_j minimizes this functional, setting, v_j as $\lambda\phi_j$ in Eq. 25 and minimizing λ must yield the result that $\lambda = 1$ at this minimum. Carrying out the substitution, taking the derivative with respect to λ and equating λ to unity after solving for it, one obtains

$$\frac{\left\langle \alpha \frac{\partial \phi_j}{\partial y_j} \right\rangle}{\langle \alpha (\nabla_y \phi_j)^2 \rangle} = -1 \tag{61}$$

Substituting Eqs. 58, 60 and 61 into Eq. 53 yields

$$A_{jj}^r < \langle \alpha \rangle_\Omega - \frac{1}{2} \psi \alpha_f \frac{\left\langle \alpha \frac{\partial \phi_j}{\partial y_j} \right\rangle}{-\alpha_f + \frac{\langle \alpha \nabla_y \phi_j \rangle^2}{\langle \alpha \, \partial \phi_j / \partial y_j \rangle}} \tag{62}$$

For a unit cell with spherical (circular) particles, the symmetry stipulates that $\partial \sigma_j / \partial y_i$ vanishes for $i \neq j$ ($\underline{A}$ is diagonal). Substituting this into Eq. 62, one obtains

$$A_{jj}^r < \langle \alpha \rangle - \frac{\psi \alpha_f}{2} \frac{\left\langle \alpha \frac{\partial \phi_j}{\partial y_j} \right\rangle}{-\alpha_f + \left\langle \alpha \frac{\partial \phi_j}{\phi y_j} \right\rangle} \tag{63}$$

where the volume integral of α is now carried out over Y rather than Ω. Since the two media have identical porosity, this is permissible. However, from Eq. 12

$$A_{jj} = \alpha_f \psi + \left\langle \alpha \frac{\partial \phi_j}{\partial y_j} \right\rangle \tag{64}$$

for periodic media.

Substituting Eq. 64 into Eq. 63, one obtains the following inequality relating A_{jj}^r, the diffusivity for random media, to A_{jj}, the corresponding value for periodic media

$$\frac{A_{jj}^r}{\alpha_f} < \frac{\psi}{2} \left[\frac{2 + \psi - A_{jj}/\alpha_f}{1 + \psi - A_{jj}/\alpha_f} \right] \tag{65}$$

In Figure 7, the data for random media (Satterfield and Sherwood, 1963) are compared to Eq. 65 with the values for simple arrays of cylinders substituted for A_{jj}. The data lie below the upper bound as expected. Although the above result is derived for a bed of uniform spheres, the same result is obtained when the medium

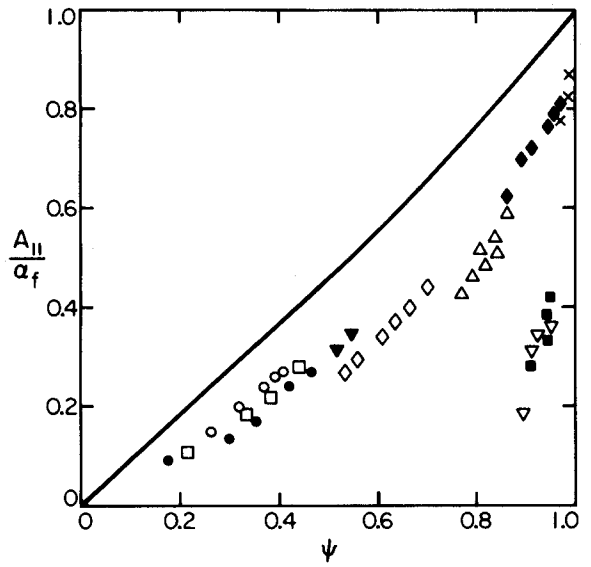

Figure 7. Theoretical upper bound for random effective diffusivity and experimental data.

contains overlapping spheres of several sizes since the medium is then a superposition of many independent media with uniform spheres of different radii.

NOTATION

$\underline{A}$ = diffusivity/conductivity tensor
$\underline{I}$ = identity matrix
n = average density of sphere (circle) centers in random media
$\underline{n}$ = unit normal pointing away from the domain of interest
O = order
x = macroscopic coordinates
y = microscopic coordinates
Y = unit cell
Y_f = fluid region in unit cell
Y_s = solid region in unit cell
t = time
u = concentration or temperature

Greek Letters

α = local diffusivity/conductivity
β = α_s/α_f
∂ = boundary of
ϵ = ratio of microscopic length scale to macroscopic one
Γ = solid-fluid interphase
ψ = porosity (void volume fraction), trial function
Ω = infinite domain for random media

Subscripts/Superscripts

f = fluid phase
s = solid phase
r = random media

LITERATURE CITED

Aris, R., "On the Dispersion of a Solute in a Fluid Flowing Through a Tube," *Proc.* R. Soc. Lond., **A235,** 67 (1956).

Batchelor, G. K., "Sedimentation in a Dilute Dispersion of Spheres," *J. Fluid Mech.*, **52,** 245 (1972).

Bensoussan, A., J.-L. Lions, and G. Papanicolaou, *Asymptotic Analysis For Periodic Structures*, North Holland Amsterdam (1978).

Brenner, H., "Dispersion Resulting From Flow Through Spatially Periodic Porous Media," *Phil. Trans.* Roy. Soc. Lond., **297,** 81 (1980).

Chang, H.-C., "Multi-Scale Analysis of Effective Transport In Periodic Heterogeneous Media," *Chem. Eng. Comm.* (In Press).

Finlayson, B. A., *Nonlinear Analysis In Chemical Engineering*, McGraw-Hill, New York (1980).

Jefferey, D. J., "Conduction Through a Random Suspension of Spheres," Proc. Roy. Soc. Lond., **A335,** 355 (1973).

Krischer, O., and K. Kröll, *Die Wissenschaftlichen Grundlagen der Trocknungstochuik*, **1,** Berlin (1956).

Mashovets, V. P., "The Effect of Nonconducting Inclusions Upon The Conductance of an Electrode," *J. App. Chem.* (USSR), **24,** 391 (1951).

McPhedran, R. C., and D. R. McKenzie, "The Conductivity of Lattices of Spheres, I. The Simple Cubic Lattice," *Proc.* R. Soc. Lond., **A359,** 45 (1978).

Meredith, R. E., and C. W. Tobias, "Resistance to Potential Flow Through a Cubical Array of Spheres," *J. Appl. Phys.*, **31,** 1270 (1960).

Nayfeh, A. H., *Perturbation Methods*, John-Wiley, New York (1975).

Perrins, W. T., D. R. McKenzie, and R. C. McPhedran, "Transport Properties of Regular Arrays of Cylinders," *Proc.* R. Soc. Lond., **A369,** 207 (1979).

Raleigh, R. S., "On the Influence of Obstacles Arranged in Rectangular Order Upon the Properties of the Medium," *Phil. Mag.*, **34,** 481 (1928).

Runge, I., "On the Electrical Conductivity of Metallic Aggregates," *Z. Tech. Physik*, **6,** 61 (1925).

Ryan, D., R. G. Carbonell, and S. Whitaker, "Effective Diffusivities for Catalyst Pellets Under Reactive Conditions," *Chem. Eng. Sci.*, **35,** 10 (1980).

Sangani, A. S., and A. Acrivos, "On the Effective Thermal Conductivity and Permeability of Regular Arrays of Spheres," *Lecture Notes in Physics*, **154,** 216, Springer-Verlag, Berlin (1982).

Scatterfield, C., and T. K. Sherwood, *The Role of Diffusion in Catalysis*, Addison-Wesley (1963).

Slattery, J. C., *Momentum, Energy and Mass Transfer in Continua*, McGraw-Hill, New York (1972).

Strieder, W., and R. Aris, *Variational Methods Applied to Problems of Diffusion and Reaction*, Springer-Verlag, New York (1973).

Tal, R., and W. A. Sirignano, "Cylinderical Cell Model for the Hydrodynamics of Particle Assemblages at Intermediate Reynolds Number," *AIChE J.*, **28,** 233 (1982).

Veverka, V., "Theorem For the Local Volume Average of a Gradient Revised," *Chem. Eng. Sci.*, **36,** 833 (1981).

Whitaker, S., "The Transport Equations for Multi-phase Systems," *Chem. Eng. Sci.*, **28,** 139 (1973).

Zuzvoski, M., and H. Brenner, "Effective Conductivities of Composite Materials Composed of Cubic Arrangements of Spherical Particles Embedded in an Isotropic Matrix," *J. App. Math. Phys.* (ZAMP), **28,** 979 (1977).

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