Diffusion and Dispersion in Porous Media

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The dispersion equation for a single, nonreacting, nonadsorbing species is derived for incompressible, laminar flow in anisotropic porous media. Direct integration of the appropriate differential equations gives rise to a dispersion vector ψ_i and a tortuosity vector τ_i, both of which must be evaluated experimentally. For the dispersion vector, this is conveniently done by representing ψ_i in terms of the velocity and gradients of the velocity and concentration. The experimental determination of τ_i is not straightforward except for the case of pure diffusion. The analysis yields a result which contains all the features of previously presented dispersion equations without making any assumptions as to the nature of the flow, that is, bypassing, cell mixing, etc., except that it be laminar. Attacking the dispersion problem in terms of the differential diffusion equation provides a rational basis for the correlation of experimental data and illustrates the connection between the microscopic and macroscopic equations.

Dispersion in porous media is of interest to chemical engineers who are generally concerned with reacting and adsorbing species, to petroleum engineers who are concerned with the miscible displacement processes that occur in oil recovery, and to civil engineers who are confronted with the problem of salt water encroachment of coastal aquifers. The analysis presented in this paper deals with the simplest case, that is, dispersion of a single, nonreacting, nonadsorbing species in the absence of density or viscosity gradients.

Previous workers (*2, 3, 8, 10, 16*) are in general agreement that the dispersion equation should take the form

$$\frac{\partial c}{\partial t} + v_i \left(\frac{\partial c}{\partial x_i} \right) = \frac{\partial}{\partial x_j} \left(D_{jk} \frac{\partial c}{\partial x_k} \right) \tag{1}$$

where the right-hand side of Equation (1) represents both convective and diffusive transport. In the absence of diffusional effects the tensor D_{jk} is generally expressed as (*8, 16*)

$$D_{jk} = D'_{jklm}\, v_l\, v_m / v \tag{2}$$

The development of Equations (1) and (2) rests largely on the cell-mixing model first discussed by Kramers and Alberda (*12*), extended by Bear (*3*) to two-dimensional flows, and generalized by de Josselin de Jong and Bossen (*8*).

While the cell-mixing model is undoubtedly connected to reality, and is especially valuable in treating turbulent flows, it has the disadvantage of being unnecessarily restrictive when laminar flows are being considered. The purpose of this paper is to attack the dispersion process directly in terms of the diffusion equation, thus providing a more flexible means of interpreting the experimental data that is always required in problems of this type.

THEORY

Since the direct solution of the diffusion equation is prohibited by the complex geometry of the porous media, we must develop equations describing average concentrations and velocities. Thus we start with the microscopic equations which hold at a point in space and develop the appropriate macroscopic equations which hold for some volume V in space. There are two ways in which one might form these macroscopic equations. The microscopic equations could be averaged over the *fluid* region, thus yielding a macroscopic equation valid over a discontinuous space, or the microscopic equations could be averaged over the *entire* region, thus providing a macroscopic equation valid over a continuous space. This latter approach has obvious advantages when the time comes to integrate the equations and compare them with experiment; however, it does require that we work with functions having jump discontinuities (*23*, p. 76; *24*, p. 492). The formulas required for treating such functions are presented in Appendix C.[†] There it is shown that the average of the derivative is equal to the derivative of the average plus $1/V$ times the interfacial area integral of the jump of the function *at the fluid-solid interface.* Thus for some vector $\mathbf{g}$

$$\overline{\nabla \cdot \mathbf{g}} = \nabla \cdot \overline{\mathbf{g}} + \frac{1}{V} \int_{A_{(i)}} [\mathbf{g}]\, \mathbf{n}\, dA \tag{C23}$$

Here $[\mathbf{g}]$ represents the value of $\mathbf{g}$ in the fluid region minus the value of $\mathbf{g}$ in the solid region, both being limiting values of $\mathbf{g}$ as the interface is approached. The unit normal $\mathbf{n}$ is taken as pointing into the solid region.

The structure of a porous media may be described in terms of the void volume distribution function $\alpha(x_i)$ where

$$\alpha(x_i) = \begin{cases} 1 & \text{if } x_i \text{ lies in the void or fluid region} \\ 0 & \text{if } x_i \text{ lies in the solid region} \end{cases} \tag{3}$$

We specify that $\alpha(x_i)$ remains constant at either zero or one as x_i approaches the fluid-solid interface; however, the value of $\alpha(x_i)$ at the interface is not defined. Under this condition we say that $\alpha(x_i)$ has a *jump discontinuity* at the fluid-solid interface.

With each point in space we associate a volume V (for example, a sphere of radius r_o) for which we wish to specify average values. The porosity Φ is then given by

$$\Phi = \frac{1}{V} \int_V \alpha(x_i)\; dV \tag{4}$$

where V must be large enough so that Φ is independent of V, although it may still be a function of x_i if the porous media is nonhomogeneous. This requires that significant variations in the structure of the porous media occur over distances which are large compared with $V^{1/3}$. If we designate $\mathcal{V}$ as the volume of the fluid contained in V, we may express the porosity as

$$\Phi = \mathcal{V}/V \tag{5}$$

For incompressible flows the total continuity equation is[‡]

[†] Deposited as document 9234 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

[‡] The developments presented in this section will be restricted to rectangular coordinates. The appropriate equations for curvilinear coordinates will be presented in Appendix *B*.

$$\left(\frac{\partial v_i}{\partial x_i}\right) = 0 \tag{6}$$

Forming the average over the volume V and using Equation (C23) one gets

$$\frac{1}{V}\int_V \left(\frac{\partial v_i}{\partial x_i}\right) dV = \frac{\partial}{\partial x_i}\left[\frac{1}{V}\int_V v_i dV\right] = \frac{\partial \bar{v}_i}{\partial x_i} = 0 \tag{7}$$

since there are no jump discontinuities in the velocity v_i. In a two-component, incompressible flow system obeying Fick's law, the diffusion equation may be written as (*4*, p. 557)

$$\frac{\partial c}{\partial t} + \frac{\partial}{\partial x_i}(v_i c) = \frac{\partial}{\partial x_j}\left(\mathcal{D}\frac{\partial c}{\partial x_j}\right) \tag{8}$$

where $\mathcal{D}$ is the molecular diffusivity and c represents the molar density of the diffusing species. In analyzing Equation (8) we will assume that it is valid everywhere, but that c is zero in the solid region.† We also assume that c and derivatives of c are continuous everywhere in the fluid region and approach definite values as the fluid-solid interface is approached.

Forming the integral over V gives

$$\frac{1}{V}\int_V \left(\frac{\partial c}{\partial t}\right) dV + \frac{1}{V}\int_V \frac{\partial}{\partial x_i}(v_i c) dV = \frac{1}{V}\int_V \frac{\partial}{\partial x_j}\left(\mathcal{D}\frac{\partial c}{\partial x_j}\right) dV \tag{9}$$

We first interchange differentiation and integration for the first term in Equation (8) to obtain

$$\frac{1}{V}\int_V \left(\frac{\partial c}{\partial t}\right) dV = \frac{\partial}{\partial t}\left[\frac{1}{V}\int_V c dV\right] = \frac{\partial \bar{c}}{\partial t} \tag{10}$$

Since $v_i c$ is a continuous function suffering no jumps at the fluid-solid interface, Equation (C23) is readily applied to yield

$$\frac{1}{V}\int_V \frac{\partial}{\partial x_i}(v_i c) dV = \frac{\partial}{\partial x_i}(\overline{v_i c}) \tag{11}$$

Application of Equation (C23) to the right-hand side of Equation (9) yields

$$\frac{1}{V}\int_V \frac{\partial}{\partial x_j}\left(\mathcal{D}\frac{\partial c}{\partial x_j}\right) dV = \frac{\partial}{\partial x_j}\left(\overline{\mathcal{D}\frac{\partial c}{\partial x_j}}\right) + \frac{1}{V}\int_{A_{(i)}}\left[\mathcal{D}\frac{\partial c}{\partial x_j}\right] n_j dA \tag{12}$$

Here the area integral of $\left[\mathcal{D}\frac{\partial c}{\partial x_j}\right] n_j$ represents the net rate at which material is adsorbed on the solid-fluid interface. A detail treatment of this term would require postulating a rate expression for mass transport between the fluid and the solid in addition to formulating an overall material balance for the adsorbed phase. For the present we restrict the analysis to a nonadsorbing species and write

$$\left[\mathcal{D}\frac{\partial c}{\partial x_j}\right] n_j = 0 \tag{13}$$

Substitution of Equations (10) to (13) into Equation (9) yields

$$\frac{\partial \bar{c}}{\partial t} + \frac{\partial}{\partial x_i}(\overline{v_i c}) = \frac{\partial}{\partial x_j}\left(\overline{\mathcal{D}\frac{\partial c}{\partial x_j}}\right) \tag{14}$$

It is well established that the diffusivity depends on the concentration for liquid systems; however, we may expect that variations of c in the volume V are not large and the diffusivity may be removed from the averaging process in Equation (14), yielding

$$\frac{\partial \bar{c}}{\partial t} + \frac{\partial}{\partial x_i}(\overline{v_i c}) = \frac{\partial}{\partial x_j}\left[\mathcal{D}\left(\overline{\frac{\partial c}{\partial x_j}}\right)\right] \tag{15}$$

While assuming $\mathcal{D}$ constant within the volume V, Equation (15) still allows for variation of $\mathcal{D}$ with x_j.

Application of Equation (C23) to the right-hand side of Equation (15) yields

$$\frac{\partial \bar{c}}{\partial t} + \frac{\partial}{\partial x_i}(\overline{v_i c}) = \frac{\partial}{\partial x_j}\left[\mathcal{D}\left(\frac{\partial \bar{c}}{\partial x_j} + \frac{1}{V}\int_{A_{(i)}} [c]\, n_j dA\right)\right] \tag{16}$$

Two distinct problems arise from this equation. One is the convective transport term on the left-hand side, and the other is the area integral of the jump in c on the right-hand side. The convective transport term can be treated in a fairly straightforward manner, and the analysis of this term is the main objective of this paper. The area integral of the jump in c represents the reduction in diffusional transport owing to the tortuosity of the porous media (*19*, p. 45). This term has not appeared in any previous discussion of diffusion in porous media, although the effect is well known and often accounted for by models of porous media (*20* to *22*).

That this term is associated with the tortuosity can easily be demonstrated by some qualitative arguments. We consider as an example pure diffusion through a porous media made up of an array of straight capillary tubes. This configuration is illustrated in Figure 1. The volume V used to obtain the averages would be the thin slab indicated, and the concentrations in the bulk fluid at $x = 0$ and $x = L$ are taken as c_{fo} and c_{fl} respectively. In utilizing Equation (16) we must be careful to remember that $\bar{c}$ is the average concentration over the total volume V and is therefore necessarily different from the average concentration over the fluid volume $\mathcal{V}$. This is defined as

$$\bar{c}_f = \frac{1}{\mathcal{V}}\int_{\mathcal{V}} c dV \tag{17}$$

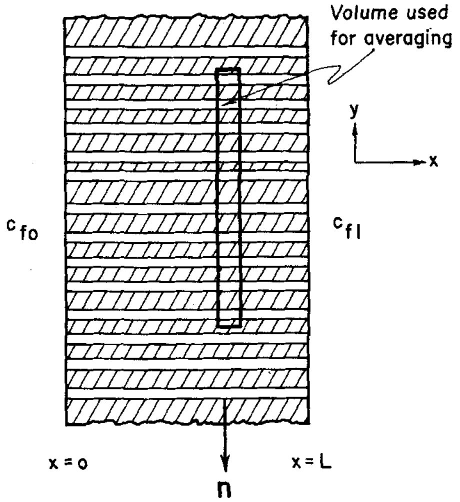

Fig. 1. Diffusion through an array of straight capillary tubes.

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† Alternatively we may multiply Equation (8) by $\alpha(x_i)$ and take the result to be valid for all x_i.

and the two concentrations are related by

$$\bar{c} = \Phi\, \bar{c}_f \tag{18}$$

Restricting Equation (16) to steady, one-dimensional diffusion, we may integrate once to obtain the diffusion flux $\bar{J}_x$:

$$\bar{J}_x = -\mathcal{D}\left(\frac{d\bar{c}}{dx} + \frac{\mathbf{i}}{V}\cdot\int_{A_{(i)}} [c]\,\mathbf{n}\,dA\right) \tag{19}$$

When one notes that the unit vectors $\mathbf{i}$ and $\mathbf{n}$ are always orthogonal, the second term on the right-hand side of Equation (19) is identically zero. Incorporating Equation (18) into this result, integrating once more and applying the appropriate boundary conditions, one obtains

$$\bar{J}_x = \mathcal{D}\left(\frac{\Phi \Delta c_f}{L}\right) \tag{20}$$

where $\Delta c_f = c_{fo} - c_{fl}$. This is a trivial example and is presented only to show that the derived equation reduces to the expected result for this simple case.

We now consider a porous media made up of an array of twisted capillary tubes such as that illustrated in Figure 2. Once again the flux is given by Equation (19); however, in this case $\mathbf{i}\cdot\mathbf{n}$ is not zero and our result reduces to

$$\bar{J}_x = -\mathcal{D}\left(\frac{\Phi\Delta c_f}{L} + \frac{1}{V}\int_{A_{(i)}} [c]\, n_x dA\right) \tag{21}$$

Here the second term, which will be strongly dependent on the geometry of the porous media, is nonzero and is the proper term for representing the decrease in the diffusion rate owing to the irregular geometry of the porous media.

The general analysis of this term would be simplified if a dimensionless area were used to yield

$$\frac{\partial \bar{c}}{\partial t} + \frac{\partial}{\partial x_i}(\overline{v_i c}) = \frac{\partial}{\partial x_j}\left[\mathcal{D}\left(\frac{\partial \bar{c}}{\partial x_j} + \frac{A_{(i)}}{V}\int_{\mathcal{A}_{(i)}} [c]\, n_j d\mathcal{A}\right)\right] \tag{22}$$

Here the differential area $d\mathcal{A}$ is equal to $dA/A_{(i)}$, and $\mathcal{A}_{(i)}$ is dimensionless with a value of unity. We define the tortuosity vector τ_j as

$$\tau_j = \int_{\mathcal{A}_{(i)}} [c]\, n_j d\mathcal{A} \tag{23}$$

and write Equation (22) as

$$\frac{\partial \bar{c}}{\partial t} + \frac{\partial}{\partial x_i}(\overline{v_i c}) = \frac{\partial}{\partial x_j}\left[\mathcal{D}\left(\frac{\partial \bar{c}}{\partial x_j} + \mathcal{R}\tau_j\right)\right] \tag{24}$$

Here the ratio of area to volume has been replaced by $\mathcal{R}$.

This form of the macroscopic mass transport equation represents a suitable starting point for the experimental study of diffusion in porous media. Experiments could be used to determine the value of τ_j and its dependence on the parameters governing the mass transfer. Note that the first term on the right-hand side depends on the geometry only through the porosity Φ, which enters this result via Equation (18). However, the second term is intimately involved in the geometry via the ratio of area to volume $\mathcal{R}$ and the tortuosity vector τ_j. Experimental determination of τ_j would appear to be quite difficult except for the case of pure diffusion. This condition is examined in Appendix A.

Our next step in the analysis requires that the convective transport term be arranged in a form amenable to experimental analysis. Expressing the point values of v_i and c as

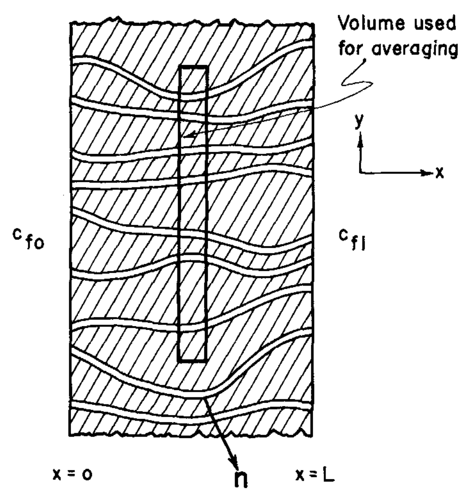

Fig. 2. Diffusion through an array of twisted capillary tubes.

$$v_i = \bar{v}_i + \tilde{v}_i \tag{25}$$

$$c = \bar{c} + \tilde{c} \tag{26}$$

where

$$\bar{\tilde{v}}_i = \bar{\tilde{c}} = 0 \tag{27}$$

allows us to express Equation (24) in terms of the dispersion vector $\bar{\psi}_i$

$$\frac{\partial \bar{c}}{\partial t} + \bar{v}_i\left(\frac{\partial \bar{c}}{\partial x_i}\right) + \frac{\partial \bar{\psi}_i}{\partial x_i} = \frac{\partial}{\partial x_j}\left[\mathcal{D}\left(\frac{\partial \bar{c}}{\partial x_j} + \mathcal{R}\tau_j\right)\right] \tag{28}$$

where

$$\bar{\psi}_i = \overline{\tilde{v}_i \tilde{c}}$$

The characteristics of $\bar{\psi}_i$ must be evaluated experimentally, just as the permeability tensor in Darcy's law must be determined by experiment. This is in effect a curve-fitting process, and by one means or another one could always fit the solution of Equation (28) to experimental data in order to determine $\bar{\psi}_i$. This would be of little help in the general analysis of dispersion problems, and what is needed is a useful functional relationship for the dispersion vector. In exploring this problem it is best to work with the dimensionless form of the equations. Denoting the characteristic length, concentration, and velocity by L, c_o, and u_o, we can write Equation (28) as

$$\frac{\partial \bar{C}}{\partial \theta} + \bar{U}_i\left(\frac{\partial \bar{C}}{\partial X_i}\right) + \left(\frac{\partial \bar{\Psi}_i}{\partial X_i}\right) = \frac{\partial}{\partial X_j}\left[\frac{1}{N_{Pe}}\left(\frac{\partial \bar{C}}{\partial X_j} + R\mathrm{T}_j\right)\right] \tag{29}$$

An examination of the differential equations for $\tilde{C}$ and $\tilde{U}_i$ will provide some useful information regarding the functional dependence of $\bar{\Psi}_i$. Substitution of Equations (25) and (26) into Equation (8) and putting the result in dimensionless form yield

$$\frac{\partial \bar{C}}{\partial \theta} + \frac{\partial \tilde{C}}{\partial \theta} + \bar{U}_i\frac{\partial \bar{C}}{\partial X_i} + \bar{U}_i\frac{\partial \tilde{C}}{\partial X_i} + \tilde{U}_i\frac{\partial \bar{C}}{\partial X_i} + \tilde{U}_i\frac{\partial \tilde{C}}{\partial X_i} = \frac{\partial}{\partial X_j}\left[\frac{1}{N_{Pe}}\left(\frac{\partial \bar{C}}{\partial X_j} + \frac{\partial \tilde{C}}{\partial X_j}\right)\right] \tag{30}$$

In obtaining Equation (30) we have made use of

$$\frac{\partial \overline{U}_i}{\partial X_i} = \frac{\partial \widetilde{U}_i}{\partial X_i} = 0 \tag{31}$$

Subtracting Equation (29) from Equation (30) yields the differential equation for $\widetilde{C}$:

$$\frac{\partial \widetilde{C}}{\partial \theta} + \overline{U}_i \frac{\partial \widetilde{C}}{\partial X_i} + \widetilde{U}_i \frac{\partial \overline{C}}{\partial X_i} + \widetilde{U}_i \frac{\partial \widetilde{C}}{\partial X_i} - \frac{\partial}{\partial X_i} (\overline{\widetilde{C}\widetilde{U}_i})$$

$$= \frac{\partial}{\partial X_j} \left[\frac{1}{N_{Pe}} \left(\frac{\partial \widetilde{C}}{\partial X_j} - R\Upsilon_j \right) \right] \tag{32}$$

On the basis of Equation (32) the functional dependence of $\widetilde{C}$ may be expressed as

$$\widetilde{C} = \widetilde{C} \left(\theta, X_i, \overline{U}_i, \widetilde{U}_i, \frac{\partial \overline{C}}{\partial X_i}, N_{Pe}, R\Upsilon_j \right) \tag{33}$$

in addition to any parameters appearing in the boundary conditions. This means that $\widetilde{C}$ would depend on the structure of the porous media via the boundary conditions on $\widetilde{C}$ in addition to the dependence on R and Υ_j. The functional dependence of $\widetilde{C}$ can be simplified by writing

$$\widetilde{C} = \widetilde{C} \left(\theta, X_i, \overline{U}_i, \widetilde{U}_j, \frac{\partial \overline{C}}{\partial X_i}, N_{Pe} \right) \tag{34}$$

where it is understood that $\widetilde{C}$ depends on the geometry.

Further information can be obtained by examining the equations of motion. In dimensionless form we have

$$\frac{\partial U_i}{\partial \theta} + \frac{\partial}{\partial X_j} (U_i U_j) = - \frac{\partial P}{\partial X_i} + \frac{1}{N_{Re}} \left(\frac{\partial^2 U_i}{\partial X_j \partial X_j} \right) \tag{35}$$

The dimensionless pressure P is defined as

$$P = \frac{p}{\rho u_o^2} + \frac{\phi}{u_o^2} \tag{36}$$

where ϕ is the gravitational potential function. In forming the average of Equation (35) we must first multiply it by $\alpha(x_i)$, since this equation is valid only in the fluid region, and then perform the integration. This yields

$$\frac{\partial \overline{U}_i}{\partial \theta} + \frac{\partial}{\partial X_j} (\overline{U_i U_j}) = - \frac{\partial \overline{P}}{\partial X_i} - \frac{1}{V} \int_{A(i)} [P] n_i dA$$

$$+ \frac{1}{N_{Re}} \left(\frac{\partial^2 \overline{U}_i}{\partial X_j \partial X_j} \right) + \frac{1}{V N_{Re}} \int_{A(i)} \left[\frac{\partial U_i}{\partial X_j} \right] n_j dA \tag{37}$$

Here the jump conditions simply represent the value of the function at the fluid-solid interface, and we may write

$$- \int_{A(i)} [P] n_i dA + \frac{1}{N_{Re}} \int_{A(i)} \left[\frac{\partial U_i}{\partial X_j} \right] n_j dA$$

$$= \int_{A(i)} \left\{ - P n_i + \frac{1}{N_{Re}} \left(\frac{\partial U_i}{\partial X_j} \right) n_j \right\} dA \tag{38}$$

$$= \begin{array}{c} \text{dimensionless force exerted} \\ \text{by the solid on the fluid} \end{array}$$

This result is exactly what one expects from a macroscopic momentum balance, the surface forces being separated into forces acting on the entrances and exits and forces acting on the solid surfaces (*4*, p. 211).

Substituting $U_i = \overline{U}_i + \widetilde{U}_i$ and $P = \overline{P} + \widetilde{P}$ into Equation (35) one gets

$$\frac{\partial \widetilde{U}_i}{\partial \theta} + \frac{\partial \overline{U}_i}{\partial \theta} + \overline{U}_j \frac{\partial \overline{U}_i}{\partial X_j} + \overline{U}_j \frac{\partial \widetilde{U}_i}{\partial X_j} + \widetilde{U}_j \frac{\partial \overline{U}_i}{\partial X_j} + \widetilde{U}_j \frac{\partial \widetilde{U}_i}{\partial X_j}$$

$$= - \frac{\partial \overline{P}}{\partial X_i} - \frac{\partial \widetilde{P}}{\partial X_i} + \frac{1}{N_{Re}} \left(\frac{\partial^2 \overline{U}_i}{\partial X_j \partial X_j} \right) + \frac{1}{N_{Re}} \left(\frac{\partial^2 \widetilde{U}_i}{\partial X_j \partial X_j} \right) \tag{39}$$

Subtracting Equation (37) from this result gives the differential equation for $\widetilde{U}_i$:

$$\frac{\partial \widetilde{U}_i}{\partial \theta} + \overline{U}_j \left(\frac{\partial \widetilde{U}_i}{\partial X_j} \right) + \widetilde{U}_j \left(\frac{\partial \overline{U}_i}{\partial X_j} \right) + \widetilde{U}_j \left(\frac{\partial \widetilde{U}_i}{\partial X_j} \right)$$

$$+ \frac{\partial}{\partial X_j} (\widetilde{U}_i \widetilde{U}_j) = - \frac{\partial \widetilde{P}}{\partial X_i} + \frac{1}{N_{Re}} \left(\frac{\partial^2 \widetilde{U}_i}{\partial X_j \partial X_j} \right)$$

$$+ \frac{1}{V} \int_{A(i)} \left\{ - P n_i + \frac{1}{N_{Re}} \left(\frac{\partial U_i}{\partial X_j} \right) n_j \right\} dA \tag{40}$$

On the basis of Equation (40) the functional dependence of $\widetilde{U}_i$ is represented by

$$\widetilde{U}_i = \widetilde{U}_i \, (\theta, X_i, N_{Re}, \overline{U}_j, \partial \overline{U}_i / \partial X_j) \tag{41}$$

plus the parameters appearing in the boundary conditions.

On the basis of Equations (34) and (41), the functional dependence of $\overline{\Psi}_i$ takes the form

$$\overline{\Psi}_i = \overline{\Psi}_i \, (\theta, X_i, \overline{U}_i, \partial \overline{U}_i / \partial X_j, \partial \overline{C} / \partial X_i, N_{Re}, N_{Pe}) \tag{42}$$

Further comments on the functional dependence of $\overline{\Psi}_i$ can be made if we examine the boundary conditions for $\widetilde{U}_i$ and $\widetilde{C}$. Considering $\widetilde{U}_i$ first, we express the boundary conditions as

$$\widetilde{U}_i = - \overline{U}_i, \; S(X_i) = 0 \tag{43}$$

$$\widetilde{U}_1 = \widetilde{U}_i(X_j), \; \theta = 0 \tag{44}$$

The first boundary condition states that the fluid velocity U_i is zero at the fluid-solid interface, since $S(X_i)$ is a function locating this interface. The second boundary condition specifies the distribution of $\widetilde{U}_i$ at some initial time. In all likelihood this latter boundary condition would take the special form $\widetilde{U}_i = 0$ at $\theta = 0$. If the volume average flow is steady after an initial acceleration, the question may be asked: "How long will it take before U_i reaches a steady value?" No precise answer can be given, but we may draw upon the solution of transient flow in a tube (*4*, p. 129) to estimate this time. In a tube, essentially steady flow occurs for times greater than t^* where

$$t^* \approx r_o^2 / \nu \tag{45}$$

Here r_o is the tube radius and ν is the kinematic viscosity. For practical purposes a lower limit on ν is 10^{-2} sq.cm./sec., and an upper limit on r_o is 10^{-1} cm. This gives a transient time t^* of 1 sec. and indicates that we may in general neglect the time dependence of $\widetilde{U}_i$. Note that if the volume average flow is unsteady, $\widetilde{U}_i$ will not depend on time explicitly but will depend on time through $\overline{U}_i$, and Equation (41) may be written as

$$\widetilde{U}_i = \widetilde{U}_i(X_i, \overline{U}_j, \partial\overline{U}_j/\partial X_i, N_{Re}) \tag{46}$$

If the porous media under consideration is homogeneous, there will be no long-range X_i dependence in the function $S(X_i)$. Under these conditions we may consider U_i to depend explicitly on X_i only at short range, while long-range X_i dependence will occur only through the functions $\overline{U}_i$ and $\partial\overline{U}_i/\partial X_j$.

Directing our attention to $\widetilde{C}$, we write the boundary conditions as

$$n_i \frac{\partial\widetilde{C}}{\partial X_i} = - n_i \frac{\partial\overline{C}}{\partial X_i}, \; S(X_i) = 0 \tag{47}$$

$$\widetilde{C} = \widetilde{C}(X_i), \; \theta = 0 \tag{48}$$

The transient time for the diffusional process will be on the order of

$$t^* = r_o^2/\mathcal{D} \tag{49}$$

which for normal liquids ($\mathcal{D} = 10^{-5}$ sq.cm./sec.) leads to transient times on the order of 10^3 sec. For geological phenomena having characteristic times on the order of hours or days, 10^3 sec. is quite a short time, and the explicit dependence of $\widetilde{C}$ on θ may be neglected. At the other extreme, dispersion processes in fixed-bed reactors (*5*) and chromatographic columns (*6*) have characteristic times on the order of seconds. Under these conditions it may be reasonable to neglect the explicit θ dependence of $\widetilde{C}$; however, it seems best to retain the time dependence until further analysis or experiments clarify the time dependence of $\widetilde{C}$.

The boundary condition expressed by Equation (47) simply indicates that there is no mass flux across the fluid-solid interface. Once again this boundary condition will yield no explicit long-range X_i dependence.

In light of the boundary conditions for $\widetilde{U}_i$ and $\widetilde{C}$ we express the functional dependence of $\overline{\Psi}_i$ as

$$\overline{\Psi}_i = \overline{\Psi}_i\;(\theta, \overline{U}_i, \partial\overline{U}_i/\partial X_j, \partial\overline{C}/\partial X_i, N_{Re}, N_{Pe}) \tag{50}$$

where the explicit X_i dependence has been removed by averaging.[†] We can further expect that $\overline{\Psi}_i$ will vary only slowly with time.

We now wish to make the following definite statements regarding the functional dependence of $\overline{\Psi}_i$.

1. $$\overline{\Psi}_i = 0 \text{ when } \overline{U}_i = 0 \tag{51}$$

This statement is not necessarily true [an abruptly stopped flow where inertial effects are important would not conform to Equation (51)], but it seems to be a reasonable assumption for most practical cases.

2. The effect of $\partial\overline{U}_i/\partial X_j$ will be neglected. Since most dispersion processes deal with uniform flows, this term is usually zero, and while the analysis definitely indicates that $\overline{\Psi}_i$ depends on $\partial\overline{U}_i/\partial X_j$ (especially at high Reynolds numbers), no experiments have been performed with the intention of investigating this effect.

3. $$\overline{\Psi}_i = 0 \text{ when } \partial\overline{C}/\partial X_i = 0 \tag{52}$$

From an intuitive point of view this assumption seems quite plausible; however, there are no theoretical arguments to support it. If the gradient of the concentration were zero *everywhere*, then $\overline{C}$ would be a constant and $\overline{\Psi}_i$ would be zero. But Equation (52) is assumed to hold at a point, and at that point Equation (29) reduces to

$$\frac{\partial\overline{C}}{\partial\theta} + \left(\frac{\partial\overline{\Psi}_i}{\partial X_i}\right) = \frac{\partial}{\partial X_j}\left[\frac{1}{N_{Pe}}\left(\frac{\partial\overline{C}}{\partial X_j} + R\tau_j\right)\right] \tag{53}$$

which certainly does not require that $\overline{\Psi}_i$ be zero. Nevertheless this assumption will be incorporated into the analysis, although it may easily be removed if future theoretical or experimental studies indicate that it is not satisfactory.

On the basis of assumptions 1, 2, and 3, the functional dependence of $\overline{\Psi}_i$ is given by

$$\overline{\Psi}_i = \overline{\Psi}_i\;(\theta, U_j, \partial\overline{C}/\partial X_j, N_{Re}, N_{Pe}) \tag{54}$$

where it is understood that $\overline{\Psi}_i$ depends on the structure of the porous media. The functional dependence given by Equation (54) is subject to the restrictions

$$\overline{\Psi}_i = 0, \quad \overline{U}_j = 0 \tag{55}$$

and

$$\overline{\Psi}_i = 0, \quad \partial\overline{C}/\partial X_j = 0 \tag{56}$$

Expanding $\overline{\Psi}_i$ in a Taylor series (*11*, p. 396) about the point $\overline{U}_i = \partial\overline{C}/\partial X_j = 0$, one gets

$$\begin{aligned}\overline{\Psi}_i = {} & \overline{\Psi}_i(0, 0) + \mathcal{A}_{ij}\overline{U}_j + \mathcal{B}_{ij}\left(\frac{\partial\overline{C}}{\partial X_j}\right) \\ & + \mathcal{C}_{ijk}\;\overline{U}_j\overline{U}_k + \mathcal{D}_{ijk}\;\overline{U}_j\left(\frac{\partial\overline{C}}{\partial X_k}\right) \\ & + \mathcal{E}_{ijk}\left(\frac{\partial\overline{C}}{\partial X_j}\right)\left(\frac{\partial\overline{C}}{\partial X_k}\right) + \mathcal{F}_{ijkl}\;\overline{U}_j\overline{U}_k\overline{U}_l \\ & + \mathcal{G}_{ijkl}\;\overline{U}_j\overline{U}_k\left(\frac{\partial\overline{C}}{\partial X_l}\right) + \mathcal{H}_{ijkl}\;\overline{U}_j\left(\frac{\partial\overline{C}}{\partial X_k}\right)\left(\frac{\partial\overline{C}}{\partial X_l}\right) \\ & + \mathcal{I}_{ijkl}\left(\frac{\partial\overline{C}}{\partial X_j}\right)\left(\frac{\partial\overline{C}}{\partial X_k}\right)\left(\frac{\partial\overline{C}}{\partial X_l}\right) + \ldots\end{aligned} \tag{57}$$

where the capital script letters indicate derivatives of $\overline{\Psi}_i$. For instance

$$\mathcal{D}_{ijk} = \left.\frac{\partial^2\overline{\Psi}_i}{\overline{U}_j\,\partial\overline{C}/\partial X_k}\right|_{\overline{U}_j = \partial\overline{C}/\partial X_k = 0} \tag{58}$$

On the basis of Equations (55) and (56) we require that terms involving only $\overline{U}_i$ or $\partial\overline{C}/\partial X_j$ be zero; thus

$$\mathcal{A}_{ij} = \mathcal{B}_{ij} = \mathcal{C}_{ijk} = \mathcal{E}_{ijk} = \mathcal{F}_{ijkl} = \text{, etc., etc.,} = 0 \tag{59}$$

We may now write Equation (57) in a more compact form:

$$\begin{aligned}\overline{\Psi}_i = {} & - \overset{I}{\mathcal{A}}_{ijk}\;\overline{U}_j\left(\frac{\partial\overline{C}}{\partial X_k}\right) - \overset{II}{\mathcal{A}}_{ijkl}\;\overline{U}_j\overline{U}_k\left(\frac{\partial\overline{C}}{\partial X_l}\right) \\ & - \overset{III}{\mathcal{A}}_{ijkl}\;\overline{U}_j\left(\frac{\partial\overline{C}}{\partial X_k}\right)\left(\frac{\partial\overline{C}}{\partial X_l}\right) \\ & - \overset{IV}{\mathcal{A}}_{ijklm}\;\overline{U}_j\overline{U}_k\overline{U}_l\left(\frac{\partial\overline{C}}{\partial X_m}\right) - \ldots .\end{aligned} \tag{60}$$

The minus sign is employed simply to insure that the final equation takes the traditional form. Here it must be remembered that the $\mathcal{A}$ tensors are not functions of X_i but are functions of the Reynolds number, the Peclet number, and the structure of the porous media. In addition we can expect the $\mathcal{A}$ tensors to be weak functions of time, and this time dependence may be quite important

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[†] It is assumed here that the spatial dependence of C is dominated by $S(X_i)$ and not by the spatial dependence of the initial condition.

if the characteristic time of the process is comparable to t^* as defined in Equation (49).

Since the $\mathfrak{R}$ tensors are derivatives of $\overline{\Psi}_i$, and the order of differentiation is of no consequence, these tensors are symmetric in all indices except the first:

$$\mathfrak{R}^{I}_{ijk} = \mathfrak{R}^{I}_{ikj} \tag{61a}$$

$$\mathfrak{R}^{II}_{ijkl} = \mathfrak{R}^{II}_{ijlk} = \mathfrak{R}^{II}_{iljk} = \mathfrak{R}^{II}_{ilkj} = \mathfrak{R}^{II}_{iklj} = \mathfrak{R}^{II}_{ikjl} \tag{61b}$$

Similar expressions may be written describing the symmetry of $\mathfrak{R}^{III}_{ijkl}$, $\mathfrak{R}^{IV}_{ijklm}$, etc. Substituting Equation (61) into Equation (29) and truncating the series after the first three terms one obtains

$$\frac{\partial \overline{C}}{\partial \theta} + \overline{U}_i \frac{\partial \overline{C}}{\partial X_i} = \frac{\partial}{\partial X_j}\left[\frac{1}{N_{Pe}}\left(\frac{\partial \overline{C}}{\partial X_j} + R\Upsilon_j\right)\right] + \frac{\partial}{\partial X_j}\left[\left(\mathfrak{R}^{I}_{jik}\,\overline{U}_i + \mathfrak{R}^{II}_{jilk}\,\overline{U}_i\overline{U}_l + \mathfrak{R}^{III}_{jikl}\,\overline{U}_i\frac{\partial \overline{C}}{\partial X_l}\right)\frac{\partial \overline{C}}{\partial X_k}\right] \tag{62}$$

If Equations (1) and (2) are put in dimensionless form, the result would correspond to Equation (62) without the molecular diffusion term, the tortuosity term, and the $\mathfrak{R}^{I}$ and $\mathfrak{R}^{III}$ tensors. Bear (3) assumed that the mixing in the cell mixing model takes place by molecular diffusion; thus a diffusive transport term does not appear explicitly in his result. The absence of the other terms in Bear's equation may result in part from the restriction to a constant value for the velocity vector $\overline{U}_i$, although this cannot completely explain the difference.

It is convenient to carry out the differentiation on the right-hand side of Equation (62) to obtain

$$\frac{\partial \overline{C}}{\partial \theta} + \left[\overline{U}_i + \mathfrak{R}^{I}_{kji}\left(\frac{\partial \overline{U}_j}{\partial X_i}\right) + 2\mathfrak{R}^{II}_{ljki}\,\overline{U}_j\left(\frac{\partial \overline{U}_k}{\partial X_l}\right) + \mathfrak{R}^{III}_{ljki}\left(\frac{\partial \overline{U}_j}{\partial X_l}\right)\left(\frac{\partial \overline{C}}{\partial X_k}\right)\right]\frac{\partial \overline{C}}{\partial X_i} = \frac{\partial}{\partial X_j}\left[\frac{1}{N_{Pe}}\left(\frac{\partial \overline{C}}{\partial X_j} + R\Upsilon_j\right)\right] + \left[\mathfrak{R}^{I}_{jik}\overline{U}_i + \mathfrak{R}^{II}_{klij}\overline{U}_l\overline{U}_i + 2\mathfrak{R}^{III}_{klij}\overline{U}_l\left(\frac{\partial \overline{C}}{\partial X_i}\right)\right]\frac{\partial^2 \overline{C}}{\partial X_j \partial X_k} \tag{63}$$

One important aspect of Equation (63) is that the convective transport term on the left-hand side always takes the simple form given in Equation (62) when $\overline{U}_i$ is a constant vector. For a pulse-injection experiment, this means that the shape of the concentration profile, or the breakthrough curve, will be altered only by the coefficient of the second-order term on the right-hand side of Equation (63).

Since the tensor $\partial^2 \overline{C}/\partial X_j \partial X_k$ is symmetric, it follows that the $\mathfrak{R}$ tensors are symmetric in the first and last indices:

$$\mathfrak{R}^{I}_{jik} = \mathfrak{R}^{I}_{kij} \tag{64a}$$

$$\mathfrak{R}^{II}_{klij} = \mathfrak{R}^{II}_{jlik} \tag{64b}$$

$$\mathfrak{R}^{III}_{klij} = \mathfrak{R}^{III}_{jlik} \tag{64c}$$

Combined with the previous symmetry condition given by Equations (61) this result indicates that the $\mathfrak{R}$ tensors are completely symmetric. This means that in general $\mathfrak{R}^{I}_{ijk}$ has ten distinct components, and $\mathfrak{R}^{II}_{ijkl}$ and $\mathfrak{R}^{III}_{ijkl}$ have fifteen distinct components. It is important to remember that the average concentration used in this development is the average over the entire volume V. If experiments are being performed where the average concentration *over the fluid volume* is being measured, it may be convenient to work with the concentration $\overline{C}_f$ which is related to $\overline{C}$ by

$$\overline{C} = \Phi\,\overline{C}_f$$

If this expression is substituted into Equation (63) and we take the porous media to be homogeneous, the dispersion equation is altered only to the extent that $\mathfrak{R}^{III}_{ijkl}$ is multiplied by Φ. If the material is nonhomogeneous, Equation (63) becomes quite complex when expressed in terms of $\overline{C}_f$.

ANALYSIS OF EXPERIMENTS: ISOTROPIC POROUS MEDIA

The experimental evaluation of the components at the $\mathfrak{R}$ tensors for an anisotropic porous media appears to be an impossible task at the present time, and further theoretical work is in order. Directing our attention to the simpler case of an isotropic media, we find that the dispersion equation is greatly simplified for the $\mathfrak{R}$ tensors must now be isotropic. There is no symmetric, third-order, isotropic tensor (*1*, p. 34); thus

$$\mathfrak{R}^{I}_{ijk} = 0, \text{ for isotropic media} \tag{65}$$

A fourth-order, symmetric, isotropic tensor has only one distinct component, and $\mathfrak{R}^{II}_{ijkl}$ and $\mathfrak{R}^{III}_{ijkl}$ take the form

$$\mathfrak{R}^{II}_{ijkl} = \mathfrak{R}^{II}\,(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \tag{66}$$

$$\mathfrak{R}^{III}_{ijkl} = \mathfrak{R}^{III}\,(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \tag{67}$$

Substitution of Equations (65), (66), and (67) into Equation (63) yields the dispersion equation for isotropic porous media:

$$\frac{\partial \overline{C}}{\partial \theta} + \left[\overline{U}_i + \left(2\mathfrak{R}^{II}\overline{U}_k + \mathfrak{R}^{III}\frac{\partial \overline{C}}{\partial X_k}\right)\left(\frac{\partial \overline{U}_k}{\partial X_i} + \frac{\partial \overline{U}_i}{\partial X_k}\right)\right]\frac{\partial \overline{C}}{\partial X_i} = \frac{\partial}{\partial X_j}\left[\frac{1}{N_{Pe}}\left(\frac{\partial \overline{C}}{\partial X_j} + R\Upsilon_j\right)\right] + \left[\mathfrak{R}^{II}\,(2\overline{U}_j\overline{U}_k + \delta_{jk}\overline{U}^2) + 2\mathfrak{R}^{III}\left(\overline{U}_k\frac{\partial \overline{C}}{\partial X_j} + \overline{U}_j\frac{\partial \overline{C}}{\partial X_k} + \delta_{jk}\overline{U}_i\frac{\partial \overline{C}}{\partial X_i}\right)\right]\frac{\partial^2 \overline{C}}{\partial X_j \partial X_k} \tag{68}$$

Thus for isotropic media we are confronted with the task of determining the two parameters, $\mathfrak{R}^{II}$ and $\mathfrak{R}^{III}$, as functions of N_{Re}, θ, N_{Pe}, and the structure of the porous media. Establishing the dependence of N_{Re} and N_{Pe} would appear to be a difficult but possible experimental task; however, the structure of the porous media is not a well-defined quantity, and this aspect of the problem does not appear to be simple. If the porous media happens to consist of an ordered array of uniform particles, the structure is easily defined in terms of a few parameters; however, the porous media generally encountered in practice may only be described statistically. Prager (14) has discussed two possible methods of description which have been used previously in the theory of light scattering by suspensions (7) and in the determination of the permeability for Darcy's law (15). Prager notes that neither method gives a complete description of the structure, and the problem invites further experimental and theoretical studies.

The time dependence of $\mathfrak{R}^{II}$ and $\mathfrak{R}^{III}$ also appears to be a difficult effect to study experimentally; however, there are quite a number of dispersion processes for which the characteristic time of the process is both much longer (geological processes) and much shorter (fixed-bed processes) than the transient diffusion time t^*. It seems quite probable that the time dependency of $\mathfrak{R}^{II}$ and $\mathfrak{R}^{III}$ can be neglected for these processes. On the other hand the initial condition $\tilde{C} = \tilde{C}(X_i)$, $\theta = 0$ may well effect the value of $\mathfrak{R}^{II}$ and $\mathfrak{R}^{III}$ for processes having a short characteristic time.

One-Dimensional Flow

If the average velocity vector is a constant, a coordinate system can always be found such that two of the components of $\overline{U}_i$ are zero:

$$\overline{U}_i = (\overline{U}_1, 0, 0) \tag{69}$$

Under this condition Equation (68) reduces to

$$\begin{aligned}\frac{\partial \overline{C}}{\partial \theta} + \overline{U}_1 \left(\frac{\partial \overline{C}}{\partial X_1}\right) &= \frac{\partial}{\partial X_j}\left[\frac{1}{N_{Pe}}\left(\frac{\partial \overline{C}}{\partial X_j} + R\Upsilon_j\right)\right] \\ &+ \left[2\mathfrak{R}^{II}\,\overline{U}_1\overline{U}_1\left(\frac{\partial^2 \overline{C}}{\partial X_1^2}\right) + \mathfrak{R}^{II}\,\overline{U}^2\left(\frac{\partial^2 \overline{C}}{\partial X_j \partial X_j}\right)\right. \\ &+ 4\mathfrak{R}^{II}\,\overline{U}_1\frac{\partial \overline{C}}{\partial X_j}\left(\frac{\partial^2 \overline{C}}{\partial X_1 \partial X_j}\right) \\ &\left. + 2\mathfrak{R}^{III}\,\overline{U}_1\frac{\partial \overline{C}}{\partial X_i}\left(\frac{\partial^2 \overline{C}}{\partial X_j \partial X_j}\right)\right]\end{aligned} \tag{70}$$

If we further restrict the equation to the case where $\overline{C}$ is only a function of X_1, Equation (70) reduces to

$$\begin{aligned}\frac{\partial \overline{C}}{\partial \theta} + \overline{U}_1\left(\frac{\partial \overline{C}}{\partial X_1}\right) &= \frac{\partial}{\partial X_1}\left[\frac{1}{N_{Pe}}\left(\frac{\partial \overline{C}}{\partial X_1} + R\Upsilon_j\right)\right] \\ &+ \left\{3\mathfrak{R}^{II}\,\overline{U}_1^2 + 6\mathfrak{R}^{III}\,\overline{U}_1\frac{\partial \overline{C}}{\partial X_1}\right\}\frac{\partial^2 \overline{C}}{\partial X_1^2}\end{aligned} \tag{71}$$

A pulse input to a system satisfying these restrictions would provide some useful information. The component $\mathfrak{R}^{III}$ could be determined by the skewness of the concentration profile. On the leading edge of the profile $\partial\overline{C}/\partial X_1$ is negative; thus the coefficient of the second-order term is decreased and the profile is steepened. On the trailing edge $\partial\overline{C}/\partial X_1$ is positive, and the slope of the profile would be decreased. Such an effect has been observed by Carberry and Bretton (5) who labeled it a *bed capacitance* effect. Although the curve-fitting process would be a difficult one, in principle one could determine $\mathfrak{R}^{III}$ by the skewness and $\mathfrak{R}^{II}$ by the change in amplitude of the pulse. Variation of the velocity while maintaining N_{Re} and N_{Pe} constant would allow one to determine $\mathfrak{R}^{II}$ and $\mathfrak{R}^{III}$ more accurately. However, if one is to maintain the structure constant during this change, the viscosity must also be varied, and this surely would give rise to a change in N_{Pe}. At best the experimental determination of $\mathfrak{R}^{II}$ and $\mathfrak{R}^{III}$ represents a difficult problem.

CONCLUSIONS

The analysis presented in this paper has led to an extended version of the dispersion equation previously derived on the basis of the cell-mixing model. The result is independent of any assumptions regarding the nature of the flow (such as the degree of mixing in a void cell), except for the restrictions of laminar, incompressible flow of a homogeneous fluid. Furthermore, there were no assumptions made regarding the structure of the porous media. Thus the terms representing dispersion and tortuosity are completely general and provide a sound basis for the interpretation of experimental results or the construction of mathematical models.

Although the development presented here has simplified the treatment of anisotropic porous media by showing that the fourth-order tensor governing dispersion is completely symmetric, this case is presently too complicated for experimental study, and further theoretical work is in order. The result for isotropic porous media leads to an expression containing two undetermined coefficients in addition to the tortuosity vector Υ_i. All of these may be determined by careful experiments, although the task is by no means a simple one.

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NOTATION

$A_{(i)}$ = interfacial area, sq.cm.
c = molar density, g. moles/cc.
c_o = characteristic molar density, g. moles/cc.
C = c/c_o, dimensionless molar density
$\overline{C}$ = $\tilde{c}/c_o$, dimensionless average molar density
$\mathcal{D}$ = molecular diffusivity, sq.cm./sec.
G^i_j = Euclidean shifter, dimensionless
L = characteristic length, cm.
N_{Re} = $\rho u_o L/\mu$, Reynolds number
N_{Pe} = $u_o L/\mathcal{D}$, Peclet number
p = pressure, dyne/sq.cm.
P = $p/\rho u_o^2 + \phi/u_o^2$, dimensionless pressure
$\mathcal{R}$ = $A_{(i)}/V$, cm.
R = $\mathcal{R}/L$, dimensionless
t = time, sec.
t^* = transient time for mass and momentum transport, sec.
v_i = velocity vector, cm./sec.
v = magnitude of velocity vector, cm./sec.
u_o = characteristic velocity, cm./sec.
U_i = v_i/u_o, dimensionless velocity vector
V = characteristic volume for defining averages, cc.
$\mathcal{V}$ = fluid volume contained in V, cc.
x_i = spatial coordinates, cm.
X_i = x_i/L, dimensionless spatial coordinates

Greek Letters

α = void volume distribution function
θ = tu_o/L, dimensionless time
μ = viscosity, (dyne)(sec.)/sq.cm.
ρ = density, g./cc.
Φ = porosity, dimensionless
ϕ = gravitational potential function, sq.cm./sec.^{2}
$[\phi]$ = jump in ϕ in going from the fluid to the solid phase

$\overline{\psi_i}$ = $\overline{\tilde{c}\tilde{v}_i}$, dispersion vector, g.-moles/(sq.cm.)

$\overline{\Psi_i}$ = $\overline{\tilde{C}\tilde{U}_i}$, dimensionless dispersion vector

τ_i = tortuosity vector, g.-moles/sq.cm.

T_i = τ_i/c_o, dimensionless tortuosity vector

Superscripts

— = average value

~ = point value minus average value

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APPENDIX *A*

The functional dependence of the concentration can be represented as

$$c = c\,(t, x_i, v_j, \mathcal{D}) \tag{A1}$$

in addition to the parameters appearing in the boundary conditions. The functional dependence of the tortuosity vector is similarly represented as

$$\tau_j = \int_{\mathcal{A}(i)} [c]\, n_j\, d\mathcal{A} = \tau_j\,(t, x_i, v_j, \mathcal{D}) \tag{A2}$$

If we assume that the spatial dependence can be uniquely represented in terms of the parameter $\partial\bar{c}/\partial x_i$, we may write

$$\tau_j = \tau_j\,(t, \frac{\partial \bar{c}}{\partial x_i}, v_j, \mathcal{D}) \tag{A3}$$

This representation is encouraged by the functional dependence of $\tilde{c}$, and it assumes that the short-range spatial variations of c and n_j are removed in the integration.

Making the intuitive assumption that

$$\tau_j = 0 \text{ when } \frac{\partial \bar{c}}{\partial x_i} = 0 \tag{A4}$$

allows us to expand τ_j in a Taylor series about the point $\partial\bar{c}/\partial x_i = 0$ to obtain

$$\tau_j = \mathcal{B}^{I}_{jk}\left(\frac{\partial \bar{c}}{\partial x_k}\right) + \mathcal{B}^{II}_{jkl}\left(\frac{\partial \bar{c}}{\partial x_k}\right)\left(\frac{\partial \bar{c}}{\partial x_l}\right) + \ldots\ldots \tag{A5}$$

Here the $\mathcal{B}$ tensors are functions of t, v_j, $\mathcal{D}$, and the geometry of the porous media. The assumption represented by Equation (*A*4) is a plausible one since it can be shown that $\tau_j = 0$ when $\bar{c}$ is a constant and the porous media is homogeneous.

If the higher order terms in Equation (*A*5) are neglected, this result can be substituted into Equation (24) to obtain

$$\frac{\partial \bar{c}}{\partial t} + \frac{\partial}{\partial x_i}\overline{(v_i c)} = \frac{\partial}{\partial x_j}\left[\left(\mathcal{D}\delta_{jk} + \mathcal{R}\,\mathcal{B}^{I}_{jk}\right)\frac{\partial \bar{c}}{\partial x_k}\right] \tag{A6}$$

Here it is apparent that $\mathcal{B}^{I}_{jk}$ is a symmetric tensor. If the porous media is isotropic, $\mathcal{B}^{I}_{jk}$ can be written as

$$\mathcal{B}^{I}_{jk} = \mathcal{B}^{I}\,\delta_{jk} \tag{A7}$$

and Equation (*A*6) reduces to

$$\frac{\partial \bar{c}}{\partial t} + \frac{\partial}{\partial x_i}\overline{(v_i c)} = \frac{\partial}{\partial x_j}\left[\left(\mathcal{D} + \mathcal{R}\,\mathcal{B}^{I}\right)\frac{\partial \bar{c}}{\partial x_j}\right] \tag{A8}$$

Thus we see that the effective diffusivity often used to describe mass transfer in porous media is given by

$$\mathcal{D}_{eff} = \mathcal{D} + \mathcal{R}\,\mathcal{B}^{I} \tag{A9}$$

It must be remembered that for the very special case of steady state, pure diffusion ($v_i = 0$) in homogeneous, isotropic porous media, the parameter $\mathcal{B}^{I}$ is function of both the structure of the porous media and the diffusivity $\mathcal{D}$.

APPENDIX *B*

The analysis presented in the body of this paper and Appendix *A* was restricted to rectangular Cartesian coordinates in order to simplify the presentation. Here we wish to express Equation (62) in a form which is valid in all coordinate systems. To do this we must express the partial derivatives as covariant derivatives (*13*, p. 140), and the average velocity vector must be interpreted as

$$\overline{U_i} = \frac{1}{V}\int_V \underset{i}{G^j}\; U_j dV \tag{B-1}$$

where $\underset{i}{G^j}$ is the Euclidean shifter (*9*). In rectangular, Cartesian coordinates

$$\underset{i}{G^j} = \underset{i}{\delta^j} \tag{B2}$$

The derivative of the average velocity must be expressed as

$$\overline{U}_{l,k} = \left(\overline{\overset{i}{G_l}\overset{j}{G_k}U_{i,j}}\right) - \frac{1}{V}\int_{A(i)} \overset{j}{G_k}\overset{i}{G_l}\,[U_i]\,n_j dA \tag{B3}$$

and a generally valid form of Equation (62) is

$$\frac{\partial \overline{C}}{\partial \theta} + \overline{U}^i\overline{C}_{,i} = \left[\frac{1}{N_{Pe}}\left(\overline{C}_{,i} + RT_i\right)\right]^{,i} + \left[\left(\overset{I}{\mathcal{A}}_{ijk}\overline{U}^{i} + \overset{II}{\mathcal{A}}_{ijkl}\overline{U}^{i}\overline{U}^{l} + \overset{III}{\mathcal{A}}_{ijkl}\overline{U}^{i}\overline{C}^{,l}\right)\overline{C}^{,j}\right]^{,k} \tag{B4}$$

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