The Effective Diffusivity of Fibrous Media

A procedure based on averaging the conservation equations in a homogeneous, disordered fibrous medium is used to demonstrate that in the limit of long times, macroscopic versions of Fick's and Fourier's laws may be used to relate the average flux to the average gradient in driving force. The asymptotic behavior in the limit of low volume fraction of the effective diffusivity (or conductivity) in such a medium is determined for all values of the Peclet number, $P = Ua/D_f$, where U is the average velocity through the bed, a is the fiber radius, and D_f is the molecular diffusivity of the solute in the fluid. The convective disturbance caused by the fibers is found to have a large influence on the rate of mass transfer even at moderate Peclet numbers and low volume fraction.

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SCOPE

Considerable attention has been devoted to the problem of determining the effective diffusivity (or conductivity) of two-phase materials in the absence of convection (Maxwell, 1873; Jeffrey, 1973; Batchelor and O'Brien, 1977; Sangani and Acrivos, 1983; to mention only a few). The theoretical understanding of diffusion in composite materials in the presence of convection is more limited, however. Leal (1973) and Nir and Acrivos (1976) studied the effect of convection on the dispersive transport of heat through a suspension of neutrally buoyant spheres in simple shear flow for temperature gradients parallel to the average velocity gradient. Although Nir and Acrivos considered the case of high Peclet number, they did not consider particle interactions and so their results are not applicable for very high Peclet numbers where the particles have a large effect on the rate of heat transfer.

Brenner (1980) developed a general theory for determining the transport properties in spatially periodic porous media, and showed that in the limit of long times the dispersion is diffusive, i.e., the mean square displacement grows linearly with time. Carbonell and Whitaker (1983) presented a volume-averaged approach for calculating the effective diffusivity and carried out specific calculations for a two-dimensional spatially periodic porous medium (Eidsath et al., 1983). While the approach of Eidsath et al. gives reasonable order-of-magnitude agreement with experiment, the predicted dependence of the effective diffusivity on Peclet number at high Peclet number is too strong. Their numerical calculations grow as $P^{1.7}$, while the experimental values grow only roughly as P. (Theoretical considerations of the relationship between Taylor dispersion theory and dispersion in spatially periodic porous media [Brenner, 1980] would suggest a P^2 dependence rather than the numerically reported 1.7 power.) Eidsath et al. point out that this strong Peclet number dependence is due to the ordered nature of the periodic porous medium; a random medium giving the weaker, roughly P, dependence. The experiments of Gunn and Pryce (1969) on random and periodic packed beds of spheres support these two different dispersion dependencies.

We have recently developed a theory (Koch and Brady, 1985) based on ensemble averages for determining the dispersion in packed beds and porous media. We applied that theory to a disordered or random medium and derived the asymptotic behavior in several limiting cases of the full effective diffusivity tensor, relating the average mass flux to the average concentration gradient in a fixed bed of spheres. Our predicted effective diffusivities agree remarkably well with experiment. In this paper the effective diffusivity of a fibrous bed is

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determined in a similar manner. This is a natural extension of our interest in dispersion in porous media and is motivated by three specific considerations:

1. Fibrous materials are often used as filter media and dispersion in such materials could affect their efficiency.

2. The solids volume fraction ϕ in fibrous materials is typically low and may be varied, facilitating a direct comparison of the low ϕ asymptotic results with experiment.

3. A study of fibrous beds allows an examination of the influence of bed anisotropy.

CONCLUSIONS AND SIGNIFICANCE

In this paper we extend the analysis of Koch and Brady (1985) to calculate the asymptotic behavior of the effective diffusivity in a fibrous material at low fiber volume fraction ϕ. The theoretical development required to calculate the effective diffusivity in any dilute, homogeneous, fibrous bed is presented. Specific results are obtained for an isotropic bed and a bed of fibers whose axes are aligned. In the absence of flow the fibers make and $O(\phi D_f)$ contribution to the effective diffusivity due to the difference in the molecular diffusivities of the fibers and the fluid. In the presence of flow a hydrodynamic dispersion arises owing to correlations between the velocity and concentration fluctuations induced by the fibers. The length over which velocity fluctuations become uncorrelated is the Brinkman screening length $k^{1/2}$, which is large in a bed of high permeability k (low ϕ). Thus, in a dilute, highly permeable bed the hydrodynamic dispersion contributions are large and actually grow with decreasing fiber volume fraction. At high Peclet numbers hydrodynamic dispersion becomes purely mechanical in the bulk of the fluid, i.e., this dispersion is independent of molecular diffusion and grows like $D_f P$. A nonmechanical mechanism for dispersion at high Peclet numbers involves the retention of solute in permeable fibers from which it can only escape by molecular diffusion, leading to an $O(\phi D_f P^2)$ contribution to the longitudinal diffusivity. Even if the fibers are impermeable, nonmechanical boundary-layer dispersion arising from the zero velocity at the fiber surfaces makes contributions to the longitudinal diffusivity which grows as $O[(\phi/\ln \phi^{-1})D_f P \ln P]$ or $O\{[(\phi/\ln \phi^{-1})D_f P](\ln P)^2\}$. The results for the effective diffusivity are summarized in tabular form in the final section. The effective diffusivities determined in this paper are valid in the limit of long times, and the characteristic times required to reach the longtime behavior are given in the Discussion section.

Introduction

Transport processes in fixed beds and porous media are subjects of considerable practical importance. Fixed beds are encountered both in engineering practice where packed beds are used as reactors and contacting devices, and in nature in the form of porous rock and soil. Fixed, fibrous materials are common in the form of filters, membranes, and polymer networks. The microscale transfer of heat and mass in each phase (solid and fluid) of these materials may often be described by Fourier's and Ficks' laws, from which, in principle, the material's behavior can be determined. The primary interest, however, is not in the detailed microscopic processes, but rather the macrotransport, i.e., transfer on a larger, macroscale. In disordered materials the complexity of the interphase boundaries make deterministic modeling of the macrotransport processes in these two-phase systems difficult.

As an alternative, these porous media can be described in terms of velocity, concentration, and temperature fields averaged over a volume that is large compared to a size characteristic of the microstructure. Macroscopic conservation equations for these averaged fields are obtained by averaging the conservation equations for the detailed, microscopic fields. These macroscopic conservation laws need not, however, take the same form as the single-phase conservation laws. For example, although the Stokes equations of motion apply in the fluid phase of a porous medium, the averaged equations of motion are Brinkman's equations, which contain a body force resulting from the drag exerted on the fixed solid (Hinch, 1977). In a previous paper (Koch and Brady, 1985) we showed that in the limit of long times the averaged equation of mass conservation in a fixed bed of spheres does take on a form similar to that given by Fick's law, but with an effective diffusivity that is a tensor, indicating that the ratio of average mass flux to the average concentration gradient depends on the direction in which the gradient is imposed. We also determined the asymptotic behavior in the limit of low solids volume fraction ϕ and/or high Peclet number P of the effective diffusivity, obtaining good agreement with experiment. In this paper we perform a similar analysis for a fixed, fibrous bed, the two-dimensional analog of the case studied previously. Because of the close analogy between the transport processes in fixed beds of spheres and of fibers, we omit much of the detailed justification of the analysis contained in the previous paper. Although we are interested in both heat and mass transfer, we speak in terms of the mass transfer problem as a matter of convenience. The heat transfer problem may be obtained by analogy, as is shown in the following section.

Our interest in fibrous beds is motivated by several factors. Fibrous materials are often used as filters to eliminate particulates from process streams and as membranes in biological systems; they also may model the behavior of polymer networks and melts. This study broadens our understanding of the general problem of dispersion in porous media. We have previously considered dispersion in a fixed bed of spheres—one possible geometry for porous media. Here we consider a second type of microstructure. Because the fibers have a direction associated with the orientation of their axes, this study allows us to examine anisotropic porous media. Finally, a theoretical study of dispersion in a fibrous medium is of interest because fibrous beds typically have a low solids volume fraction, and the volume fraction may be varied over a large range. This facilitates a direct comparison between experiment and the theoretical results of a low fiber volume fraction analysis. This last point is particularly interesting because, as we show, the effective diffusivity in a fibrous bed actually increases with decreasing volume fraction.

In a fibrous bed a purely two-dimensional problem is obtained if one considers infinitely long cylindrical fibers whose axes are parallel, Figure 1. We consider fibrous beds without long-range order—so-called disordered beds, i.e., beds in which the fibers do not lie in a regular lattice. (Note that fibers that are aligned may still be disordered in directions perpendicular to the direction of alignment.) This distinction is important because the mechanism that will be developed for the hydrodynamic contribution to the effective diffusivity depends on the stochastic velocity field that is induced by the randomly positioned fibers. We treat fibers of circular cross section, although the method presented here can easily be generalized to apply to fibers of any cross-sectional shape and to a distribution of fiber radii. With one exception (noted below) the shape of the cross section affects only the numerical coefficients, not the functional relationships.

In general, the individual fibers are not perfectly straight nor are they perfectly aligned. Rather, they are often randomly coiled and twisted, giving some distribution of fiber orientations, Figure 1. If the radius of curvature of the fibers is much larger than the cross-sectional radius and much larger than an interaction length to be discussed below, the fibers may still be treated as infinitely long cylinders. In this case the overall bed geometry is three-dimensional, but it will be shown that the effective diffusivity can be derived from a superposition of one-fiber problems each of which is two-dimensional. The theoretical development below is applicable to any distribution of fiber orientations. In addition to the case of aligned fibers mentioned above, specific results will be obtained for the case of an isotropic, fibrous bed.

In the following section we average the detailed, microscopic mass conservation equations to obtain a macroscopic Fick's law and give a general expression for the effective diffusivity in a homogeneous bed. In the third section the approximations required to obtain the low fiber volume fraction asymptotic behavior of the effective diffusivity are introduced. It should be noted, that in a disordered, homogeneous, fibrous bed, the volume fraction is equal to the areal fraction.

The fibers contribute to the effective diffusivity to leading order in three ways:

1. A pure conduction contribution arising from the difference in the molecular diffusivity of the tracer in the fluid and in the fibers.
2. A hydrodynamic contribution resulting from the velocity disturbance induced by the fibers.
3. Nonmechanical dispersion contributions resulting from the tendency of the zero velocity in and near the fibers to retain the tracer and hold it back against the bulk flow.

The pure conduction contribution, which is the two-dimensional analog of the effective conductivity of a material with spherical inclusions calculated by Maxwell (1873), is $O(\phi D_f)$ and is thus always a small correction in the dilute limit to the molecular diffusivity in the fluid D_f. The latter contributions, however, may cause a significant enhancement of the effective diffusivity.

It will be shown that the second, convective contribution to the effective diffusivity can be related to an integral overall space of the product of the velocity and concentration disturbances caused by a fiber times the fiber number density, which is $O(\phi)$. Thus, if the velocity and concentration disturbances decayed near the fiber one would expect this contribution to be $O[\phi D_f F(P)]$, where $F(P)$ is some as yet undetermined function of the Peclet number. The velocity disturbance decays only at large $O[a(\ln \phi^{-1}/\phi)]$ distances from the fiber. This distance, known as the Brinkman screening length, is the length at which the porous media term, related to the drag exerted by the fibers on the fluid, becomes comparable in magnitude to the viscous

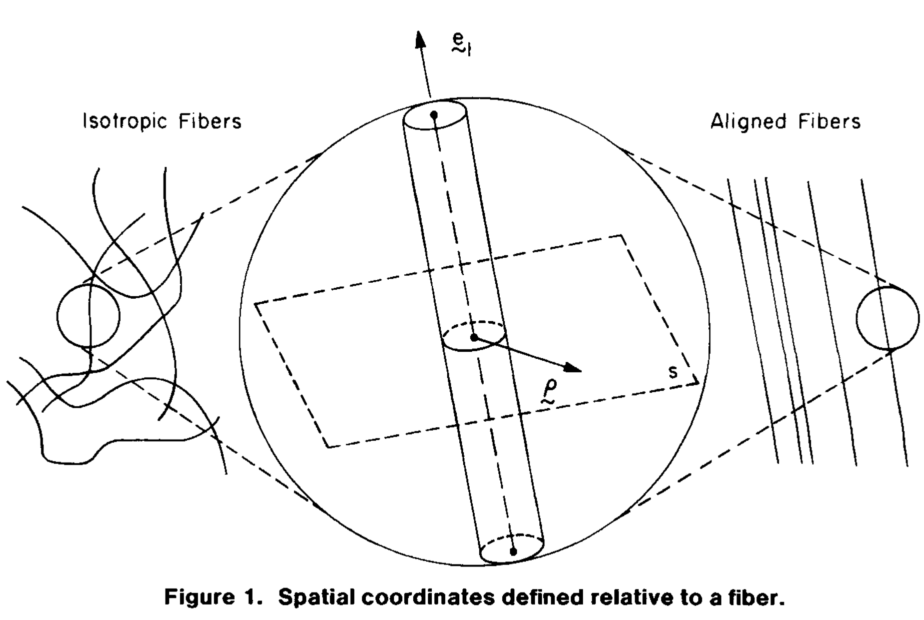

Figure 1. Spatial coordinates defined relative to a fiber.

term in the averaged momentum conservation equation. For lengths smaller than the Brinkman screening length the bed acts like a viscous fluid obeying the Stokes equations, and the velocity and concentration disturbances do not decay. For lengths larger than the screening length the bed acts like a porous medium obeying Darcy's law, and the velocity and concentration disturbances do decay sufficiently rapidly to assure convergence of the integral for the convective contribution to the effective diffusivity. Thus each fiber influences mass transfer over the large region within one Brinkman screening length, and the hydrodynamic contribution to the effective duffisivity is much larger than the $O[\phi D_f F(P)]$ estimate made earlier; in fact, this contribution actually increases with decreasing fiber volume fraction. In the limit of high Peclet numbers—large flow rates—it will be seen that the hydrodynamic dispersion mechanism becomes independent of molecular diffusion. This contribution to the dispersion is caused by the stochastic velocity field induced by the randomly positioned fibers, a phenomenon commonly referred to as mechanical dispersion.

The third, nonmechanical dispersion contributions to the longitudinal diffusivity arise when part of the solute is trapped in a region from which it cannot escape by convection alone. The solute may be trapped in the fibers, from which it can only escape by molecular diffusion, leading to an $O(\phi D_f P^2)$ holdup dispersion contribution. If the fibers are impermeable to the solute, holdup dispersion is absent, but a second type of nonmechanical dispersion becomes important. This nonmechanical, boundary-layer type of dispersion occurs because solute can only escape the diffusive boundary layer near the fiber by a combination of convection and diffusion. The boundary-layer contributions to the longitudinal diffusivity are $O[(\phi/\ln \phi^{-1})D_f P \ln P]$ or $O\{[(\phi/\ln \phi^{-1})D_f P](\ln P)^2\}$ depending on the orientation distribution of the fibers.

Macrotransport Equations

We are interested in the transport of a dilute solute through a bed of fibers of radius a in the presence of a uniform bulk convective motion throughout the bed. On the microscale, i.e., at each point in the bed, the tracer concentration $c(\boldsymbol{x}, t)$ satisfies

$$\frac{\partial c}{\partial t} + \nabla \cdot \boldsymbol{q} = 0, \tag{1a}$$

where the mass flux $\boldsymbol{q}$ is

$$\boldsymbol{q} = \boldsymbol{u}c - D_f \nabla c \quad \text{in the fluid} \tag{1b}$$

and

$$\boldsymbol{q} = D_p \nabla c \quad \text{in the fibers} \tag{1c}$$

and $\boldsymbol{u}(\boldsymbol{x})$ is the fluid velocity. On the fiber surface the continuity of mass flux and solubility conditions are

$$D_p \boldsymbol{n} \cdot \nabla c_{|\text{in}} = D_f \boldsymbol{n} \cdot \nabla c_{|\text{out}}, \quad \text{and} \quad m c_{|\text{in}} = c_{|\text{out}}. \tag{1d, e}$$

Here, m is the ratio of the solubilities of the solute in the fluid and in the fibers, and $\boldsymbol{n}$ is the outward normal to the fiber surfaces.

Equations 1b–e may also be written

$$\boldsymbol{q} = \boldsymbol{u}c - \frac{D}{M} \nabla (Mc), \tag{1f}$$

where the mass conductivity D/M and the activity coefficient M are generalized functions that take on the values D_f and 1 in the fluid, and the values D_p/m and m in the fibers. Equation 1f reduces to Eqs. 1b, c in the two phases. Because of the jump in M at the interface, a jump in c—equivalent to the solubility condition, Eq. 1e—is required if Eq. 1f is to be nonsingular. Finally, the requirement that the flux, Eq. 1f, be continuous, so that its divergence in Eq. 1a is nonsingular is equivalent to Eq. 1d.

To determine the macrotransport, we shall develop macroscopic conservation equations that apply to concentration and velocity fields averaged over a volume large enough to contain sections of many different fibers. To this end we define an ensemble average $\langle\ (\boldsymbol{x}, t)\rangle_0$ as the unconditional average over an ensemble of realizations of the bed, each realization having a different microstructural configuration. Similarly, we define the conditional ensemble average $\langle\ (\boldsymbol{x}, t|\boldsymbol{r}_1, \boldsymbol{e}_1)\rangle_1$ as the average over those realizations for which a fiber axis of orientation $\boldsymbol{e}_1$ passes through the point $\boldsymbol{r}_1$. The unconditional ensemble average is equal to the volume average if the average velocity and concentration fields are nearly constant within this volume. We shall consider bulk fields that satisfy this condition and are constant or vary linearly on the scale of the microstructure, i.e., the Brinkman screening length, which should be true everywhere except within one screening length of the boundaries of the bed.

Averaging mass conservation Eq. 1 gives

$$\frac{\partial \langle c(\boldsymbol{x}, t)\rangle_0}{\partial t} + \nabla \cdot \langle \boldsymbol{q}(\boldsymbol{x}, t)\rangle_0 = 0, \tag{2a}$$

where

$$\langle \boldsymbol{q}\rangle_0 = \langle \boldsymbol{u}c\rangle_0 - \left\langle \frac{D}{M} \nabla (Mc)\right\rangle_0. \tag{2b}$$

In the absence of fibers the nonlinear terms $\langle \boldsymbol{u}c\rangle_0$ and $\langle (D/M)\nabla(Mc)\rangle_0$ in Eq. 2b would simply equal the product of the averaged quantities $\langle u\rangle_0\langle c\rangle_0$ and $\langle D\rangle_0\nabla\langle c\rangle_0$, respectively. The presence of the fibers, however, causes $\boldsymbol{u}$, c, D, and M to fluctuate and the correlations in these fluctuating fields give rise to an excess mass flux—a flux in addition to that given by an average Fick's law. Nevertheless, Eq. 2b may be rewritten in a form similar to Fick's law (Koch and Brady, 1985):

$$\langle \boldsymbol{q}\rangle_0 = (1 + \gamma)\langle \boldsymbol{u}\rangle_0\langle c\rangle_0 - \boldsymbol{D} \cdot \nabla\langle c\rangle_0. \tag{3}$$

The first term in Eq. 3 represents the bulk convective flux of the solute. The effect $\gamma\langle \boldsymbol{u}\rangle_0\langle c\rangle_0$ of the fibers on this term is equivalent to replacing the concentration averaged over the bed with the average concentration in the fluid, and replacing the bed average velocity with the superficial velocity, reflecting the fact that the velocity is nonzero only within the fluid. For convenience in the analysis we have chosen to define averages over the entire bed—fluid and fiber phases—and so γ appears. γ is given exactly by

$$\gamma \equiv \frac{\phi(1 - m^{-1})}{1 - \phi + \phi m^{-1}}. \tag{4}$$

The second term in Eq. 3 is the dispersive flux and serves as the definition of the effective diffusivity $\boldsymbol{D}$. The tensorial nature of $\boldsymbol{D}$ reflects both the directionality imposed by the average velocity and the anisotropy of the bed. In general, $\boldsymbol{D}$ is a tensorial operator rather than a constant tensor, due to the nonlocal nature of dispersion. There are many effects that contribute to the dispersive flux, but in general the effective diffusivity operator may be written as the sum of three (not independent) terms:

$$\boldsymbol{D} \equiv \boldsymbol{D}^m + \boldsymbol{D}^\alpha + \boldsymbol{D}^*, \tag{5a}$$

where

$$\boldsymbol{D}^m \cdot \nabla\langle c\rangle_0 \equiv D_f \nabla\langle Mc\rangle_0 \tag{5b}$$

is the effective diffusivity in the absence of convection and differences in the mass conductivity D/M of the two phases. This term differs from D_f because the driving force for diffusion is actually the gradient in activity Mc rather than concentration.

The contribution $\boldsymbol{D}^\alpha$ arises from the difference in the mass conductivities of the solute in the fibers and in the fluid. It is given by

$$\boldsymbol{D}^\alpha \cdot \nabla\langle c\rangle_0 \equiv mD_f(\alpha - 1) \int_{|x-r_1|\le a} dr_1 de_1 P(r_1, e_1) \cdot \nabla\langle c(x, t|r_1, e_1)\rangle_1 \delta[(x - r_1)\cdot e_1], \tag{5c}$$

where $\alpha = D_p/mD_f$, and $P(r_1, e_1)$ is the probability density function for finding a fiber axis of orientation e_1 passing through the point r_1. The delta function $\delta[(x - r_1)\cdot e_1]$ has the effect of converting the volume integral dr_1 into an area integral in the plane s normal to the fiber axis e_1 as illustrated in Figure 1.

For the case of a bed of aligned fibers, $P(r_1, e_1) = (\phi/\pi a^2)[\delta(\hat{z}\cdot e_1)]$, where each fiber is parallel to every other, the microscopic mass transfer problem, Eq. 1, is entirely two-dimensional; i.e., the velocity and concentration only depend on x and y, not on z. Thus, the effective diffusivity may be determined entirely by solving a two-dimensional problem. For any other orientation distribution the full problem is three-dimensional. The one-fiber conditionally averaged problem (Eq. 8) is, however, a two-dimensional problem defined in the plane s normal to that particular fiber's axis, if one neglects (as we do here) the fiber's curvature. Thus, although the overall problem is three-dimensional, the effective diffusivity can be determined in the dilute limit by solving a set of two-dimensional, single-fiber problems.

The final contribution $\boldsymbol{D}^*$ to the effective diffusivity is caused by the velocity fluctuations induced by the fibers and is given by

$$-\boldsymbol{D}^* \cdot \nabla\langle c\rangle_0 \equiv \langle u'c'\rangle_0 - \gamma\langle u\rangle_0\langle c\rangle_0. \tag{5d}$$

Note that our division of the effective diffusivity in Eq. 5 does not imply that $\boldsymbol{D}^\alpha$ is independent of convection or that $\boldsymbol{D}^*$ is independent of the effects of molecular diffusion; both molecular diffusion and convection affect the concentration required to evaluate Eqs. 5c, d.

Equations 3, 4, and 5a–d are strictly valid for all volume fractions, and are equivalent to Eq. 2b under any circumstances in which an ensemble average may be defined. If we are to interpret the operator $\boldsymbol{D}$ as an effective diffusivity in the usual sense, however, we should require that it be a constant tensor independent of time and position, and independent of the bulk concentration field $\langle c(x, t)\rangle_0$. These conditions are satisfied if the bed is homogeneous, i.e., $P(r_1, e_1)$ is independent of position r_1, if (as we shall assume here) sufficient time is allowed, and if the bulk concentration field varies slowly with position on the scale of the Brinkman screening length. In a future paper we shall consider mass transfer in fixed beds in the presence of bulk concentrations that do not vary slowly in time and space.

The dispersive flux defining $\boldsymbol{D}$ can be determined by subjecting the bed to a constant bulk concentration gradient. A concentration field that is time-independent and has a constant gradient perpendicular to the bulk flow ($\langle u\rangle_0 \cdot \nabla\langle c\rangle_0 = 0$) is a solution of the bulk mass conversion equation 2a with Eq. 3. The presence of the bulk convection term $\gamma\langle u\rangle_0\langle c\rangle_0$ in Eq. 3, however, requires that a concentration gradient that is constant in the direction of the bulk flow must also vary linearly with time. Thus, the solution of Eqs. 2a and 3 that has a constant gradient is

$$\langle c\rangle_0(x, t) = \nabla\langle c\rangle_0 \cdot x - \nabla\langle c\rangle_0 \cdot \langle u\rangle_0(1 + \gamma)t. \tag{6}$$

Although this bulk concentration field is time-dependent, the gradient $\nabla\langle c\rangle_0 = \nabla\langle c(x, t)\rangle_0$ is independent of both time and position, and we shall find that this determines an effective diffusivity that is also independent of time and position.

We can now evaluate $\boldsymbol{D}^m$ exactly for all volume fractions. The equilibrium concentration field that corresponds to a constant average concentration $\langle c\rangle_0$ obtained by solving Eq. 1 is

$$c_{eq} = \frac{1}{1 - \phi + \phi m^{-1}}\langle c\rangle_0 \quad \text{in the fluid,}$$

and

$$c_{eq} = \frac{1}{m[1 - \phi + \phi m^{-1}]}\langle c\rangle_0 \quad \text{in the fibers.}$$

Substituting c_{eq} for the concentration in Eq. 5b gives

$$\boldsymbol{D}^m = \frac{D_f}{1 - \phi + \phi m^{-1}} \boldsymbol{I}, \tag{5e}$$

where $\boldsymbol{I}$ is the identity dyadic. In writing Eq. 5e we have neglected the term $D_f\nabla\langle M(c - c_{eq})\rangle$. However, as $c - c_{eq}$ is driven by the constant concentration gradient, the averaged quantity $\langle M(c - c_{eq})\rangle$ has no spatial variation, its gradient is zero, and thus Eq. 5e is equivalent to Eq. 5b for constant bulk concentration gradients.

At this point we shall begin to introduce the approximations required to obtain the low ϕ asymptotic behavior of the effective diffusivity. Velocity-concentration correlations involving two or more fibers may be neglected in the dilute limit, so that Eq. 5d is approximated by

$$-D^* \cdot \nabla\langle c\rangle_0 = \int_{|x-r_1|>a} dr_1 de_1 P(r_1, e_1)\langle u'(x|r_1, e_1)\rangle_1 \cdot \langle c'(x, t|r_1, e_1)\rangle_1 \delta[(x - r_1)\cdot e_1] + \int_{|x-r_1|\le a} dr_1 de_1 P(r_1, e_1)\langle u'\rangle_1 \cdot \left[\langle c\rangle_1 - \frac{1}{m}(1+\gamma)\langle c\rangle_0\right] \cdot \delta[(x - r_1)\cdot e_1], \tag{5f}$$

where $\langle u'(x|r_1, e_1)\rangle_1 = \langle u(x|r_1, e_1)\rangle_1 - \langle u(x)\rangle_0$ is the disturbance velocity field—the difference between the velocity averaged with and without a fiber fixed at r_1—and $\langle c'(x, t|r_1, e_1)\rangle_1 = \langle c(x, t|r_1, e_1)\rangle_1 - \langle c(x, t)\rangle_0$ is the disturbance concentration field.

Further approximations are required to evaluate the conditionally averaged velocity and concentration fields. The conditionally averaged concentration $\langle c(x, t|r_1, e_1)\rangle_1$ satisfies the equations

$$\frac{\partial\langle c\rangle_1}{\partial t} + \langle u\rangle_1 \cdot \nabla\langle c\rangle_1 - D_f\nabla^2\langle c\rangle_1 = \nabla \cdot \left\{mD(\alpha - 1)\int_{|x-r_2|\le a} dr_2 de_2 P(r_2, e_2|r_1, e_1)\nabla\langle c\rangle_2 \cdot \delta[(x - r_2)\cdot e_2]\right\} - \nabla \cdot \langle(u - \langle u\rangle_1)(c - \langle c\rangle_1)\rangle_1 \tag{7a}$$

for points in the fluid, and

$$\frac{\partial\langle c\rangle_1}{\partial t} - D_p\nabla^2\langle c\rangle_1 = 0 \tag{7b}$$

for points in the fiber that is fixed at r_1 with orientation e_1. The symbol $\langle\ \rangle_2$ indicates a conditional ensemble average with two fibers fixed. The one-fiber convective diffusion problem obtained by neglecting the righthand side of Eq. 7a is usually adequate to give the leading behavior of the diffusivity. (An exception to this general statement is discussed later.) These and the additional approximations that will be required in the following section may be justified by analogy to the fixed-sphere problem (Koch and Brady, 1985). It should be noted, however, that whereas the asymptotic analysis produces an algebraic series in ϕ for the effective diffusivity in a fixed bed of spheres, the asymptotic series for the effective diffusivity in a fibrous bed contains terms that are only logarithmically small in ϕ.

The equations of motion in the fluid phase are taken to be the Navier-Stokes equations, which may be approximated by the creeping-flow Stokes equations at low Reynolds number. Taking the conditional average of the Stokes equations with one fiber fixed gives (Hinch, 1977)

$$\nabla \cdot \langle u(x|r_1, e_1)\rangle_1 = 0 \tag{8a}$$

$$\mu\nabla^2\langle u\rangle_1 - \nabla\langle p\rangle_1 - \mu k^{-1}\cdot\langle u\rangle_1 = \int_{|x-r_2|\le a} dr_2 de_2 \left\{P(r_2, e_2|r_1, e_1) \int_{|x-r_2|=a} dx'\langle\sigma(x'|r_1, e_1, r_2, e_2)\rangle_1 \cdot n'\delta(x' - x) - \mu k^{-1}\cdot\langle u(r_2|r_1, e_1)\rangle_1\delta(r_2 - x)\right\}\delta[(x - r_2)\cdot e_2], \tag{8b}$$

where $\sigma = -pI + \mu(\nabla u + \nabla u\dagger)$ is the stress tensor, and the resistivity k^{-1} which is the inverse of the permeability tensor for anisotropic media, is given by

$$-\mu k^{-1}\cdot\langle u\rangle_0 = \int de_1 P(r_1, e_1)\langle f(r_1, e_1)\rangle_0. \tag{8c}$$

Here $\langle f(r_1, e_1)\rangle_0$ is the drag per unit length exerted by a fiber of orientation e_1.

The porous media term $-\mu k^{-1}\cdot\langle u\rangle_1$ on the lefthand side of Eq. 8b is proportional to the fiber volume fraction. It cannot, however, be neglected in the low volume fraction asymptotic analysis, because it decays more slowly with radial distance $|x - r_1|$ than does the viscous term $\mu\nabla^2\langle u\rangle$. These two terms are of the same order of magnitude at radial separations of one screening length $|k^{-1}|^{-1/2}$, where $|k^{-1}|$ is the trace of the resistivity k^{-1}. The velocity disturbance resulting from holding a fiber fixed in a medium described by Eq. 8a and the lefthand side of Eq. 8b grows as $\ln(|x - r_1|)$ for small radial distance $|x - r_1|$, but is screened by the other fibers and decays as $|x - r_1|^{-2}$ at distances large compared to the screening length. Through this screening, the Stokes paradox is avoided and the drag on the fibers may be determined (Spielman and Goren, 1968). In the appendix we reproduce the results of Spielman and Goren that are required to calculate the effective diffusivity.

The remaining terms involving fiber interactions—those on the righthand side of Eq. 8b—decay more rapidly than $-\mu k^{-1}\cdot\langle u\rangle_1$ and may be safely neglected (Koch and Brady, 1985; Hinch, 1977; Acrivos et al., 1981).

Effective Diffusivity

In this section we make use of the definition of the effective diffusivity Eq. 5, and the approximate expressions for the conditionally averaged concentration and velocity fields, Eqs. 7 and 8, to obtain the asymptotic behavior at low fiber volume fraction of the effective diffusivity as a function of the Peclet number $P = Ua/D_f$, where U is the magnitude of the average velocity, i.e., $U = |\langle u\rangle_0|$. In each of the three following subsections we shall consider one of the three contributions that the fibers make to the effective diffusivity: the pure conduction, the hydrodynamic, and the nonmechanical contributions. The theoretical development for each contribution will be applicable to any distribution of fiber orientations. Explicit results will be presented for two cases: an isotropic bed, and a bed of aligned fibers with flow perpendicular to the fiber axes. It will also be shown that for the special case of flow parallel to the axes in a bed of aligned fibers there is no time-independent solution for the effective diffusivity.

Pure conduction

In the absence of convection, $u = 0$, the fibers still affect the macroscopic mass transfer rate if the diffusivity D_p of the solute in the fibers is different from its diffusivity D_f in the fluid. In this case, however, the fibers have only a small effect on the effective diffusivity, and the conditionally averaged concentration may be approximated by solving a pure conduction problem for an isolated fiber subject to a constant concentration gradient $\nabla\langle c\rangle_0$ at infinite separation from the fiber:

$$-D_p\nabla^2\langle c\rangle_1 = 0 \quad \rho < a, \tag{9a}$$

$$-D_p\nabla^2\langle c\rangle_1 = 0 \quad \rho > a, \tag{9b}$$

$$D_f\frac{\partial\langle c\rangle_1}{\partial\rho}\bigg|_{\rho=a_+} = D_p\frac{\partial\langle c\rangle_1}{\partial\rho}\bigg|_{\rho=a_-}, \tag{9c}$$

$$m\langle c\rangle_1|_{\rho=a_-} = \langle c\rangle_1|_{\rho=a_+} \tag{9d}$$

$$\nabla\langle c\rangle_1 \sim \nabla\langle c\rangle_0 \quad \text{as} \quad \rho \longrightarrow \infty, \tag{9e}$$

where $\boldsymbol{\rho} = (\boldsymbol{x} - \boldsymbol{r}_1) - \boldsymbol{e}_1[\boldsymbol{e}_1 \cdot (\boldsymbol{x} - \boldsymbol{r}_1)]$ is the radial distance from the fiber (Figure 1); $\rho = |\boldsymbol{\rho}|$. The concentration gradient in the fiber obtained by solving Eq. 9 is

$$\begin{aligned}\nabla\langle c(\boldsymbol{x}|\boldsymbol{r}_1, \boldsymbol{e}_1)\rangle_1 &= (\boldsymbol{e}_1 \cdot \nabla\langle c\rangle_0)\boldsymbol{e}_1\frac{1}{m} \\ &+ [\boldsymbol{I} - \boldsymbol{e}_1\boldsymbol{e}_1] \cdot \nabla\langle c\rangle_0\frac{1}{m}\left(\frac{2}{\alpha+1}\right)\end{aligned} \quad \text{for } \rho < a. \tag{10}$$

Using this result with the proper orientation distribution in Eq. 5c, one obtains the pure-conduction contribution $\boldsymbol{D}^\alpha$ in the dilute limit.

Isotropic Bed. In an isotropic bed, $P(\boldsymbol{r}, \boldsymbol{e}_1) = \phi/4\pi^2a^2$, and there is no preferred direction in the absence of convection. Thus, the pure-condition contribution is isotropic and is given by

$$\boldsymbol{D}^\alpha = \boldsymbol{I}D_f\left[\frac{1}{3}\phi\frac{(\alpha-1)(\alpha+5)}{\alpha+1} + 0(\phi^2)\right]. \tag{11}$$

Aligned Fibers. In general, the pure-conduction contribution will not be isotropic in an anisotropic bed even in the absence of convection. For the case of fibers aligned with the z-axis, $P(\boldsymbol{r}_1, \boldsymbol{e}_1) = (\phi/\pi a^2)\delta(\hat{\boldsymbol{z}} \cdot \boldsymbol{e}_1)$, the pure-conduction contribution is

$$\begin{aligned}\boldsymbol{D}^\alpha &= \hat{\boldsymbol{z}}\hat{\boldsymbol{z}}\phi D_f(\alpha - 1) \\ &+ (\hat{\boldsymbol{x}}\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}}\hat{\boldsymbol{y}})D_f\left[2\phi\left(\frac{\alpha-1}{\alpha+1}\right) + 0(\phi^2)\right].\end{aligned} \tag{12}$$

The first term on the righthand side of Eq. 12 has the effect of replacing the molecular diffusivity D_f in the fluid with the average molecular diffusivity $D_f(1 - \phi) + \phi(D_p/m)$ for diffusion parallel to the fiber axes. This term is exact, independent of the volume fraction. The above results are equivalent to the effective conductivity in a bed of spheroids presented by Batchelor (1974) in the limit as the aspect ratio of the spheroids becomes large. The result for the pure-conduction contribution Eq. 12, is also equivalent to the low ϕ asymptote of the effective conductivities calculated by Runge (1925) and by Perrins et al. (1979) for aligned cylinders in square and hexagonal arrays. The leading behavior of the pure-conduction contribution is the same in ordered and disordered beds, because this leading behavior does not depend on the nature of fiber-fiber interactions, and hence does not depend on the bed microstructure. In the next section we shall see that the leading order hydrodynamic contribution does depend on fiber-fiber interactions, and so the ordered and disordered cases are expected to give different hydrodynamic contributions even in the dilute limit.

Hydrodynamic dispersion

The leading effect of convection on the effective diffusivity comes from the correlation in the velocity and concentration fluctuations contained in $\boldsymbol{D}^*$, which is defined by Eq. 5d and approximated in the dilute limit by Eq. 5f. We noted in the introduction that the concentration and velocity disturbances caused by a fiber decay only at large radial distances from the fiber, distances comparable to the Brinkman screening length $k^{1/2} \sim O[a(\ln\phi^{-1}/\phi)^{1/2}]$, where k is the permeability. Thus, the Brinkman screening length is an important parameter affecting hydrodynamic dispersion. The relationship between the permeability and the volume fraction is given by Eqs. A2 and A4 in the appendix. The errors inherent in these implicit expressions are $O(1/\ln\phi^{-1})$ at low volume fraction ϕ. On the other hand, the explicit expressions Eqs. A3 and A5 of the appendix, for the permeability in terms of the volume fraction have much larger $O[\ln(\ln\phi^{-1})/\ln\phi^{-1}]$ errors. Thus, it is more convenient and more accurate to express the hydrodynamic contribution in terms of the Brinkman screening length (or permeability) rather than expressing it directly in terms of the volume fraction.

The convective flux integral, Eq. 5f, must be integrated over a large cylindrical volume with a radius comparable to the screening length. The dominant hydrodynamic contributions to the effective diffusivity occur at this large radial distance, because it is only here that the velocity and concentration disturbances induced by the fiber decay. As a consequence, several simplifications may be introduced:

1. The velocity disturbance caused by a fiber $\langle\boldsymbol{u}'\rangle_1$ may be approximated as that due to a point force.
2. The boundary conditions on the concentration field at the surface of the fiber need not be satisfied.
3. The second integral in Eq. 5f over the area inside the fiber may be neglected.

The coordinate transform $\boldsymbol{R} = k^{-1/2}\boldsymbol{\rho} = k^{-1/2}\{(\boldsymbol{x} - \boldsymbol{r}_1) - \boldsymbol{e}_1[\boldsymbol{e}_1 \cdot (\boldsymbol{x} - \boldsymbol{r}_1)]\}$ places the dominant contribution to the convective mass flux integral, Eq. 5f, at $R \sim O(1)$. Using the spatial homogeneity of the bed, $P(\boldsymbol{r}_1, \boldsymbol{e}_1) = (\phi/\pi a^2)P(\boldsymbol{e}_1)$, the transformed flux integral, Eq. 5f, becomes

$$\begin{aligned}&-\boldsymbol{D}^* \cdot \nabla\langle c\rangle_0 \\ &= \int d\boldsymbol{e}_1\frac{\phi}{\pi a^2}kP(\boldsymbol{e}_1)\int d\boldsymbol{R}\langle\boldsymbol{u}'(\boldsymbol{R})\rangle_1\langle c'(\boldsymbol{R}, t)\rangle_1.\end{aligned} \tag{13}$$

The convolution theorem may be used to transform this real-space integral into an integral involving the Fourier transforms of the velocity and concentration disturbance fields:

$$\begin{aligned}&-\boldsymbol{D}^* \cdot \nabla\langle c\rangle_0 \\ &= \int d\boldsymbol{e}_1\frac{\phi}{\pi a^2}\frac{k}{(2\pi)^2}P(\boldsymbol{e}_1)\int d\boldsymbol{\xi}\langle\hat{\boldsymbol{u}}'(-\boldsymbol{\xi})\rangle_1\langle\hat{c}'(\boldsymbol{\xi})\rangle_1,\end{aligned} \tag{14}$$

where the Fourier transform is denoted by ^, and ξ is the two-dimensional transform variable corresponding to $\boldsymbol{R}$.

The transform of the point-force velocity disturbance $\langle \hat{\boldsymbol{u}}'(\boldsymbol{\xi})\rangle_1$ is obtained by solving the transformed equations of motion, i.e., the transform of Eq. 8 with the appropriate point-force driving term $k^{-1}\langle \boldsymbol{f}(\boldsymbol{e}_1)\rangle_0 \delta(\boldsymbol{R})$, and, in general, is given by

$$\langle \hat{\boldsymbol{u}}'(\boldsymbol{\xi})\rangle_1 = -\frac{k^{-1}}{\mu}\left[k^{-1}\xi^2 \boldsymbol{I} + \boldsymbol{k}^{-1} - \frac{\boldsymbol{\xi\xi}\cdot \boldsymbol{k}^{-1}}{\xi^2}\right]^{-1} \cdot \left[\boldsymbol{I} - \frac{\boldsymbol{\xi\xi}}{\xi^2}\right]\cdot \langle \boldsymbol{f}(\boldsymbol{e}_1)\rangle_0, \quad (15)$$

where $k^{-1} = |\boldsymbol{k}^{-1}|$. Here, $\langle \boldsymbol{f}(\boldsymbol{e}_1)\rangle_0$ is the average drag per unit length on a fiber of orientation $\boldsymbol{e}_1$.

Low Peclet numbers: $|P| \ll \phi \ln \phi^{-1}$

The equation for the concentration disturbance at low P may be obtained by subtracting the mass conservation equation, Eq. 2a, averaged with no fibers fixed from that, Eq. 7a, averaged with one fiber fixed, neglecting the interfiber interactions on the righthand side of Eq. 7a to give, in screening length variables $\boldsymbol{R}$,

$$k\frac{\partial \langle c'\rangle_1}{\partial t} + k^{1/2}\langle \boldsymbol{u}\rangle_1 \cdot \nabla_R \langle c'\rangle_1 - D_f \nabla_R^2 \langle c'\rangle_1 = -k\langle \boldsymbol{u}'\rangle_1 \cdot \nabla\langle c\rangle_0 \quad (16)$$

We have retained the time derivative in Eqs. 7a and 16 because the bulk average concentration $\langle c\rangle_0$ given by Eq. 6 is time-dependent. Note, however, that only $\nabla\langle c\rangle_0$ appears in Eq. 16. We have seen that this gradient is a constant independent of time, and so the concentration disturbance has a steady solution. As shown by Koch and Brady (1985), $\langle \boldsymbol{u}\rangle_1$ in the second term on the lefthand side of Eq. 16 may be approximated to leading order in ϕ (large k) by $\langle \boldsymbol{u}\rangle_0$, and Eq. 16 may be solved in Fourier space, using the fact that $\nabla\langle c\rangle_0$ is a constant, to give

$$\langle \hat{c}'\rangle_1(\boldsymbol{\xi}) = -\frac{k\langle \hat{\boldsymbol{u}}'\rangle_1(\boldsymbol{\xi})\cdot \nabla\langle c\rangle_0}{D_f \xi^2 - ik^{1/2}\langle \boldsymbol{u}\rangle_0 \cdot \boldsymbol{\xi}} \quad (17)$$

The leading-order hydrodynamic contribution to the effective diffusivity at all values of the Peclet number may be obtained by integrating Eq. 14 with the concentration disturbance, Eq. 17, and the velocity disturbance given by Eq. 15. Since $\langle \hat{c}'\rangle_1$ is proportional to $\nabla\langle c\rangle_0$, and since Eq. 14 must hold for any constant $\nabla\langle c\rangle_0$, the effective diffusivity $\boldsymbol{D}^*$ is space- and time-independent and is given by

$$\boldsymbol{D}^* = \int d\boldsymbol{e}_1 \frac{\phi}{\pi a^2}\frac{1}{k^2}\frac{P(\boldsymbol{e}_1)}{(2\pi)}\int d\boldsymbol{\xi}\frac{\langle \hat{\boldsymbol{u}}'\rangle_1(-\boldsymbol{\xi})\langle \hat{\boldsymbol{u}}'\rangle_1(\boldsymbol{\xi})}{D_f\xi^2 - ik^{1/2}\langle \boldsymbol{u}\rangle_0\cdot \boldsymbol{\xi}} \quad (18)$$

Isotropic Bed. In an isotropic bed the permeability is a scalar, $\boldsymbol{k}^{-1} = k^{-1}\boldsymbol{I}$, indicating that the overall structure of the bed has no preferred direction, and the velocity disturbance, Eq. 15, reduces to

$$\langle \boldsymbol{u}'\rangle_1(\boldsymbol{\xi}) = -\frac{\langle \boldsymbol{f}(\boldsymbol{e}_1)\rangle_0\cdot\left(\boldsymbol{I} - \frac{\boldsymbol{\xi\xi}}{\xi^2}\right)}{\mu(\xi^2+1)}. \quad (19)$$

Using Eq. 19 with the orientation distribution $P(\boldsymbol{e}_1) = 1/4\pi$, the convective contribution, Eq. 18, to the effective diffusivity may be written in the form

$$\boldsymbol{D}^* = \frac{\phi D_f}{16\pi^4}\frac{\mathcal{P}^2 k}{\mu^2 U^2 a^2}\int_{d\boldsymbol{e}_1} d\boldsymbol{\xi}\frac{\left[\langle \boldsymbol{f}(\boldsymbol{e}_1)\rangle_0\cdot\left(\boldsymbol{I} - \frac{\boldsymbol{\xi\xi}}{\xi^2}\right)\right]^2}{(\xi^2+1)^2(\xi^2 - i\mathcal{P}\langle \boldsymbol{1}\rangle_0\cdot\boldsymbol{\xi})},$$
$$|\boldsymbol{P}| \ll [\phi \ln \phi^{-1}]^{1/2}, \quad \phi \ll 1, \quad (20)$$

where $\mathcal{P} = Pa^{-1}k^{1/2} = Uk^{1/2}/D_f$ is the Peclet number based on the Brinkman screening length and $\langle \boldsymbol{1}\rangle_0$ is a unit vector in the direction of the bulk flow, which we take to be the x-direction. $\langle \boldsymbol{f}(\boldsymbol{e}_1)\rangle_0$ is the drag per unit length in an isotropic bed and is given by Eq. A1. In order of magnitude $|\langle \boldsymbol{f}\rangle_0| \sim O(Ua^2/\phi k)$. The integral in Eq. 20 may be evaluated numerically to give the hydrodynamic contribution to the effective diffusivity in terms of the screening length Peclet number $\mathcal{P}$, and the results are given in Figure 2. Note that it is the Peclet number $\mathcal{P}$ based on the screening length that is the appropriate nondimensional parameter which measures the relative importance of convection and conduction in determining the effective diffusivity. $\mathcal{P}$ also arises naturally upon nondimensionalizing Eq. 16. Depending on the relative magnitudes of particle Peclet number P and the volume fraction ϕ (i.e. k^{-1}), the screening length Peclet number $\mathcal{P}$ may be large, even though P is small.

In the limit of high $\mathcal{P}$ convection dominates in the Brinkman screening length region, while at low $\mathcal{P}$ conduction dominates. Equation 20 can be evaluated analytically in these limits, and these asymptotic forms are indicated by the dotted lines in Figure 2. Explicitly, the low $\mathcal{P}$ results are:

$$\left.\begin{aligned} D^*_{xx} &= S_0\mathcal{P}^2\pi\left[\frac{19}{30}\ln\frac{1}{|\mathcal{P}|} + \frac{599}{900}\right] \\ D^*_{zz} &= D^*_{yy} = S_0\mathcal{P}^2\pi\left[\frac{1}{10}\ln\frac{1}{|\mathcal{P}|} - \frac{137}{900}\right]\end{aligned}\right\} \quad |\mathcal{P}| \ll 1,$$

where S_0 is a function of the volume fraction given by $S_0 = (9/25)(a^2/k\phi)$.

If we could neglect the bulk convective term $i\mathcal{P}\langle \boldsymbol{1}\rangle_0\cdot\boldsymbol{\xi}$ in the denominator of the integrand of Eq. 20 in the limit of low $\mathcal{P}$, the hydrodynamic contribution would be $O[D_f(a^2/k\phi)\mathcal{P}^2]$. However, the integral is only conditionally convergent in the limit of small wave number ξ (large distances R from the fiber) when the convective term is neglected. We have stated that the velocity and concentration disturbances begin to decay at radial distances comparable to the screening length, $\rho \sim O(k^{1/2})$, $R \sim O(1)$. In the low $\mathcal{P}$ limit, however, the velocity and concentration disturbance fields each decay only as R^{-1} upon screening, and the convective flux integral is only conditionally convergent. It is only at a still larger radial distance $\rho \sim O(P^{-1}a)$, $R \sim O(\mathcal{P}^{-1})$ that the bulk convection term becomes more important than the conduction term, so that the concentration disturbance begins to decay like R^{-2}, and the convective flux integral becomes absolutely convergent. As a result the actual asymptotic form of $\boldsymbol{D}^*$ at low $\mathcal{P}$ contains a factor of $\ln|\mathcal{P}^{-1}|$, and is $O[D_f(a^2/k\phi)\mathcal{P}^2\ln|\mathcal{P}^{-1}|]$.

In terms of the fiber Peclet number, the low $\mathcal{P}$ asymptote of the effective diffusivity $\boldsymbol{D}^*$ is $O[D_f(1/\phi)P^2\ln|Pk^{1/2}a^{-1}|]$,

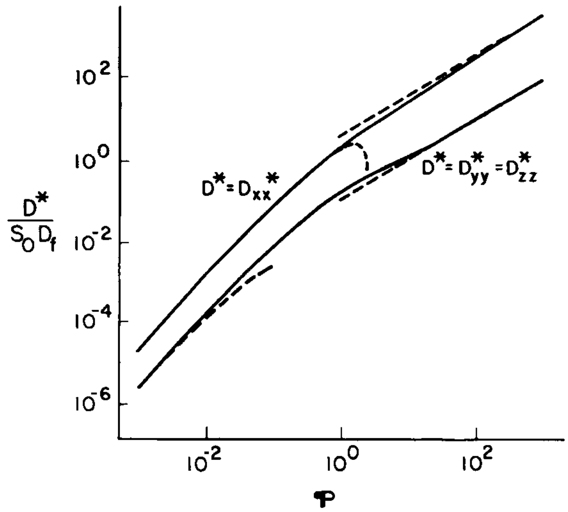

Figure 2. Hydrodynamic contribution D^* to the effective diffusivity for an isotropic bed with flow in the x-direction at low Peclet numbers, $P \ll [\phi \ln \phi^{-1}]^{1/2}$.
----, high and low P asymptotes.

which increases as the volume fraction decreases. This surprising result comes from the fact that the velocity disturbance in a fibrous bed is long-ranged and increases in range as ϕ decreases. It should be noted, however, that we must wait an increasingly long time, $O(a/U\phi^{1/2})$, for the effective diffusivity to reach its longtime asymptotic value as the volume fraction decreases.

The high $\mathcal{P}$ asymptote in Figure 2 applies to the range $[\phi/\ln \phi^{-1}]^{1/2} \ll P \ll [\phi \ln \phi^{-1}]^{1/2}$. In this range of Peclet numbers the convective contribution to the effective diffusivity may be calculated using either the methods for low Peclet numbers just discussed above, or those for high Brinkman screening length Peclet numbers discussed later; for convenience we shall consider this limit in the later discussion.

Aligned Fibers. In the case where the fiber axes are aligned in the z-direction, the resistivity is a tensor, i.e., $\boldsymbol{k}^{-1} = k_\perp^{-1} (\hat{x}\hat{x} + \hat{y}\hat{y}) + k_\parallel^{-1} \hat{z}\hat{z}$. For an arbitrary bulk velocity $\langle \boldsymbol{u} \rangle_0$, it is necessary to use the general form of the velocity disturbance, Eq. 15. It is possible to use a simpler form of the velocity disturbance similar to Eq. 19 in two cases. These correspond to bulk flow parallel to and perpendicular to the fiber axes.

When the bulk velocity $\langle \boldsymbol{u} \rangle_0$ is perpendicular to the fibers, the velocity disturbance $\langle \boldsymbol{u}' \rangle_1$ has no component in the z-direction. As a result only the perpendicular components of the resistivity tensor enter the problem, and $\boldsymbol{k}^{-1} \cdot \langle \boldsymbol{u}' \rangle_1 = k_\perp^{-1} \langle \boldsymbol{u}' \rangle_1$. Thus, the velocity disturbance may be written in a form similar to Eq. 19:

$$\langle \boldsymbol{u}'(\boldsymbol{\xi}) \rangle_1 = - \frac{\langle \boldsymbol{f}_\perp \rangle_0 \cdot \left(\boldsymbol{I} - \frac{\boldsymbol{\xi}\boldsymbol{\xi}}{\xi^2} \right)}{\mu(\xi^2 + 1)}, \tag{21}$$

where $\langle \boldsymbol{f}_\perp \rangle_0 = - \phi^{-1} k_\perp^{-1} \pi \mu a^2 \langle \boldsymbol{u} \rangle_0$ is the average drag per unit length on a fiber, and $k_\perp^{-1}$ is given by Eq. A4b. Using Eq. 21 and the orientation distribution $P(\boldsymbol{e}_1) = \delta(\boldsymbol{e}_1 \cdot \hat{z})$, the convective contribution, Eq. 18, to the effective diffusivity becomes, upon integration in $\boldsymbol{e}_1$,

$$\boldsymbol{D}^* = \frac{\phi D_f \mathcal{P}_\perp^2 k_\perp}{4\pi^3 \mu^2 a^2 U^2} \frac{\int d\boldsymbol{\xi} \left[\langle \boldsymbol{f}_\perp \rangle_0 \cdot \left(\boldsymbol{I} - \frac{\boldsymbol{\xi}\boldsymbol{\xi}}{\xi^2} \right) \right]^2}{(\xi^2 + 1)^2 (\xi^2 - i\mathcal{P}_\perp \langle \boldsymbol{1} \rangle_0 \cdot \boldsymbol{\xi})}, \quad |\boldsymbol{P}| \ll [\phi \ln \phi^{-1}]^{1/2}, \ \phi \ll 1, \tag{22}$$

where $\mathcal{P}_\perp = P k_\perp^{1/2} a^{-1}$, and $\langle \boldsymbol{1} \rangle_0$ is a unit vector in the direction of bulk flow, the x-direction. The results of Eq. 22 are presented in Figure 3. The behavior of the effective diffusivity is similar to that for the isotropic bed given in Figure 2. The low screening length Peclet number asymptotes of the hydrodynamic contribution to the effective diffusivity are given by:

$$\left. \begin{aligned} D_{xx}^* &= \frac{S_1}{\pi} \mathcal{P}_\perp^2 \left[\frac{3}{16} \ln \frac{2}{|\mathcal{P}_\perp|} + \frac{3}{64} \right] \\ D_{yy}^* &= \frac{S_1}{\pi} \mathcal{P}_\perp^2 \left[\frac{1}{16} \ln \frac{2}{|\mathcal{P}_\perp|} + \frac{3}{64} \right] \end{aligned} \right\} \quad |\mathcal{P}_\perp| \ll 1,$$

where $S_1 = a^2 \pi / k_\perp \phi$, and differ from the isotropic case only by a numerical factor. Note, however, that there is no hydrodynamic contribution to the diffusivity parallel to the aligned fibers, $D_{zz}^* = 0$, because there is no component of the velocity disturbance in this direction. Also, there is a quantitative difference in the high screening length Peclet number behavior of D_{yy}^*, the hydrodynamic contribution to the diffusivity transverse to the bulk flow in the two cases. We discuss this behavior in the following section.

We shall now consider the case of a bulk flow parallel to the fiber axes in a bed of aligned fibers. The velocity disturbance here is entirely in the z-direction, parallel to the fiber axes.

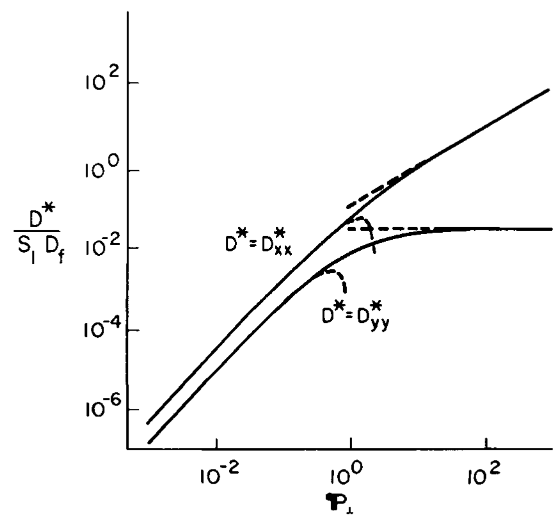

Figure 3. Hydrodynamic contribution D^* to effective diffusivity for a bed of fibers aligned in the z-direction with flow in the x-direction at low Peclet numbers, $P \ll [\phi \ln \phi^{-1}]^{1/2}$.
----, high and low $P_\perp$ asymptotes.

Thus, only the parallel component of the resistivity tensor affects the velocity disturbance, and $k^{-1} \cdot \langle u' \rangle_1 = k_\parallel^{-1} \langle u' \rangle_1$. The hydrodynamic contribution to the effective diffusivity may be written in a form similar to Eq. 22, but with $k_\perp$ replaced by $k_\parallel$. We have noted that it is necessary to involve the effect of the bulk convective term in Eq. 16 on the concentration disturbance in order to obtain a convergent expression for D^* even in the limit of low screening length Peclet numbers. The concentration disturbance varies only in the plane (s in Figure 1) normal to the fiber axis. Thus when the bulk flow is parallel to the axis, the convective term in Eq. 16 $\langle u \rangle_0 \cdot \nabla \langle c' \rangle \equiv 0$, indicating that the concentration disturbance is not convected away from the fiber by the bulk flow. Thus, the concentration disturbance grows with time and with distance along the fiber and there is no time- and space-independent effective diffusivity for this case.

If a fiber is nearly parallel to the bulk flow, its contribution to the effective diffusivity is large $O(\ln \theta^{-1})$ where θ is the angle between the bulk flow direction and the fiber axis. Here, bulk convection does carry the concentration disturbance away from the fiber, but only slowly for small θ. The requirement that a given orientation distribution give a constant time- and space-independent diffusivity is that the orientation distribution, $P(\theta)$, is less singular than $(\sin \theta)^{-1} \ln \theta^{-1}$ as $\theta \rightarrow 0$. For the isotropic case considered above $P(\theta) \sim O(1)$ as $\theta \rightarrow 0$, confirming the existence of a constant effective diffusivity for that case. We shall see, however, that fibers orientated nearly parallel $[\theta \sim O(\rho^{-1})]$ to the bulk flow make a large contribution to the boundary-layer dispersion in an isotropic bed, examined later.

High Brinkman screening length Peclet numbers: $1 \ll |\mathcal{P}|, [\ln \phi^{-1}/\phi]^{1/2} \ll |P|$

In this subsection we evaluate the hydrodynamic contribution to the effective diffusivity in the convection-dominated region, $\mathcal{P} \gg 1$. We shall see that this contribution may generally be evaluated by simply neglecting the $O(\mathcal{P}^{-1})$ small molecular diffusion term in Eq. 16 for the concentration disturbance, to give the one-fiber purely mechanical equation:

$$\langle u \rangle_1 \cdot \nabla \langle c' \rangle_1 = -k^{1/2} \langle u' \rangle_1 \cdot \nabla \langle c \rangle_0. \tag{23}$$

In the Brinkman screening length region $R \sim O(1)$ far from the fiber, $\langle u \rangle_1 \approx \langle u \rangle_0$. From symmetry considerations, however, $e_1 \cdot \nabla_R \langle c' \rangle_1 = 0$, so $\langle u \rangle_1 \cdot \nabla_R \langle c' \rangle_1 = \langle u \rangle_0 \cdot \nabla_R \langle c' \rangle_1 = [\langle u \rangle_0 - e_1(e_1 \cdot \langle u \rangle_0)] \cdot \nabla_R \langle c' \rangle_1$, and the solution of Eq. 23 is

$$\langle c'(R, e_1) \rangle_1 = -\frac{k^{1/2}}{|\langle u \rangle_0 - e_1(e_1 \cdot \langle u \rangle_0)|} \cdot \int_{-\infty}^{X} dX' \langle u'(X', Y, e_1) \rangle_1 \cdot \nabla \langle c \rangle_0, \tag{24}$$

where X and Y are Cartesian coordinates corresponding to R, and X is the direction corresponding to the projection of the flow direction onto the plane s (Figure 1). Substituting Eq. 24 for the concentration disturbance in Eq. 13, we obtain

$$D^* = \frac{\phi k^{1/2}}{\pi a^2} \int de_1 P(e_1) \frac{1}{|\langle u \rangle_0 - e_1(e_1 \cdot \langle u \rangle_0)|} \cdot \int dX dY \langle u'(X, Y) \rangle_1 \int_{-\infty}^{X} dX' \langle u'(X', Y) \rangle_1. \tag{25}$$

Equation 25 is an integral over all space and over all fiber orientations of the velocity disturbance correlation function

$$\int_{-\infty}^{X} dX' \langle u'(X, Y) \rangle_1 \langle u'(X', Y) \rangle_1, \tag{26}$$

which measures the correlation of the velocity disturbances experienced by a fluid element at a given time, i.e., given X, with the fluid element's velocity disturbance at all previous times—previous X.

The integration in X and X' in Eq. 25 can be carried out giving

$$D^* = \frac{1}{2} \frac{\phi k^{1/2}}{\pi a^2} \int de_1 P(e_1) \frac{1}{|\langle u \rangle_0 - e_1(e_1 \cdot \langle u \rangle_0)|} \cdot \int dY \langle u'(Y) \rangle_{1x} \langle u'(Y) \rangle_{1x}, \tag{27}$$

where

$$\langle u'(Y) \rangle_{1x} = \int_{-\infty}^{\infty} dX \langle u'(X, Y) \rangle_1. \tag{28}$$

An equation for $\langle u'(Y) \rangle_{1x}$ is obtained by integrating the equations of motion, Eq. 8, with respect to X. In Fourier space $\langle u'(Y)_{1x}$ is

$$\langle \hat{u}'(\eta) \rangle_1 = \langle f(e_1) \rangle_0 \frac{1}{\eta^2 + 1}, \tag{29}$$

where η is the one-dimensional Fourier transform variable corresponding to Y. The convolution theorem can be used to write Eq. 27 as

$$D^* = \frac{\phi k^{1/2}}{\pi a^2} \frac{1}{2\pi} \int de_1 P(e_1) \frac{1}{|\langle u \rangle_0 - e_1(e_1 \cdot \langle u \rangle_0)|} \cdot \int d\eta \langle \hat{u}'(\eta, e_1) \rangle_1 \langle \hat{u}'(\eta, e_1) \rangle_1. \tag{30}$$

The leading behavior at low ϕ of the convective contribution to the effective diffusivity for $|\mathcal{P}| \gg 1$ is given explicitly by Eq. 30 provided that the righthand side is nonzero.

The mechanism we have just presented for hydrodynamic dispersion in the high $\mathcal{P}$ limit is completely independent of molecular diffusion. Each fiber's velocity disturbance gives rise to a convectively determined mass flux. When this effect is averaged over the randomly distributed fiber positions and orientations it gives a contribution to the effective diffusivity that is independent of the molecular diffusivity. Such a purely hydrodynamic dispersion is commonly referred to as mechanical dispersion.

Isotropic Beds. For the case of an isotropic bed with the bulk flow in the x-direction the hydrodynamic contribution obtained by evaluating Eq. 30 is

$$D^*_{xx} = \frac{171}{3{,}200} \pi^3 \frac{a^2}{k^{1/2}\phi} U, \tag{31a}$$

$$D^*_{yy} = D^*_{zz} = \frac{9}{6{,}400} \pi^3 \frac{a^2}{k^{1/2}\phi} U, \qquad |\mathcal{P}| \gg 1, \phi \ll 1. \tag{31b}$$

These expressions give the high $\mathcal{P}$ asymptotes in Figure 2.

Aligned Fibers. For a bed of fibers with their axes aligned in the z-direction, the mechanical contribution given by Eq. 30 is

$$D^*_{xx} = \frac{\pi}{8}\frac{a^2}{k_\perp^{1/2}\phi}U, \quad |\mathcal{P}| \gg 1, \phi \ll 1. \tag{32a}$$

$$D^*_{yy} = D^*_{zz} = 0, \tag{32b,c}$$

These expressions give the high $\mathcal{P}$ asymptotes in Figure 3. There is no hydrodynamic contribution to the effective diffusivity D^*_{zz} parallel to the fiber axes, because the z-component of the velocity is identically zero. Thus, Eq. 32c holds independent of ϕ and $\mathcal{P}$. The contribution D^*_{xx} to the parallel diffusivity differs only by a numerical coefficient from the contributions D^*_{xx}, D^*_{yy}, and D^*_{zz} to the effective diffusivity in the isotropic case. However, Eq. 30 gives no contribution to D^*_{yy}, the coefficient for diffusivity perpendicular to both the bulk flow and the fiber axes.

From Eqs. 29 and 30 it can be seen that at the level of approximation considered above, a fiber continues to dispersion only in the direction in which it exerts a drag on the fluid. In the case of circular fibers aligned perpendicular to the flow, the average drag on each fiber, $\langle f_\perp \rangle_0 = -\phi^{-1}k_\perp^{-1}\pi\mu a^2 \langle \boldsymbol{u} \rangle_0$, is antiparallel to the flow. As a result, there is no contribution to D^*_{yy} at the level of a one-fiber, purely mechanical analysis. Note that if the fibers were noncircular, or if they were not perfectly aligned, there would be a component of the drag in the y-direction and there would thus be a contribution to D^*_{yy} from the one-fiber, purely mechanical analysis above.

For perfectly aligned, circular fibers, however, the leading behavior of D^*_{yy} comes from considering the corrections to the purely mechanical concentration disturbance obtained by including the effects of molecular diffusion or fiber interactions, Eq. 23. The relative importance of diffusion and fiber interactions depends on the magnitude of the Peclet number.

For $[\phi/\ln \phi^{-1}]^{1/2} \ll |\boldsymbol{P}| \ll [\phi \ln \phi^{-1}]^{1/2}$ the diffusive correction gives the dominant contribution to D^*_{yy}. This correction may be obtained by expanding the concentration disturbance in inverse powers of $\mathcal{P}$,

$$\langle c' \rangle_1 = \langle c' \rangle_{1,0} + \mathcal{P}^{-1} \langle c' \rangle_{1,1} + \cdots$$

The first term $\langle c' \rangle_{1,0}$ is just Eq. 24, but the $O(\mathcal{P}^{-1})$ obtained by solving

$$\langle \boldsymbol{u} \rangle_1 \cdot \nabla \langle c' \rangle_{1,1} = \nabla^2 \langle c' \rangle_{1,0}, \tag{33}$$

does contribute to D^*_{yy}, giving

$$D^*_{yy} = \frac{1}{8}\frac{a^2}{k_\perp \phi} D_f, \quad \left[\frac{\phi}{\ln \phi^{-1}}\right]^{1/2} \ll |\boldsymbol{P}| \ll [\phi \ln \phi^{-1}]^{1/2} \tag{34}$$

Next, we turn to the corrections to Eq. 32b due to fiber interactions. We have noted that the null result $D^*_{yy} = 0$ in Eq. 32b arises because there is no component of the drag on the fiber in the y-direction at the level of the one-fiber problem in a bed of aligned fibers. One fiber's velocity disturbance, however, induces a drag on a second fiber that has a component in the y-direction, normal to the flow. Thus, the inclusion of fiber interactions in the analysis results in a purely mechanical contribution to the transverse diffusivity. These interactions enter the analysis through the previously neglected righthand side of mass conservation Eq. 7a, and through the two-fiber velocity-concentration correlations neglected in writing Eq. 5d as Eq. 5f. It may be shown by analogy to Koch and Brady (1985) that these contributions to D^*_{yy} are $O(Ua^4/k_\perp^{3/2}\phi^2) - O[Ua\phi^{-1/2}(\ln \phi^{-1})^{3/2}]$. Thus for $[\phi/\ln \phi^{-1}]^{1/2} \ll |\boldsymbol{P}| \ll [\phi \ln \phi^{-1}]^{1/2}$, the diffusively driven transverse diffusivity, Eq. 34, is dominant, while for $|\boldsymbol{P}| \gg [\phi \ln \phi^{-1}]^{1/2}$, D^*_{yy} is determined by fiber interactions.

A self-consistent renormalization, which takes account of these fiber interactions, involves using the same effective diffusivity $\boldsymbol{D}$ that we have calculated for the bulk diffusion problem in the equation for the concentration disturbance:

$$k^{1/2}\langle \boldsymbol{u} \rangle_1 \cdot \nabla_R \langle c' \rangle_1 - \nabla_R \cdot \boldsymbol{D} \cdot \nabla_R \langle c' \rangle_1 = -k\langle \boldsymbol{u}' \rangle_1 \cdot \nabla \langle c \rangle_0. \tag{35}$$

This self-consistent approximation does not fully account for all the effects of fiber interactions. It does, however, give the functional dependence of D^*_{yy} on ϕ, $k_\perp$, and $\boldsymbol{P}$, and it has a certain intuitive appeal. Equation 35 may be solved in a manner similar to our solution of Eq. 16 above. Here we expand $\langle c' \rangle_1$ in powers of $|\boldsymbol{D}|/\mathcal{P}$ rather than $\mathcal{P}^{-1}$. The transverse diffusivity obtained by substituting the solution of Eq. 35 into the expression for the convective flux Eq. 13, is

$$D^*_{yy} = \frac{1}{32}\frac{a^2}{k_\perp \phi} D_{xx} + \frac{3}{32}\frac{a^2}{k_\perp \phi} D_{yy}, \quad |\mathcal{P}| \gg 1. \tag{36}$$

Inserting Eq. 32a into Eq. 36 we obtain, to leading order in ϕ,

$$D^*_{yy} = \frac{1}{8}\frac{a^2}{k_\perp \phi} D_f + \frac{\pi}{256}\frac{a^4}{k_\perp^{3/2}\phi^2} U, \quad |\mathcal{P}| \gg 1, \tag{37}$$

which includes the diffusive correction, Eq. 34, and the anticipated $O(Ua^4/k_\perp^{3/2}\phi^2)$ mechanical dispersion term caused by interfiber interactions.

In the limit of high Peclet number all of the contributions to the effective diffusivity considered in this section grow linearly with the flow rate and are independent of molecular diffusion. This phenomenon is referred to as mechanical dispersion because it is caused by the stochastic velocity field alone, without need for a consideration of molecular diffusion. This mechanical dispersion mechanism adequately describes the dispersion that occurs in the bulk fluid between the fibers. As we shall see in the next section, however, this mechanism is not valid within and near the fibers.

Nonmechanical dispersion

The effects of the finite cross-sectional area of the fibers on the effective diffusivity are small in the volume fraction ϕ in a dilute bed. However, some of these effects grow faster with the Peclet number as $|\boldsymbol{P}| \rightarrow \infty$ than the $O[D_f|\boldsymbol{P}|(\phi^{-1} \ln \phi^{-1})^{1/2}]$ purely hydrodynamic, or mechanical, contributions obtained in the previous section.

These nonmechanical, finite-size effects arise when the mechanical dispersion mechanism examined above breaks down. This breakdown occurs when the concentration disturbance given by the purely mechanical mass conservation Eq. 23 is not finite. The three regions of the bed where this occurs are:

1. The interior of the fibers were $\langle \boldsymbol{u} \rangle_1 = 0$.

2. A boundary layer of fluid near the fiber surfaces where $\langle u \rangle_1 \rightarrow 0$ as one approaches the surfaces.

3. Any regions of closed streamlines where $\langle u \rangle_1 \neq 0$, but the integral of $\langle u \rangle_1$ over a circuit of a closed streamline is zero.

In each of these regions the stochastic velocity field alone is not sufficient to remove any solute and allow it to be convected downstream. As a result the contributions to dispersion arising from these regions do depend on molecular diffusion in the limit $P \rightarrow \infty$.

Holdup dispersion

When the tracer permeates the fibers, $1/m \neq 0$, the most important nonmechanical contribution to dispersion results from portions of the solute being retained in the fibers and held back against the bulk flow. The magnitude of this holdup dispersion contribution can be rationalized by a simple physical argument. In the limit of high Peclet number the resistance to mass transfer in the fluid is negligible compared to the diffusive resistance within the fiber. The residence time of a solute molecule in the fiber is the diffusive time scale for the fiber $t_{res} \sim (a^2/D_p)$. A solute molecule in the fluid has a velocity $|\langle u \rangle_0| = U$ relative to the solute in the fiber, so the distance by which the solute in the fibers is displaced from the solute in the fluid, i.e., its mean free path, is $\lambda \sim Ut_{res} \sim (a^2U/D_p)$. At any time the fraction of the solute in the fibers is $f_f \sim (1/m\phi)$. The resulting diffusive contribution is the product of the velocity, the mean free path, and the fraction of the solute being held back, $D^*_{h,xx} \sim f_f \lambda U \sim (a^2U^2/D_p)\,\phi\,(1/m)$.

The correct numerical coefficient for this holdup dispersion contribution is obtained by evaluating the portion of the convective dispersion integral from the interior of the fiber, Eq. 7, i.e.,

$$-\boldsymbol{D}^* \cdot \nabla \langle c \rangle_0 = \int_{\rho<a} de_1 d\rho \frac{\phi}{\pi a^2} P(e_1) \langle u' \rangle_1 \left[\langle c \rangle_1 - \frac{1}{m}(1+\gamma)\langle c \rangle_0 \right]. \quad (38)$$

Inside the fiber the conditionally averaged velocity $\langle u(\rho) \rangle_1 = 0$, so the velocity disturbance is $\langle u'(\rho) \rangle_1 = \langle u \rangle_1 - \langle u \rangle_0 = -\langle u \rangle_0$. Because the primary resistance to mass transfer is in the fiber, the conditionally averaged concentration field may be determined by solving Eq. 7 with the boundary condition

$$\langle c(\rho, t) \rangle_1 = \frac{1}{m}(1+\gamma)\langle c \rangle_0 = \frac{1}{m}(1+\gamma)^2 \nabla \langle c \rangle_0 \cdot \langle u \rangle_0 t \quad \text{at } \rho = a, \quad (39)$$

where we have used Eq. 6 and chosen $x = 0$. The boundary condition at the fiber surface is $(1/m)(1+\gamma)\langle c \rangle_0$, rather than simply $(1/m)\langle c \rangle_0$, because at high Peclet number a fiber sees the average fluid phase concentration, not the average bed concentration. Although $\langle c \rangle_0$ and $\langle c \rangle_1$ are time-dependent, the integrand of Eq. 38 is independent of time. Thus, the holdup dispersion contribution is time-dependent and is given by

$$D^*_{h,xx} = \frac{1}{8}(1+\gamma)^2 \frac{\phi a^2 U^2}{mD_p} \qquad |P| \gg 1. \quad (40a)$$

$$D^*_{h,yy} = D^*_{h,zz} = 0, \quad (40b, c)$$

This result applies to all fibrous beds independent of the orientation distribution $P(e_1)$. It is also valid independent of the volume fraction ϕ as long as the Peclet number is sufficiently high so that the primary resistance to mass transfer is internal diffusion within the fiber.

We have described holdup dispersion arising from the direct absorption of the solute into the solid fiber. If the fibers are made of a porous solid material, however, holdup dispersion may result from retention of the solute in the solvent-filled dead end pores in the fibers. The velocity of the fluid in these dead end pores is zero, and so the trapped fluid plays the same role as the solid in holding the solute back against the bulk flow. To determine the magnitude of this holdup dispersion we can use Eq. 40 with D_p replaced by an effective diffusivity for diffusion through fiber pores, and ϕ replaced by an appropriate measure of the relative amount of pore volume.

Boundary-layer dispersion

When the fibers are impermeable to the solute, $1/m = 0$, the holdup dispersion discussed above is absent. This simply means that solute cannot be dispersed by retention in the fibers when the fibers do not absorb the solute. In the heat transfer problem the equivalent criterion for the absence of holdup dispersion is that the volumetric heat capacity of the fibers is small compared to the heat capacity of the fluid.

Even when the fibers are impermeable there are nonmechanical contributions to the longitudinal diffusivity from regions of closed streamlines and from a boundary layer near the fiber. When the distance between two fibers is sufficiently small, we expect there to be regions of closed streamlines between them. [See Hasimoto and Sano (1980) for a discussion of separation and the formation of regions of closed streamlines for two bodies that are nearly in contact.] Closed streamlines are finite regions from which the solute can only escape by molecular diffusion. As a result, these regions are expected to give a holdup dispersion contribution similar to that discussed in the preceding section. Since this is a two-fiber effect, however, this closed streamline dispersion is expected to be $O(\phi^2 P^2)$.

At the level of the one-fiber problem there are no finite regions of closed streamlines or of stagnant fluid, but we shall see that the mechanical dispersion analysis still breaks down near the fiber surface, leading to a nonmechanical, $O(\phi P \ln P)$, boundary-layer dispersion contribution.

The purely mechanical mass conservation Eq. 23 reduces near the fiber to

$$-\frac{1}{2} y^2 \cos\theta \frac{\partial \langle c' \rangle_1}{\partial y} + y \sin\theta \frac{\partial \langle c' \rangle_1}{\partial \theta} = \frac{2\pi\mu}{|\langle f \rangle_0 - e_1(e_1 \cdot \langle f \rangle_0)|} \langle \mathbf{1} \rangle_0 \cdot \nabla \langle c \rangle_0, \quad (41)$$

where $y = (\rho/a) - 1 \ll 1$, ρ and θ are polar coordinates in the plane normal to the fiber, and $\theta = 0$ is the upstream direction. Equation 41 may be solved by the method of characteristics, giving

$$\langle c' \rangle_1 = \frac{2\pi\mu}{|\langle f \rangle_0 - e_1(e_1 \cdot \langle f \rangle_0)|} \cdot \langle \mathbf{1} \rangle_0 \cdot \nabla \langle c \rangle_0 \frac{1}{y \sin^{1/2}\theta} \int_{\theta'=0}^{\theta} \frac{d\theta'}{\sin^{1/2}\theta'}. \quad (42)$$

Substituting Eq. 42 into the portion of the convective flux integral, Eq. 7, in the boundary layer, the purely mechanical analysis gives

$$D^*_{xx,b\ell} = \frac{Ua\phi}{\pi}\int de_1\, d\theta\, dy P(e_1) \cdot \frac{2\pi\mu}{|\langle f\rangle_0 - e_1(e_1\cdot\langle f\rangle_0)|}\frac{1}{y\sin^{1/2}\theta}\int_{\theta'=0}^{\theta}\frac{d\theta'}{\sin^{1/2}\theta'}. \quad (43)$$

Aligned Bed. In a bed of aligned fibers $P(e_1) = \delta(\langle 1\rangle_0 \cdot e_1)$, and $\langle f\rangle_0 = f_\perp\langle 1\rangle_0$, so Eq. 43 reduces to

$$D^*_{xx,b\ell} = \frac{2Ua\phi}{\pi}\int_{\theta=0}^{\pi}\int_{y=0}^{\epsilon} d\theta\, dy \frac{2\pi\mu}{f_\perp} \cdot \frac{1}{y\sin^{1/2}\theta}\int_{\theta'=0}^{\theta}\frac{d\theta'}{\sin^{1/2}\theta'}. \quad (44)$$

The upper limit of $\epsilon \ll 1$ in the range of integration in y is introduced so that the integral is restricted to the region near the fiber where Eq. 41 is valid. The integral in Eq. 44 is only conditionally convergent as $y \to 0$, because the concentration disturbance becomes infinite at the surface $y = 0$. The problem is that close to the surface, $y \sim O(P^{-1/3})$, there is a boundary layer where diffusion must be taken into account even as $P \to \infty$. The equation for the concentration disturbance in this diffusive boundary layer is

$$-\frac{1}{2}Y^2\cos\theta\frac{\partial\langle c'\rangle_1}{\partial Y} + Y\sin\theta\frac{\partial\langle c'\rangle_1}{\partial\theta} - \frac{\partial^2\langle c'\rangle_1}{\partial Y^2} + O(P^{-1/3}) = P^{1/3}\frac{2\pi\mu}{|\langle f\rangle_0 - e_1(e_1\cdot\langle f\rangle_0)|}\langle 1\rangle_0\cdot\nabla\langle c\rangle_0, \quad (45)$$

where $Y = yP^{1/3}$. The leading effect of the boundary layer on the diffusivity can be determined without obtaining the full solution of Eq. 45, however. The correct $O[(\phi/\ln\phi^{-1})P\ln P)]$ contribution to the longitudinal diffusivity is obtained if we simply recognize that due to molecular diffusion the concentration disturbance does not become infinite as $y \to 0$, but approaches a finite, $O(P^{1/3})$ value. An approximate concentration disturbance that captures this effect is

$$\langle c'\rangle_{1,a} = \langle 1\rangle_0\cdot\nabla\langle c\rangle_0 \cdot \left(\frac{2\pi\mu}{|f_\perp|}\right)\min\left[\frac{1}{y\sin^{1/2}\theta}\int_{\theta'=0}^{\theta}\frac{d\theta'}{\sin^{1/2}\theta'},\ b_1P^{1/3}\right], \quad (46)$$

where b_1, is an $O(1)$ constant. Substituting Eq. 46 into the convective flux integral, the boundary-layer contribution to the longitudinal diffusivity is

$$D^*_{xx,b\ell} = \frac{1}{3}\left[B\left(\frac{1}{4},\frac{1}{4}\right)\right]^2\frac{\mu}{|f_\perp|}\phi|P|\ln|P| + O\left(\frac{\phi}{\ln\phi^{-1}}P\right) = 18.33\frac{\mu}{|f_\perp|}\phi|P|\ln|P| + O\left(\frac{\phi}{\ln\phi^{-1}}P\right), \quad (47)$$

where $B(1/4, 1/4)$ is the Beta function. Note that the $O(\phi/|f_\perp|P\ln P)$ term in Eq. 47 is independent of b_1, indicating that the exact form of the concentration disturbance in the boundary layer does not affect the leading behavior of $D^*_{xx,b\ell}$.

Isotropic Bed. In an isotropic bed $P(e_1) = 1/4\pi$ and $|\langle f\rangle_0 - e_1(e_1\cdot\langle f\rangle_0)| = (1-\cos\omega)f_\perp$, where ω is the angle between e_1 and $\langle 1\rangle_0$, so Eq. 43 reduces to

$$D^*_{xx,b\ell} = \frac{2Ua\phi}{\pi}\int_{\omega=0}^{\pi/2} d\omega\frac{\sin\omega}{4}\frac{2\pi\mu}{|f_\perp|(1-\cos\omega)} \int_{\theta=0}^{\pi}\int_{y=0}^{\epsilon} d\theta dy\frac{1}{y\sin^{1/2}\theta}\int_{\theta'=0}^{\theta}\frac{d\theta'}{\sin^{1/2}\theta'} \quad (48)$$

Equation 48 fails to converge not only near the fiber surface, $y \to 0$, but also for fibers that are nearly parallel to the flow, $\cos\omega \to 1$. In this case the strength of the convective field normal to the fiber is $O[(1/\mu)Uy|f_\perp|(1-\cos\omega)]$, so the boundary-layer thickness is $O\{[(1/\mu)|f_\perp|(1-\cos\omega)P]^{-1/3}\}$, and the concentration disturbance in the boundary layer is $O\{[(1/\mu)|f_\perp|(1-\cos\omega)P]^{1/3}\}$. Thus, for fibers that are nearly parallel to the flow the boundary-layer thickness and the concentration disturbance both become larger than in an aligned bed. However, the concentration disturbance cannot grow larger than $O(P)$, the value that holds when the solute is transported away from the fiber by molecular diffusion alone. The approximate concentration disturbance in the isotropic case is thus

$$\langle c'\rangle_{1,a} = \langle 1\rangle_0\cdot\nabla\langle c\rangle_0\min\left[\frac{2\pi\mu}{|f_\perp|(1-\cos\omega)}\frac{1}{y\sin^{1/2}\theta} \cdot \int_{\theta'=0}^{\theta}\frac{d\theta'}{\sin^{1/2}\theta'},\ b_2\left(\frac{\mu P}{|f_\perp|(1-\cos\omega)}\right)^{1/3},\ b_3P\right]. \quad (49)$$

Substituting Eq. 49 into the convective flux integral in the boundary layer gives

$$D^*_{xx,b\ell} = \frac{1}{3}\left[B\left(\frac{1}{4},\frac{1}{4}\right)\right]^2\phi\frac{\mu}{|f_\perp|}|P|[\ln|P|]^2 + O\left(\frac{\phi P\ln P}{\ln\phi^{-1}}\right), = 18.33\,\phi\frac{\mu}{|f_\perp|}|P|[\ln|P|]^2, \quad (50)$$

where the leading $O(\phi P[\ln P]^2/\ln\phi^{-1})$ term comes from the thick boundary layers of the fibers that are nearly parallel to the flow.

The linearity of the mass conservation equation allows us to superimpose the solutions from the holdup and boundary-layer dispersion sections above, so the corresponding nonmechanical effects are additive to leading order.

Discussion

We have applied ensemble-averaging techniques to the basic conservation equations in a fibrous medium to derive a macroscopic mass conservation equation. In the limit of long times for slowly varying bulk concentration fields, this averaged mass conservation equation was shown to take the form of a macroscopic version of Fick's law with a time- and space-independent effective diffusivity. We presented a procedure by which the leading effect of the fibers on the effective diffusivity could be determined in a homogeneous fibrous material with any orientation distribution.

Specific results were calculated for the isotropic case and for

Table 1. **Leading Behavior of the Effective Diffusivity in an Isotropic Bed for all Values of Peclet Number**

Flow Regime	Isotropic Bed (Flow in x-direction)	
	D_{xx}	$D_{yy} = D_{zz}$
$P \equiv 0$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + \frac{1}{3}\phi\frac{(\alpha-1)(\alpha+5)}{\alpha+1}\right\}$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + \frac{1}{3}\frac{(\alpha-1)(\alpha+5)}{\alpha+1}\right\}$
$\lvert\mathcal{P}\rvert \ll 1, \lvert P\rvert \ll \left[\frac{\phi}{\ln\frac{1}{\phi}}\right]^{1/2}$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + \frac{1}{3}\phi\frac{(\alpha-1)(\alpha+5)}{\alpha+1} + \frac{9}{25}\pi\frac{a^2}{k\phi}\mathcal{P}^2\left[\frac{19}{30}\ln\frac{1}{\lvert\mathcal{P}\rvert} + \frac{599}{900}\right]\right\}$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + \frac{1}{3}\phi\frac{(\alpha-1)(\alpha+5)}{\alpha+1} + \frac{9}{25}\pi\frac{a^2}{k\phi}\mathcal{P}^2\left[\frac{1}{10}\ln\frac{1}{\lvert\mathcal{P}\rvert} - \frac{137}{900}\right]\right\}$
$\lvert\mathcal{P}\rvert \sim 0(1), \lvert P\rvert \ll \left[\phi\ln\frac{1}{\phi}\right]^{1/2}$	D^*_{xx} (given by Fig. 2) + $D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + \frac{1}{3}\phi\frac{(\alpha-1)(\alpha+5)}{\alpha+1}\right\}$	D^*_{yy} (given by Fig. 2) + $D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + \frac{1}{3}\phi\frac{(\alpha-1)(\alpha+5)}{\alpha+1}\right\}$
$\lvert\mathcal{P}\rvert \gg 1$, $\left[\frac{\phi}{\ln\frac{1}{\phi}}\right]^{1/2} \ll \lvert P\rvert \ll \frac{1}{\phi^{3/2}\left(\ln\frac{1}{\phi}\right)^{1/2}}$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + \frac{171}{3{,}200}\pi^3\frac{a^2}{k\phi}\lvert\mathcal{P}\rvert\right\}$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + \frac{9}{6{,}400}\pi^3\frac{a^2}{k\phi}\lvert\mathcal{P}\rvert\right\}$
$\lvert P\rvert \gg 1$	$D_f\left\{\frac{171}{3{,}200}\pi^3\frac{a}{k^{1/2}\phi}\lvert P\rvert + \frac{1}{8}\phi\frac{D_f}{mD_p}P^2 + 4.862\frac{\phi^2a^2}{k}\lvert P\rvert[\ln\lvert P\rvert]^2\right\}$	$D_f\left\{\frac{9}{6{,}400}\pi^3\frac{a}{k^{1/2}\phi}\lvert P\rvert\right\}$

$k^{1/2}$, screening length in an isotropic bed, is given by Eq. A3, more accurately by Eq. A2.
$\mathcal{P} = Pk^{1/2}$ is screening length Peclet number in an isotropic bed.

a bed of fibers with their axes aligned perpendicular to the bulk flow, and these are summarized in Tables 1 and 2. In the absence of flow (first row in the tables) the fibers have a small effect on mass transfer because the diffusivity of the tracer in the fibers is different from that in the fluid.

In the presence of convection there is a hydrodynamic contribution to the effective diffusivity (second through fourth rows of the tables) that results from the stochastic velocity field induced by the randomly distributed fibers. This hydrodynamic contribution is larger than one might have expected, and may actually increase with decreasing volume fraction, because each fiber enhances mass transfer in a large cylindrical volume with a radius comparable to the Brinkman screening length $k^{1/2} \sim O[(\phi^{-1}\ln\phi^{-1})^{1/2}]$. This hydrodynamic dispersion is more important than the difference in the molecular diffusivities for all $\lvert P\rvert \gg \phi$. When the Peclet number based on the screening length, $\mathcal{P}$, is large the hydrodynamic dispersion occurs primarily in a convection-dominated region far from the fiber, even though the fiber Peclet number P may still be small. For sufficiently large Peclet numbers the hydrodynamic dispersion mechanism is independent of molecular diffusion, a phenomenon known as mechanical dispersion.

This purely mechanical analysis breaks down, however, in regions of the bed where the solute cannot escape by convection alone even at high flow rates. Such regions include the interior of fibers, the boundary layer near the fibers, and regions of closed streamlines. The solute can escape these regions only with the aid of molecular diffusion, leading to nonmechanical contributions to the longitudinal dispersion, i.e., contributions that depend on molecular diffusion even at high Peclet numbers. These nonmechanical contributions dominate the behavior of the longitudinal diffusivity at sufficiently high Peclet numbers (row five of the tables).

The overall effective diffusivity in an isotropic bed is illustrated in Figure 4 for the case $\phi = 0.02$, $1/m = 0$ (impermeable fibers), and $\phi = 0.02$, $1/m = 1$, $D_f/D_p = 1$ (permeable fibers). At low Peclet numbers the only effect of the fibers on dispersion is a slight 3.3% decrease in the diffusivity in the impermeable case. This decrease cannot be detected on the scale used in Figure 4. At Peclet numbers of 0.1–10 the hydrodynamic dispersion becomes important and the effective diffusivity begins to increase. At moderately high Peclet numbers (10–1,000) hydrodynamic and boundary-layer dispersion control the longitudinal diffusivity, which grows slightly faster than linearly with the Peclet number. At very high Peclet numbers (over 1,000) holdup dispersion becomes important if the fibers are permeable or porous and the longitudinal diffusivity grows as P^2. At some still higher value of the Peclet number we would expect dispersion due to closed streamlines to affect the longitudinal diffusivity in a bed of impermeable particles, making $D_\parallel$ also grow as P^2. This $O(\phi^2P^2)$ closed-streamline contribution is not included in Figure 4 because of the uncertainty in its numerical coefficient. The transverse diffusivity is unaffected by nonmechanical effects and grows linearly with P for all $P \geqq 100$.

Table 2. Leading Behavior of the Effective Diffusivity in a Bed of Aligned Fibers for all Values of Peclet Number

Flow Regime	Fibers Aligned in z-direction (Flow in x-direction) D_{xx}	D_{yy}	D_{zz}
$P \equiv 0$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + 2\phi\left(\frac{\alpha-1}{\alpha+1}\right)\right\}$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + 2\phi\left(\frac{\alpha-1}{\alpha+1}\right)\right\}$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + \phi(\alpha-1)\right\}$
$\lvert\mathcal{P}_\perp\rvert \ll 1, \lvert P\rvert \ll \left[\frac{\phi}{\ln\frac{1}{\phi}}\right]^{1/2}$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + 2\phi\left(\frac{\alpha-1}{\alpha+1}\right) + \frac{a^2}{k_\perp\phi}\mathcal{P}_\perp^2\left[\frac{3}{16}\ln\frac{2}{\lvert\mathcal{P}_\perp\rvert} + \frac{3}{64}\right]\right\}$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + 2\phi\left(\frac{\alpha-1}{\alpha+1}\right) + \frac{a^2}{k_\perp\phi}\mathcal{P}_\perp^2\left[\frac{1}{16}\ln\frac{2}{\lvert\mathcal{P}_\perp\rvert} - \frac{3}{64}\right]\right\}$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + \phi(\alpha-1)\right\}$
$\lvert\mathcal{P}_\perp\rvert \sim 0(1), \lvert P\rvert \ll \left[\phi\ln\frac{1}{\phi}\right]^{1/2}$	D^*_{xx} (given by Fig. 3) + $D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + 2\phi\left(\frac{\alpha-1}{\alpha+1}\right)\right\}$	D^*_{yy} (given by Fig. 3) + $D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + 2\phi\left(\frac{\alpha-1}{\alpha+1}\right)\right\}$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + \phi(\alpha-1)\right\}$
$\lvert\mathcal{P}_\perp\rvert \gg 1$, $\left[\frac{\phi}{\ln\frac{1}{\phi}}\right]^{1/2} \ll \lvert P\rvert \ll \frac{1}{\phi^{3/2}\left(\ln\frac{1}{\phi}\right)^{1/2}}$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + \frac{\pi}{8}\frac{a^2}{k_\perp\phi}\lvert\mathcal{P}_\perp\rvert\right\}$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + \frac{1}{8}\frac{a^2}{k_\perp\phi} + \frac{\pi}{256}\frac{a^4}{k_\perp^2\phi}\lvert\mathcal{P}_\perp\rvert\right\}$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + \phi(\alpha-1)\right\}$
$\lvert P\rvert \gg 1$	$D_f\left\{\frac{\pi}{8}\frac{a}{k_\perp^{1/2}\phi}\lvert P\rvert + \frac{1}{8}\phi\frac{D_f}{mD_p}P^2 + 5.835\frac{\phi_2 a^2}{k_\perp}\lvert P\rvert\ln\lvert P\rvert\right\}$	$D_f\left\{\frac{1}{256}\frac{a^3}{k_\perp^{3/2}\phi}\lvert P\rvert\right\}$	$D_f\left\{\frac{1}{1-\phi-\phi m^{-1}} + \phi(\alpha-1)\right\}$

$k_\perp^{1/2}$, screening length for flow perpendicular to the axes of aligned fibers, is given by Eq. A5a, more accurately by Eq. A5b.
$\mathcal{P}_\perp = Pk_\perp^{1/2}$ is screening length Peclet number in an aligned bed.

The effective diffusivities derived herein describe dispersion only in the longtime limit. We have noted that the hydrodynamic dispersion contributions to the effective diffusivity grow with decreasing fiber volume fraction, but the characteristic time, $a/U\phi^{1/2}$, required to reach this longterm diffusive behavior also grows with decreasing ϕ. The nonmechanical dispersion mechanisms discussed above have characteristic times that do not scale with ϕ, but that do scale with the Peclet number. The characteristic time for boundary-layer dispersion is the diffusive time in the boundary layer, $a^2P^{-2/3}/D_f = aP^{1/3}/U$, while the characteristic time for holdup dispersion is $a^2/D_p = (aP/U)(D_p/D_f)$. At high Peclet number when these nonmechanical dispersion mechanisms are most important, the time required for them to reach their asymptotic diffusive behavior is large. Thus, in applying the results obtained here it is important to allow sufficient time for the asymptotic limits to be achieved.

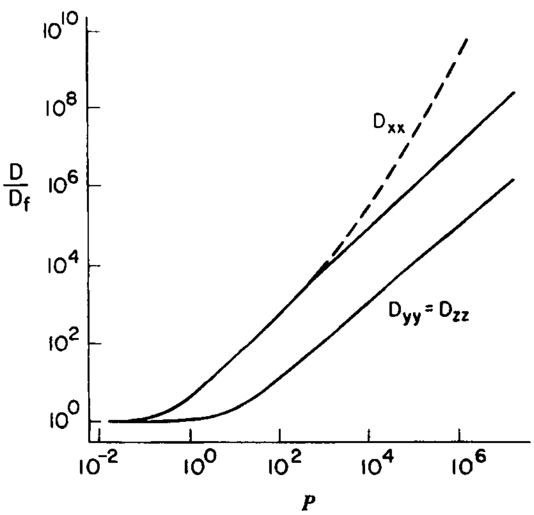

Figure 4. Ratio of effective diffusivity D to the molecular diffusivity D_f plotted as a function of Peclet number P for an isotropic bed.
—, impermeable; ---, permeable.

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Notation

- a = fiber radius
- $B(\ ,\ )$ = Beta function
- $c(x, t)$ = concentration of the tracer
- $D(x)$ = molecular diffusivity of the tracer at position x, a generalized function that takes on the value D_p in the fibers and D_f in the fluid
- $(D/M)(x)$ = mass conductivity, a generalized function that takes on the value D_f in the fluid and D_p/m in the solid
- $\boldsymbol{D}$ = effective diffusivity tensor
- $\boldsymbol{D}^m$ = $D_f\boldsymbol{I}$, contribution to $\boldsymbol{D}$ from the molecular diffusivity in the fluid
- $\boldsymbol{D}^\alpha$ = pure conduction contribution to $\boldsymbol{D}$ resulting from the difference in the molecular diffusivity of the tracer in the fibers and in the fluid

D^* = contribution to D from the correlation of the velocity and concentration disturbances induced by the fibers
D_h^* = holdup dispersion contribution to D^*
D_{bl}^* = boundary-layer contribution to D^*
D_f = molecular diffusivity of the tracer in the fluid
D_p = molecular diffusivity of the tracer in the fibers
D_{xx} = component of D relating the flux in the x-direction to the concentration gradient in the x-direction
e_1 = unit vector indicating the orientation of a fiber
f = drag on a fiber per unit length
f_f = fraction of the tracer held in the fibers
$f_\perp$ = component of drag perpendicular to fiber axis
I = identity tensor
k^{-1} = resistivity tensor
k = scalar permeability for an isotropic bed
$k^{1/2}$ = square root of the permeability, known as the Brinkman screening length
$k_\perp^{-1}$ = component of the resistivity tensor k^{-1} for flow perpendicular to aligned fibers
m = ratio of the solubility of the tracer in the fluid to the solubility in the fiber
$M(x)$ = activity coefficient of the solute, a generalized function that takes on the value 1 in the fluid and m in the solid.
n = unit normal pointing outward (into the fluid) on the fiber surface
P = Ua/D_f, Peclet number based on fiber radius a, diffusivity in the fluid D_f, and average velocity U
$\mathcal{P}$ = $Uk^{1/2}/D_f$, Peclet number based on Brinkman screening length $k^{1/2}$
$P(r_1, e_1)$ = probability density of fibers at position r_1 with orientation e_1
$P(e_1)$ = probability density of fibers of orientation e_1
q = mass flux
r = point through which a fiber axis passes
R = radial position relative to fiber axis scaled with the Brinkman screening length $k^{1/2}$, i.e., $R = \rho k^{-1/2}$
S_0 = $(9/25)(a^2/\phi k)$, a scale factor for D^*
S_1 = $\pi(a^2/\phi k_\perp)$, a scale factor for D^*
s = plane normal to fiber axis, Figure 1
t = time
t_{res} = average residence time for a tracer element in a fiber
$u(x)$ = fluid velocity
x = position in the bed
X, Y = Cartesian coordinates for the scale radial position R

Greek letters

α = D_p/mD_f
γ = fractional change in bulk convective term induced by the fibers
λ = mean free path of tracer in holdup dispersion, i.e., distance that the tracer in the fluid traverses while a tracer element is held in one fiber
μ = fluid viscosity
η = Fourier transform variable corresponding to Y
θ = angular coordinate
ξ = Fourier transform variable corresponding to R
ρ = two-dimensional variable for the position relative to the fiber axis, defined in a plane normal to the fiber axis
ϕ = volume fraction of fibers (equals areal fraction in disordered beds)
ω = angle between flow direction $\langle 1\rangle_0$ and fiber axis e_1

Special Expressions

$\langle(x,t)\rangle_0$ = ensemble average evaluated at position x and time t
$\langle(x,t|r_1,e_1)\rangle_1$ = ensemble average at x and t conditioned on the presence of a fiber of orientation e_1 at position r_1
$\langle'(x,t|r_1,e_1)\rangle_1$ = conditionally averaged disturbance caused by a fiber $\langle(x,t|r_1,e_1)\rangle_1 - \langle(x,t)\rangle_0$
$\langle 1\rangle_0$ = unit vector in the direction of the bulk flow $\langle u\rangle_0$
$\hat{}$ = Fourier transform
$\delta(\ )$ = Delta function

Appendix: Hydrodynamic Resistivity of Fibrous Media (Spielman and Gorin, 1968)

Isotropic media

The drag on a fiber in an isotropic medium may be written

$$\langle f(r_1, e_1)\rangle_0 = e_1(e_1 \cdot \langle u\rangle_0)f_\parallel + (I - e_1e_1)\cdot\langle u\rangle_0 f_\perp, \quad \text{(A1a)}$$

where

$$f_\perp = -4\pi\mu\left[ak^{-1/2}\frac{K_1(ak^{-1/2})}{K_0(ak^{-1/2})} + \frac{1}{2}a^2k^{-1}\right], \quad \text{(A1b)}$$

$$f_\parallel = -2\pi\mu ak^{-1/2}\frac{K_1(ak^{-1/2})}{K_0(ak^{-1/2})}, \quad \text{(A1c)}$$

and $K_0(x)$ and $K_1(x)$ are the modified Bessel functions or order zero and one. The resistitivy is $k^{-1} = Ik^{-1}$, where

$$k^{-1} = -\frac{\phi}{\pi a^2\mu}\left[\frac{2}{3}f_\perp + \frac{1}{3}f_\parallel\right] + O\left(\frac{\phi}{a^2\left(\ln\frac{1}{\phi}\right)^2}\right), \quad \text{(A2)}$$

and $f_\parallel$ and $f_\perp$ are given by Eqs. A1b, c. In the limit of low volume fraction ϕ or high permeability k, this reduces to

$$k^{-1} = \frac{20}{3a^2}\frac{\phi}{\ln\frac{1}{\phi}} + O\left(\frac{\phi\ln\left[\ln\frac{1}{\phi}\right]}{a^2\left[\ln\frac{1}{\phi}\right]}\right). \quad \text{(A3)}$$

Note that the errors in the explicit expression A3 are larger than those in the implicit expression A2 for the permeability k. The size of the error in Eq. A2, which results from the neglected fiber-interaction terms on the righthand side of Eq. 8b is not given by Spielman and Goren (1968), but may easily be determined through an analysis analogous to that performed by Hinch (1977) for fixed beds of spheres.

Aligned fibers

The resistivity resulting from flow through an array of fibers whose positions are randomly distributed, but whose axes are aligned with the z-axis is

$$k^{-1} = k_\perp^{-1/2}(\hat{x}\hat{x} + \hat{y}\hat{y}) + k_\parallel^{-1}\hat{z}\hat{z}, \quad \text{(A4a)}$$

where $\hat{x}$, $\hat{y}$, and $\hat{z}$ are unit vectors in the x, y, and z directions and

$$k_\perp^{-1} = \frac{4\phi}{a^2}\left[ak_\perp^{-1/2}\frac{K_1(ak_\perp^{-1/2})}{K_0(ak_\perp^{-1/2})} + \frac{1}{2}a^2k_\perp^{-1}\right], \quad \text{(A4b)}$$

$$k_\parallel^{-1} = \frac{2\phi}{a^2}\left[ak_\parallel^{-1/2}\frac{K_1(ak_\parallel^{-1/2})}{K_0(ak_\parallel^{-1/2})}\right]. \quad \text{(A4c)}$$

In the limit of low ϕ or high $k_\parallel$, $k_\perp$, Eqs. A4b, c reduce to

$$k_\perp^{-1} = \frac{8\phi}{a^2\ln\frac{1}{\phi}}, \quad \text{(A5a)}$$

and

$$k_{\mathrm{I}}^{-1} = \frac{4\phi}{a^2 \ln \frac{1}{\phi}}. \tag{A5b}$$

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