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Dispersion in fixed beds

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A macroscopic equation of mass conservation is obtained by ensemble-averaging the basic conservation laws in a porous medium. In the long-time limit this 'macrotransport' equation takes the form of a macroscopic Fick's law with a constant effective diffusivity tensor. An asymptotic analysis in low volume fraction of the effective diffusivity in a bed of fixed spheres is carried out for all values of the Péclet number $\mathbb{P} = Ua/D_{\mathrm{f}}$, where U is the average velocity through the bed, a is the particle radius and D_{f} is the molecular diffusivity of the solute in the fluid. Several physical mechanisms causing dispersion are revealed by this analysis. The stochastic velocity fluctuations induced in the fluid by the randomly positioned bed particles give rise to a convectively driven contribution to dispersion. At high Péclet numbers, this convective dispersion mechanism is purely mechanical, and the resulting effective diffusivities are independent of molecular diffusion and grow linearly with $\mathbb{P}$. The region of zero velocity in and near the bed particles gives rise to non-mechanical dispersion mechanisms that dominate the longitudinal diffusivity at very high Péclet numbers. One such mechanism involves the retention of the diffusing species in permeable particles, from which it can escape only by molecular diffusion, leading to a diffusion coefficient that grows as $\mathbb{P}^2$. Even if the bed particles are impermeable, non-mechanical contributions that grow as $\mathbb{P}\ln\mathbb{P}$ and $\mathbb{P}^2$ at high $\mathbb{P}$ arise from a diffusive boundary layer near the solid surfaces and from regions of closed streamlines respectively. The results for the longitudinal and transverse effective diffusivities as functions of the Péclet number are summarized in tabular form in §6. Because the same physical mechanisms promote dispersion in dilute and dense fixed beds, the predicted Péclet-number dependences of the effective diffusivities are applicable to all porous media. The theoretical predictions are compared with experiments in densely packed beds of impermeable particles, and the agreement is shown to be remarkably good.

1. 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. The 'microscopic' transfer of heat and mass in each phase (solid and fluid) of these materials may often be described by Fourier's and Fick's laws. The primary interest, however, is not the detailed microscopic processes, but rather the 'macrotransport', i.e. transfer on a lengthscale larger than that of the detailed microstructure of the porous medium. Previous work on macrotransport in the absence of convection has focused primarily on the heat-transfer problem, while work in the presence of convection has dealt with mass transfer. As a matter of convenience, we shall speak principally in terms of the mass-transfer problem; the heat-transfer results may be obtained by analogy, as we show in §2.

In the absence of convection in an isotropic medium the effective thermal conductivity is a scalar which depends on the molecular thermal conductivities in the fluid and particulate phases, as well as on the distribution of the included particles (Batchelor 1974). Maxwell (1873) determined the first effect of spherical inclusions of different conductivity on the effective conductivity in a dilute, *stagnant* suspension. Jeffrey (1973) extended these results by calculating the effect of particle interactions on the conductivity for randomly distributed particles.

Although only strictly valid in the limit of low particle volume fraction, the results of Maxwell and Jeffrey provide a good estimate of the effective conductivity of more concentrated systems unless the particles are nearly close-packed or the conductivity of the particles is large compared with that of the continuous phase. The effective conductivity of very densely packed suspensions may be estimated by studying periodic arrays of particles (see e.g. Sangani & Acrivos 1983). The case in which the conductivity of the particles greatly exceeds that of the continuous phase is particularly important, because the effective conductivity may be significantly larger than the conductivity of the continuous phase. Batchelor & O'Brien (1977) addressed this case through an asymptotic analysis for $k_p/k_f \gg 1$ and $\phi/\phi_{max}-1 \ll 1$, where ϕ is the volume fraction of the included particles, ϕ_{max} is the volume fraction at closest packing, and k_p and k_f are the respective thermal conductivities of the particulate and continuous phases. Thus, good estimates of the effective conductivity may be obtained at all values of the volume fraction. All of these studies, however, are valid only in the absence of convection.

Brenner (1980) developed a general theory for determining the transport properties in spatially periodic porous media in the presence of convection, and showed that in the limit of long times the dispersion of a tracer particle is diffusive, i.e. the mean-square displacement grows linearly with time. Carbonell & Whitaker (1983) presented a volume-average approach for calculating the effective diffusivity, and carried out specific calculations for a two-dimensional spatially periodic porous medium (Eidsath *et al.* 1983). The longitudinal diffusivities (describing dispersion in the direction of the bulk flow) calculated numerically by Eidsath *et al.* are in reasonable agreement with the experiments of Gunn & Pryce (1969) for a periodic cubic array of spheres. It should be noted, however, that theoretical considerations of the relationship between Taylor dispersion and dispersion in spatially periodic porous media (Brenner 1980) suggest a stronger $\mathbb{P}^2$ dependence of the longitudinal diffusivity on the Péclet number than the $\mathbb{P}^{1.7}$ dependence found by Eidsath *et al.* Here the Péclet number is defined as $\mathbb{P} = Ua/D_f$, where U is the average velocity through the bed, a is a characteristic size of the particles or grains in the porous medium and D_f is the molecular diffusivity of the tracer in the fluid.

The overwhelming body of experimental data on dispersion in packed beds and porous media (Fried & Combarnous 1971) that are *not* spatially periodic shows, however, that both the longitudinal and transverse effective diffusivities grow approximately as $\mathbb{P}$ at high Péclet number. The longitudinal diffusivities calculated by Eidsath *et al.* for periodic media show a Péclet-number dependence that is too strong, while their transverse diffusivities are much lower and have a weaker Péclet-number dependence than experiment. Thus, while there is good agreement between theory and experiment for spatially periodic porous media, the theory of dispersion in such media does not correctly model the Péclet-number dependence of the effective diffusivity in the 'random' media that are commonly encountered in practice.

These observations suggest a fundamental difference between the mechanisms for dispersion in periodic and random porous media. In dimensional terms the experimentally observed diffusivities at high Péclet numbers in random media are roughly proportional to Ua and independent of the molecular diffusivity D_f. This suggests that at high $\mathbb{P}$ in a random medium the dispersion mechanism depends only on the stochastic velocity field in the medium and does not involve molecular diffusion; a phenomenon known as mechanical dispersion. In contrast, the random element introduced by molecular diffusion is required in the theory of dispersion in periodic porous media (at least for flow parallel to a line contained in a plane of symmetry) in order that a tracer particle should sample all points in the unit cell and in order that the dispersion be diffusive. The stochastic element in the distribution of pores or of particles in a random porous medium introduces an alternative mechanism by which a tracer may sample all positions with respect to the bed microstructure.

Note, however, that it is not necessarily true that an arbitrary stochastic velocity field leads to mechanical dispersion, i.e. a true diffusive behaviour independent of molecular diffusion. Kesten & Papanicolaou (1979) have demonstrated that mechanical dispersion *is* obtained for any incompressible velocity field in the limit as the magnitude of the fluctuating portion of the velocity becomes small compared with its average. We shall see, however, that, if a stochastic velocity field contains regions of zero velocity or regions of closed streamlines, there is no purely hydrodynamic mechanism by which a tracer injected into these regions can reach the rest of the microstructural space, and the dispersion depends on molecular diffusion even in the limit of high Péclet number. An example of such behaviour is the 'holdup' dispersion examined in §5.

Saffman (1959) modelled the microstructure of a porous medium as a network of capillary tubes of random orientation. At high Péclet number and at very long time, Saffman found that the dispersion never becomes truly mechanical, the effective diffusivity growing as $\mathbb{P} \ln \mathbb{P}$. The logarithmic dependence results from the zero velocity of the fluid at the capillary walls. The time required for a tracer particle to leave a capillary would become infinite as its distance from the walls goes to zero, if molecular diffusion did not allow the tracer to escape the region of low velocity near the wall. This phenomenon is similar to the 'holdup' dispersion mentioned above, although in this case there is no finite region of zero velocity.

A capillary network may provide a reasonable model for consolidated porous media – media in which the solid phase is continuous. In this paper we model the microstructure of the porous medium as a bed of fixed particles – an unconsolidated medium in which the solid phase is discrete. Unconsolidated media are common in the form of packed beds and sandstone formations, and this model provides an alternate approach to the study of dispersion.

Our interest is in heat and mass transfer through a bed of particles whose positions are held fixed at randomly distributed points in the bed, when the average velocity U through the bed is constant. We shall approach the problem through an asymptotic analysis, determining the leading effect of the particles at low particle volume fraction (or, equivalently, at high permeability) on the dispersive behaviour of the bed for all values of the Péclet number. It will be seen that this particle-induced dispersion is truly diffusive, i.e. the effective diffusivity defined as the ratio of the ensemble-average mass flux to the average concentration gradient is a time- and space-independent constant in the limit of long times for slowly varying average concentration fields. The asymptotic analysis will enable us to elucidate the fundamental physical mechanisms causing dispersion and to predict the dependence of the diffusivity on the Péclet number even in porous media that do not satisfy the low-volume-fraction restriction.

In §2 we present the microscopic transport equations and the averaging procedure used to derive the macrotransport equations and the definition of the effective diffusivity. In §3 we obtain the first effect of the velocity disturbance induced by the particles on mass transfer at low Péclet number $\mathbb{P}$ based on the particle radius. We shall see that the use of the Stokes velocity disturbance for flow past an *isolated* sphere leads to a non-convergent expression for the effective diffusivity. This difficulty is overcome when the momentum-conservation equation is renormalized to obtain Brinkman's equation for viscous flow through a porous medium. In a dilute, highly permeable bed the Brinkman velocity disturbance is the same as the Stokes velocity disturbance near the particle, but it becomes screened at a large distance $k^{\frac{1}{2}} = O(\phi^{-\frac{1}{2}}a)$ known as the Brinkman screening length, where k is the permeability and ϕ is the solid's volume fraction. This screening phenomenon enables us to formulate a convergent one-particle convection–diffusion problem. The observation that each particle's contribution to macrotransport extends over a large $O(k^{\frac{3}{2}})$ volume leads to several important simplifications in the analysis, including the use of a point-particle approximation. It will be seen that the Péclet number $\mathscr{P} = Uk^{\frac{1}{2}}/D_{\mathrm{f}}$ based on the Brinkman screening length $k^{\frac{1}{2}}$ is the appropriate parameter for determining whether convection or conduction (molecular diffusion) is dominant in the $O(k^{\frac{3}{2}})$ volume that contributes to the effective diffusivity. In §4 we examine the purely mechanical dispersion that occurs at high $\mathscr{P}$, developing a dispersion mechanism based on the stochastic velocity field alone and obtaining a contribution to the diffusivity that grows like $\mathbb{P}$.

This purely mechanical analysis breaks down, however, in the region of zero velocity inside the particles, giving rise to 'holdup' dispersion, which does depend on molecular diffusion even in the limit of high Péclet numbers. Although holdup dispersion occurs only in the volume ϕ within the particles, it is important at high Péclet numbers because of its strong $\mathbb{P}^2$ dependence. If the fixed particles are impermeable to the tracer, this holdup dispersion contribution is absent. However, even for such impermeable particles there is an $O(\phi \mathbb{P} \ln \mathbb{P})$ non-mechanical dispersion contribution, similar to that obtained by Saffman, arising from the zero fluid velocity at the particle surfaces. These non-mechanical holdup dispersion results are derived in §5.

The results of the asymptotic analysis are summarized in tabular form in §6 and are compared with the available experimental data for transverse and longitudinal diffusion in beds of impermeable particles. The agreement with experiment is shown to be excellent.

2. Macrotransport equations

We are interested in mass transfer through a monodisperse, random bed of fixed spheres of radii a in the presence of a bulk convective motion. The particle Reynolds number is assumed small so that the inertial terms in the momentum conservation equation may be neglected, and the concentration of the diffusing species or solute is assumed sufficiently small so that Fick's law describes the conservation of mass. The equations of motion for the steady velocity $\boldsymbol{u}$ and pressure p fields are the well-known Stokes equations

$$\nabla \cdot \boldsymbol{u} = 0, \quad -\nabla p + \mu \nabla^2 \boldsymbol{u} = 0, \qquad (2.1\,a,b)$$

where μ is the fluid viscosity. Equations (2.1 *a, b*) are valid for any point lying in the fluid, while within the fixed particles

$$\boldsymbol{u} = 0, \tag{2.1c}$$

and the pressure is indeterminate. The no-slip condition requires the fluid velocity to be zero on the particle surfaces. The average or bulk velocity through the bed will be denoted by $\boldsymbol{U}$ (or $\langle \boldsymbol{u} \rangle_0$), and is equal to the volume flux per unit cross-sectional area of the bed. In the engineering literature the flow rate through a bed is usually given in terms of the superficial velocity – the average velocity per unit area of the fluid part of the bed, but our definition of $\boldsymbol{U}$ simplifies the analysis.

The solute concentration field $c(\boldsymbol{x}, t)$ satisfies

$$\frac{\partial c}{\partial t} + \nabla \cdot \boldsymbol{q} = 0, \tag{2.2a}$$

with the mass flux $\boldsymbol{q}$ given by

$$\boldsymbol{q} = \boldsymbol{u}c - D_\mathrm{f} \nabla c \quad \text{in the fluid,} \tag{2.2b}$$

and by

$$\boldsymbol{q} = -D_\mathrm{p} \nabla c \quad \text{in the particles.} \tag{2.2c}$$

On the particle surfaces the continuity of flux and solubility conditions are

$$D_\mathrm{p} \boldsymbol{n} \cdot \nabla c|_\mathrm{in} = D_\mathrm{f} \boldsymbol{n} \cdot \nabla c|_\mathrm{out}, \quad mc|_\mathrm{in} = c|_\mathrm{out}. \tag{2.2d, e}$$

Here m is the ratio of the solubilities of the solute in the fluid and in the particles, D_p is the molecular diffusivity of the solute in the particles, and $\boldsymbol{n}$ is the outward (into the fluid) normal to the particle surfaces. The time dependence must be retained in the mass-conservation equation even though we seek only the long-time behaviour of the effective diffusivity, because the bulk convective motion requires that a concentration field that varies linearly with the spatial coordinate parallel to the direction of flow also vary linearly with time. Although we have formulated the problem in terms of mass transfer, the effective thermal diffusivity, defined as the ratio of the heat flux to the gradient in enthalpy, is obtained if the ratio of solubilities is replaced by the ratio of the volumetric heat capacities in the fluid and in the particles, the concentration is replaced with the enthalpy, and the mass diffusivity is replaced with the thermal diffusivity. (The thermal conductivity is simply the product of the thermal diffusivity and the volumetric heat capacity.)

We wish to determine the relationship between the average mass flux and average concentration gradient in a fixed bed in the presence of a constant average velocity field. We shall define these averages by averaging over an ensemble of realizations of the bed, each realization having a different configuration of particles, but with the same statistics of their relative positions. Such an average will be denoted by $\langle \, \rangle_0$ and be called an unconditional or bulk average, or simply the average. Thus the averaged mass-conservation equation is

$$\frac{\partial \langle c(\boldsymbol{x}, t) \rangle_0}{\partial t} + \nabla \cdot \langle \boldsymbol{q}(\boldsymbol{x}, t) \rangle_0 = 0, \tag{2.3a}$$

with the bulk average of the mass flux $\langle \boldsymbol{q}(\boldsymbol{x}, t) \rangle_0$ at any point $\boldsymbol{x}$ within the bed at time t given by

$$\langle \boldsymbol{q}(\boldsymbol{x}, t) \rangle_0 = \langle \boldsymbol{u} \rangle_0 \langle c \rangle_0 - \langle D \rangle_0 \nabla \langle c \rangle_0 + \langle \boldsymbol{u}' c' \rangle_0 - \langle D' \nabla c' \rangle_0, \tag{2.3b}$$

where $\boldsymbol{u}' = \boldsymbol{u} - \langle \boldsymbol{u} \rangle_0$, $c' = c - \langle c \rangle_0$, $D' = D - \langle D \rangle_0$, and $D(\boldsymbol{x})$ is a generalized function which takes on the value D_f when $\boldsymbol{x}$ lies in the fluid and D_p when $\boldsymbol{x}$ lies in a particle.

The non-convective terms in (2.3) can be written in a form in keeping with previous work (Jeffrey 1973; Acrivos, Hinch & Jeffrey 1980) by making use of the conditional ensemble average $\langle(\boldsymbol{x},t\,|\,\boldsymbol{r}_1)\rangle_1$. This is an ensemble average at the point $\boldsymbol{x}$ at time t conditioned on the presence of a particle centred at $\boldsymbol{r}_1$. Thus, using the analogy between heat and mass transfer, we can write

$$-\langle D\rangle_0\nabla\langle c(\boldsymbol{x},t)\rangle_0-\langle(D-\langle D\rangle_0)\nabla(c-\langle c\rangle_0(\boldsymbol{x},t))\rangle_0$$
$$=-D_\mathrm{f}\nabla\langle c\rangle_0-D_\mathrm{f}(\alpha-1)\int_{|\boldsymbol{x}-\boldsymbol{r}_1|\leqslant a}\mathrm{d}\boldsymbol{r}_1\,P(\boldsymbol{r}_1)\nabla\langle c(\boldsymbol{x},t\,|\,\boldsymbol{r}_1)\rangle_1. \qquad (2.4)$$

In (2.4) $\alpha=D_\mathrm{p}/mD_\mathrm{f}$, $P(\boldsymbol{r}_1)$ is the probability density for finding a particle at $\boldsymbol{r}_1$, which we shall take to be uniform $P(\boldsymbol{r}_1)=\phi/\frac{4}{3}\pi a^3$, and the integral is over the volume of the particle centred at $\boldsymbol{r}_1$. The use of D_f in place of $\langle D\rangle_0$ in (2.3) allows the integral in (2.4) to be over the particle volume only, for $(D-D_\mathrm{f})\nabla(c-\langle c\rangle_0)$ is non-zero only within the particles.

In order to obtain a macroscopic law of mass transfer, we must express the bulk mass flux purely in terms of macroscopic variables. Because the detailed mass flux $\boldsymbol{q}$ is a linear function of the detailed concentration field c and the ensemble average is a linear operation, the average mass flux is in general a linear functional of the average concentration, which we shall write in the form

$$\langle\boldsymbol{q}\rangle_0=(1+\gamma)\langle\boldsymbol{u}\rangle_0\langle c\rangle_0-\mathbf{D}\cdot\nabla\langle c\rangle_0. \qquad (2.5)$$

Here γ is a constant and $\mathbf{D}$ is in general a tensorial operator, reflecting, among other factors, that dispersion in the direction of the bulk flow is different from that in the transverse direction.

If we are to interpret the operator $\mathbf{D}$ as an effective diffusivity in the usual sense, we should require that it be a constant tensor independent of time and position, and independent of the bulk concentration field. We shall see that these conditions are satisfied in a homogeneous bed in the limit of long time, if the bulk concentration field varies slowly with position. In a future paper we shall consider mass transfer when the bulk concentration does not vary slowly in time and space, a case in which non-local effects are expected.

The effect $\gamma\langle\boldsymbol{u}\rangle_0\langle c\rangle_0$ of the particles on the convective term may be isolated by considering a bed with no bulk concentration gradient. Under these circumstances, one might expect that the disturbance concentration would be zero throughout the bed. The equilibrium condition (2.2*e*) at the particle surfaces, however, gives rise to concentration disturbances in the particles $\langle c\rangle_\mathrm{p}-\langle c\rangle_0$ and in the fluid $\langle c\rangle_\mathrm{f}-\langle c\rangle_0$. Here $\langle c\rangle_\mathrm{p}$ and $\langle c\rangle_\mathrm{f}$ are the average concentrations in the particulate and fluid phases respectively, and are given by

$$\langle c\rangle_\mathrm{f}=\frac{\langle c\rangle_0}{1-\phi(1-m^{-1})},\quad\langle c\rangle_\mathrm{p}=\frac{\langle c\rangle_0}{m(1-\phi(1-m^{-1}))}. \qquad (2.6a, b)$$

Since the concentrations are constant within each phase, we may write

$$\langle\boldsymbol{u}'c'\rangle_0=\phi\langle\boldsymbol{u}'\rangle_\mathrm{p}\langle c'\rangle_\mathrm{p}+(1-\phi)\langle\boldsymbol{u}'\rangle_\mathrm{f}\langle c'\rangle_\mathrm{f},$$

where the velocity disturbance within the fixed-particle phase is $\langle\boldsymbol{u}'\rangle_\mathrm{p}=-\langle\boldsymbol{u}\rangle_0$, while in the fluid phase $\langle\boldsymbol{u}'\rangle_\mathrm{f}=\phi\langle\boldsymbol{u}\rangle_0/(1-\phi)$. Hence γ is given by

$$\gamma=\frac{\phi(1-m^{-1})}{1-\phi(1-m^{-1})}. \qquad (2.6c)$$

This correction to the convective mass flux 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 non-zero only within the fluid.

Equation (2.5) serves as the *definition* of the diffusivity operator $\mathbf{D}$. Comparing (2.5) with (2.3*b*) and (2.4), the effective diffusivity may be written as the sum of three terms, each reflecting a different physical phenomenon:

$$\mathbf{D} = \mathbf{D}^{\mathrm{m}} + \mathbf{D}^{\alpha} + \mathbf{D}^{*}, \tag{2.7a}$$

where

$$\mathbf{D}^{\mathrm{m}} \equiv D_{\mathrm{f}}\,\mathbf{I} \tag{2.7b}$$

is the molecular diffusivity of the fluid, $\mathbf{I}$ is the isotropic tensor,

$$\mathbf{D}^{\alpha}\cdot\nabla\langle c\rangle_0 \equiv D_{\mathrm{f}}(\alpha-1)\int_{|\boldsymbol{x}-\boldsymbol{r}_1|\leqslant a} \mathrm{d}\boldsymbol{r}_1\, P(\boldsymbol{r}_1)\,\nabla\langle c(\boldsymbol{x},t\,|\,\boldsymbol{r}_1)\rangle_1 \tag{2.7c}$$

is the particles' contributions from the difference in diffusivities, and

$$-\mathbf{D}^{*}\cdot\nabla\langle c\rangle_0 \equiv \langle \boldsymbol{u}'c'\rangle_0 - \gamma\langle \boldsymbol{u}\rangle_0\langle c\rangle_0 \tag{2.7d}$$

is the particles' contribution from the nonlinear convection term. Equation (2.7*a*) is just an identity resulting from the way in which we defined the effective diffusivity in (2.5).

In the long-time limit considered here, we expect a true diffusive behaviour. Thus, we postulate subject to confirmation that $\mathbf{D}$ is a constant, so that (2.3*a*) and (2.5) have a solution of the form

$$\langle c(\boldsymbol{x},t)\rangle_0 = \nabla\langle c\rangle_0\cdot\boldsymbol{x} - \nabla\langle c\rangle_0\cdot\langle \boldsymbol{u}\rangle_0(1+\gamma)\,t, \tag{2.8}$$

where $\nabla\langle c\rangle_0$ is a constant vector. The time-dependence in (2.8) is necessitated by the presence of the bulk convective term $(1+\gamma)\langle \boldsymbol{u}\rangle_0\langle c\rangle_0$ in (2.5). Although the bulk concentration field is time-dependent, it is significant that the gradient $\nabla\langle c\rangle_0 = \nabla\langle c(\boldsymbol{x},t)\rangle_0$ is independent of both time and space.

3. Dispersion at low Péclet numbers

3.1. *Pure conduction*

Even in the absence of convection, $\boldsymbol{u} = 0$, the particles affect the macrotransport through the term $\mathbf{D}^{\alpha}$ involving the difference in the molecular diffusivities D_{f} and D_{p} of the solute in the fluid and in the particles respectively. In order to evaluate (2.7*c*) for $\mathbf{D}^{\alpha}$, we require an equation for the conditionally averaged concentration field $\langle c(\boldsymbol{x},t\,|\,\boldsymbol{r}_1)\rangle_1$. This equation, obtained by conditionally averaging the detailed mass-conservation equation, is

$$\frac{\partial\langle c\rangle_1}{\partial t} + \mathbb{P}\langle \boldsymbol{u}\rangle_1\cdot\nabla\langle c\rangle_1 - \nabla^2\langle c\rangle_1$$

$$= (\alpha-1)\int_{|\boldsymbol{x}-\boldsymbol{r}_2|\leqslant 1} \mathrm{d}\boldsymbol{r}_2\, P(\boldsymbol{r}_2\,|\,\boldsymbol{r}_1)\,\nabla\langle c(\boldsymbol{x},t\,|\,\boldsymbol{r}_1,\boldsymbol{r}_2)\rangle_2 - \mathbb{P}\,\nabla\cdot\langle(\boldsymbol{u}-\langle \boldsymbol{u}\rangle_1)(c-\langle c\rangle_1)\rangle_1 \tag{3.1a}$$

for points, $|\boldsymbol{x}-\boldsymbol{r}_1| > 1$, outside the particle, and

$$\frac{\partial\langle c\rangle_1}{\partial t} - \frac{D_{\mathrm{p}}}{D_{\mathrm{f}}}\nabla^2\langle c\rangle_1 = 0 \tag{3.1b}$$

for the points, $|\boldsymbol{x}-\boldsymbol{r}_1| < 1$, inside the particle. Here, and in all subsequent expressions, all lengths have been made dimensionless with the particle radius a, the velocity with the bulk average U, and the time with the diffusive timescale a^2/D_f. In addition to satisfying the boundary conditions (2.2*d*, *e*) at the surface of the fixed particle, the conditionally averaged field must sum to the bulk as $|\boldsymbol{x}-\boldsymbol{r}_1| \rightarrow \infty$, i.e.

$$\langle c(\boldsymbol{x},t\,|\,\boldsymbol{r}_1)\rangle_1 \sim \langle c(\boldsymbol{x},t)\rangle_0 \quad \text{as } |\boldsymbol{x}-\boldsymbol{r}_1| \rightarrow \infty. \tag{3.1c}$$

In the absence of convection (3.1*a*) reduces to

$$\frac{\partial\langle c\rangle_1}{\partial t}-\nabla^2\langle c\rangle_1 = (\alpha-1)\int_{|\boldsymbol{x}-\boldsymbol{r}_2|\leqslant 1} \mathrm{d}\boldsymbol{r}_2\, P(\boldsymbol{r}_2\,|\,\boldsymbol{r}_1)\,\nabla\langle c(\boldsymbol{x},t\,|\,\boldsymbol{r}_1,\boldsymbol{r}_2)\rangle_2. \tag{3.2}$$

The leading behaviour of $\mathbf{D}^{\alpha}$ may be evaluated by neglecting the right-hand side of (3.2) to give the one-sphere pure-conduction problem solved by Maxwell. Substituting the resultant conditionally averaged concentration into (2.7*c*) gives the classic result

$$\mathbf{D}^{\alpha} = \mathbf{I}\left[\frac{3(\alpha-1)}{\alpha+2}\phi+O(\phi^2)\right] \quad (\phi \ll 1). \tag{3.3}$$

Note that here and throughout the rest of the paper the effective diffusivity is non-dimensionalized with the molecular diffusivity in the fluid D_f. The $O(\phi^2)$ correction to (3.3) was evaluated by Jeffrey (1973) by including the two-particle interactions on the right-hand side of (3.2).

3.2. *The first effects of convection*

In this subsection we seek the first effects at low ϕ and low $\mathbb{P}$ of convection on macrotransport in a fixed bed. The detailed justification of the approximations made in this asymptotic analysis will be presented in the Appendix. Although the velocity disturbance affects the concentration within the particle and thus makes an indirect contribution to $\mathbf{D}^{\alpha}$, the leading effect of convection on the diffusivity is through $\mathbf{D}^{*}$. Using the definition of the conditional average, this contribution (2.7*d*) can be written in the dimensional form

$$-\mathbf{D}^{*}\cdot\nabla\langle c\rangle_0 = -\gamma\langle \boldsymbol{u}\rangle_0\langle c\rangle_0+\int \mathrm{d}\boldsymbol{r}_1\, P(\boldsymbol{r}_1)\,\langle \boldsymbol{u}'c'\rangle_1, \tag{3.4}$$

where the integral is over all $\boldsymbol{r}_1$ space. Neglecting two-particle velocity–concentration correlations, (3.4) may be approximated as

$$-\mathbf{D}^{*}\cdot\nabla\langle c\rangle_0 = \mathbb{P}\int \mathrm{d}\boldsymbol{r}_1\, P(\boldsymbol{r}_1)\,\langle \boldsymbol{u}'\rangle_1\langle c'\rangle_1-\mathbb{P}\int_{|\boldsymbol{x}-\boldsymbol{r}_1|\leqslant 1} \mathrm{d}\boldsymbol{r}_1\, P(\boldsymbol{r}_1)\left(1-\frac{1}{m}\right)\langle \boldsymbol{u}\rangle_0\langle c\rangle_0, \tag{3.5}$$

where $\langle \boldsymbol{u}'\rangle_1 = \langle \boldsymbol{u}\rangle_1-\langle \boldsymbol{u}\rangle_0$ and $\langle c'\rangle_1 = \langle c\rangle_1-\langle c\rangle_0$ are the disturbances to the velocity and concentration fields caused by the fixed particle. We shall see that at low $\mathbb{P}$ the particles cause only a small enhancement of diffusion, and as a result the effect of the other particles on any particle's concentration disturbance is small and the right-hand side of (3.1*a*) may be neglected.

We shall now see, however, that it is necessary to consider many-body hydrodynamic interactions even in a dilute (low-ϕ) bed. To demonstrate this fact, we first adopt the contrary assumption that the leading effect of convection on the effective diffusivity may be derived from a problem involving a single, isolated particle; a problem similar to that solved by Maxwell to determine the conductivity in the absence of convection. The velocity disturbance caused by a single isolated sphere held fixed in an unbounded fluid moving at a constant velocity is the well-known Stokes velocity field, which decays only as r^{-1} far from the particle, where r is the radial distance measured from the particle centre. Solving (3.1) with the Stokes velocity field, one obtains a concentration disturbance that does not decay with radial distance far from the particle. The expression (3.5) for the convective contribution to the effective diffusivity involves an integral over all space of the product of the velocity and concentration disturbances. This integral fails to converge at large radial distances, indicating that it is not adequate to treat the particles in a fixed bed as if they were isolated in an unbounded fluid.

This convergence difficulty results from our neglect of the strong hydrodynamic, interparticle interactions characteristic of porous media. Hinch (1977) showed that conditionally averaging the equation of motion (1) yields

$$\nabla\cdot\langle \boldsymbol{u}(\boldsymbol{x}\,|\,\boldsymbol{r}_1)\rangle_1 = 0, \tag{3.6a}$$

$$\begin{aligned} -\nabla\langle p_{\mathrm{f}}\rangle_1 + \mu\nabla^2\langle \boldsymbol{u}\rangle_1 - \frac{\mu}{k}\langle \boldsymbol{u}\rangle_1 \\ = \int_{|\boldsymbol{r}_2-\boldsymbol{r}_1|\geqslant 2a} \mathrm{d}\boldsymbol{r}_2 \Big\{ P(\boldsymbol{r}_2\,|\,\boldsymbol{r}_1) \int_{|\boldsymbol{x}'-\boldsymbol{r}_2| = a} \mathrm{d}\boldsymbol{x}' \,\langle \boldsymbol{\sigma}(\boldsymbol{x}'\,|\,\boldsymbol{r}_1,\boldsymbol{r}_2)\rangle_2\cdot\boldsymbol{n}'\delta(\boldsymbol{x}'-\boldsymbol{x}) \\ -\frac{\mu}{k}\langle \boldsymbol{u}(\boldsymbol{r}_2|\boldsymbol{r}_1)\rangle_1\,\delta(\boldsymbol{r}_2-\boldsymbol{x})\Big\}, \end{aligned} \tag{3.6b}$$

where $\boldsymbol{\sigma} = -p_{\mathrm{f}}\,\mathbf{I} + \mu(\nabla\boldsymbol{u}+\nabla\boldsymbol{u}^{\dagger})$ is the stress tensor. In the dilute limit the right-hand side may now be safely neglected, and (3.1 *a*, *b*) become Brinkman's equations for viscous flow in a porous medium. These equations differ from Stokes equations by the inclusion of the porous-media term $(\mu/k)\langle \boldsymbol{u}\rangle_1$, which results from the body force exerted by the fixed particles on the fluid. The drag exerted by each particle in a dilute bed is approximately Stokes drag $6\pi\mu a\langle \boldsymbol{u}\rangle_1$, while the number density of particles is $\phi/\frac{4}{3}\pi a^3$. Thus the permeability is approximately $k = \frac{2}{9}\phi^{-1}a^2$ or in dimensionless form $k = \frac{2}{9}\phi^{-1}$. The solution to Brinkman's equations that satisfies the no-slip boundary condition on the particle surface and sums to the bulk far away was given by Acrivos *et al.* (1980):

$$\begin{aligned} \langle \boldsymbol{u}\rangle_1 = \langle \boldsymbol{u}\rangle_0\left\{1-\frac{3}{2\kappa^2r^3}[(1+\kappa r+\kappa^2r^2)\,\mathrm{e}^{\kappa(1-r)}-(1+\kappa+\tfrac{1}{3}\kappa^2)]\right\} \\ +\tfrac{3}{2}\boldsymbol{r}(\langle \boldsymbol{u}\rangle_0\cdot\boldsymbol{r})\frac{9}{\kappa^2r^5}[(3+3\kappa r+\kappa^2r^2)\,\mathrm{e}^{\kappa(1-r)}-(3+3\kappa+\kappa^2)], \end{aligned} \tag{3.7}$$

where $\boldsymbol{r} = \boldsymbol{x}-\boldsymbol{r}_1$, $r = |\boldsymbol{r}|$ and $\kappa = k^{-\frac{1}{2}}$. This solution is identical with the Stokes velocity near the particle, i.e. in the limit $\phi\rightarrow 0$, $r = O(1)$, but at a large radial distance $r = O(k^{\frac{1}{2}})$, known as the Brinkman screening length, the velocity disturbance is screened and decays like kr^{-3}, rather than as r^{-1}. This effect causes the expression (3.5) for the effective diffusivity to become convergent, but only after integration has been carried out over a large $O(k^{\frac{3}{2}})$ volume.

As a result, the dominant contribution to the effective diffusivity in (3.5) occurs at large distances $r = O(k^{\frac{1}{2}})$. This allows us to make several important simplifications in the asymptotic analysis for small ϕ: (1) in this region the particle appears as a point, allowing the velocity field $\langle \boldsymbol{u}\rangle_1$ to be that of a point force rather than the full expression (3.7); (2) no boundary conditions on the concentration field $\langle c\rangle_1$ need to be satisfied at the particle surface, and no solution is needed inside the fixed particle; and (3) the $1-m^{-1}$ particle contribution in (3.5) can be neglected, and the integral can be carried out over all space using only the point-particle velocity and concentration disturbances.

An equation for the concentration disturbance $\langle c'\rangle_1 = \langle c\rangle_1 - \langle c\rangle_0$ appropriate for a point particle may be found by subtracting the bulk equation (2.3) from (3.1*a*):

$$\begin{aligned}&\mathbb{P}\langle \boldsymbol{u}\rangle_1\cdot\nabla\langle c'\rangle_1-\nabla^2\langle c'\rangle_1+\mathbb{P}\langle \boldsymbol{u}'\rangle_1\cdot\nabla\langle c\rangle_0\\&\quad=(\alpha-1)\int_{|\boldsymbol{x}-\boldsymbol{r}_2|\leqslant 1}\mathrm{d}\boldsymbol{r}_2\Big[P(\boldsymbol{r}_2\,|\,\boldsymbol{r}_1)\,\nabla\langle c(\boldsymbol{x},t\,|\,\boldsymbol{r}_1,\boldsymbol{r}_2)\rangle_2-P(\boldsymbol{r}_2)\,\nabla\langle c(\boldsymbol{x},t\,|\,\boldsymbol{r}_2)\rangle_1\Big]\\&\qquad+\mathbb{P}\nabla\cdot[\langle(\boldsymbol{u}-\langle\boldsymbol{u}\rangle_1)\,(c-\langle c\rangle_1)\rangle_1-\langle\boldsymbol{u}'c'\rangle_0].\end{aligned}\tag{3.8}$$

Note that, although the bulk average and conditionally averaged concentration fields are time-dependent, the concentration disturbance depends only on $\nabla\langle c\rangle_0$, which is independent of time, and so $\langle c'\rangle_1$ is also time-independent at long times.

Since $\nabla\langle c\rangle_0$ and $\langle \boldsymbol{u}\rangle_0$ are constant and $\langle \boldsymbol{u}\rangle_1$ is a function only of $\boldsymbol{x}-\boldsymbol{r}_1$, $\langle c'\rangle_1$ is only a function of $\boldsymbol{x}-\boldsymbol{r}_1$. The transformation $\boldsymbol{R} = k^{-\frac{1}{2}}(\boldsymbol{x}-\boldsymbol{r}_1)$ exploits this fact and places the dominant convective contribution to the effective diffusivity at $R = O(1)$. Thus, neglecting the particle–particle interaction terms on the right-hand side (which is justified in the Appendix), (3.8) becomes

$$\mathscr{P}\langle\boldsymbol{u}\rangle_1\cdot\nabla_R\langle c'\rangle_1-\nabla_R^2\langle c'\rangle_1=-\mathscr{P}k^{\frac{1}{2}}\langle\boldsymbol{u}'\rangle_1\cdot\nabla\langle c\rangle_0.\tag{3.9}$$

Note that the bulk concentration gradient $\nabla\langle c\rangle_0$, being constant, has not been transformed. The appearance of the screening-length Péclet number $\mathscr{P} = \mathbb{P}k^{\frac{1}{2}}$ in (3.9) reflects the fact that the screening length is the characteristic length over which the excess mass flux caused by a particle decays, and thus the magnitude of $\mathscr{P}$ determines whether convection or conduction is dominant in the region of interest. At these large radial distances, $r \sim k^{\frac{1}{2}}$, the conditionally averaged velocity is approximately equal to the bulk velocity. Thus approximating $\langle\boldsymbol{u}\rangle_1$ on the left-hand side of (3.9) by

$$\langle\boldsymbol{u}\rangle_1\sim\langle\boldsymbol{u}\rangle_0+O(k^{-\frac{1}{2}}),$$

and solving by Fourier transform, we obtain

$$\langle\hat{c}'(\boldsymbol{\xi})\rangle_1=-\mathscr{P}k^{\frac{1}{2}}\frac{\langle\hat{\boldsymbol{u}}'(\boldsymbol{\xi})\rangle_1\cdot\nabla\langle c\rangle_0}{\xi^2-\mathrm{i}\mathscr{P}\langle\boldsymbol{u}\rangle_0\cdot\boldsymbol{\xi}},\tag{3.10}$$

where the transform is denoted by ˆ and $\boldsymbol{\xi}$ is the transform variable of $\boldsymbol{R}$. $\langle\hat{\boldsymbol{u}}'(\boldsymbol{\xi})\rangle_1$, the transform of the point-force velocity disturbance in a fixed bed, is (Saffman 1973)

$$\langle\hat{\boldsymbol{u}}(\boldsymbol{\xi})\rangle_1=6\pi k^{-\frac{1}{2}}\frac{\langle\boldsymbol{u}\rangle_0\cdot(\boldsymbol{I}-\boldsymbol{\xi}\boldsymbol{\xi}/\xi^2)}{\xi^2+1}.\tag{3.11}$$

The integral for the convective contribution (3.5) to the effective diffusivity may be extended over all space, and when transformed into R-variables it becomes

$$-\mathbf{D}^*\cdot\nabla\langle c\rangle_0=\frac{\mathbb{P}\phi k^{\frac{3}{2}}}{\frac{4}{3}\pi}\int\mathrm{d}\boldsymbol{R}\,\langle\boldsymbol{u}'(\boldsymbol{R})\rangle_1\,\langle c'(\boldsymbol{R})\rangle_1.\tag{3.12a}$$

Using the convolution theorem in $\boldsymbol{\xi}$, we have

$$-\mathbf{D}^*\cdot\nabla\langle c\rangle_0=\frac{\mathbb{P}\phi k^{\frac{3}{2}}}{\frac{4}{3}\pi(2\pi)^3}\int\mathrm{d}\boldsymbol{\xi}\,\langle\hat{\boldsymbol{u}}'(-\boldsymbol{\xi})\rangle_1\,\langle\hat{c}'(\boldsymbol{\xi})\rangle_1.\tag{3.12b}$$

Since $\nabla\langle c\rangle_0$ is constant, (3.10)–(3.12) show that $\mathbf{D}^*$ is indeed a constant, and is given explicitly by

$$\mathbf{D}^* = \frac{3}{4\pi^2}\mathscr{P}^2 k^{-\frac{1}{2}} \int \mathrm{d}\boldsymbol{\xi} \frac{\langle \boldsymbol{u}\rangle_0 \cdot (\boldsymbol{I}-\boldsymbol{\xi\xi}/\xi^2)\,\langle \boldsymbol{u}\rangle_0 \cdot (\boldsymbol{I}-\boldsymbol{\xi\xi}/\xi^2)}{(\xi^2+1)^2\,(\xi^2-\mathrm{i}\mathscr{P}\langle \boldsymbol{u}\rangle_0 \cdot \boldsymbol{\xi})}. \tag{3.13}$$

An expression equivalent to the transverse component of (3.13) was given by Carton, DuBois-Violette & Prost (1983) for the transverse diffusivity in a dilute fixed bed, defined as the rate of increase with time of the second moment of the probability distribution for a single Brownian particle in a fixed bed in the limit of long times. Unfortunately, these authors misinterpreted the origin of the velocity disturbances, and instead of using the Brinkman velocity field for both the $\langle \boldsymbol{u}'\rangle_1$ in (3.10) and the $\langle \boldsymbol{u}'\rangle_1$ appearing explicitly in (3.12) they used a Stokes velocity field for one and a Brinkman field for the other. This led to subsequent errors in their final expression for $D^*_\perp$, the transverse diffusivity. It is reassuring, however, that the definition of the diffusivity based on the response to a steady concentration gradient used in this paper and the definition based on a moments approach used by Carton *et al.* yield equivalent integral expressions for the long-time transverse diffusivity.

Carrying out the integration in (3.13) explicitly shows that the off-diagonal elements of $\mathbf{D}^*$ are zero, as one would expect from symmetry considerations. The transverse (perpendicular to the bulk-flow direction) component of the convective contribution to the effective diffusivity is

$$D^*_\perp = k^{-\frac{1}{2}}[\tfrac{1}{4}+\tfrac{3}{4}|\mathscr{P}|^{-1}-\tfrac{3}{4}|\mathscr{P}|^{-2}+\tfrac{3}{2}(|\mathscr{P}|^{-3}-\tfrac{1}{2}|\mathscr{P}|^{-1})\ln(|\mathscr{P}|+1)], \tag{3.14a}$$

while the longitudinal (in the direction of the bulk flow) component is

$$D^*_\parallel = k^{-\frac{1}{2}}[\tfrac{3}{4}|\mathscr{P}|-2-\tfrac{3}{2}|\mathscr{P}|^{-1}+3|\mathscr{P}|^{-2}+3(|\mathscr{P}|^{-1}-|\mathscr{P}|^{-3})\ln(|\mathscr{P}|+1)]. \tag{3.14b}$$

The absolute value of $\mathscr{P}$ appears in (3.14) directly as a result of the integration, and reflects the fact that reversing the direction of the bulk flow does not change the effective diffusivity. $D^*_\perp k^{\frac{1}{2}}$ and $D^*_\parallel k^{\frac{1}{2}}$ are plotted as functions of $\mathscr{P}$ in figure 1. The asymptotic limits at low and high $\mathscr{P}$ are indicated by dotted lines.

The low-$\mathscr{P}$ asymptotic behaviour is obtained by neglecting the convective term $\mathscr{P}\langle \boldsymbol{u}\rangle_1 \cdot \nabla_R \langle c'\rangle_1$ on the left-hand side of (3.9), or equivalently neglecting the convective term $-\mathrm{i}\mathscr{P}\langle \boldsymbol{u}\rangle_0 \cdot \boldsymbol{\xi}$ in the denominator of the integrand in (3.13). The resulting asymptotic form, which may also be derived directly from (3.14), is

$$\left.\begin{aligned} D^*_\perp &= \frac{\sqrt{2}}{60}\frac{\mathbb{P}^2}{\phi^{\frac{1}{2}}}, \qquad (3.15a)\\ D^*_\parallel &= \frac{\sqrt{2}}{15}\frac{\mathbb{P}^2}{\phi^{\frac{1}{2}}} \qquad (3.15b) \end{aligned}\right\}\quad (\mathscr{P} \ll 1,\ \mathbb{P}^2 \ll \phi \ll 1).$$

It is interesting to note that this convective contribution to the effective diffusivity becomes larger than the pure-conduction contribution, (3.3), even at very low particle Péclet numbers $\phi^{\frac{3}{4}} \ll \mathbb{P} \ll \phi^{\frac{1}{2}}$. This surprising behaviour occurs because the convective flux occurs over a large $O(k^{\frac{3}{2}}) = O(\phi^{-\frac{3}{2}})$ volume, while the pure-conduction contribution comes only from a region of the order of the particle size.

While we have treated the low-$\mathscr{P}$ asymptote of (3.14) in this section, the high-$\mathscr{P}$ asymptote is particularly important, and we discuss it separately in §4.

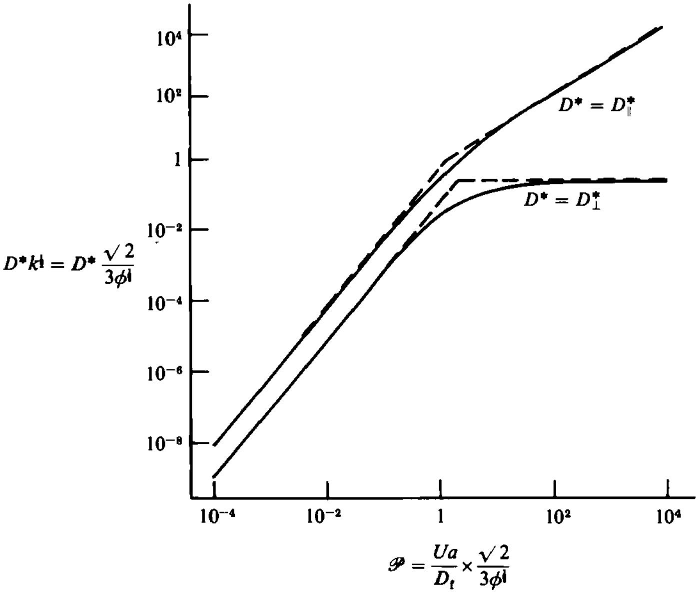

FIGURE 1. The convective contributions (3.14*a*, *b*) to the transverse and longitudinal diffusivities at low P are plotted as functions of the Péclet number $\mathscr{P}$ based on the screening length $k^{\frac{1}{2}}$. The dotted lines indicate the asymptotes (3.15*a*, *b*), (4.8*a*) and (4.9) at low and high $\mathscr{P}$.

4. Mechanical dispersion at high screening-length Péclet numbers

In this section we consider dispersion at high screening-length Péclet numbers $\mathscr{P}$, where convection is expected to dominate over molecular diffusion. The most straightforward mechanism obtained by neglecting the small molecular-diffusion and particle-interaction terms in the concentration disturbance equation (3.8) is developed in §4.1. There are two limitations to this analysis, however. (1) There is no contribution to the transverse diffusivity from the one-sphere mechanical analysis. This problem may be addressed by including molecular diffusion, particle interactions or non-spherical particles in the analysis, as discussed in §4.2. (2) There are regions in the bed where the concentration disturbance determined through the purely mechanical analysis of §4.1 is singular, and these regions make important contributions to the effective diffusivity at very high Péclet numbers. This forms the basis of our discussion of 'holdup' dispersion in §5.

4.1. *Longitudinal diffusivity*

The purely mechanical one-particle convection–diffusion problem is obtained by neglecting the diffusion and particle-interaction terms in (3.8), giving in R-variables

$$\langle \boldsymbol{u} \rangle_1 \cdot \nabla_R \langle c' \rangle_1 = -k^{\frac{1}{2}} \langle \boldsymbol{u}' \rangle_1 \cdot \nabla \langle c \rangle_0. \tag{4.1}$$

Justification of the neglect of particle interaction terms can be found in the Appendix.

The solution to (4.1) is

$$\langle c' \rangle_1 = -k^{\frac{1}{2}} \int_{-\infty}^{\eta} \mathrm{d}\eta' \frac{1}{h_\eta |\langle \boldsymbol{u}(\psi, \eta', \theta) \rangle_1|} \langle \boldsymbol{u}'(\psi, \eta', \theta) \rangle_1 \cdot \nabla \langle c \rangle_0, \tag{4.2}$$

where η is the coordinate along the streamlines of the conditionally averaged velocity field $\langle \boldsymbol{u} \rangle_1$, with metric coefficient h_η, θ is the coordinate in the direction of rotational invariance, and ψ is the third orthogonal coordinate. We have imposed the condition that the particle does not affect the concentration far upstream, i.e. $\langle c' \rangle_1 \sim 0$ as $\eta \rightarrow -\infty$. Substituting the mechanically determined concentration disturbance (4.2) into the expression (3.12*a*) for the effective diffusivity gives

$$\mathbf{D}^* = \frac{\mathbb{P}\phi k^2}{\frac{4}{3}\pi} \int \mathrm{d}\boldsymbol{R} \, \langle \boldsymbol{u}'(\psi, \eta, \theta) \rangle_1 \int_{-\infty}^{\eta} \mathrm{d}\eta' \frac{1}{h_\eta \, | \langle \boldsymbol{u}(\psi, \eta', \theta) \rangle_1 |} \langle \boldsymbol{u}'(\psi, \eta', \theta) \rangle_1. \tag{4.3}$$

Equation (4.3) is nothing more than the volume integral of the velocity-disturbance correlation function

$$\int_{-\infty}^{\eta} \mathrm{d}\eta' \langle \boldsymbol{u}'(\psi, \eta, \theta) \rangle_1 \frac{1}{h_\eta \, | \langle \boldsymbol{u}(\psi, \eta', \theta) \rangle_1 |} \langle \boldsymbol{u}'(\psi, \eta', \theta) \rangle_1,$$

which measures the correlation between the velocity disturbance experienced by a fluid element at a given time, i.e. given η, and the fluid element's velocity disturbance at all previous times – previous η. A similar expression may be used to relate the *Brownian* diffusivity of a tracer particle to the tracer particle's velocity correlation function.

Far from the fixed particle, where we expect the dominant contribution to the diffusivity (4.3) to occur, the conditionally averaged velocity is approximately the same as the bulk velocity, and the streamlines are nearly straight lines parallel to the bulk-flow direction, i.e. $\langle \boldsymbol{u} \rangle_1 \approx \langle \boldsymbol{u} \rangle_0$ and $\eta \approx Z$, where Z is measured along the flow direction. Thus (4.3) becomes

$$\mathbf{D}^* = \frac{\mathbb{P}\phi k^2}{\frac{4}{3}\pi} \int \rho \, \mathrm{d}\rho \, \mathrm{d}\Theta \, \mathrm{d}Z \, \langle \boldsymbol{u}'(\rho, \Theta, Z) \rangle_1 \int_{-\infty}^{Z} \mathrm{d}Z \, \langle \boldsymbol{u}'(\rho, \Theta, Z') \rangle_1, \tag{4.4}$$

where (ρ, Θ, Z) form a cylindrical coordinate system. The integrations in Z and Z' can be carried out to give

$$\mathbf{D}^* = \frac{1}{2} \frac{\mathbb{P}\phi k^2}{\frac{4}{3}\pi} \int \rho \, \mathrm{d}\rho \, \mathrm{d}\Theta \, \langle \boldsymbol{u}' \rangle_{1z} \langle \boldsymbol{u}' \rangle_{1z}, \tag{4.5}$$

where
$$\langle \boldsymbol{u}'(\rho, \Theta) \rangle_{1z} = \int_{-\infty}^{\infty} \mathrm{d}Z \, \langle \boldsymbol{u}'(\rho, \Theta, Z) \rangle_1.$$

An equation for this 'two-dimensional' velocity disturbance $\langle \boldsymbol{u}' \rangle_{1z}$ can be obtained by integrating Brinkman's equation (3.6) with respect to Z from $-\infty$ to $+\infty$. The point particle at the origin forces the velocity disturbance. In Fourier space $\langle \boldsymbol{u}' \rangle_{1z}$ is given by

$$\langle \hat{\boldsymbol{u}}' \rangle_{1z}(\boldsymbol{\lambda}) = 6\pi k^{-\frac{1}{2}} \langle \boldsymbol{u} \rangle_0 \frac{1}{\lambda^2 + 1}, \tag{4.6}$$

where $\boldsymbol{\lambda}$ is the two-dimensional transform variable corresponding to (ρ, Θ). The convolution theorem in $\boldsymbol{\lambda}$ can be used to write (4.5) as

$$\mathbf{D}^* = \frac{1}{2} \frac{\mathbb{P}\phi k^2}{\frac{4}{3}\pi} \frac{1}{(2\pi)^2} \int \mathrm{d}\boldsymbol{\lambda} \, \langle \hat{\boldsymbol{u}}' \rangle_{1z} \langle \hat{\boldsymbol{u}}' \rangle_{1z}. \tag{4.7}$$

Integrating (4.7) with (4.6), $\mathbf{D}^*$ is

$$\left. \begin{aligned} D_{\parallel}^* &= \tfrac{3}{4} |\mathbb{P}|, & (4.8a) \\ D_{\perp}^* &= 0 & (4.8b) \end{aligned} \right\} \quad (\mathscr{P} \gg 1, \ \phi \ll 1).$$

Equation (4.8*a*) can also be obtained directly from the asymptotic behaviour of (3.13). In evaluating (3.13) for high $\mathscr{P}$, it is necessary to retain the asymptotically small diffusive term ξ^2 compared with $\mathrm{i}\mathscr{P}\langle \boldsymbol{u}\rangle_0 \cdot \boldsymbol{\xi}$ in order to avoid a singularity at $\langle \boldsymbol{u}\rangle_0 \cdot \boldsymbol{\xi} = 0$, even though the final result does not depend on diffusion. In fact, any small number ϵ may be used in the denominator of (3.13) to remove the singularity at $\langle \boldsymbol{u}\rangle_0 \cdot \boldsymbol{\xi} = 0$, and then letting $\epsilon \rightarrow 0$ in the final result will show independence of ϵ. The development presented in this section has the advantage that it demonstrates unequivocally that molecular diffusion plays no role in determining the asymptotic behaviour at high $\mathscr{P}$ of $D_{\parallel}^*$. In dimensional form, $D_{\parallel}^* = \frac{3}{4}|U|a$, independent of D_{f}. This dispersion is of a purely *mechanical* origin caused by the stochastic velocity field in a random fixed bed.

4.2. *Transverse diffusivity*

There is no contribution to the transverse diffusivity from the one-particle, purely mechanical, analysis presented above. This null result occurs because the integral of the transverse component of the velocity disturbance along any streamline is zero, as it must be for streamlines that possess fore–aft symmetry. If we considered a fixed bed of particles that do not possess fore–aft symmetry (such as spheroids with their axes oriented at oblique angles to the direction of the bulk flow), the one-particle hydrodynamic analysis would yield contributions to the transverse diffusivity. For the bed of spheres considered here, however, contributions to $D_{\perp}^*$ are obtained only through consideration of molecular diffusion or particle interactions.

4.2.1. *Diffusion correction*

The diffusive correction to (4.8) may be obtained by expanding the concentration disturbance in inverse powers of $\mathscr{P}$:

$$\langle c'\rangle_1 = \langle c'\rangle_{1,0} + \mathscr{P}^{-1}\langle c'\rangle_{1,1} + \dots .$$

The first term $\langle c'\rangle_{1,0}$ is just the hydrodynamically determined concentration disturbance (4.2). The second term $\langle c'\rangle_{1,1}$ is obtained by solving

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

$\langle c'\rangle_{1,1}$, unlike $\langle c'\rangle_{1,0}$, does contribute to transverse dispersion. Since $\langle c'\rangle_{1,1}$ is $O(\mathscr{P}^{-1})$ smaller than $\langle c'\rangle_{1,0}$ the leading behaviour of $D_{\perp}^*$,

$$D_{\perp}^* = \frac{3\sqrt{2}}{8}\phi^{\frac{1}{2}} \quad (\mathscr{P} \gg 1,\ \mathbb{P} \ll 1,\ \phi \ll 1), \tag{4.9}$$

is smaller than the $O(\mathbb{P})$ longitudinal diffusivity (4.8*a*). Equation (4.9) is surprising in that $D_{\perp}^*$ is independent of the bulk velocity, even though it is caused by the convective motion within the bed. This anomalous behaviour can be explained in the following way. Because of the fore–aft symmetry of the one-particle streamlines, transverse diffusion in the absence of particle interactions can occur only by molecular diffusion normal to the streamlines at high $\mathscr{P}$. The particles affect this transverse dispersion by distorting the streamlines. Thus the effect of the particles is independent of the magnitude of the velocity as long as $\mathscr{P} \gg 1$ and particle interactions may be neglected.

4.2.2. *Correction due to particle interactions*

We have noted that the null result for the transverse diffusivity obtained from the one-particle hydrodynamic analysis in §4.1 is related to the fore–aft symmetry of the streamlines for flow past a sphere. The streamlines for flow past *two* spheres do not have fore–aft symmetry in general, however. Thus we expect that the inclusion of particle interactions in the analysis will result in a purely mechanical contribution to the transverse diffusivity. In the Appendix we show that these contributions are $O(\mathbb{P}\phi^{\frac{1}{2}})$. Thus for $\phi^{\frac{1}{2}} \ll \mathbb{P} \ll 1$ the diffusively driven contribution to the transverse diffusivity, (4.9), obtained in §4.2.1 is dominant, while for $\mathbb{P} \gg 1$ particle interactions are more important and $D_\perp^* = O(\mathbb{P}\phi^{\frac{1}{2}})$.

We can include these particle interactions in a self-consistent manner by renormalizing the equation (3.8) for the concentration disturbance using the same effective diffusivity that we have calculated for the bulk diffusion problem:

$$\begin{aligned}\mathbb{P}\langle \boldsymbol{u}\rangle_1\cdot\nabla\langle c'\rangle_1-\nabla\cdot\mathbf{D}\cdot\nabla\langle c'\rangle_1+\mathbb{P}\langle \boldsymbol{u}'\rangle_1\cdot\nabla\langle c\rangle_0 \\ = (\alpha-1)\int_{|\boldsymbol{x}-\boldsymbol{r}_2|\leqslant 1} \mathrm{d}\boldsymbol{r}_2\, P(\boldsymbol{r}_2\,|\,\boldsymbol{r}_1)\nabla\langle c(\boldsymbol{x},t\,|\,\boldsymbol{r}_1,\boldsymbol{r}_2)\rangle_2 \\ -\mathbb{P}\nabla\cdot\langle(\boldsymbol{u}-\langle\boldsymbol{u}\rangle_1)(c-\langle c\rangle_1)\rangle_1-\nabla\cdot(\mathbf{D}^*+\mathbf{D}^\alpha)\cdot\nabla\langle c'\rangle_1. \qquad (4.10)\end{aligned}$$

It is not clear whether this self-consistent renormalization approximation *fully* accounts for all the two-particle effects that influence the effective diffusivity at leading order. However, it does give the correct functional dependence of the effective diffusivity on $\mathbb{P}$ and ϕ, and we shall see in §6 that the result compares well with experimental data.

Neglecting the right-hand side, which is shown to be small in the Appendix, (4.10) can be solved in a manner analogous to that used in §4.2.1, so long as $|\mathbf{D}| \ll \mathscr{P}$, a requirement that will be justified *a posteriori*. If we expand the concentration in inverse powers of $\mathscr{P}$, $\langle c'\rangle_{1,0}$ again gives no contribution to the transverse diffusivity. The leading behaviour of $D_\perp^*$ then comes from substituting $\langle c'\rangle_{1,1}$, obtained by solving

$$\langle \boldsymbol{u}\rangle_1\cdot\nabla_R\langle c'\rangle_{1,1}=\nabla\cdot\mathbf{D}\cdot\nabla\langle c'\rangle_{1,0}$$

into the integral (3.12) for the effective diffusivity. The resultant transverse diffusivity is

$$D_\perp = 1+\frac{21\sqrt{2}}{80}\phi^{\frac{1}{2}}D_\parallel+\frac{9\sqrt{2}}{80}D_\perp \quad (\mathscr{P}\gg 1,\ \phi\ll 1). \qquad (4.11a)$$

This result reduces to the result

$$D_\perp = 1+\frac{3\sqrt{2}}{8}\phi^{\frac{1}{2}} \quad \text{or} \quad D_\perp^* = \frac{3\sqrt{2}}{8}\phi^{\frac{1}{2}}$$

obtained in §4.2.1 when $\mathbb{P} \ll 1$ and $\mathscr{P} \gg 1$, so that $D_\parallel \approx D_\perp \approx 1$. Solving (4.11$a$) for $D_\perp$ and using (4.8a) for $D_\parallel$,

$$D_\perp = \frac{1+\dfrac{63\sqrt{2}}{320}|\mathbb{P}|\phi^{\frac{1}{2}}+\dfrac{21\sqrt{2}}{80}\phi^{\frac{1}{2}}}{1-\dfrac{9\sqrt{2}}{80}\phi^{\frac{1}{2}}} \quad (\mathscr{P}\gg 1,\ \phi\ll 1). \qquad (4.11b)$$

At high $\mathbb{P}$, $D_\perp$ becomes

$$D_\perp = D_\perp^* = \frac{63\sqrt{2}}{320}|\mathbb{P}|\phi^{\frac{1}{2}} \quad (\phi^{\frac{1}{2}}|\mathbb{P}|\gg 1,\ \phi\ll 1), \qquad (4.11c)$$

indicating that at sufficiently high Péclet numbers the dimensional transverse diffusivity is independent of the molecular diffusivity, i.e.

$$D_\perp = \frac{63\sqrt{2}}{320}\phi^{\frac{1}{2}}|U|a.$$

5. Non-mechanical dispersion at high Péclet numbers

In §4 we derived a diffusive behaviour that is based solely on the stochastic velocity field in the bed. In doing so we neglected the details of the problem near and inside the particle, treating it as a point. This point-particle approximation was based on the fact that the $O(1)$ region near the particle makes a contribution to the diffusivity that is of smaller order in the volume fraction than that of the $O(\phi^{-\frac{3}{2}})$ region over which the velocity-disturbance-driven flux occurs. Some of these finite-particle contributions to the diffusivity are non-mechanical, however, i.e. they depend on the molecular diffusivity even at large Péclet numbers, and they are thus of higher order in the Péclet number than the purely hydrodynamic results obtained in §4. These non-mechanical contributions influence the leading behaviour of the diffusivity at very high Péclet numbers.

In qualitative terms non-mechanical dispersion arises when a solute molecule introduced at some point in the bed cannot sample all points within the microstructure, i.e. all positions relative to the fixed particles, by convection alone. Such points exist inside and on the surface of the fixed particles and within any region of closed streamlines. The solute can escape the region of closed streamlines or the particle surface or interior only by molecular diffusion. A quantitative criterion for non-mechanical dispersion is that the purely hydrodynamic integral (4.3) for the effective diffusivity fails to converge.

5.1. *Dispersion due to holdup of solute in particles*

The conditionally averaged velocity $\langle \boldsymbol{u} \rangle_1$ is zero inside the particles, so the hydrodynamically determined concentration disturbance (4.2) and the integral (4.3) for the diffusivity are singular in the particle interior. This indicates that molecular diffusion must be considered in order to obtain a finite time-independent diffusivity.

At high Péclet numbers the particle interiors contribute to dispersion primarily by trapping portions of the diffusing species and holding them back against the bulk flow. The magnitude of this 'holdup' dispersion, which we shall denote by $\mathbf{D}_{\mathrm{h}}^*$, can be rationalized by a simple physical argument. In the limit of high Péclet number, where this contribution is important, the resistance to mass transfer in the fluid is $O\,(\mathbb{P}^{-\frac{1}{3}})$ smaller than the diffusive resistance within the particle (Acrivos & Taylor 1962). The residence time of the diffusing species or solute in a single particle is $t_{\mathrm{res}} \sim a^2/D_{\mathrm{p}}$, the diffusive time for the particle. The solute in the fluid has a velocity U relative to the solute in the particle, so the displacement of the solute in the particle relative to that in the fluid, i.e. its mean free path, is $\lambda \sim Ut_{\mathrm{res}} = a^2U/D_{\mathrm{p}}$. At any time the fraction of the solute in the particles is $f_{\mathrm{p}} \sim m^{-1}\phi$. The resulting diffusive contribution is the product of the velocity, the mean free path and the fraction of solute being held back at any given time

$$D^*_{\parallel,\mathrm{h}} \sim f_{\mathrm{p}} \lambda U \sim \frac{a^2U^2}{D_{\mathrm{p}}} \phi \frac{1}{m}.$$

The correct numerical coefficient for this holdup dispersion contribution is obtained by evaluating the portion of the convective flux integral (3.5) inside the particle, i.e.

$$-\mathbf{D}_{\mathrm{h}}^* \cdot \nabla \langle c \rangle_0 = \frac{\mathbb{P}\phi}{\frac{4}{3}\pi} \int_{|\boldsymbol{x}-\boldsymbol{r}_1|<1} \mathrm{d}\boldsymbol{r}_1 \, \langle \boldsymbol{u}' \rangle_1 [\langle c \rangle_1 - \langle c \rangle_{\mathrm{p}}], \tag{5.1a}$$

where $\langle c \rangle_{\mathrm{p}}$ is the solute concentration at equilibrium. Making use of the fact that $\langle \boldsymbol{u} \rangle = -\langle \boldsymbol{u} \rangle_0$ inside the particle and substituting (2.6b) for $\langle c \rangle_{\mathrm{p}}$, (5.1$a$) becomes

$$-\mathbf{D}_{\mathrm{h}}^* \cdot \nabla \langle c \rangle_0 = -\frac{\mathbb{P}\phi}{\frac{4}{3}\pi} \langle \boldsymbol{u} \rangle_0 \int_{|\boldsymbol{x}-\boldsymbol{r}_1|<1} \mathrm{d}\boldsymbol{r}_1 \left[\langle c \rangle_1 - \frac{1}{m}(1+\gamma) \langle c \rangle_0 \right]. \tag{5.1b}$$

The concentration field $\langle c\rangle_1$ within the particle obeys (3.1*b*). The boundary conditions (2.2*d*, *e*) may be replaced by

$$\langle c\rangle_1 = \frac{1}{m}\langle c\rangle_\mathrm{f} = \frac{1}{m}(1+\gamma)\langle c\rangle_0 \quad \text{at } |\boldsymbol{x}-\boldsymbol{r}_1| = 1, \tag{5.2}$$

with an $O(\mathbb{P}^{-\frac{1}{3}})$ error, since the primary resistance to mass transfer is within the particle.

Defining a particle-interior concentration disturbance

$$\langle c'_\mathrm{h}\rangle_1 = \langle c\rangle_1 - \frac{1}{m}(1+\gamma)\langle c\rangle_0,$$

as suggested by the convective flux integral, the equation for $\langle c'_\mathrm{h}\rangle_1$ is, in place of (3.1*b*) and (5.2),

$$\nabla^2\langle c'_\mathrm{h}\rangle_1 = -\frac{1}{m}\mathbb{P}(1+\gamma)^2\langle \boldsymbol{u}\rangle_0\cdot\nabla\langle c\rangle_0, \tag{5.3a}$$

$$\langle c'_\mathrm{h}\rangle_1 = 0 \quad \text{at } |\boldsymbol{x}-\boldsymbol{r}_1| = 1. \tag{5.3b}$$

Because the bulk concentration (2.8) decays linearly with time in response to the bulk convection, and $\langle c'_\mathrm{h}\rangle_1$ is assumed time-independent at long times, the time derivative in (3.1*b*) is replaced by a steady source term in equation (5.3*a*) for the concentration disturbance in the particle. This source reflects the fact that solute must diffuse out of the particle in order to maintain a constant concentration disturbance in the presence of a decaying fluid concentration. The solution for $\langle c'_\mathrm{h}\rangle_1$ is easily obtained, and when substituted in (5.1*b*) it gives

$$\left.\begin{aligned} D^*_{\parallel,\mathrm{h}} &= \frac{1}{15}\frac{1}{m}(1+\gamma)^2\frac{D_\mathrm{f}}{D_\mathrm{p}}\mathbb{P}^2\phi, && (5.4a)\\ D^*_{\perp,\mathrm{h}} &= 0 && (5.4b)\end{aligned}\right\} \quad (\mathbb{P}\gg 1).$$

When the particles are impermeable to the solute ($m^{-1} = 0$) this holdup dispersion is absent. This simply means that the solute cannot be dispersed by retention in the fixed particles when it cannot penetrate the particles. The equivalent criterion for the absence of holdup dispersion in the heat-transfer problem is that the heat capacity of the particles be small compared with that of the fluid. Note also that holdup dispersion acts only parallel to the bulk flow.

Reis *et al.* (1979) studied dispersion in a bed of fixed spheres assuming uniform one-dimensional flow in the fluid phase and assuming that the rate of mass transfer from the spheres to the fluid could be written in terms of the product of a mass-transfer coefficient and the concentration difference between the spheres and the fluid. They obtained an expression for the effective diffusivity that reduces to (5.4*a*) in the present limit $\mathbb{P}\gg 1$.‡ Reis *et al.* found neither the hydrodynamic dispersion of §§3 and 4 nor the logarithmic dispersion that we shall examine in §5.2, because they neglected the effect of the particles on the velocity field in the fluid.

Although we have presented this holdup dispersion on the context of the dilute results on §§3 and 4, it should be clear that these results are not limited to dilute systems. Since the leading effect in $\mathbb{P}$ occurs within the particles and the particle surfaces are at constant concentration, (5.4*a*, *b*) are valid in fixed beds of *any* volume fraction.

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‡ The expression (122) for the holdup dispersion contribution presented by Reiss *et al.* differs from (5.4*a*) by a factor of $1+\gamma$ because they defined the effective diffusivity in terms of the fluid concentration rather than the bed-average concentration, and by a factor of $(1-\phi)^2$ because their expression is written in terms of the superficial velocity rather than the bed-average velocity.

5.2. *Non-mechanical dispersion in the fluid*

Even if the fixed particles are impermeable to the diffusing species, non-mechanical dispersion arises owing to stagnant regions and to regions of closed streamlines in the fluid. We do not expect regions of stagnant fluid in a bed of solid spheres, but a porous medium with a more complex microstructure, particularly one that contains dead-end pores, might well possess regions of stagnant fluid. If they exist these stagnant regions make $O(\mathbb{P}^2\phi_s)$ holdup dispersion contributions to the longitudinal diffusivity, where ϕ_s is the volume fraction of such stagnant regions in the bed.

In a bed of fixed spheres no stagnant fluid regions are expected, but regions of closed streamlines do arise for Stokes flow past two fixed spheres (Davis *et al.* 1976). In the dilute limit the flow *near* two fixed spheres in a fixed bed satisfies Stokes equations approximately, although the full Brinkman equations must be used far from the particles. Thus we can infer that regions of closed streamlines enter the fixed-bed analysis at the level of the two-particle problem. Because the solute can only escape a region of closed streamlines by molecular diffusion normal to the streamlines, these regions are expected to make an $O(\phi^2\mathbb{P}^2)$ holdup contribution to the effective diffusivity.

At the level of a one-sphere problem there are no regions of closed streamlines and no stagnant fluid. As we shall now see, however, the hydrodynamically determined concentration is singular at the particle surface, and this leads to an $O(\phi\mathbb{P}\ln\mathbb{P})$ 'boundary-layer' contribution to the longitudinal diffusivity.

The purely hydrodynamic mass-conservation equation

$$\langle \boldsymbol{u}\rangle_1\cdot\nabla\langle c'\rangle_1 = -\langle \boldsymbol{u}'\rangle_1\cdot\nabla\langle c\rangle_0$$

reduces near the particle surface to

$$-\tfrac{3}{2}y^2\cos\theta\frac{\partial\langle c'\rangle_1}{\partial y}+\tfrac{3}{2}y\sin\theta\frac{\partial\langle c'\rangle_1}{\partial\theta}+O(y^2) = \langle \boldsymbol{u}\rangle_0\cdot\nabla\langle c\rangle_0, \tag{5.5}$$

where $y = r-1 \ll 1$. Solving (5.5) by the method of characteristics, the streamlines (or characteristic curves) are

$$\psi = y\sin\theta, \tag{5.6a}$$

where ψ is the stream function, which is constant along streamlines. The hydrodynamically determined concentration disturbance is

$$\langle c'\rangle_1 = \frac{2}{3\psi}\theta\langle \boldsymbol{u}\rangle_0\cdot\nabla\langle c\rangle_0 = \frac{2\theta}{3y\sin\theta}\langle \boldsymbol{u}\rangle_0\cdot\nabla\langle c\rangle_0. \tag{5.6b}$$

Substituting (5.6*b*) and $\langle \boldsymbol{u}'\rangle_1 = -\langle \boldsymbol{u}\rangle_0$ into the portion of (3.5) near the particle, and using the volume element $\mathrm{d}V = \mathrm{d}y\sin\theta\,\mathrm{d}\theta$, this purely mechanical analysis gives a contribution near the surface of

$$D^*_{\parallel,\mathrm{BL}} = \int_0^\pi \sin\theta\,\mathrm{d}\theta\int_0^\epsilon \mathrm{d}y\frac{2\theta}{3y\sin\theta}, \quad D^*_{\perp,\mathrm{BL}} = 0. \tag{5.7a, b}$$

Here ϵ is an arbitrary small constant ($\epsilon \ll 1$) introduced to avoid carrying the integration in (5.7*a*) outside the region $y \ll 1$ where the present approximation is valid. The integral in (5.7*a*) is conditionally convergent at $y = 0$, indicating that the purely mechanical analysis does indeed break down near the particle surface.

The problem is that, even at high $\mathbb{P}$, diffusion becomes important in a thin boundary layer $y = O(\mathbb{P}^{-\frac{1}{3}})$ near the particle surface. In this boundary layer the convection–diffusion equation is

$$-\tfrac{3}{2}Y^2\cos\theta\frac{\partial\langle c'\rangle_1}{\partial Y}+\tfrac{3}{2}Y\sin\theta\frac{\partial\langle c'\rangle_1}{\partial\theta}-\frac{\partial^2\langle c'\rangle_1}{\partial Y^2}+O(\mathbb{P}^{-\frac{1}{3}}) = \mathbb{P}^{\frac{1}{3}}\langle \boldsymbol{u}\rangle_0\cdot\boldsymbol{\nabla}\langle c\rangle_0, \quad (5.8)$$

where the stretched coordinate $Y = y\mathbb{P}^{\frac{1}{3}}$. This equation is similar to the boundary-layer equation obtained in the problem of determining the coefficient of mass transfer from a sphere in Stokes flow (Acrivos & Taylor 1962). However, the source on the right-hand side of (5.8) makes finding the solution of this boundary-layer problem more difficult.

Fortunately, we can obtain the leading effect of the particle surface boundary layer on dispersion without determining the full solution of (5.8). The most important effect of diffusion is to eliminate the singularity in the hydrodynamically determined concentration (5.6*b*). An approximation to the concentration disturbance that reflects this important effect of diffusion is

$$\langle c'\rangle_{1,\,\mathrm{app}} = \langle \boldsymbol{u}\rangle_0\cdot\boldsymbol{\nabla}\langle c\rangle_0 \min\left[\frac{2\theta}{3y\sin\theta}, b\mathbb{P}^{\frac{1}{3}}\right], \quad (5.9)$$

where b is an $O(1)$ constant. Equation (5.9) is identical with the hydrodynamic solution (5.6) outside the boundary layer, but the concentration disturbance becomes an $O(\mathbb{P}^{\frac{1}{3}})$ constant in the boundary layer. Substituting (5.9) in the portion of (3.5) near the particle gives the boundary-layer contribution

$$D^*_{\parallel,\,\mathrm{BL}} = \tfrac{1}{6}\pi^2\phi\mathbb{P}\ln\mathbb{P}+O(\phi\mathbb{P}), \quad D^*_{\perp,\,\mathrm{BL}} = 0. \quad (5.10a, b)$$

In the Appendix we show that the use of the approximate concentration disturbance (5.9), which is constant in the boundary layer, rather than the full solution of (5.8), causes a small $O(\phi\mathbb{P})$ error. Note also that the leading term in (5.10*a*) is independent of the constant b. This indicates that the exact form of the concentration disturbance in the boundary layer does not affect the leading $O(\phi\mathbb{P}\ln\mathbb{P})$ term in (5.10). We only need to recognize that the singularity in $\langle c'\rangle_1$ as $y\rightarrow 0$ is eliminated and that $\langle c'\rangle_1 = O(\mathbb{P}^{\frac{1}{3}})$ in the boundary layer.‡

Boundary-layer dispersion will occur in any porous medium owing to the no-slip condition at solid surfaces. The $\frac{1}{6}\pi^2\phi$ in (5.10*a*) will in general be replaced by a factor that depends on the nature of the microstructure, but the $\mathbb{P}\ln\mathbb{P}$ behaviour is independent of the details of the microstructure. Because the boundary-layer dispersion and the permeability are both related to the velocity gradient at the particle surfaces, one might hope to generalize (5.10*a*) by finding a correlation between $D^*_{\parallel,\,\mathrm{BL}}$ and the permeability k. However, while the permeability is related to an integral of the velocity gradient over the solid surfaces, and is influenced primarily by regions of high velocity gradients, such as in the narrow gaps where two particles are nearly touching, the dispersion occurs primarily in regions of low velocity gradients, such as in the junctions connecting the narrow gaps, where the diffusive boundary layer is thickest. Thus, no general correlation between dispersion and permeability can be drawn.

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‡ Saffman (1959) used a similar scheme to obtain the analogous logarithmic term in his pore model for a consolidated porous medium, placing a diffusively determined maximum value on the time taken for a solute molecule to pass through a pore. However, Saffman was apparently not aware of the $\mathbb{P}^{\frac{1}{3}}$ scaling of the diffusive boundary layer (this scaling was first worked out three years later by Acrivos & Taylor 1962). As a result Saffman chose the wrong maximum transit time, causing an error in his expression (his (4.5) with (4.3*a*)) for the long-time longitudinal diffusivity. The second and third terms in his (4.3*a*) are too large by a factor of three.

Because of the linearity of the mass-conservation equation (3.1), the solutions of (5.1) and (5.2) can be superimposed. Thus the full form of the longitudinal diffusivity at high Péclet numbers including the mechanical contribution and the various non-mechanical (holdup and boundary-layer) terms is

$$D_{\parallel} = \tfrac{3}{4}|\mathbb{P}| + \tfrac{1}{6}\pi^2\phi\,|\mathbb{P}|\ln|\mathbb{P}| + \frac{1}{15}\frac{D_{\mathrm{f}}}{mD_{\mathrm{p}}}(1+\gamma)^2\phi\mathbb{P}^2. \tag{5.11}$$

6. Results and conclusions

In this final section we summarize the results derived in the present theoretical analysis and compare them with the experimental work reported by Fried & Combarnous (1971). It has been shown that macrotransport in a fixed bed may be described by a macroscopic Fick's law in the long-time limit, provided that the concentration gradient varies slowly over the lengthscale of the one-particle problem. The results of §§3–5 taken together provide a description of the leading effect of the particles on the effective diffusivity. These results are summarized in table 1.

The asymptotic analysis presented here demonstrates the diversity of physical processes leading to diffusion in porous media. In the absence of convection, the particles affect diffusion through the difference in diffusivities of the fluid and particulate phases. In the presence of a bulk convective motion, however, even at low Péclet numbers, $\phi^{\frac{3}{4}} \ll \mathbb{P} \ll \phi^{\frac{1}{2}}$, the stochastic velocity field induced by the particles becomes a more important factor affecting macrotransport than the difference in diffusivities. The effect of convection is unexpectedly strong because velocity disturbances in a porous medium are correlated over a lengthscale $k^{\frac{1}{2}} \sim a\phi^{-\frac{1}{2}}$ that is large in a dilute (highly permeable) medium.

In either a theoretical or experimental study of the effect of such a stochastic velocity field on dispersion it is important to be sure that one obtains a truly diffusive behaviour, i.e. one in which the mean-squared displacement of a tracer particle grows linearly with time. Such a diffusive behaviour is obtained in general only if there is a mechanism by which a tracer particle may sample all possible values of the stochastic velocity field. In a porous medium this means sampling all points in the microstructure of the medium. At sufficiently low Péclet numbers $\mathscr{P} = \mathbb{P}k^{\frac{1}{2}} \sim \mathbb{P}\phi^{-\frac{1}{2}} \ll 1$, molecular diffusion plays the role of transporting the tracer particle through the microstructure. Because molecular diffusion causes the velocity fluctuations experienced by the tracer to become uncorrelated, it inhibits the convective transport, and the resulting diffusivity grows as $U^2a^2/D_{\mathrm{f}}\phi^{\frac{1}{2}}$, as we saw in §3.

At high Péclet numbers the bulk convective motion in the bed becomes a more important mechanism for transporting the tracer throughout *most* of the bed. As a result molecular diffusion has no role in the dispersive mechanism, giving rise to the $O(Ua)$ purely mechanical diffusivity derived in §4.

There are, however, regions in the bed that the tracer cannot sample by convection alone. These include regions where the velocity is zero no matter how strong the bulk flow, such as the interior of fixed particles and dead-end pores, and regions of closed streamlines. Molecular diffusion is the only mechanism by which the tracer can sample these regions, and so they contribute a dispersivity that grows like U^2a^2/D even in the high Péclet-number limit as discussed in §5.1. Here D may be either D_{f} or D_{p}, depending on whether the region in question is in the fluid or the particles.

Finally, yet another mechanism discussed in §5.2 governs dispersion in the fluid near surfaces where the fluid satisfies a no-slip boundary condition. Here there is no

Flow regime	Longitudinal $D_{\parallel}/D_{\mathrm{f}}$	Transverse $D_{\perp}/D_{\mathrm{f}}$
$\mathbb{P} \ll \phi^{\frac{1}{2}} \ll 1$ $(\mathscr{P} \ll 1)$	$1+\dfrac{3(\alpha-1)}{\alpha+2}\phi+\dfrac{\sqrt{2}}{15}\dfrac{\mathbb{P}^2}{\phi^{\frac{1}{2}}}$	$1+\dfrac{3(\alpha-1)}{\alpha+2}\phi+\dfrac{\sqrt{2}}{60}\dfrac{\mathbb{P}^2}{\phi^{\frac{1}{2}}}$
$\phi^{\frac{3}{4}} \ll \mathbb{P} \ll 1$	figure 1, (3.14*b*)	figure 1, (3.14*a*)
$\phi^{\frac{1}{2}} \ll \mathbb{P} \ll 1$ $(\mathscr{P} \gg 1)$	$1+\frac{3}{4}\lvert\mathbb{P}\rvert$	$1+\dfrac{3\sqrt{2}}{8}\phi^{\frac{1}{2}}$
$\mathbb{P} \gg 1$	$1+\frac{3}{4}\lvert\mathbb{P}\rvert+\frac{1}{6}\pi^2\phi\lvert\mathbb{P}\rvert\ln\lvert\mathbb{P}\rvert+\frac{1}{15}(1+\gamma)^2\dfrac{D_{\mathrm{f}}}{mD_{\mathrm{P}}}\phi\mathbb{P}^2$	$1+\dfrac{63\sqrt{2}}{320}\phi^{\frac{1}{2}}\lvert\mathbb{P}\rvert$

TABLE 1. The leading behaviour of the effective diffusivity is given for all values of the Péclet number $\mathbb{P} = Ua/D_{\mathrm{f}}$. $\mathscr{P} = \mathbb{P}a^{-1}k^{\frac{1}{2}}$ is the Péclet number based on the screening length. The factor γ is given by (2.6*c*).

finite region of zero velocity, but the velocity goes to zero at the surface. The tracer samples this region by a combination of convection and diffusion normal to the surface. As a result the contribution to the effective diffusivity from this region, $O(Ua\ln(Ua/D_{\mathrm{f}}))$, depends on the diffusivity, but the dependence on D_{f} is much weaker than the $O(U^2a^2/D)$ dispersion obtained in finite regions of zero velocity.

Although the dispersion mechanisms discussed above were discovered through an asymptotic analysis in low solids volume fraction, these same physical processes occur in more densely packed beds. Thus the predicted Péclet-number dependence of the effective diffusivity obtained here is applicable to densely packed beds and porous media. In fact, the holdup dispersion contribution is given by (5.4*a*) independent of the volume fraction at high Péclet number. The volume-fraction dependence of the mechanical and boundary-layer dispersion contributions in dense beds cannot, however, be determined from the dilute-bed analysis. The similarities between the mechanisms of dispersion in dilute and dense systems indicates that it is reasonable to compare these calculations with experimental data taken in densely packed beds.

Fried & Combarnous (1971) have collected the results of several experimental investigations of dispersion in packed beds of impermeable particles. The experimental procedure was to introduce a step change in the concentration of a dilute solute and observe the resultant concentration profile downstream from the inlet. It was found that sufficiently far downstream the concentration profiles were well fitted by the exponential profiles that would be obtained by substituting step functions as the initial condition in the macroscopic Fick's law (2.3*a*) and (2.5) with a constant diffusivity. The experimentally determined diffusivities are taken to be those values of the diffusivity which give the best fit of the experimentally observed concentration profiles. The resultant longitudinal and transverse diffusivities are plotted as functions of the Péclet number in figure 2.

At sufficiently large distances from the inlet, the experimental concentration profiles satisfy the condition that the concentration gradient vary slowly over a distance $a\phi^{-\frac{1}{2}}$, so the present long-time analysis is applicable. A uniformly valid approximation for the transverse diffusivity in a bed of impermeable particles may be obtained by summing the diffusivities given by (3.3), (3.14*a*) and (4.11*b*) and subtracting the behaviour (4.9) of these solutions in their overlap region $\phi^{\frac{1}{2}} \ll \mathbb{P} \ll 1$. The leading behaviour of the longitudinal diffusivity is given by the sum of (3.3), (3.14*b*) and (5.10*a*). The theoretical results plotted in figure 2 were obtained by

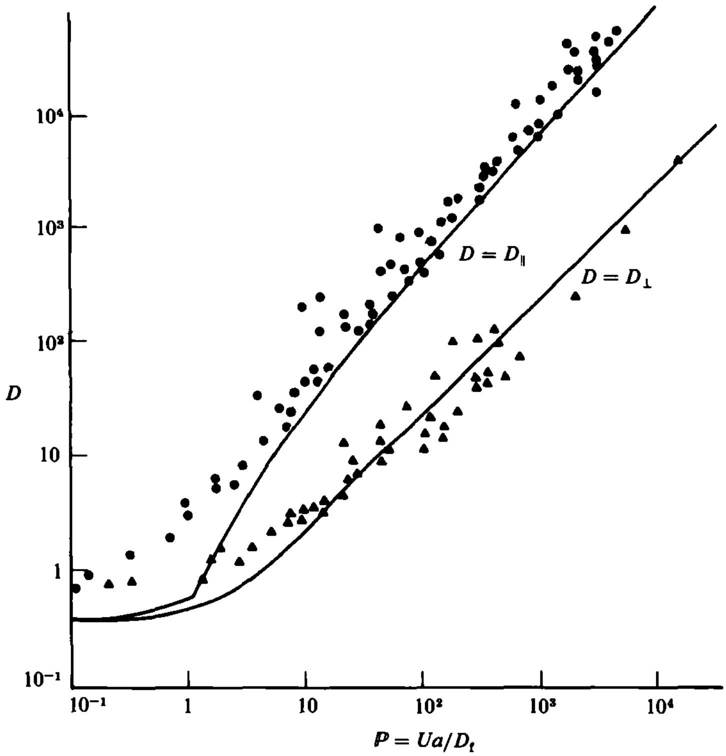

FIGURE 2. The theoretically predicted values of the effective diffusivity (solid lines) obtained through the present asymptotic analysis are compared with the experimental values reported by Fried & Combarnous (1971). ▲ indicates an experimentally obtained transverse diffusivity and ● an experimental value for the longitudinal diffusivity. We have arbitrarily chosen $P = 1$ as the point where the high-P asymptotic result (5.11) for the longitudinal diffusivity becomes valid, and this causes the change in slope evident at $P = 1$.

substituting the volume fraction $\phi = 0.5$, typical of packed beds, into these uniformly valid approximations.‡

The theory shows very good agreement with the experiments, even as far as the numerical coefficients are concerned. In particular, both theory and experiment show a transition from a low-P behaviour, where the effective diffusivity is independent of P and of the same order as the molecular diffusivity, to a high-P behaviour, where the effective diffusivity grows with P. The theoretical prediction of the transverse diffusivity is quite close to the experimentally measured values at high P; both theory and experiment indicate that $D_{\perp}$ grows linearly with P. At very high P the theory predicts that the longitudinal diffusivity grows like $P \ln P$. Considering the scatter in the data, it is not easy to distinguish this $O(P \ln P)$ behaviour from the $O(P)$ diffusivity predicted by mechanical dispersion. It does appear, however, that the experimentally measured longitudinal diffusivities grow faster than P for $10^2 < P < 10^4$. Note that the good agreement between theory and experiment has been obtained here without any adjustable parameters.

We have not included the $O(\phi^2 P^2)$ contribution to the longitudinal diffusivity that

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‡ Both the $O(\phi)$ Maxwell term and the $O(\phi^2)$ Jeffrey correction were included in the calculated results in figure 2. Thus for impermeable particles $\mathbf{D}^{\alpha} = \mathbf{I}(-1.5\phi + 0.588\phi^2)$.

is expected to arise from the holdup of solute in regions of closed streamlines in the theoretical curve in figure 2. This holdup dispersion is not detectable from the presently available experimental data on longitudinal dispersion in fixed beds of impermeable particles. Two possible explanations for the failure of experimentalists to observe this $O(P^2)$ behaviour are as follows. (1) The numerical coefficient of the $O(P^2)$ term in the longitudinal diffusivity may be quite small owing to the small fraction of the bed that is made up of regions of closed streamlines. It would then be necessary to obtain data at higher Péclet numbers than those contained in figure 2. (2) The data at very high Péclet number contained in figure 2 may have been taken without allowing sufficient time to reach the long-time diffusive behaviour.

Han, Bhakta & Carbonell (1984) noted that in the experiments of several previous investigators insufficient time was allowed for the final diffusive behaviour to be observed. Their own time-dependent experiments indicated that the apparent longitudinal diffusivity increased with time before reaching its long-time asymptote. They observed no time-dependent behaviour for the transverse diffusivity, however. These observations can be explained in terms of the present theoretical results.

Transverse dispersion is caused by mechanical mechanisms alone, so the characteristic time for $D_\perp$ to reach its long-time behaviour is $a/U\phi^{\frac{1}{2}}$. On the other hand the longitudinal diffusivity depends on non-mechanical mechanisms arising from the no-slip boundaries and on holdup dispersion. The characteristic time required for the boundary dispersion to reach its long-time behaviour is the diffusive time in the boundary layer, $a^2 P^{-\frac{2}{3}}/D_f = aP^{\frac{1}{3}}/U$, while the characteristic time for holdup dispersion is $a^2/D_f = aP/U$. At high Péclet numbers the mechanical dispersion that determines the transverse diffusivity reaches its long-time behaviour much faster that the boundary and holdup dispersion terms that influence longitudinal diffusion. Thus it is not surprising that Han *et al.* observed a time-dependent $D_\parallel$, but a time-independent $D_\perp$. We plan to address the problem of time- and space-dependent diffusivities in more detail in a future paper.

The present analysis suggests that longitudinal dispersion in heterogeneous media in the presence of convection is inherently non-mechanical in the limit of high Péclet numbers. Even in the absence of the $O(P^2)$ holdup dispersion contributions, the longitudinal diffusivity is non-mechanical at high P owing to the $O(P \ln P)$ boundary-layer dispersion. The only prerequisite for the appearance of such non-mechanical, boundary-layer, dispersion effects is a bulk convective motion relative to solid surfaces on which no-slip boundary conditions must be satisfied. Thus this type of non-mechanical dispersion is expected in all types of porous media, both unconsolidated and consolidated. Note that Saffman (1959) observed this type of behaviour in a capillary network model of a consolidated porous medium. Some recent studies of convective transport in lattice or network models of porous media (e.g. Adler & Brenner 1984; Gavalas & Kim 1981; Sahimi *et al.* 1983) and even in fractal models (Adler 1984) have simplified the convective motion into a 'conductance' formulation, and have thus overlooked this important non-mechanical boundary-layer dispersion, which is expected to be the dominant mechanism for longitudinal dispersion at high Péclet numbers.

In addition to being restricted to long times, the present analysis describes only the macrotransport or macromixing of the solute. The macrotransport equations (2.3*a*) and (2.5) derived herein describe the evolution of the ensemble-average concentration, which is equivalent to the volume-average concentration for a volume containing many particles. Information concerning the micromixing of the solute, i.e. mixing on lengthscales equal to or smaller than the interparticle separation, is lost in the averaging process. This distinction is particularly important when macromixing is accomplished primarily by mechanical or hydrodynamic dispersion. Here macromixing is completed in a time $a/U\phi^{\frac{1}{2}}$ that is short at high $\mathcal{P}$. Micromixing, however, requires the aid of molecular diffusion to achieve a uniform concentration down to the molecular lengthscale, and thus requires a much longer time a^2/D_f. As a result, for times $a/U\phi^{\frac{1}{2}} \ll t \ll a^2/D_f$ the concentration is uniform on the macroscale $l \gg a$, but fluctuates rapidly on the microscale $l \ll a$. This phenomenon is important, for example, when the solute undergoes chemical reaction.

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Appendix. Justification of the asymptotic analysis

A 1. *Justification of the low-Péclet-number analysis of* §3

We first turn to the task of justifying the assumptions made in the one-particle problem used in §3 to derive the low-ϕ low-$\mathcal{P}$ behaviour of the effective diffusivity.

Two basic types of error have been made: those due to the finite size of the particles, and those due to neglecting various convective terms in the excess-flux expression and in the concentration-disturbance equation. In estimating the errors of these latter terms, the particle can again be treated as a point. We begin by examining the contributions from the finite size of the particle.

There will be a contribution to Maxwell's correction to the effective diffusivity, $\mathbf{D}^{\alpha}$ in (2.7*c*), from the perturbation to $\nabla\langle c\rangle_1$ *inside* the particle at $\boldsymbol{r}_1$ caused by the convective motion. The perturbation to $\nabla\langle c\rangle_1$ is clearly $O(\mathcal{P})$, and since the integral in (2.7*c*) is over the particle volume, this contribution is $O((\alpha-1)\,\mathcal{P}\phi)$, which is always small compared with $\mathbf{D}^*$ as given by (3.14) or (2.7*d*). Note that the Péclet number $\mathcal{P}$ based on the particle size is appropriate for estimating the influence of convection near the particle. There is also of course the $O((\alpha-1)\,\phi^2)$ pure-conduction correction to Maxwell's result calculated by Jeffrey (1973).

In solving (3.8) for the disturbance concentration field no boundary conditions were satisfied at the particle surface. There are corrections to $\langle c'\rangle_1$ that are $O((\alpha-1)\,r^{-2})$ from the source dipole that arises in Maxwell's conduction problem and $O(\mathcal{P}r^{-1})$ from a source term that arises from the time-dependent nature of the bulk field. (The origin of this source is clarified in §A 2.) Using these in the excess-flux integral (3.5) gives corrections $O((\alpha-1)\,\mathcal{P}\phi)$ and $O(\mathcal{P}^2\phi^{\frac{1}{2}})$ respectively, which are small compared with $|\mathbf{D}^*|$.

Neglecting the particle size in using the convolution theorem and in using the point-force velocity disturbance creates errors that are $O(\phi)$ and $O(k^{-\frac{1}{2}} \sim \phi^{\frac{1}{2}})$ smaller than $|\mathbf{D}^*|$ respectively. As discussed by Hinch (1977) and Acrivos *et al.* (1980), the error in neglecting terms on the right-hand side of the momentum equation (3.6*b*) is also $O(\phi^{\frac{1}{2}})$ smaller than the terms that have been retained.

The final particle contributions come from the neglected $\gamma\langle \boldsymbol{u}\rangle_0\langle c\rangle_0$ term used in defining $\mathbf{D}^*$ and from not evaluating $\langle \boldsymbol{u}'\rangle_1\langle c'\rangle_1$ within the particle, as required by the excess-flux integral. It is the difference of these two terms inside the particle as written in (3.5) that contributes to the dispersive flux

$$\mathcal{P}\int_{|\boldsymbol{x}-\boldsymbol{r}_1|\leqslant 1} \mathrm{d}\boldsymbol{r}_1\, P(\boldsymbol{r}_1)\,\langle \boldsymbol{u}'\rangle_1\,[\langle c\rangle_1-\langle c\rangle_{\mathrm{p}}]. \tag{A 1}$$

$\langle \boldsymbol{u}' \rangle_1 = -\langle \boldsymbol{u} \rangle_0$ within the particle and the difference $\langle c \rangle_1 - \langle c \rangle_{\mathrm{p}}$ will be $O(\alpha - 1)$ from the Maxwell conduction problem and $O(\mathbb{P})$ from the velocity-disturbance-driven concentration field outside the particle. Hence this dispersion due to the fixed particles holding back the tracer relative to the bulk flow is $O((\alpha-1)\,\mathbb{P}\phi)$ or $O(\mathbb{P}^2\phi)$, both of which are small.

There are three convective errors that must be addressed. Since these corrections enter on the scale of the Brinkman screening length $R = O(1)$, they are most easily discussed in terms of point particles and the Péclet number $\mathscr{P}$ based on the screening length. The first correction is that due to approximating the conditionally averaged velocity $\langle \boldsymbol{u} \rangle_1$ by the bulk-average $\langle \boldsymbol{u} \rangle_0$ on the left-hand side of (3.9), thus neglecting $\mathbb{P}k^{-\frac{1}{2}}\langle \boldsymbol{u}' \rangle_1 \cdot \nabla_R \langle c' \rangle_1$. Using the already-determined solution for $\langle c' \rangle_1$, the neglected term drives an $O(\mathscr{P}k^{-\frac{1}{2}}R^{-3})$ correction to $\langle c' \rangle_1$ when conduction dominates, $\mathscr{P} \ll 1$, and an $O(k^{-\frac{1}{2}}R^{-5})$ correction when convection dominates, $\mathscr{P} \gg 1$. Substituting into the excess-flux integral (3.5), these corrections are $O(\mathscr{P}^3k^{-1}, \mathscr{P}k^{-1})$ respectively, which are $O(\mathscr{P}k^{-\frac{1}{2}})$ and $O(k^{-\frac{1}{2}})$ smaller than $D^*_{\parallel}$ and $O(\mathscr{P}k^{-\frac{1}{2}}, \mathscr{P}k^{-\frac{1}{2}})$ smaller than $D^*_{\perp}$.

The next correction comes from approximating the exact convective-flux integral (3.4) by (3.5), giving rise to an error

$$\int \mathrm{d}\boldsymbol{r}_1\, P(\boldsymbol{r}_1)\,[\langle \boldsymbol{u}'c' \rangle_1 - \langle \boldsymbol{u}' \rangle_1 \langle c' \rangle_1]. \tag{A 2}$$

Using the definition of the ensemble average, (A 2) may be written as

$$\iint \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2\, P(\boldsymbol{r}_1, \boldsymbol{r}_2)\,\langle \boldsymbol{u}'c' \rangle_2 - \int \mathrm{d}\boldsymbol{r}_1\, P(\boldsymbol{r}_1)\,\langle \boldsymbol{u}' \rangle_1 \langle c' \rangle_1, \tag{A 3}$$

or, upon rearrangement,

$$\iint \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2\, P(\boldsymbol{r}_1, \boldsymbol{r}_2)\,\langle \boldsymbol{u}''c'' \rangle_2 + \iint \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2\, [P(\boldsymbol{r}_1, \boldsymbol{r}_2) - \tfrac{1}{2}P(\boldsymbol{r}_1)\,P(\boldsymbol{r}_2)]\,\langle \boldsymbol{u}'(\boldsymbol{x}\,|\,\boldsymbol{r}_1) \rangle_1 \langle c'(\boldsymbol{x}\,|\,\boldsymbol{r}_2) \rangle_1, \tag{A 4}$$

where $\boldsymbol{u}'' = \boldsymbol{u}' - \langle \boldsymbol{u}'(\boldsymbol{x}\,|\,\boldsymbol{r}_1) \rangle_1 - \langle \boldsymbol{u}'(\boldsymbol{x}\,|\,\boldsymbol{r}_2) \rangle_1$ and $c'' = c' - \langle c'(\boldsymbol{x}\,|\,\boldsymbol{r}_1) \rangle_1 - \langle c'(\boldsymbol{x}\,|\,\boldsymbol{r}_2) \rangle_1$ are the velocity and concentration disturbances caused by groups of two or more particles.[†] The leading contribution to the two-particle velocity disturbance $\boldsymbol{u}''$ comes from the change in the force strength of the particle at $\boldsymbol{r}_2$ due to the point-force velocity disturbance of the particle at $\boldsymbol{r}_1$ and *vice versa*. In screening-length variables

$$\boldsymbol{u}'' = O(k^2\,|\boldsymbol{R}_1 - \boldsymbol{R}_2|^{-2}\,R_2^{-3}),$$

where $\boldsymbol{R}_1 = k^{-\frac{1}{2}}(\boldsymbol{x} - \boldsymbol{r}_1)$ and $\boldsymbol{R}_2 = k^{-\frac{1}{2}}(\boldsymbol{x} - \boldsymbol{r}_2)$. This gives for the first term in (A 4)

$$\mathscr{P}k^{\frac{1}{2}} \iint \mathrm{d}\boldsymbol{R}_1\, \mathrm{d}\boldsymbol{R}_2\, |\boldsymbol{R}_1 - \boldsymbol{R}_2|^{-3}\,R_2^{-3} \langle c'' \rangle_2,$$

where we have taken $P(\boldsymbol{r}_1, \boldsymbol{r}_2) = O(\phi^2)$ in the screening-length region. An equation analogous to (3.8) can be written for $\langle c'' \rangle_2$. It is easy to show that the leading contribution to $\langle c'' \rangle_2$ is driven by $\mathscr{P}k^{\frac{1}{2}}\langle \boldsymbol{u}'' \rangle_2 \cdot \nabla \langle c \rangle_0$, leading to a two-particle concentration disturbance of

$$\langle c'' \rangle_2 = O(\mathscr{P}k^{-\frac{1}{2}}\,|\boldsymbol{R}_1 - \boldsymbol{R}_2|^{-3}\,R_2^{-1},\ k^{-\frac{1}{2}}\,|\boldsymbol{R}_1 - \boldsymbol{R}_2|^{-3}\,R_2^{-2})$$

[†] The factor of $\frac{1}{2}$ in (A 4) arises because the number of groups of two particles is $\frac{1}{2}N^2$, in the limit $N \rightarrow \infty$, where N is the number of particles in the bed.

in the conduction- and convection-dominated regions respectively. Thus the first term in (A 4) gives corrections

$$O(\mathscr{P}^2 k^{-1}, \mathscr{P} k^{-1}),$$

which are $O(k^{-\frac{1}{2}}) = O(\phi^{\frac{1}{2}})$ smaller than $D^*_{\parallel}$, and $O(\phi^{\frac{1}{2}}, \mathscr{P}\phi^{\frac{1}{2}})$ small compared with $D^*_{\perp}$ at low and high $\mathscr{P}$ respectively.

The second term in (A 4) involves the correlation between the positions of two particles. For example, the condition that the particles do not overlap requires that the centres of no two particles be closer than two particle radii apart, i.e. $P(\boldsymbol{r}_1, \boldsymbol{r}_2) = 0$ for $|\boldsymbol{r}_1 - \boldsymbol{r}_2| < 2$. We expect that the correlation between particle positions will decay, $P(\boldsymbol{r}_1, \boldsymbol{r}_2) \rightarrow \frac{1}{2} P(\boldsymbol{r}_1)\, P(\boldsymbol{r}_2)$, in an $O(1)$ distance independent of the permeability. Thus the second term in (A 4) arises only near the two particles and is $O(\mathbb{P}^2 \phi^2)$.

The final convective correction comes from neglecting the nonlinear average

$$\mathbb{P}\nabla \cdot [\langle(\boldsymbol{u} - \langle \boldsymbol{u}\rangle_1)(c - \langle c\rangle_1)\rangle_1 - \langle(\boldsymbol{u} - \langle \boldsymbol{u}\rangle_0)(c - \langle c\rangle_0)\rangle_0]$$

on the right-hand side of (3.8). In the limit of small ϕ this term can be approximated as

$$\mathbb{P}\nabla \cdot \int \mathrm{d}\boldsymbol{r}_2 \, [P(\boldsymbol{r}_2 | \boldsymbol{r}_1)\langle \boldsymbol{u} - \langle \boldsymbol{u}\rangle_1\rangle_2 \langle c - \langle c\rangle_1\rangle_2 - P(\boldsymbol{r}_2)\langle \boldsymbol{u}'(\boldsymbol{x}|\boldsymbol{r}_2)\rangle_1 \langle c'(\boldsymbol{x}|\boldsymbol{r}_2)\rangle_1. \quad \text{(A 5)}$$

As $|\boldsymbol{x} - \boldsymbol{r}_1| \rightarrow \infty$, with $|\boldsymbol{x} - \boldsymbol{r}_2|$ fixed, $P(\boldsymbol{r}_2|\boldsymbol{r}_1) \sim P(\boldsymbol{r}_2)$, $\langle \boldsymbol{u} - \langle \boldsymbol{u}(\boldsymbol{x}|\boldsymbol{r}_1)\rangle_1\rangle_2 \sim \langle \boldsymbol{u}'(\boldsymbol{x}|\boldsymbol{r}_2)\rangle_1$, $\langle c - \langle c(\boldsymbol{x}|\boldsymbol{r}_1)\rangle_1\rangle_2 \sim \langle c'(\boldsymbol{x}|\boldsymbol{r}_2)\rangle_1$, and the integrand of (A 5) vanishes. The form of the concentration field $\langle c'\rangle_1$ driven by (A 5) will depend on how fast $P(\boldsymbol{r}_2|\boldsymbol{r}_1) \sim P(\boldsymbol{r}_2)$ and on the corrections to representing $\langle \boldsymbol{u} - \langle \boldsymbol{u}\rangle_1\rangle_2$ as $\langle \boldsymbol{u}'(\boldsymbol{x}|\boldsymbol{r}_2)\rangle_1$, etc. We have assumed that the bed is sufficiently random for $P(\boldsymbol{r}_2|\boldsymbol{r}_1)$ to asymptote to $P(\boldsymbol{r}_2)$ on a lengthscale small compared with the screening length. In screening-length variables then (A 5) becomes

$$\mathscr{P} k^{-\frac{1}{2}} \nabla_R \cdot \int \mathrm{d}\boldsymbol{R}_2 \, [\langle \boldsymbol{u} - \langle \boldsymbol{u}\rangle_1\rangle_2 \langle c - \langle c\rangle_1\rangle_2 - \langle \boldsymbol{u}'(\boldsymbol{x}|\boldsymbol{R}_2)\rangle_1 \langle c'(\boldsymbol{x}|\boldsymbol{R}_2)\rangle_1]. \quad \text{(A 6)}$$

The leading terms in (A 6) come from $\langle \boldsymbol{u}''\rangle_2 \langle c'(\boldsymbol{x}|\boldsymbol{R}_2)\rangle_1$ and $\langle \boldsymbol{u}'(\boldsymbol{x}|\boldsymbol{R}_2)\rangle_1 \langle c''\rangle_2$. Using the previous estimates of $\langle \boldsymbol{u}''\rangle_2$ and $\langle c''\rangle_2$ and the known results for $\langle \boldsymbol{u}'\rangle_1$ and $\langle c'\rangle_1$, these terms yield upon integration of (A 6) contributions

$$O(\mathscr{P} k^{-\frac{1}{2}} R_1^{-5}, \mathscr{P} k^{-\frac{1}{2}} R_1^{-6})$$

in the conduction- and convection-dominated regions respectively. This right-hand side in (3.8) drives $O(\mathscr{P}^3 k^{-\frac{1}{2}} R_1^{-3}, k^{-\frac{1}{2}} R_1^{-5})$ corrections to $\langle c'\rangle_1$, resulting in $O(\mathscr{P}^3 k^{-1}, \mathscr{P} k^{-1})$ contributions to the convective excess flux (3.5), which are $O(\mathscr{P} k^{-\frac{1}{2}})$ and $O(k^{-\frac{1}{2}})$ smaller than $D^*_{\parallel}$, and $O(\mathscr{P} k^{-\frac{1}{2}}, \mathscr{P} k^{-\frac{1}{2}})$ smaller than $D^*_{\perp}$. The convective errors are thus all small in ϕ. This completes our justification that all the errors made in §3 are asymptotically small as $\phi \rightarrow 0$.

A 2. *Justification of the high-Péclet-number analysis*

In §A 1 we showed that the corrections to evaluating the effective diffusivity from a problem involving one point-particle in a medium described by Brinkman's equations of motion are of lower order in ϕ. There are, however, two such effects, which are of lower order in ϕ, but of higher order in $\mathbb{P}$ and must be included in the high-$\mathbb{P}$ behaviour of the diffusivity. These are the effect of particle interactions on transverse dispersion, and the non-mechanical dispersion due to the finite size of the particle.

A 2.1. *Hydrodynamic corrections*

The convective corrections to the effective diffusivity that occur in the Brinkman screening-length region are independent of the particle size, depending only on the screening-length Péclet number $\mathscr{P}$, not the particle Péclet number $\mathbb{P}$. Thus the analysis of these convective corrections presented in §A 1 is valid at high $\mathbb{P}$ as well. These corrections are all small compared with the $O(\mathbb{P})$ one particle longitudinal diffusivity calculated in §4.1 in the limit of high Péclet numbers. The one-particle transverse diffusivity calculated in §4.2.1 is only $O(\phi^{\frac{1}{2}})$, however, and two $O(\mathbb{P}\phi^{\frac{1}{2}})$ convective corrections resulting from particle interactions become more important than the one-particle contribution at high $\mathbb{P}$. These important two-particle effects are the two-particle velocity–concentration correlations in the convective-flux integral (the first term in (A 4)), and the effect of particle interactions on the one-particle concentration disturbance through the nonlinear average (A 5). The renormalization involving the use of $\mathbf{D}$ in the equation for the concentration disturbance (4.10) captures a part of the latter effect. The resulting estimate of $D_{\perp}^{*}$ (4.11) has the correct $\mathbb{P}\phi^{\frac{1}{2}}$ functional dependence, but the numerical coefficient is uncertain.

A 2.2. *Non-mechanical effects in beds of permeable particles, $m^{-1} \neq 0$*

We now turn to the contributions to the effective diffusivity due to the finite size of the particle when the particles are permeable. The effect of convection on $\mathbf{D}^{\alpha}$ is $O(\phi(\alpha-1)\mathbb{P})$, as it was at low $\mathbb{P}$, and is thus always smaller than $\mathbf{D}^{*}$.

The finite size of the particle causes it to act as a source and a source dipole of mass, leading to contributions to $\mathbf{D}^{*}$. The source dipole of strength $O(\alpha-1)$ results from the difference in the molecular diffusivities in the fluid and in the particles. This source dipole leads to an $O(\alpha-1)$ concentration disturbance in the particle, which gives in (3.5) an $O(\phi(\alpha-1)\mathbb{P})$ contribution to the diffusivity, which is small compared with the purely hydrodynamic diffusivity.

The source behaviour results from the time-dependent nature of the bulk concentration field: $\langle c\rangle_0$ in (2.8) varies linearly with time as a result of the bulk convective motion. The steady decrease in the bulk concentration $\langle c\rangle_0$ leads to a constant source of mass in the equation for the concentration disturbance

$$\langle c'\rangle_1 = \langle c\rangle_1 - m^{-1}(1+\gamma)\langle c\rangle_0.$$

This source requires a steady mass flux $\frac{4}{3}\pi m^{-1}(1+\gamma)^2(D_{\mathrm{f}}/D_{\mathrm{p}})\,\mathbb{P}\langle \boldsymbol{u}\rangle_0\cdot\nabla\langle c\rangle_0$ out of the particle in order to maintain a time-independent concentration disturbance.

This source problem is similar to Acrivos & Taylor's (1962) investigation of heat and mass transfer from a fixed particle in Stokes flow. They demonstrated that the concentration disturbance decays exponentially in an $O(\mathbb{P}^{-\frac{1}{3}})$ boundary layer near the particle surface, except in the wake downstream from the particle. Sih & Newman (1967) studied the nature of the wake in more detail. The source drives an $O(\mathbb{P}m^{-1}D_{\mathrm{f}}/D_{\mathrm{p}})$ concentration disturbance in the $O(1)$ volume of the particle, resulting in the $O(m^{-1}(D_{\mathrm{f}}/D_{\mathrm{p}})\,\mathbb{P}^2\phi)$ diffusivity calculated in §5.1. Since the source strength depends only on the longitudinal concentration gradient $\langle \boldsymbol{u}\rangle_0\cdot\nabla\langle c\rangle_0$, it only affects the longitudinal diffusivity. The diffusivity in §5.1 was calculated using the boundary condition $\langle c_{\mathrm{h}}'\rangle_1 = 0$ at the particle surface. The correction to (5.4*a*) comes from satisfying the continuity of mass flux condition (2.2*d*). This requires that $\nabla\langle c'\rangle_1$ be $O(\mathbb{P})$ in the boundary layer, which in turn requires $\langle c_{\mathrm{h}}'\rangle_1 = O(\mathbb{P}^{\frac{2}{3}})$. Thus the contribution $D_{\parallel,\mathrm{h}}^{*}$ from the boundary layer is $O(m^{-1}(D_{\mathrm{f}}/D_{\mathrm{p}})\,\mathbb{P}^{\frac{4}{3}}\phi)$, and is thus small compared with

(5.4a). An additional $O(m^{-1}(D_{\mathrm{f}}/D_{\mathrm{p}})\,\mathbb{P}^{\frac{5}{3}}\phi)$ correction to (5.4a) results from the correction to the concentration disturbance in the particle because $\langle c'_{\mathrm{h}}\rangle_1$ is not actually zero, but rather $O(\mathbb{P}^{\frac{2}{3}})$ at the surface.

In the wake downstream from the particle, the concentration decays as $m^{-1}(D_{\mathrm{f}}/D_{\mathrm{p}})\,\mathbb{P}r^{-1}$. The characteristic dimensions of the wake are $x/z \approx y/z = O(\mathbb{P}^{-\frac{1}{2}})$, where x and y are coordinates normal to the bulk flow. If the Stokes velocity field is used with this concentration disturbance in the convective flux integral (3.5), the integral is not convergent in the wake. As before, the Brinkman velocity field must be used, and the resulting integral converges at a distance of a screening length $z = O(\phi^{-\frac{1}{2}})$ behind the particle. Thus from the wake we obtain an $O(m^{-1}(D_{\mathrm{f}}/D_{\mathrm{p}})\,\mathbb{P}\phi^{\frac{1}{2}})$ contribution to the longitudinal diffusivity. Thus (5.4) gives the leading effect of the particles finite size on the diffusivity in a bed of permeable particles, $m^{-1} \neq 0$.

A 2.3. *Non-mechanical effects in beds of impermeable particles*, $m^{-1} = 0$

When the particles are impermeable, $m^{-1} = 0$, the concentration inside the particles and the source strength described in §A 2.2 are zero, and the $O(m^{-1}(D_{\mathrm{f}}/D_{\mathrm{p}})\,\mathbb{P}^2\phi)$, $O(m^{-1}(D_{\mathrm{f}}/D_{\mathrm{p}})\,\mathbb{P}^{\frac{5}{3}}\phi)$ and $O(m^{-1}(D_{\mathrm{f}}/D_{\mathrm{p}})\,\mathbb{P}^{\frac{4}{3}}\phi)$ contributions to the longitudinal diffusivity described above are absent. There is, however, an $O(\phi\mathbb{P}\ln\mathbb{P})$ non-mechanical contribution to the longitudinal diffusivity discussed in §5.2 resulting from a source in the boundary layer (cf. (5.8)). In §5.2 we argued that this contribution could be evaluated by using an approximate concentration disturbance $\langle c'\rangle_{1,\mathrm{app}}$. Here we shall demonstrate that the contributions to $D^*_{\parallel,\mathrm{BL}}$ due to the difference between $\langle c'\rangle_{1,\mathrm{app}}$ and the exact concentration disturbance $\langle c'\rangle_{1,\mathrm{BL}}$ are smaller than the result (5.10) obtained above. $\langle c'\rangle_{1,\mathrm{app}}$ is by design identical with $\langle c'\rangle_{1,\mathrm{BL}}$ in the hydrodynamically controlled region outside the boundary layer. Thus $\langle c'\rangle_{1,\mathrm{BL}}-\langle c'\rangle_{1,\mathrm{app}}$ is non-zero only in the $O(\mathbb{P}^{-\frac{1}{3}})$ volume of the diffusive boundary layer, where $\langle c'\rangle_{1,\mathrm{BL}}-\langle c'\rangle_{1,\mathrm{app}} = O(\mathbb{P}^{\frac{1}{3}})$. The convective-flux integral (3.5), with $\langle c'\rangle_{1,\mathrm{BL}}-\langle c'\rangle_{1,\mathrm{app}}$ inserted for the concentration, and $\langle \boldsymbol{u}'\rangle_1 \approx -\langle \boldsymbol{u}\rangle_0$, is

$$-\mathbf{D}^*_{\parallel,\mathrm{BL}}\cdot\nabla\langle c\rangle_0 = -\tfrac{3}{2}\mathbb{P}\phi\int \mathbb{P}^{-\frac{1}{3}}\,\mathrm{d}Y\sin\theta\,\mathrm{d}\theta\,\langle\boldsymbol{u}\rangle_0[\langle c'\rangle_{1,\mathrm{BL}}-\langle c'\rangle_{1,\mathrm{app}}], \tag{A 7}$$

where $Y = y\mathbb{P}^{\frac{1}{3}} = \mathbb{P}^{\frac{1}{3}}(r-1)$.

As long as (A 7) converges, this correction will be $O(\phi\mathbb{P})$. The solution of the boundary-layer equation that satisfies a no-flux boundary condition $\partial\langle c'\rangle_{1,\mathrm{BL}}/\partial Y = 0$ at the impermeable surface $Y = 0$ behaves as

$$\langle c'\rangle_{1,\mathrm{BL}} \sim \mathbb{P}^{\frac{1}{3}}\langle\boldsymbol{u}\rangle_0\cdot\nabla\langle c\rangle_0[b'-\tfrac{1}{2}Y^2] \quad \text{as } Y\to 0, \tag{A 8a}$$

and as
$$\langle c'\rangle_{1,\mathrm{BL}} \sim \mathbb{P}^{\frac{1}{3}}\langle\boldsymbol{u}\rangle_0\cdot\nabla\langle c\rangle_0\left[\frac{2\theta}{3Y\sin\theta}+O(Y^{-3})\right] \quad \text{as } Y\to\infty, \tag{A 8b}$$

where b' is determined from matching with the outer solution. Subtracting (5.9) from (A 8), we get the asymptotic behaviours

$$\langle c'\rangle_{1,\mathrm{BL}}-\langle c'\rangle_{1,\mathrm{app}} \sim \mathbb{P}^{\frac{1}{3}}\langle\boldsymbol{u}\rangle_0\cdot\nabla\langle c\rangle_0(b'-b) \quad \text{as } Y\to 0, \tag{A 9a}$$

$$\langle c'\rangle_{1,\mathrm{BL}}-\langle c'\rangle_{1,\mathrm{app}} \sim \mathbb{P}^{\frac{1}{3}}\langle\boldsymbol{u}\rangle_0\cdot\nabla\langle c\rangle_0\,O(Y^{-3}) \quad \text{as } Y\to\infty. \tag{A 9b}$$

Substituting (A 9) into (A 7) results in a convergent integral, and an $O(\phi\mathbb{P})$ correction to the longitudinal diffusivity that is always small compared with (5.10) or (4.8a). There is also an $O(\phi\mathbb{P}^{\frac{4}{3}}m^{-1}D_{\mathrm{f}}/D_{\mathrm{p}})$ correction to (5.10a) due to the $O(\mathbb{P}^{\frac{1}{3}}m^{-1}D_{\mathrm{f}}/D_{\mathrm{p}})$ concentration disturbance inside the particle required to satisfy the equilibrium concentration (2.2e) at the particle surface.

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