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The effect of order on dispersion in porous media

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The effect of spatial periodicity in grain structure on the average transport properties resulting from flow through porous media are derived from the basic conservation equations. At high Péclet number, the mechanical dispersion that is induced by the stochastic fluid velocity field in disordered media and is independent of the molecular diffusivity is absent in periodic media where the velocity field is deterministic. Instead, the fluid motion enhances diffusion by an amount proportional to U^2l^2/D when the bulk flow is in certain directions (of which there are an infinite number), and to D otherwise. The non-mechanical dispersion mechanisms associated with the zero velocity of the fixed grains is qualitatively similar in ordered and disordered media.

1. Introduction

The study of spatially periodic porous media is of theoretical interest because the problem of determining the transport properties of such media may be reduced to a convection–diffusion problem in a single unit cell. Thus, it is straightforward to treat transport in ordered media in relative completeness. Brenner (1980) and Brenner & Adler (1982) have applied generalized Taylor dispersion theory to provide a framework for determining the effective diffusivity in spatially periodic porous media. The purpose of the present paper is to calculate this diffusivity and elucidate its dependence on the Péclet number $P = Ul/D$, where U is the average flow rate through the medium, l is a lengthscale characteristic of the microscale (for periodic media it will be the lattice spacing h), and D is the molecular diffusivity of the tracer or diffusing species in the fluid.

Porous media normally encountered in practice do not possess long-range order, so it is important to understand what aspects of the dispersion mechanisms predicted in spatially periodic media are artifacts of the periodicity constraint. Koch & Brady (1985) used a method based on ensemble averaging the basic conservation equations over the possible configurations of the grain structure to predict the effective diffusivity in *disordered* porous media. It was shown that there are three types of mechanisms causing dispersion at high Péclet number in disordered media: (i) Mechanical dispersion, which is proportional to Ul and results from the stochastic velocity field induced by the randomly distributed solid boundaries independent of molecular diffusion. (ii) Holdup dispersion which grows as U^2l^2/D and occurs when the solute is trapped in regions from which it can escape only by molecular diffusion.

These include the interior of the solid, and regions of stagnant or recirculating fluid. (iii) Boundary-layer dispersion, which grows as $Ul(\ln(Ul/D))$ and arises from the diffusive boundary layers near the solid surfaces where both convection and molecular diffusion influence solute transport. The boundary-layer and holdup mechanisms arise owing to the local boundary conditions at the solid grains, and so they are present in both ordered and disordered media.

However, we shall see that the dispersion that occurs owing to the fluid motion (outside the solid and the boundary layers near solid surfaces) is qualitatively different in ordered and disordered media. In a disordered medium the macroscopic transport results from a purely mechanical process on the microscale in which the solute particle's velocity disturbance becomes uncorrelated with its initial position as the particle is convected through the random microstructure. In an ordered medium this mechanism is absent as the microstructure is spatially periodic, and it will be seen that molecular diffusion must always be considered in order that the solute particle may forget its initial position.

In §2 we briefly review the theoretical framework required for the calculation of the effective diffusivity. In §3 we show that in general the dispersion occurring in the bulk fluid gives rise to either an $O(U^2l^2/D)$ Taylor dispersion contribution or an $O(D)$ enhanced molecular diffusion contribution to the effective diffusivity. The latter $O(D)$ contribution is influenced by the flow field, although it is of the same order of magnitude as the molecular diffusivity. We obtain a criterion for whether Taylor dispersion or enhanced molecular diffusion is obtained.

In §4 we examine two examples: that of (i) bulk flow parallel to one of the primary axes of a simple cubic array of spheres for which Taylor dispersion is obtained, and (ii) flow parallel to no axis of symmetry for the lattice giving enhanced molecular diffusion. The results are compared with the experiments of Gunn & Pryce (1969) on ordered porous media.

2. Theoretical framework

In this section we shall give a brief derivation of the effective diffusivity. More detailed developments for systems with spatial periodicity are to be found in Brenner (1980) and Brenner & Adler (1982) and for systems of arbitrary structure in Koch & Brady (1985, 1987) and Koch (1986).

If the Reynolds number based on a typical lengthscale for the grain structure is small, the equations of motion are Stokes equations

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

for points in the fluid phase, and for points in the solid

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

where p is the dynamic pressure in the fluid, $\boldsymbol{u}$ the velocity and μ the viscosity; p is indeterminate in the particles.

If we neglect any variation in the molecular diffusivity and solubility of the diffusing species in the fluid and solid phases and assume that the concentration of this species is small, its concentration c satisfies

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

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

$$\boldsymbol{q} = \boldsymbol{u}c - D\nabla c, \tag{2.2b}$$

where D is the molecular diffusivity of the solute or diffusing species.

We wish to determine the relationship between the average flux and average concentration. Thus, we average (2.2) to obtain

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

$$\langle\boldsymbol{q}\rangle = \langle\boldsymbol{u}c\rangle - D\nabla\langle c\rangle = \langle\boldsymbol{u}\rangle\langle c\rangle + \langle\boldsymbol{u}'c'\rangle - D\nabla\langle c\rangle, \tag{2.3b}$$

where $c' = c - \langle c\rangle$ is the concentration fluctuation about its mean, and $\boldsymbol{u}' = \boldsymbol{u} - \langle\boldsymbol{u}\rangle$ is the velocity fluctuation.

The average indicated by $\langle\ \rangle$ may be considered as a 'configurational' average over an ensemble of media with different detailed structures (Koch & Brady 1987). This configurational average is most convenient for treating *non*-periodic media. In spatially periodic media this average reduces to a volume average over a single unit cell

$$\langle\ \rangle = \frac{1}{V}\int_{\substack{\text{unit}\\ \text{cell}}} \mathrm{d}\boldsymbol{x},$$

where V is the volume of the unit cell. (In a periodic medium the configurational average is taken over an ensemble of media each with identical periodic structures but with their structures translated relative to the coordinate frame in which the average concentration field is defined.)

The equation for the concentration disturbance is obtained by subtracting (2.3) from (2.2) to give

$$\frac{\partial c'}{\partial t} + \nabla\cdot[\boldsymbol{u}c' - D\nabla c'] = -\boldsymbol{u}'\cdot\nabla\langle c\rangle + \nabla\cdot\langle\boldsymbol{u}'c'\rangle. \tag{2.4}$$

Thus, in general the concentration fluctuation c' is a linear functional of the average concentration gradient. When the average concentration gradient is a constant independent of space and time and $\langle\ \rangle$ is interpreted as a configurational ensemble average, $\boldsymbol{u}'$ and c' are stationary random functions so that $\langle\boldsymbol{u}'c'\rangle$ is independent of position and the second term on the right-hand side of (2.4) is zero. (Alternatively, this term may be seen to be zero by applying $\langle\ \rangle$ interpreted as a volume average over the unit cell, applying the divergence theorem, and noting that $\boldsymbol{u}'c'$ is a spatially periodic function.) The concentration disturbance is then simply proportional to the average concentration gradient

$$c' = \boldsymbol{B}\cdot\nabla\langle c\rangle, \tag{2.5}$$

where we have introduced the so-called '$\boldsymbol{B}$-field' of Brenner (1980).†

Inserting (2.5) with (2.4) into the average mass conservation equation (2.3*b*), we obtain

$$\langle\boldsymbol{q}\rangle = \langle\boldsymbol{u}\rangle\langle c\rangle - \boldsymbol{D}\cdot\nabla\langle c\rangle, \tag{2.6a}$$

where

$$\boldsymbol{D} = D\boldsymbol{I} - \langle\boldsymbol{u}'\boldsymbol{B}\rangle, \tag{2.6b}$$

and

$$\nabla\cdot[\boldsymbol{u}\boldsymbol{B} - D\nabla\boldsymbol{B}] = -\boldsymbol{u}'. \tag{2.6c}$$

The retention of the time derivative in (2.2) and (2.3) is essential because the average concentration field

$$\langle c\rangle = \nabla\langle c\rangle\cdot[\boldsymbol{x} - \langle\boldsymbol{u}\rangle t]$$

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† This is actually the spatially periodic field $\tilde{\boldsymbol{B}}$ in Brenner's notation.

possessing a constant gradient, $\nabla\langle c\rangle$, is time dependent owing to the effects of bulk convection. The $\boldsymbol{B}$-field, however, is time independent for a constant concentration gradient.

We have used an Eulerian definition of the effective diffusivity as the average flux due to a given concentration gradient. If the gradient is not constant but varies slowly on the lengthscale of the bed microstructure, (2.6) may be derived through a multiple scales analysis (Koch & Brady 1987). The Lagrangian or moments diffusivity (Brenner 1980), defined as the time rate of change of the mean-squared displacement of the distribution of a tracer at long times, is the symmetric part of the Eulerian diffusivity (2.6*b*). This distinction is significant, and antisymmetric components of the Eulerian diffusivity arise in media whose structures lack reflectional symmetry (Koch & Brady 1987). We shall restrict ourselves here to the determination of the symmetric part of the diffusivity. Brenner (1980) defined the diffusivity in terms of an average over an ensemble of tracer experiments in which a tracer particle is introduced at the same position in the same medium and showed that in the limit of long times following the release of this tracer in a periodic medium its mean-squared displacement grew as $\frac{1}{2}\boldsymbol{D}_{\mathrm{L}}\,t$, where $\boldsymbol{D}_{\mathrm{L}} = \operatorname{sym}\boldsymbol{D}$ and $\boldsymbol{D}$ is given by (2.6*b*) with the average $\langle\ \rangle$ defined as a volume average over a unit cell (2.6*d*). Thus, with the exception of the possible antisymmetric components of the effective diffusivity the Eulerian and Lagrangian definitions give the same diffusivity.

3. General behaviour of the effective diffusivity

In this section we shall examine the functional dependence of the effective diffusivity (2.6*b*) on the Péclet number $P = Uh/D$ in the limit of high Péclet number. Here h is the characteristic size of the unit cell. We are interested here in the dispersion that arises in the *bulk* fluid phase and not in the boundary-layer dispersion that will arise in the slow moving fluid near solid surfaces. Thus, in the following development it will be assumed that the leading contributions to the dispersion come from finite wavenumber contributions to the $\boldsymbol{B}$-field. Any boundary-layer dispersion contributions would arise from infinitely large wavenumbers in the high-Péclet-number limit. It will be seen that the bulk fluid phase dispersion is most sensitive to the presence of order.

The symmetric part $\boldsymbol{D}_{\mathrm{s}}$ of the effective diffusivity (2.6*b*) is

$$\boldsymbol{D}_{\mathrm{s}} = \boldsymbol{I} - \frac{1}{2P}\int_{\substack{\text{unit}\\\text{cell}}} \mathrm{d}\boldsymbol{x}[\boldsymbol{u}'\boldsymbol{B} + \boldsymbol{B}\boldsymbol{u}'], \tag{3.1}$$

where we have non-dimensionalized the effective diffusivity with the molecular diffusivity D, the velocity with its average U, and all lengths with $h = V^{\frac{1}{3}}$. Using (2.6*c*), (3.1) may be written as

$$\boldsymbol{D}_{\mathrm{s}} = \boldsymbol{I} + \tfrac{1}{2}P\frac{1}{V}\int_{\substack{\text{unit}\\\text{cell}}} \mathrm{d}\boldsymbol{x}\left\{\nabla\cdot\left[\boldsymbol{u}\boldsymbol{B} - \frac{1}{P}\nabla\boldsymbol{B}\right]\boldsymbol{B} + \boldsymbol{B}\nabla\cdot\left[\boldsymbol{u}\boldsymbol{B} - \frac{1}{P}\nabla\boldsymbol{B}\right]\right\}. \tag{3.2}$$

Integration by parts followed by application of the divergence theorem yields

$$\boldsymbol{D}_{\mathrm{s}} = \boldsymbol{I} + \frac{1}{V}\int_{\substack{\text{unit}\\\text{cell}}} \mathrm{d}\boldsymbol{x}[\nabla\boldsymbol{B}\cdot\nabla\boldsymbol{B}^{\dagger}] + \tfrac{1}{2}P\frac{1}{V}\int_{\substack{\text{unit}\\\text{cell}}} \mathrm{d}S\boldsymbol{n}\cdot\left[\boldsymbol{u}\boldsymbol{B}\boldsymbol{B} - \frac{1}{P}\nabla(\boldsymbol{B}\boldsymbol{B})\right], \tag{3.3}$$

where $\boldsymbol{n}$ is the outward unit normal of the unit cell. The quantity in brackets in the final integral is spatially periodic so the integral over opposite faces of the cell cancel, and the entire integral is zero. Thus, we obtain

$$\boldsymbol{D}_{\mathrm{s}} = \boldsymbol{I} + \frac{1}{V}\int_{\substack{\text{unit}\\\text{cell}}} \mathrm{d}\boldsymbol{x}[\nabla\boldsymbol{B}\cdot\nabla\boldsymbol{B}^{\dagger}]. \tag{3.4}$$

This is just the form given by Brenner (1980) in his equation (6.13) with (8.14).

Introducing the three-dimensional finite Fourier transform denoted by ^ and using its convolution theorem, (3.4) may be written as

$$\boldsymbol{D}_{\mathrm{s}} = \boldsymbol{I} + \sum_{\boldsymbol{k}} 4\pi^2 k^2 \hat{\boldsymbol{B}}(\boldsymbol{k})\,\hat{\boldsymbol{B}}(-\boldsymbol{k}), \tag{3.5}$$

where the summation is over all integral values of n_1, n_2, and n_3 in

$$\boldsymbol{k} = n_1\boldsymbol{b}_1 + n_1\boldsymbol{b}_2 + n_3\boldsymbol{b}_3.$$

Here, $\boldsymbol{b}_1 = \boldsymbol{h}_2 \times \boldsymbol{h}_3/V$ etc. are the vectors defining the reciprocal lattice, $\boldsymbol{h}_1, \boldsymbol{h}_2, \boldsymbol{h}_3$ are the sides of the real space unit cell, and $V = \boldsymbol{h}_1\cdot(\boldsymbol{h}_2 \times \boldsymbol{h}_2)$ is the volume of the unit cell (Hasimoto 1959). The transform is defined by

$$\hat{\boldsymbol{u}}(\boldsymbol{k}) = \int_{\substack{\text{unit}\\\text{cell}}} \mathrm{d}\boldsymbol{x}\,\mathrm{e}^{-2\pi\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}}\,\boldsymbol{u}(\boldsymbol{x}),$$

and the inverse transform by

$$\boldsymbol{u}(\boldsymbol{x}) = \sum_{\boldsymbol{k}} \mathrm{e}^{2\pi\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}}\,\hat{\boldsymbol{u}}(\boldsymbol{k}).$$

Transforming the equation (2.6*c*) for the $\boldsymbol{B}$-field yields

$$4\pi^2\frac{1}{P}k^2\hat{\boldsymbol{B}}(\boldsymbol{k}) + 2\pi\sum_{\boldsymbol{k}'}\hat{\boldsymbol{u}}(\boldsymbol{k}-\boldsymbol{k}')\cdot\mathrm{i}\boldsymbol{k}'\hat{\boldsymbol{B}}(\boldsymbol{k}') = -\hat{\boldsymbol{u}}'(\boldsymbol{k}). \tag{3.6}$$

From (3.5) and (3.6) it is apparent that the effective diffusivity is independent of the Péclet number in the limit of high Péclet number, if

$$2\pi\sum_{\boldsymbol{k}'}\hat{\boldsymbol{u}}(\boldsymbol{k}-\boldsymbol{k}')\cdot\mathrm{i}\boldsymbol{k}'\hat{\boldsymbol{B}}(\boldsymbol{k}') = -\boldsymbol{u}'(\boldsymbol{k}), \tag{3.7}$$

has a solution. This correspond to the requirement that a matrix $\boldsymbol{A} = 2\pi\hat{\boldsymbol{u}}(\boldsymbol{k}-\boldsymbol{k}')\cdot\mathrm{i}\boldsymbol{k}'$, having as its rows all the possible values of $\boldsymbol{k}$ and as its columns all possible values of $\boldsymbol{k}'$, should be non-singular. This in turn requires that

$$\boldsymbol{A}\hat{\boldsymbol{B}} = 2\pi\sum_{\boldsymbol{k}'}\hat{\boldsymbol{u}}(\boldsymbol{k}-\boldsymbol{k}')\cdot\mathrm{i}\boldsymbol{k}'\hat{\boldsymbol{B}}(\boldsymbol{k}') = 0 \tag{3.8}$$

should have no non-trivial solutions or that

$$\boldsymbol{u}\cdot\nabla\boldsymbol{B} = 0 \tag{3.9}$$

should have no non-trivial periodic solutions. (By non-trivial solution we mean a solution for which $\boldsymbol{B}$ is not a constant everywhere.) The solution of (3.9) is that $\boldsymbol{B}$ is constant along any streamline. Equation (3.9) has no non-trivial solutions and $|\boldsymbol{D}_{\mathrm{s}}| \sim O(P^0)$, if all streamlines are equivalent in the sense that each and every streamline when plotted within a single cell fills the space within the cell completely. In other words, (3.9) has no non-trivial solutions if a tracer particle released anywhere in the unit cell eventually samples the entire unit cell by convection alone.

If there are at least two non-equivalent streamlines (3.9) has non-trivial solutions and (3.7) has no solution. In this case it is necessary to retain the diffusive term in (3.6) even in the limit of high Péclet number. Equation (3.6) may be written as a matrix equation

$$\left(\boldsymbol{A}+4\pi^2\frac{1}{P}k^2\boldsymbol{I}\right)\hat{\boldsymbol{B}}=-\boldsymbol{u}', \tag{3.10}$$

where $\boldsymbol{I}$ is the identity matrix. The singularity of the $\boldsymbol{A}$-matrix means that it has at least one zero eigenvalue. Adding $4\pi^2(1/P)k^2\boldsymbol{I}$ to $\boldsymbol{A}$ has the effect of adding $4\pi^2(1/P)k^2$ to each eigenvalue. Thus, the smallest eigenvalue of $\boldsymbol{A}+4\pi^2(1/P)k^2\boldsymbol{I}$ is $O(1/P)$ and the largest eigenvalue of $(\boldsymbol{A}+4\pi^2(1/P)k^2\boldsymbol{I})^{-1}$ is $O(P)$ (Stewart 1973, p. 266). The largest eigenvalue $\lambda_{\max}$ is known as the spectral radius of a matrix and has the property that for any positive constant ϵ there exists a consistent matrix norm $\|\ \|$ (Stewart 1973, p. 284), such that

$$\lambda_{\max}\leqslant\left\|\left(\boldsymbol{A}+4\pi^2\frac{1}{P}k^2\boldsymbol{I}\right)^{-1}\right\|\leqslant\lambda_{\max}+\epsilon.$$

Thus,

$$\left.\begin{aligned}|\hat{\boldsymbol{B}}|&=-\left(\boldsymbol{A}+4\pi^2\frac{1}{P}k^2\boldsymbol{I}\right)^{-1}\hat{\boldsymbol{u}}'\sim O\left(\left\|\left(\boldsymbol{A}+4\pi^2\frac{1}{P}k^2\boldsymbol{I}\right)^{-1}\right\||\hat{\boldsymbol{u}}'|\right)\\ |\hat{\boldsymbol{B}}|&\sim O(P),\end{aligned}\right\} \tag{3.11}$$

where $\|\ \|$ and $|\ |$ denote compatible matrix and vector norms. From (3.11) and (3.5), it can be seen that $|\boldsymbol{D}_s|\sim O(P^2)$, when there are at least two non-equivalent streamlines, so that (3.9) has non-trivial periodic solutions.

3.1. *Interpretation in terms of tracer particle motion*

The high-Péclet-number behaviour of the effective diffusivity in ordered media and the absence of mechanical dispersion may be understood by examining the mechanical dispersion hypothesis and seeing why it does not apply to ordered media.

The $\boldsymbol{B}$-field may be written as

$$\boldsymbol{B}=-\int_{-\infty}^{t}\mathrm{d}t_1\int\mathrm{d}\boldsymbol{x}_1\,P(\boldsymbol{x},t\,|\,\boldsymbol{x}_1,t_1)\,\boldsymbol{u}'(\boldsymbol{x}_1),$$

where P, the Green's function for (2.6*c*), is the transition probability giving the probability that a tracer at point $\boldsymbol{x}_1$ at time t_1 transits to $\boldsymbol{x}$ at time t. Thus, (2.6*b*) may be written as a velocity correlation function

$$\boldsymbol{D}=D\boldsymbol{I}+\left\langle\boldsymbol{u}'(\boldsymbol{x})\int_{-\infty}^{t}\mathrm{d}t_1\int\mathrm{d}\boldsymbol{x}_1\,P(\boldsymbol{x},t\,|\,\boldsymbol{x}_1t_1)\,\boldsymbol{u}'(\boldsymbol{x}_1)\right\rangle. \tag{3.12}$$

If we neglect the effects of molecular diffusion the transition probability satisfies

$$\frac{\partial P}{\partial t}+\boldsymbol{\nabla}\cdot(\boldsymbol{u}P)=\delta(\boldsymbol{x}-\boldsymbol{x}_1)\,\delta(t-t_1). \tag{3.13}$$

The solution of (3.13) is simply a delta function,

$$P=\delta\left(\eta-\eta_1-\int_{t_1}^{t}\mathrm{d}t'h_\eta|\boldsymbol{u}|,\Psi-\Psi_1,\vartheta-\vartheta_1\right), \tag{3.14}$$

which indicates that the solute's path is a streamline. (η,Ψ,ϑ) constitute an orthogonal curvilinear coordinate system with η as the coordinate measured along the streamline and h_η the metric coefficient for the streamline. This characteristic is in the direction of the fluid velocity $\boldsymbol{u}$. Substituting (3.14) into (3.12) gives

$$\boldsymbol{D} = D\boldsymbol{I} + \left\langle \boldsymbol{u}' \int_{-\infty}^{\eta} \frac{\mathrm{d}\eta_1}{h_\eta |\boldsymbol{u}|} \boldsymbol{u}'(\eta_1, \Psi_1, \vartheta_1) \right\rangle. \tag{3.15}$$

This is the form the effective diffusivity takes under the mechanical dispersion hypothesis.

In a disordered medium the integral in (3.15) is a stochastic variable, which has zero mean, but is correlated with the stochasic variable $\boldsymbol{u}'$ leading to a non-zero symmetric, mechanical diffusivity. The solute experiences a stochastic velocity, which becomes uncorrelated after a large enough length of the streamline has been traversed.

In ordered media, on the other hand, the structure of the medium and, therefore, the velocity experienced by a solute traversing a streamline, remain correlated throughout all space. Here, there are two possibilities: (i) All streamlines are equivalent and the entire unit cell is sampled by translating along a single streamline.† In this case the integral in (3.15) is zero. As the streamline fills the available space uniformly the integral of the velocity disturbance is equal to the volume-average velocity disturbance, which is zero. If two solute particles are released at time zero at two different points within the unit cell, they will initially disperse, with their separation increasing linearly with time. But, since all streamlines are identical, each particle follows the same trajectory and their separation does not grow at long times. The integral of the velocity along a particle path and thus the symmetric mechanical diffusivity is, then, zero and dispersion only occurs in the presence of molecular diffusion, so that $|\boldsymbol{D}_\mathrm{s}| \sim O(D)$. (ii) At least two non-equivalent streamlines exist, and no one streamline fills the entire unit cell. In this case the velocity averaged over a particle path is non-zero, so the integral in (3.15) diverges and the mechanical diffusivity is infinite. The solute's velocity remains correlated for all time, and the distance between two solute particles released on different streamlines (the non-equivalent ones) increases linearly with time. Thus, a diffusive process is obtained only if molecular diffusion across streamlines is considered. As a result the dispersion is non-mechanical and grows as U^2h^2/D like Taylor dispersion in a tube. Thus, there are two possible mechanisms for fluid-phase dispersion in ordered media, but neither resembles the mechanical dispersion encountered in disordered media.

4. Examples

In this section we shall illustrate the dispersion mechanisms discussed above by examining specific spatially periodic microstructures. There is no difficulty in principle in calculating the transport properties of periodic media of high volume fraction as only the solution on a unit cell is required. In order to simplify the analysis, however, we shall obtain the asymptotic behaviour of the effective diffusivity at low solids volume fraction. This asymptotic analysis will allow us to illustrate the

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† Of course this fluid streamline cannot sample the space within the solid, and the solid always leads to a contribution to the diffusivity of $O([U^2l^2/D_\mathrm{p}]\ m^{-1})$, where l is the particle radius, D_p is the molecular diffusivity of the tracer in the solid, and m is the ratio of the solubility of the tracer in the solid and fluid phases (Koch & Brady 1985); cf. the discussion in §4.4.

qualitative features of the transport process. We shall study a simple cubic array of spheres and a square array of cylinders, showing that at high Péclet number the fluid-phase dispersion may be of the Taylor-dispersion type $|\boldsymbol{D}_s| \sim O(U^2h^2/D)$ or enhanced molecular diffusion $|\boldsymbol{D}_s| \sim O(D)$, depending on the orientation of the average flow relative to the periodic lattice.

4.1. *Derivation of expressions for the effective diffusivity in ordered arrays*

In a periodic bed of low solids volume fraction the radii a of the particles non-dimensionalized by the lattice spacing h is small. The velocity disturbance caused by the particles may be approximated as that due to a point force

$$\hat{\boldsymbol{u}}'(\boldsymbol{k}) = \frac{a}{4\pi^2}\frac{\boldsymbol{f}\cdot\left[\boldsymbol{I}-\dfrac{\boldsymbol{kk}}{k^2}\right]}{k^2} + O(a^3), \qquad \boldsymbol{k} \neq 0, \tag{4.1a}$$

$$\boldsymbol{u}'(\boldsymbol{k}) = 0, \qquad \boldsymbol{k} = 0. \tag{4.1b}$$

Equation (4.1*a*) possesses errors of order a^3 since in real space $\boldsymbol{u}'$ differs from that due to a point force by an $O(1)$ amount at $O(a)$ distances from the sphere and by an $O(a^3)$ amount at $O(1)$ distances (Hasimoto 1959). Here the force $\boldsymbol{f}$ exerted by the sphere on the fluid is non-dimensionalized by μhU. A cubic array of spheres is not isotropic as far as velocity-induced dispersion is concerned, as will be indicated by the profound influence that the orientation of the average velocity relative to the medium structure has on dispersion. The bed permeability, however, is isotropic – the force $\boldsymbol{f}$ is antiparallel to the average velocity. Equation (4.1*a*) may be approximated as

$$\hat{\boldsymbol{u}}' = -\frac{3}{2\pi}a\frac{\boldsymbol{U}\cdot\left[\boldsymbol{I}-\dfrac{\boldsymbol{kk}}{k^2}\right]}{k^2} + O(a^3), \quad \boldsymbol{k} \neq 0. \tag{4.2}$$

Except near the particle that makes a contribution $O(a)$ smaller than the one we shall calculate, the velocity field on the left-hand side of (3.6) or (2.6*c*) for the $\boldsymbol{B}$-field may be approximated by the average velocity, $\boldsymbol{u} \approx \boldsymbol{U}$, so that (3.6) has the solution

$$\hat{\boldsymbol{B}}(\boldsymbol{k}) = -\frac{\hat{\boldsymbol{u}}'(\boldsymbol{k})}{4\pi^2\dfrac{1}{P}k^2 + 2\pi\mathrm{i}\boldsymbol{U}\cdot\boldsymbol{k}}. \tag{4.3}$$

Inserting (4.3) into the expression (3.5) for the effective diffusivity yields

$$\boldsymbol{D}_s = \boldsymbol{I} + \sum_{\boldsymbol{k}} \frac{\hat{\boldsymbol{u}}'(\boldsymbol{k})\,\hat{\boldsymbol{u}}'(\boldsymbol{k})\,k^2}{4\pi^2\dfrac{1}{P^2}k^4 + (\boldsymbol{U}\cdot\boldsymbol{k})^2}, \tag{4.4}$$

or, substituting (4.2) for the velocity disturbance,

$$\boldsymbol{D}_s = \boldsymbol{I} + \frac{9a^2}{4\pi^2}\sum_{\boldsymbol{k}\neq 0} \frac{\left[\left(\boldsymbol{I}-\dfrac{\boldsymbol{kk}}{k^2}\right)\cdot\boldsymbol{U}\right]^2}{k^2\left(4\pi^2\dfrac{1}{P^2}k^4 + (\boldsymbol{U}\cdot\boldsymbol{k})^2\right)}. \tag{4.5}$$

Expression (4.5) bears a close resemblance to equation (3.13) of Koch & Brady (1985) for dispersion in disordered media, the major difference being an integral in the latter rather than a discrete sum as in (4.5).

The two-dimensional analogue of the simple cubic array of spheres considered above is a square array of cylinders of infinite length. The only changes required in the preceding analysis in order to treat dispersion due to flow perpendicular to the axes of an array of cylinders are to replace the drag $6\pi a U$ on a sphere with the drag per unit length on a cylinder at low volume fraction $4\pi U/[\ln(a^{-1})-1.3015]$ (Hasimoto 1959), and to interpret $\boldsymbol{k}$ as a two-dimesional reciprocal lattice vector. The resulting effective diffusivity is, in place of (4.5),

$$\boldsymbol{D}_s = \boldsymbol{I} + \left(\frac{4\pi}{\ln(a^{-1})-1.3015}\right)^2 \sum_{k\neq 0} \frac{\left[\left(\boldsymbol{I}-\frac{\boldsymbol{kk}}{k^2}\right)\cdot \boldsymbol{U}\right]^2}{16\pi^4 k^2\left(4\pi^2 \frac{1}{P^2}k^4 + (\boldsymbol{U}\cdot\boldsymbol{k})^2\right)}. \tag{4.6}$$

The low-Péclet-number behaviour of the convective contribution to the diffusivity may be obtained by neglecting the convective term $(\boldsymbol{U}\cdot\boldsymbol{k})^2$ in the denominator of (4.5) or (4.6), resulting in a contribution proportional to P^2. This result is similar to that obtained in disordered media (Koch & Brady 1985). At low Péclet number the solute samples the microstructure primarily by molecular diffusion in both ordered and disordered structures. In addition to the convectively enhanced dispersion considered here, the difference in the molecular diffusivity in the fluid and solid phases affects dispersion. This contribution, which is proportional to the molecular diffusivity, has been calculated by Sangani & Acrivos (1983) for period arrays of spheres and by Rayleigh (1892) and Perrins, McKenzie & McPhedran (1979) for periodic arrays of cylinders. In the present analysis we have avoided treating these effects by assuming that the molecular diffusivity and solubility of the solute are equal in the fluid and solid phases.

4.2. *Justification for the presence of Taylor dispersion in certain medium structures using symmetric arguments*

In the preceding analysis we have neglected terms of $O(a)$ in the velocity field on the left-hand side of (2.6*c*) or (3.6) for the $\boldsymbol{B}$-field and retained the $O(P^{-1})$ diffusive terms. The diffusive term differs qualitatively from the convective term (involving a second derivative rather than a first derivative of the $\boldsymbol{B}$-field), and it must be retained no matter how high the Péclet number. Successively higher approximation in small a may be obtained by including better approximations to the velocity field in (3.6), but in each successive calculation the diffusive term must be retained. Superficially, it would appear that the first approximation in small a is only valid if $P \ll a^{-1}$. However, the results (4.5) and (4.6) obtained may be justified at arbitrarily large Péclet number if it can be shown that the neglected terms do not change the Péclet-number dependence of the effective diffusivity. That this is so will now be demonstrated.

According to (4.5) and (4.6), $O(P^2)$ Taylor-dispersion contributions for the effective diffusivity are obtained if $\boldsymbol{U}\cdot\boldsymbol{k} = 0$ for any $\boldsymbol{k}$, i.e. if the bulk flow is perpendicular to any vector in the reciprocal lattice structure. In a cubic array the lattice structure in real space is identical to the reciprocal lattice structure and $\boldsymbol{U}\cdot\boldsymbol{k} = 0$ if the velocity is perpendicular to any separation vector in the real-space lattice. In §3 we showed that the necessary and sufficient criterion for Taylor dispersion at high Péclet

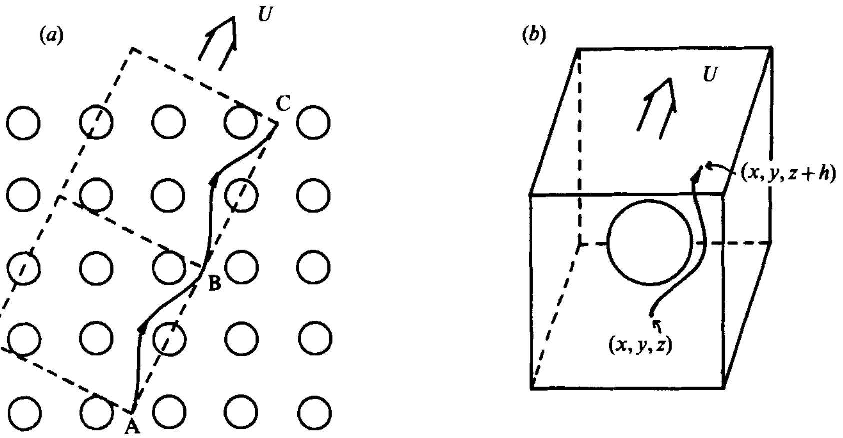

FIGURE 1. (*a*) The lines of translational symmetry parallel and perpendicular to the bulk flow direction in a square array are illustrated. The streamlines repeat themselves in the interval between each of the lines of symmetry perpendicular to the flow. (*b*) A typical streamline in the unit cell of a cubic array of spheres is illustrated for flow parallel to a primary axis for the lattice. The faces of the unit cell are planes of reflectional and translational symmetry. The symmetry of the bed structure and the reversibility of low-Reynolds-number flows require that a streamline that passes through a point (x, y, z) on one face of the unit cell must pass through the corresponding point $(x, y, z+h)$ on the opposite face.

numbers is that $\boldsymbol{u}\cdot\nabla\boldsymbol{B} = 0$ (equation (3.9)) have non-trivial periodic solutions. If we approximate the fluid velocity $\boldsymbol{u}$ by its average $\boldsymbol{U}$ this criterion reduces to $\boldsymbol{U}\cdot\boldsymbol{k} = 0$. In order to justify the use of (4.5) and (4.6) at high Péclet numbers, however, we must show that (3.9) also has non-trivial solutions if we retain the full velocity field $\boldsymbol{u}$. It can be shown through arguments based on symmetry and continuity that Taylor dispersion is obtained and (4.6) is valid at high Péclet number for the case of flow parallel to an axis of translational symmetry in the two-dimensional array of cylinders.

In a square array $\boldsymbol{U}\cdot\boldsymbol{k} = 0$ implies that the bulk velocity $\boldsymbol{U}$ is parallel to a set of lines of translational symmetry and perpendicular to a second set of lines of translational symmetry, as illustrated in figure 1(*a*). From the definition of the average flow it is clear that there can be no net flow across any of the lines of translational symmetry which are parallel to the average flow. Further, there can be no net flow across the line segment AB in figure 1(*a*) formed by the intersection with lines of translational symmetry perpendicular to the flow. As the streamlines cannot cross, this requires that a streamline that goes through A must go through B and then through C, etc. Thus, the streamlines repeat themselves and there are non-trivial solutions to (3.9) if the flow in a two-dimensional square array is parallel to any axis of translational symmetry. This result is independent of the configuration of the fluid–solid boundaries in the unit cell.

When the average flow is perpendicular to a set of planes of both translational and reflectional symmetry, such as the (100)-planes in a cubic array of spheres, symmetry and reversibility require that the streamlines repeat themselves. Here (100) is the Miller index notation for the planes parallel to one of the primary axes of the array. If (x, y, z) is a Cartesian coordinate system with its axes parallel to the primary axes of the array and the bulk flow is in the z-direction, the streamlines must intersect each symmetry plane at the same (x, y)-coordinates, as illustrated in figure 1(*b*). If the streamlines did not pass through the same (x, y)-coordinates, then upon reversal the fluid would not return to its original position, thus violating the principle of reversibility of low-Reynolds-number flow. Thus, for flows perpendicular to planes of translational and reflectional symmetry such as the flow parallel to the primary axis of a cubic array of spheres, streamlines repeat themselves, (3.9) has non-trivial solutions and Taylor dispersion is obtained. The only effect of including the $O(a)$ convective terms on the right-hand side of (3.6) would be to deflect the streamlines slightly making a small change in the coefficient in the $O(P^2)$ Taylor-dispersion contribution to the effective diffusivity.

4.3. *Justification for the presence of Taylor dispersion in a wider class of structures for $P \ll a^{-2}$*

For the cubic array of spheres (3.6), with the terms of $O(a)$ included, may be written as

$$\sum_{\boldsymbol{k}'\neq 0} \boldsymbol{A}(\boldsymbol{k},\boldsymbol{k}')\,\hat{\boldsymbol{B}}(\boldsymbol{k}') = \frac{3a}{2\pi}\frac{1}{k^2}\left(\boldsymbol{I}-\frac{\boldsymbol{k}\boldsymbol{k}}{k^2}\right)\cdot \boldsymbol{U}, \tag{4.7}$$

where, for $\boldsymbol{k} = \boldsymbol{k}'$

$$\boldsymbol{A}(\boldsymbol{k},\boldsymbol{k}') = \{2\pi \mathrm{i}\boldsymbol{U}\cdot\boldsymbol{k} + 4\pi P^{-1}k^2\}, \tag{4.8a}$$

and for $\boldsymbol{k} \neq \boldsymbol{k}'$

$$\boldsymbol{A}(\boldsymbol{k},\boldsymbol{k}') = -3\mathrm{i}a\frac{1}{|\boldsymbol{k}-\boldsymbol{k}'|^2}\boldsymbol{k}'\cdot\left(\boldsymbol{I}-\frac{(\boldsymbol{k}-\boldsymbol{k}')(\boldsymbol{k}-\boldsymbol{k}')}{(\boldsymbol{k}-\boldsymbol{k}')^2}\right)\cdot \boldsymbol{U}. \tag{4.8b}$$

Thus

$$\hat{\boldsymbol{B}}(\boldsymbol{k}) = \frac{3a}{2\pi}\sum_{\boldsymbol{k}'\neq 0} \boldsymbol{A}^{-1}(\boldsymbol{k},\boldsymbol{k}')\cdot\frac{1}{k'^2}\left(\boldsymbol{I}-\frac{\boldsymbol{k}'\boldsymbol{k}'}{k^2}\right)\cdot \boldsymbol{U}, \tag{4.9}$$

which upon neglect of the terms of $O(a)$ reduces to (4.5).

If the bulk flow velocity $\boldsymbol{U}$ is such that

$$\boldsymbol{U}\cdot\boldsymbol{k} = 0 \tag{4.10}$$

possesses no non-trivial solutions for $\boldsymbol{k}$, it may be shown after a straightforward but lengthy consideration of the form of the elements of $\boldsymbol{A}$ and hence of $\boldsymbol{A}^{-1}$ for small a and P^{-1}, that $\boldsymbol{D}_s - \boldsymbol{I}$ is of $O(a^2)$, being

$$\boldsymbol{D}_s - \boldsymbol{I} = \frac{9a^2}{4\pi^2}\sum_{\boldsymbol{k}\neq 0}\frac{\left[\left(\boldsymbol{I}-\frac{\boldsymbol{k}\boldsymbol{k}}{k^2}\right)\cdot \boldsymbol{U}\right]^2}{k^2(\boldsymbol{U}\cdot\boldsymbol{k})^2}, \tag{4.11}$$

which is, at lowest order, identical to (4.5).

If $\boldsymbol{U}$ is in a direction for which (4.10) does possess non-trivial solutions for $\boldsymbol{k}$, two situations can occur. Either the solution for $\boldsymbol{k}$ is a line of points

$$\boldsymbol{k} = r\boldsymbol{a} \quad (r \text{ is a non-zero integer}) \tag{4.12}$$

(as occurs if $\boldsymbol{U}$ is in the direction $\boldsymbol{n}_1 + \lambda\boldsymbol{n}_2$ where $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$ are vectors with integer elements and λ is irrational) or the solution for $\boldsymbol{k}$ is a plane of points

$$\boldsymbol{k} = r\boldsymbol{a} + s\boldsymbol{b} \quad (r, s \text{ are integers which are not both zero}) \tag{4.13}$$

(as occurs if $\boldsymbol{U}$ is in the direction $\boldsymbol{n}_1$, where $\boldsymbol{n}_1$ is a vector with integer elements). Again we consider the form of the elements of $\boldsymbol{A}$ and hence $\boldsymbol{A}^{-1}$ for small a and P^{-1}, but now, at least for $P \ll a^{-2}$, we find that for both cases $\boldsymbol{D}_s - \boldsymbol{I}$ is of $O(a^2P^2)$. For the former case for which $\boldsymbol{k}$ is of the form (4.12), one obtains

$$\boldsymbol{D}_s - \boldsymbol{I} = \frac{\pi^2 a^2 P^2}{840}|\boldsymbol{a}|^{-6}\boldsymbol{U}\boldsymbol{U}, \tag{4.14}$$

whilst for the latter case for which $\boldsymbol{k}$ is of the form (4.13),

$$\boldsymbol{D}_{\mathrm{s}}-\boldsymbol{I}=\frac{9a^2P^2}{16\pi^4}\sum_{r=-\infty}^{\infty}\sum_{\substack{s=-\infty \\ (r,\, s \text{ not both zero})}}^{\infty}(r^2|\boldsymbol{a}|^2+s^2|\boldsymbol{b}|^2+2rs\boldsymbol{a}\cdot\boldsymbol{b})^{-3}\,\boldsymbol{U}\boldsymbol{U} \qquad (4.15)$$

Again, at lowest order, these results are identical to (4.5). It is interesting to note that when (4.10) possesses non-trivial solutions so that $\boldsymbol{D}_{\mathrm{s}}-\boldsymbol{I}$ is of order P^2a^2 the dispersion due to the flow is purely longitudinal.

We have thus shown that for a square array of cylinders and for a cubic array of spheres, any bulk flow velocity $\boldsymbol{U}$ for which $\boldsymbol{U}\cdot\boldsymbol{k}=0$ has non-trivial solutions, gives rise to an effective diffusivity of $O(P^2)$ as $P\rightarrow\infty$ independently of the solid volume fraction (except perhaps for flows for a cubic array of spheres without reflectional symmetry for which this result has been proved only for $P \ll a^{-2}$).

4.4. *Results and discussion*

In figure 2 we compare the results of the present theoretical analysis with experimental measurements of the longitudinal diffusivity due to flow parallel to the one of the axes of a simple cubic array of spherical particles (Gunn & Pryce 1969). The theoretical curves (solid lines) are the sum of the convective contribution obtained from (4.5) and the purely conductive contribution calculated by Sangani & Acrivos (1983). Although (4.5) is strictly valid only in the limit of small solids volume fraction, for the purposes of this comparison we have evaluated it for a volume fraction 0.52 corresponding to a close-packed simple cubic array. Both theory and experiment indicate that the longitudinal diffusivity grows as P^2 at high Péclet numbers. The theoretical prediction of the magnitude of the diffusivity is a factor of four smaller than the experimental measurement. This discrepancy is not surprising as we have not satisfied the boundary conditions on the particle surfaces, which would be expected to enhance the dispersion. For the high value of a in a bed of close-packed spheres we cannot predict the precise value of the diffusivity from the present analysis, but we can predict the functional dependence of the diffusivity on the Péclet number.

A precise value of the diffusivity is obtainable by solving the full boundary-value convective–diffusive problem in a unit cell. Eidsath *et al.* (1983) carried out such a numerical calculation for flow parallel to an axis of a square array of cylinders. Unfortunately, the calculations of Eidsath *et al.* do not exhibit the proper asymptotic behaviour at the high- and low-Péclet-number limits. At high Péclet number they found the longitudinal diffusivity growing roughly as $P^{1.7}$ rather than as P^2, and although they found a weak dependence of the transverse diffusivity on the Péclet number, they did not reach a constant transverse diffusivity at high Péclet numbers. Their results also fail to match the pure-conduction results of Rayleigh (1892) and Perrins *et al.* (1979) in the limit of low Péclet numbers. It is not known whether these discrepancies are due to numerical inaccuracies, to not having achieved the high-P limit, or reflect a more serious error.

If the average flow is not perpendicular to any vector in the reciprocal lattice, i.e. if $\boldsymbol{U}\cdot\boldsymbol{k}\neq 0$ for all $\boldsymbol{k}$, then both the axial and transverse diffusivities are independent of the Péclet number at high flow rates. In simple cubic and square arrays this condition implies that the flow is not perpendicular to any axis of the *real* lattice, but this result does not hold for a general lattice structure. In this case (4.5) or (4.6) give the contributions to the effective diffusivity arising in the bulk fluid away from the

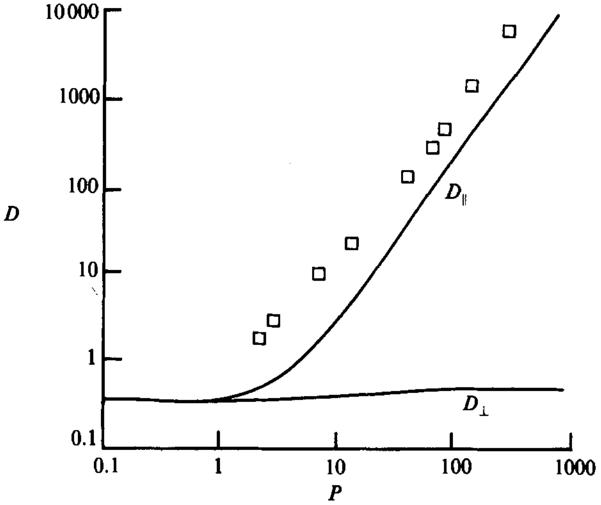

FIGURE 2. Effective diffusivity for flow parallel to an axis of a cubic array of spheres. The theoretical values (solid curves) of the longitudinal diffusivity $D_\parallel$ and the transverse diffusivity $D_\perp$ and the experimental values (squares) of the longitudinal diffusivity measured by Gunn & Pryce (1969) are plotted as a function of the Péclet number P. A solids volume fraction of 0.2 was used.

diffusive boundary layer near solid surfaces. The $O(a^3)$ contributions resulting from the finite size of the particle may be calculated to leading order in large Péclet number as if the particles were isolated in an unbounded fluid (Koch & Brady 1985). Thus, these contributions are independent of the structure of the medium and are the same in ordered and disordered media. The full behaviour of the effective diffusivity at high Péclet number and small a for off-axis flow is obtained by adding (4.5) to the $O(a^4 P \ln(Pa))$ and $O(a^5 P^2 (D/D_p)\, m^{-1})$ contributions from the diffusive boundary layer and the interior of the particle, respectively. The latter contributions have been calculated in Koch & Brady (1985). Here, D_p is the diffusivity of the tracer in the solid phase, and m is the solubility ratio of the tracer in the solid and fluid phases. In the subsequent discussion and in figures 3 and 4 we refer only to the contribution to the effective diffusivity from the bulk fluid, i.e. from (4.5) or (4.6).

In figure 3 we plot the effective diffusivity due to off-axis flow in a square array of cylinders. The average velocity is

$$U = \frac{\epsilon}{\pi} \mathbf{1}_x + (1 - \epsilon/\pi^2)^{\frac{1}{2}} \mathbf{1}_y, \tag{4.16}$$

with $\epsilon = 1$, where x and y are the axes of the square array. The irrationality of π assures that the velocity is not perpendicular to any of the lattice vectors, which must be rational. At non-zero flow rates the effective diffusivity is non-diagonal both in the axes (x, y) of the lattice and in the axes defined by the flow. Thus, in figure 3 we must include three components D_{xx}, D_{yy}, and $D_{xy} = D_{yx}$ of the diffusivity.

At high Péclet numbers the diffusivities approach constant values as expected, but these values may be quite large. In fact, if the flow is nearly parallel to an axis of symmetry – deviating by a small angle ϵ – the longitudinal diffusivity grows as P^2 up to a Péclet number of order $1/\epsilon$.

At $P \gg 1/\epsilon$, the longitudinal diffusivity asymptotes to a constant value of order

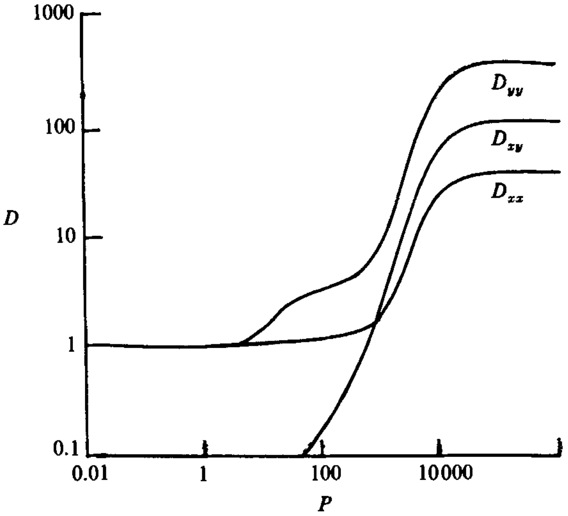

FIGURE 3. Effective diffusivity for off-axis flow in a square array of cylinders. The diffusivities D_{xx} and D_{yy} for transport parallel to the axes of the array and the cross-diffusivity $D_{xy} = D_{yx}$ are plotted as a function of the Péclet number for flow (described by equations (4.16) with $\epsilon = 1$) which is not parallel to any symmery axis for the array. The solids volume fraction is $\phi = 0.02$.

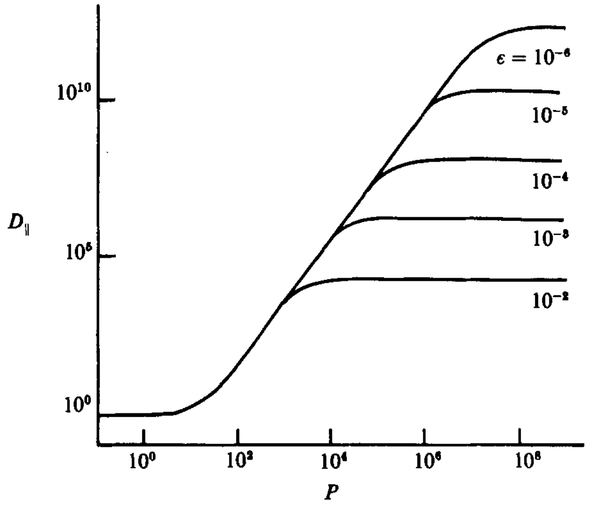

FIGURE 4. Longitudinal diffusivity due to flow deviating slightly from an axis of a square array of cylinders. The longitudinal diffusivity $D_{\parallel}$ is plotted as a function of the Péclet number for flow described by equation (4.16) with ϵ varying from 10^{-2} to 10^{-6}. The sine of the angle between the average flow direction and the lattice axis is proportional to ϵ. The solids volume fraction is $\phi = 0.02$.

$1/\epsilon^2$. This situation is illustrated in figure 4, where the longitudinal diffusivity in a square array of cylinders is plotted as a function of Péclet number for the flow (4.16) with ϵ ranging from 10^{-2} to 10^{-6}. This behaviour occurs because a tracer must pass through many $O(1/\epsilon)$ unit cells before it samples the entire microstructure by convection. Thus, the characteristic time for convective sampling is $h/U\epsilon$, while the time for diffusive sampling is h^2/D; the criterion for convective sampling to dominate is then $h/U\epsilon \ll h^2/D$, or $P \gg 1/\epsilon$. For $P \ll 1/\epsilon$ diffusive sampling dominates and we have Taylor dispersion just as in the on-axis-flow case; for $P \gg 1/\epsilon$ the convective sampling becomes important and the longitudinal diffusivity reaches a constant value. (In the foregoing discussion we have considered only values of ϵ that are not products of π and a rational number, so that $\boldsymbol{U}\cdot\boldsymbol{k} \neq 0$.)

In an actual experiment with a periodic porous medium it may not be possible to ensure flow along a direction for which $\boldsymbol{U}\cdot\boldsymbol{k} = 0$, and then one might expect to always observe a diffusivity that is independent of P as $P \rightarrow \infty$. However, since the off-axis diffusivity initially grows as P^2, a sample size much greater than $1/\epsilon$ would be required before the final asymptotic behaviour was reached. Hence, one should expect to see P^2 behaviour in periodic porous media unless care is taken to ensure off-axis flow with a large enough sample.

In this section we have obtained results for periodic media with the simplest structures. The general discussion in §3, however, applies to any structure within the unit cell. Specifically, the presence of a periodic structure precludes the possibility of mechanical dispersion, which arises owing to the stochastic nature of the solid boundaries in a disordered medium.

We have not specifically considered the possible consequences of deterministic chaos on dispersion in periodic porous media. Studies of tracer particle trajectories in other systems (Aref 1984) suggest the possibility that a tracer in a three-dimensional periodic medium (a system with three degrees of freedom) might sample all or part of the space within the unit cell in an apparently random manner. One might further speculate that the resulting 'chaotic dispersion' might be independent of the molecular diffusivity (like mechanical dispersion in a disordered medium). Nonetheless, there is a fundamental qualitative difference between chaotic dispersion (if it exists) and mechanical dispersion. Physically, mechanical dispersion results from the stochastic nature of the solid structure and the resulting velocity field in a disordered medium, while chaotic dispersion must result from the complexity of the tracer trajectories despite the deterministic nature of the solid structure and velocity field in a periodic medium. Mathematically, mechanical dispersion arises from the small-wavenumber (large-wavelength) limit of the integral (Koch & Brady 1985, eq. 3.13) for the effective diffusivity in a disordered medium. From the arguments in §3 of this paper it is clear that no similar behaviour can occur at small or moderate wavenumbers in a periodic system. Chaotic dispersion could only manifest itself mathematically as a large-wavenumber (small-wavelength) divergence of the sum (3.5) for the effective diffusivity. This fundamental difference is further illustrated by the fact that mechanical dispersion occurs in random two-dimensional systems, while deterministic chaos *cannot* occur in two dimensions. Furthermore, in many systems for which deterministic chaos has been found only part of space can be sampled by the chaotic motion (see, for example, Aref 1984). If part of the unit cell in a periodic medium were not reached by the chaotic motion it could only be sampled by molecular diffusion, leading to $O(P^2)$ Taylor-dispersion contributions to the effective diffusivity. It is clear then that the mechanisms of dispersion in ordered and disordered porous media differ qualitatively and it is dangerous to draw conclusions about dispersion in disordered media from studies of ordered media.

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