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A non-local description of advection–diffusion with application to dispersion in porous media

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When the lengthscales and timescales on which a transport process occur are not much larger than the scales of variations in the velocity field experienced by a tracer particle, a description of the transport in terms of a local, averaged macroscale version of Fick's law is not applicable. Here, a *non-local* transport theory is developed in which the average mass flux is not simply proportional to the average local concentration gradient, but is given by a convolution integral over space and time of the average concentration gradient times a spatial- and temporal-wavelength-dependent diffusivity. The non-local theory is applied to the transport of a passive tracer in the advective field that arises in the bulk fluid of a porous medium, and the complete residence–time distribution – space–time response to a unit source input – of the tracer is determined. It is also shown how the method of moments may be simply recovered as a special case of the non-local theory. While developed in the context of and applied to tracer dispersion in porous media, the non-local theory presented here is applicable to the general problem of determining the average transport behaviour in advection–diffusion-type systems in which spatial and temporal variations are occurring on scales comparable with the scale of interest.

1. Introduction

Many important physical processes involve the transport of a passive scalar quantity in the presence of a complex advective field that fluctuates on lengthscales and timescales comparable to those on which the transport process occurs. For example, the initial dissipation of a pollutant in the atmosphere, in rivers, or in ground-water flows occurs on a lengthscale comparable to or smaller than the scale of the advective motion. The mean residence time of a species in a reservoir or chemical reactor may be smaller than the time required for the tracer to experience the full range of velocity fluctuations present in such a heterogeneous medium. The oscillatory flows in the pulmonary and cardiovascular systems as well as in tidal estuaries give rise to time-dependent dispersive effects that depend fundamentally on the inherent unsteadiness.

When the timescales and lengthscales on which a transport process occurs are not much larger than the scales of variations in the velocity field experienced by a tracer particle, a description of the transport in terms of an averaged, macroscale version of Fick's law is not applicable. In this paper a more general, 'non-local' description of transport is derived. In the non-local theory the average mass flux is not simply proportional to the average local concentration gradient, but is given by a convolution integral over space and all previous times of the average concentration gradient

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times a temporal- and spatial-wavelength-dependent diffusivity. The average mass conservation equation then is a second-order integrodifferential equation, which takes on a particularly simple form upon Fourier transformation in time and space.

Wavelength-dependent properties have long been used to treat non-local effects in physics. For example, the electric displacement in a dielectric may be related to the electric field through a dielectric constant, which is in general a function of temporal and spatial wavelengths (Jackson 1975; Landau, Lifshitz & Pitaevskií 1984). Indeed, the overall linearity of Maxwell's equations of electromagnetism require that the dielectric displacement be a linear functional of the imposed field, and the non-local wavelength-dependent representation is an appropriate manner of expressing this functionality. In situations much closer to ours, non-local theories have been developed to study wave propagation in random media (Keller 1962; Frisch 1968), and a general approach to such non-local problems for steady second-order linear stochastic differential equations has been developed by Beran & McCoy (1970).

While such non-local approaches are widespread in the physics and applied physics literature, they do not seem to have been applied to advection–diffusion problems. Previous analyses of transient effects in advectively enhanced dispersion for Taylor dispersion in a tube (Gill & Sankarasubramanian 1970; Chatwin 1970; Smith 1981), for generalized Taylor dispersion theory (Pagitsas, Nadim & Brenner 1986) and for an *ad hoc*, one-dimensional model of a packed bed with adsorption (Reis *et al.* 1979) have been based on an expansion of the concentration field in moments. The resulting expression relates the mass flux to an infinite expansion in time- and space-derivatives of the concentration field. This procedure requires the determination of an infinite set of phenomenological coefficients, which are in general tensors. It is unclear how one would obtain the infinite set of boundary conditions required to solve a boundary-value problem involving an infinite-dimensional mass conservation equation. In addition, it is difficult to calculate more than the first few phenomenological coefficients, so the method is not applicable at short times and short spatial wavelengths when the non-Fickian effects are expected to be most pronounced. (Smith's analysis goes further than a moments expansion by writing an effective diffusion coefficient in terms of a time-delay integral, but the limitations of this approach for short times are still present.)

In this paper we recognize the inherent coupling between spatial and temporal variations and follow the non-local approaches in generalizing the conventional local Fick's law expression for mass conservation. This approach represents a generalization of the Eulerian description of transport, as opposed to the moments or Lagrangian approaches discussed above, and will be seen to have significant advantages.

The non-local conservation equation derived in §2 gives the ensemble-average field of a scalar quantity in any advection–diffusion problem for which the quantity's velocity $\boldsymbol{v}$ is known (at least in a statistical sense). This conservation equation is applicable regardless of the lengthscales and timescales over which the scalar quantity varies, and it allows a complete determination of the concentration field for all space–time positions. Thus, the full residence–time distribution of a tracer being transported through the advective field can be predicted. In §2 we also discuss how the ensemble-average approach taken here reduces to an average over a unit cell for spatially periodic systems and can be modified to treat problems whose structure is formally similar to Taylor dispersion in a tube. We also show how the integro-differential formulation can be locally expanded to recover the method of moments used in previous studies.

In §§3 and 4 we demonstrate the application of this general theory to the transport of a solute in the advective field that arises in the bulk fluid of a porous medium consisting of fixed spheres whose positions are randomly distributed. In a previous paper (Koch & Brady 1985) we showed that one can capture the correct qualitative nature of this transport process through an asymptotic analysis in small solids volume fraction. In this limit the effect of the particles on the fluid velocity may be approximated as that due to point forces in a medium that obeys Brinkman's equations of motion. The residence–time distributions (RTDs) – the concentration field resulting from a point source impulse – predicted here show the complete spatial and temporal evolution of the transport process and the approach to the long-time limit. In the long-time limit (long times and large lengthscales), we recover, of course, the classical local Fickian behaviour. The velocity field considered here is a simple example of a stochastic velocity field, and as such it may be viewed as a crude model of turbulence.

The general theory presented here has much broader application than determining the RTDs resulting from the fluid-induced dispersion – the so-called mechanical dispersion – in a porous medium. In particular, the dispersion in porous media caused by the non-mechanical mechanisms associated with the retention of the solute species in regions of zero velocity (Koch & Brady 1985) has a pronounced affect on the RTDs and the approach to the long-time limit. These issues are addressed in a separate work (Koch 1986; Koch & Brady 1987*a*). The theory presented here is also the natural starting point for examining transport in systems which are not spatially homogeneous. An application to dispersion in heterogeneous porous media is given in Koch & Brady (1987*b*).

2. The non-local transport equations

In this section we shall follow the non-local approach used in other physical settings (Keller 1962; Frisch 1968; Beran & McCoy 1970) and derive the general averaged conservation equation for a scalar quantity c (such as a solute concentration) that satisfies, at each point in the medium, the detailed conservation equation

$$\frac{\partial c}{\partial t}+\nabla\cdot\boldsymbol{q}=S, \tag{2.1a}$$

where

$$\boldsymbol{q}\equiv\boldsymbol{v}c\equiv\boldsymbol{u}c-\frac{D}{M}\nabla(Mc) \tag{2.1b}$$

is the flux, $\boldsymbol{u}$ is the sum of the fluid velocity and the velocity resulting from any external force that may be acting on the solute, D is the molecular diffusivity, and M is the solubility (or solute's activity coefficient). The source S of solute is taken to be independent of concentration and includes the solute injected into the bed initially. In general the diffusivity and solubility are functions of position and are different, for example, in the various phases of a multiphase medium. Thus, D and M are both generalized functions, which may undergo a step change at interphase boundaries.

The writing of the contribution to the flux from the effects of diffusion and solubility as $(D/M)\nabla(Mc)$ has been done for convenience to remove any specific reference to boundary conditions. Thus, (2.1) applies throughout the entire medium. In the application to dispersion in porous media consisting of a fixed solid phase and a mobile fluid phase, the requirement that this term be non-singular gives continuity of mass flux and solute equilibrium at the interphase boundaries. A step change in solubility M at an interphase boundary necessitates a step change in c in order that the solute activity Mc is continuous and $\nabla(Mc)$ is non-singular; this step change in c is the interphase partitioning of the solute at local interphase equilibrium. A step change in D/M due to different molecular diffusivities in the two phases in turn requires a step change in $\nabla(Mc)$, so that the flux $(D/M)\nabla(Mc)$ is continuous at the boundary and its divergence is non-singular. Thus, the solute velocity $\boldsymbol{v}$ defined by (2.1*b*) must be interpreted as a differential operator, which includes the effects of convection, molecular diffusion, and the interphase boundary conditions on the solute transport.

We are interested in cases in which the spatial variations in the velocity field are complex and/or the precise position of the source relative to the velocity field is uncertain, so that the solute velocity is best described stochastically. Thus, we define an ensemble average $\langle\ \rangle$ as the average over an ensemble of velocity fields. The precise specification of this ensemble necessarily depends on the application. For example, in a spatially periodic medium this ensemble average reduces to an average over a unit cell (Koch 1986). In applying (2.1) and (2.2) below to Taylor dispersion in a channel or tube, the ensemble average would be replaced by an average over the channel or tube cross-section. In this context it may also prove more convenient to explicitly use boundary conditions at the tube wall rather than incorporate them in the differential equation as we have done here. This requires no change in the development below, because the interpretation of the solute velocity $\boldsymbol{v}$ as an operator implies the imposition of boundary conditions.

Averaging (2.1*a*) yields

$$\frac{\partial\langle c\rangle}{\partial t}+\nabla\cdot\langle \boldsymbol{q}\rangle = \langle S\rangle. \tag{2.2}$$

In order to obtain an equation relating the average concentration to the source, we must express the average flux $\langle \boldsymbol{q}\rangle = \langle \boldsymbol{v}c\rangle$ in terms of the average or 'macroscale' properties of the medium. To this end, we write the concentration as

$$c = P_{\mathrm{eq}}\langle c\rangle + c', \tag{2.3}$$

where P_{eq}, the equilibrium distribution of the solute in the absence of an average concentration gradient, is defined by

$$\nabla\cdot(\boldsymbol{v}P_{\mathrm{eq}}) = \nabla\cdot\left[\boldsymbol{u}P_{\mathrm{eq}}-\frac{D}{M}\nabla(MP_{\mathrm{eq}})\right] = 0, \tag{2.4a}$$

$$\langle P_{\mathrm{eq}}\rangle = 1, \tag{2.4b}$$

and c' is the deviation of the concentration from local equilibrium. In a two-phase medium (fluid–solid) the solubility requirement for local, microscale thermodynamic equilibrium at the interphase boundaries takes the form

$$c_{\mathrm{f}} = mc_{\mathrm{p}},$$

i.e. $M = 1$ in the fluid phase and m in the solid phase. P_{eq} gives the partitioning of the solute between the phases on the macroscopic scale, and in the case considered here of a solenoidal fluid velocity field $\boldsymbol{u}$ in a multiphase medium, P_{eq} is constant in each phase, but undergoes a step change at interphase boundaries, such that MP_{eq} is constant, i.e.

$$P_{\mathrm{eq}} = \begin{cases} \dfrac{1}{1-\phi+\phi m^{-1}} & \text{in the fluid,} \\ \dfrac{1}{m(1-\phi+\phi m^{-1})} & \text{in the solid,} \end{cases}$$

where ϕ is the volume fraction of the solid phase. If the fluid were compressible, the fluid motion could cause the equilibrium distribution to vary within the fluid phase. Substituting (2.3) in the equation for the average mass flux gives

$$\langle \boldsymbol{q}\rangle = \langle \boldsymbol{v}P_{\mathrm{eq}}\rangle\langle c\rangle + \langle \boldsymbol{v}c'\rangle. \tag{2.5}$$

In interpreting (2.5), we must recall that the solute velocity $\boldsymbol{v}$ is an operator. Thus, the first term on the right-hand side of (2.5), obtained by operating on $P_{\mathrm{eq}}\langle c\rangle$ with the operator $\boldsymbol{v}$ and then averaging, is

$$\langle \boldsymbol{u}P_{\mathrm{eq}}\rangle\langle c\rangle - \left\langle\left(\frac{D}{M}\right)\nabla(MP_{\mathrm{eq}}\langle c\rangle)\right\rangle = \boldsymbol{V}\langle c\rangle - \langle DP_{\mathrm{eq}}\rangle\nabla\langle c\rangle,$$

where

$$\boldsymbol{V} \equiv \langle \boldsymbol{u}P_{\mathrm{eq}}\rangle \tag{2.6}$$

is defined to be the solute average velocity at equilibrium. Thus, using (2.3) and (2.4) we may rewrite (2.5) as

$$\langle \boldsymbol{q}\rangle = \boldsymbol{V}\langle c\rangle - \langle DP_{\mathrm{eq}}\rangle\nabla\langle c\rangle + \langle \boldsymbol{v}'c'\rangle, \tag{2.7}$$

where $\boldsymbol{v}' = \boldsymbol{v} - \boldsymbol{V}$.

An equation for the concentration disturbance may be obtained by substituting (2.3) into (2.1) and using (2.4) to give

$$\frac{\partial c'}{\partial t} + \nabla\cdot(\boldsymbol{v}c') = -\boldsymbol{v}P_{\mathrm{eq}}\cdot\nabla\langle c\rangle - P_{\mathrm{eq}}\frac{\partial\langle c\rangle}{\partial t} + S_{\mathrm{d}}\langle S\rangle, \tag{2.8}$$

where $S \equiv S_{\mathrm{d}}\langle S\rangle$, i.e. S_{d} is the distribution of the source relative to its average in the microstructure. The solution of (2.8) is

$$c' = \int \mathrm{d}\boldsymbol{x}_1 \int_{-\infty}^{t} \mathrm{d}t_1\, P(\boldsymbol{x}-\boldsymbol{x}_1, t-t_1)\left\{-\boldsymbol{v}'P_{\mathrm{eq}}\cdot\nabla\langle c\rangle - P_{\mathrm{eq}}\left[\frac{\partial\langle c\rangle}{\partial t} + \boldsymbol{V}\cdot\nabla\langle c\rangle\right] + S_{\mathrm{d}}\langle S\rangle\right\}, \tag{2.9a}$$

where

$$\frac{\partial P}{\partial t} + \nabla\cdot(\boldsymbol{v}P) = \frac{\partial P}{\partial t} + \nabla\cdot(\boldsymbol{u}P) - \nabla\cdot\left[\frac{D}{M}\nabla(MP)\right] = \delta(\boldsymbol{x}-\boldsymbol{x}_1)\,\delta(t-t_1). \tag{2.9b}$$

Here P, the Green function for the left-hand side of (2.8), is the transition probability: the probability of finding a tracer particle at $\boldsymbol{x}$ at time t given that it was at $\boldsymbol{x}_1$ at time t_1.

Using the solution (2.9) for the concentration disturbance the average mass flux (2.7) may be written as

$$\begin{aligned}\langle \boldsymbol{q}\rangle = \boldsymbol{V}\langle c\rangle - \int \mathrm{d}\boldsymbol{x}_1 \int_{-\infty}^{t} \mathrm{d}t_1 \Big\{&\mathsf{D}(\boldsymbol{x}-\boldsymbol{x}_1, t-t_1)\cdot\nabla\langle c(\boldsymbol{x}_1, t_1)\rangle \\ &+ \boldsymbol{w}(\boldsymbol{x}-\boldsymbol{x}_1, t-t_1)\left[\frac{\partial\langle c(\boldsymbol{x}_1, t_1)\rangle}{\partial t_1} + \boldsymbol{V}\cdot\nabla_1\langle c(\boldsymbol{x}_1, t_1)\rangle\right] - \boldsymbol{\sigma}(\boldsymbol{x}-\boldsymbol{x}_1, t-t_1)\langle S(\boldsymbol{x}_1, t_1)\rangle\Big\},\end{aligned} \tag{2.10a}$$

where

$$\mathbf{D} \equiv \langle DP_{\mathrm{eq}}\rangle \mathbf{I}\delta(\boldsymbol{x}-\boldsymbol{x}_1)\,\delta(t-t_1)+\langle \boldsymbol{v}'(\boldsymbol{x},t)\,P(\boldsymbol{x}-\boldsymbol{x}_1,t-t_1)\,\boldsymbol{v}'(\boldsymbol{x}_1,t_1)\,P_{\mathrm{eq}}(\boldsymbol{x}_1)\rangle, \tag{2.10b}$$

$$\boldsymbol{w} \equiv \langle \boldsymbol{v}'(\boldsymbol{x},t)\,P(\boldsymbol{x}-\boldsymbol{x}_1,t-t_1)\,P_{\mathrm{eq}}(\boldsymbol{x}_1)\rangle, \tag{2.10c}$$

$$\boldsymbol{\sigma} \equiv \langle \boldsymbol{v}'(\boldsymbol{x},t)\,P(\boldsymbol{x}-\boldsymbol{x}_1,t-t_1)\,S_{\mathrm{d}}(\boldsymbol{x}_1,t_1)\rangle, \tag{2.10d}$$

$\mathbf{I}$ is the identity dyadic, and $\delta(\;)$ denotes the Dirac delta function. In deriving (2.10) we have used the fact the $\langle \boldsymbol{V}c'\rangle$ and $\langle\langle DP_{\mathrm{eq}}\rangle \nabla c'\rangle$ are zero.

Equation (2.2) with (2.10) relates the average concentration to the source. The average flux depends not only on the local average concentration $\langle c(\boldsymbol{x},t)\rangle$ but on the average concentration at other positions $\boldsymbol{x}_1$ and at previous times t_1. In addition to the solute average velocity $\boldsymbol{V}$, which is a constant in a statistically homogeneous medium, the flux depends on three transport properties $\mathbf{D}$, $\boldsymbol{w}$, and $\boldsymbol{\sigma}$, which are functions of the spatial separation $\boldsymbol{x}-\boldsymbol{x}_1$ and time lag $t-t_1$ between a change in the average concentration and the flux response. The non-local nature of these properties results from the finite correlation distance of the velocity fluctuations and the finite time required for the detailed concentration field to respond to changes in the average concentration. These correlation lengths and times depend on the fundamental microscale transport processes that are occurring and on the statistical properties of the solute velocity field (see §4 for a discussion).

The local description of dispersion used in most studies of average transport properties (Koch & Brady 1985; Koch 1986) is recovered in the absence of sources when the average concentration gradient is constant, so that the expression $(\partial\langle c\rangle/\partial t)+\boldsymbol{V}\cdot\nabla\langle c\rangle$ is zero. The average flux then reduces to

$$\langle \boldsymbol{q}\rangle = \boldsymbol{V}\langle c\rangle - \mathbf{D}_l\cdot\nabla\langle c\rangle, \tag{2.11a}$$

where

$$\mathbf{D}_l = \int \mathrm{d}\boldsymbol{x}_1 \int_{-\infty}^{t} \mathrm{d}t_1\, \mathbf{D}(\boldsymbol{x}-\boldsymbol{x}_1,t-t_1). \tag{2.11b}$$

Thus, $\mathbf{D}$ is simply a non-local generalization of the traditional local or Fickian diffusivity. The second non-local function $\boldsymbol{w}$ gives the response to temporal and spatial changes in the average concentration. Finally, $\boldsymbol{\sigma}$ gives the flux that results when a source causes the detailed concentration field to deviate from local equilibrium. As the source includes the solute injected into the bed initially, $\boldsymbol{\sigma}$ includes the effect of the initial concentration distribution on the average concentration. The local expression (2.11) can also be obtained as the first term in a multiple-scales expansion when the average concentration gradient $\nabla\langle c\rangle$ is not strictly constant but slowly varying (Keller 1977; Koch 1986; Koch & Brady 1987*c*).

In evaluating the average flux (2.10) we must recall that the solute velocity disturbance, $\boldsymbol{v}' \equiv \boldsymbol{u}'-(D/M)\nabla(M)$, is a linear operator. Here $\boldsymbol{u}' \equiv \boldsymbol{u}-\boldsymbol{V}$ is the fluid velocity disturbance. Thus, written out in full, the transport properties (2.10*c*, *d*) are

$$\boldsymbol{w} = \left\langle \left[\boldsymbol{u}'P-\frac{D}{M}\nabla(MP)\right]P_{\mathrm{eq}}(\boldsymbol{x}_1)\right\rangle, \tag{2.12a}$$

$$\boldsymbol{\sigma} = \left\langle \left[\boldsymbol{u}'P-\frac{D}{M}\nabla(MP)\right]S_{\mathrm{d}}(\boldsymbol{x}_1,t_1)\right\rangle, \tag{2.12b}$$

and the diffusivity (2.10*b*) is an operator given by

$$\mathsf{D} = \langle DP_{\mathrm{eq}}\rangle \mathsf{I}\delta(\boldsymbol{x}-\boldsymbol{x}_1)\,\delta(t-t_1) + \left\langle\left[\boldsymbol{u}'P-\frac{D}{M}\boldsymbol{\nabla}(MP)\right][\boldsymbol{u}'(\boldsymbol{x}_1)\,P_{\mathrm{eq}}(\boldsymbol{x}_1)-D(\boldsymbol{x}_1)\,P_{\mathrm{eq}}(\boldsymbol{x}_1)\,\boldsymbol{\nabla}_1]\right\rangle. \qquad (2.12c)$$

Note that the first factor of the solute velocity $\boldsymbol{v}'(\boldsymbol{x},t)$ in the definition of D in (2.10*b*) and the solute velocity in the definitions (2.10*c*, *d*) of $\boldsymbol{w}$ and $\boldsymbol{\sigma}$ are operators in $\boldsymbol{x}$. Thus, they do not act on the $\boldsymbol{x}_1$ dependence of the equilibrium distribution P_{eq} or the concentration gradient $\boldsymbol{\nabla}_1\langle c\rangle$. As a result, $\boldsymbol{w}$ and $\boldsymbol{\sigma}$ are not operators. The second factor of the solute velocity $\boldsymbol{v}'(\boldsymbol{x}_1,t_1)$ in the definition of D is an operator in $\boldsymbol{x}_1$, however, so D is itself a differential operator.

These transport properties take on a simpler form and the diffusivity is simply a function (not an operator) when we neglect the effect of molecular diffusion on the solute velocity. In this case (2.12) reduces to

$$\boldsymbol{w} = \langle \boldsymbol{u}'(\boldsymbol{x},t)\,P(\boldsymbol{x}-\boldsymbol{x}_1,t-t_1)\,P_{\mathrm{eq}}(\boldsymbol{x}_1)\rangle, \qquad (2.13a)$$

$$\boldsymbol{\sigma} = \langle \boldsymbol{u}'(\boldsymbol{x},t)\,P(\boldsymbol{x}-\boldsymbol{x}_1,t-t_1)\,S_{\mathrm{d}}(\boldsymbol{x}_1,t_1)\rangle, \qquad (2.13b)$$

and

$$\mathsf{D} = D\mathsf{I}\delta(\boldsymbol{x}-\boldsymbol{x}_1)\,\delta(t-t_1)+\langle \boldsymbol{u}'(\boldsymbol{x},t)\,P(\boldsymbol{x}-\boldsymbol{x}_1,t-t_1)\,\boldsymbol{u}'(\boldsymbol{x}_1,t_1)\,P_{\mathrm{eq}}(\boldsymbol{x}_1)\rangle. \qquad (2.13c)$$

The averaged conservation equations (2.2) and (2.10*a*) take on a simple form upon Fourier transforming in space and time, because the convolution integrals in (2.9*a*) are replaced by products in Fourier space. The transform of the average concentration is

$$\langle \hat{c}(\boldsymbol{\xi},\omega)\rangle = \frac{\langle\hat{S}\rangle(1-\mathrm{i}\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{\xi})}{\mathrm{i}\omega+\mathrm{i}\boldsymbol{\xi}\cdot\boldsymbol{V}+\boldsymbol{\xi}\cdot\hat{\mathsf{D}}\cdot\boldsymbol{\xi}+(\boldsymbol{\xi}\cdot\hat{\boldsymbol{w}})\,(\omega+\boldsymbol{\xi}\cdot\boldsymbol{V})}, \qquad (2.14)$$

where ^ indicates the transform in both time and space, $\boldsymbol{\xi}$ is the spatial and ω the temporal transform variable, and we have restricted the application to statistically homogeneous media so that $\boldsymbol{V}$ is constant. Equation (2.14) provides a convenient way of calculating the average concentration for a given source if we know the transformed properties $\hat{\mathsf{D}}$, $\hat{\boldsymbol{\sigma}}$, and $\hat{\boldsymbol{w}}$.

This completes the general derivation of the non-local transport problem. The evaluation of D, $\boldsymbol{w}$ and $\boldsymbol{\sigma}$ requires knowledge of $\boldsymbol{v}'$ and the solution of (2.4) for P_{eq} and (2.9*b*) for the transition probability P for each realization of the ensemble, followed by the appropriate averaging $\langle\ \rangle$. This direct method of solution is generally quite difficult. Instead, one normally derives averaged equations of $\boldsymbol{v}'$, P etc. and then seeks to break the nonlinear average inherent in (2.10) by an appropriate closure scheme. This we shall do in the following application to dispersion in disordered porous media. The direct method can, however, be used in the relatively simple problems of Taylor dispersion in a tube or transport in spatially periodic porous media (Koch 1986). Here, the average reduces to an average over a cross-section or a unit cell, and the closure problem is absent. (Simple is used here in a conceptual sense; carrying out specific calculations may pose a difficult mathematical boundary-value problem.)

The expression (2.10*a*, *b*) for the frequency- and wavelength-dependent diffusivity (or its local approximation (2.11*b*)) indicates that the macroscopic or effective diffusivity is given in terms of the solute's velocity correlation function, which measures the correlation between the solute's velocity disturbance at a given point and time and its velocity disturbance at all other points and all previous times. In this context, (2.10) bears a close resemblance to the Green–Kubo expressions for determining 'molecular' transport properties from linear response theory (McQuarrie 1976). An approach such as that taken here can actually be used to write the diffusivity as a more general integral and average, which incorporates variations on both molecular and continuum scales.

Before closing this section we shall briefly show how the moments expansions used previously may be simply recovered from our analysis. In Fourier space the $\langle \hat{\boldsymbol{q}} \rangle$ from (2.10a) is (neglecting $\boldsymbol{w}$ and $\boldsymbol{\sigma}$ for clarity)

$$\langle \hat{\boldsymbol{q}} \rangle = \boldsymbol{V}\langle \hat{c} \rangle - \hat{\mathbf{D}}\cdot\widehat{\nabla\langle c \rangle}. \tag{2.15}$$

The traditional moments approach (Gill & Sankarasubramanian 1970; Chatwin 1970; Pagitsas *et al.* 1986) is simply obtained by expanding $\hat{\mathbf{D}}(\boldsymbol{\xi}, \omega)$ in a Taylor series about $\boldsymbol{\xi} = 0$, $\omega = 0$. Indeed, from (2.11b) we have $\mathbf{D}_l = \hat{\mathbf{D}}(0,0)$; the long-time or local diffusivity is given by the zero-frequency (ξ and ω going to zero) limit of the non-local dispersivity. The more involved time-integral approach of Smith (1981) is obtained by expanding about $\boldsymbol{\xi} = 0$, but retaining the ω dependence to recover the time integral upon Fourier inversion.

3. Transport properties in porous media

In this section we demonstrate the general non-local transport theory derived in §2 for the case of a porous medium consisting of a fixed solid phase and a Newtonian fluid. We shall see that the non-local theory is capable of predicting the complete space–time response (RTD) in such a medium.

If the Reynolds number based on a characteristic size of the microstructure is small, the equations of motion for the fluid velocity $\boldsymbol{u}$ are Stokes equations

$$\nabla\cdot\boldsymbol{u} = 0, \tag{3.1a}$$

$$-\nabla p + \mu\nabla^2\boldsymbol{u} = 0, \tag{3.1b}$$

with

$$\boldsymbol{u} = 0 \quad \text{on solid boundaries.} \tag{3.1c}$$

Here p is the dynamic pressure, μ is the fluid viscosity, and the average velocity in the medium is a constant denoted by U. The ensemble average in a porous medium consists of an average over possible configurations $\boldsymbol{\zeta}$ of the solid phase, i.e.

$$\langle f \rangle \equiv \int \mathrm{d}\boldsymbol{\zeta} f(\boldsymbol{x} \,|\, \boldsymbol{\zeta})\, g(\boldsymbol{\zeta}), \tag{3.2}$$

where $g(\boldsymbol{\zeta})$ is the probability that the solid phase has configuration $\boldsymbol{\zeta}$. The vector $\boldsymbol{\zeta}$ contains all of the information – such as the relative positions and orientations of grains – required to specify the bed structure.

In principle we may now calculate the transport properties (2.10) by solving (3.1) for the fluid velocity and (2.9b) for the transition probability for each configuration $\boldsymbol{\zeta}$ of the microstructure and using (3.2) to evaluate the ensemble average. In order to obtain a simple analytic solution for the transport properties, however, we require a closure scheme that allows us to relate the averages of the nonlinear terms in (2.10) to a suitable product of the individual averages. This closure is obtained here for disordered or random media through an asymptotic analysis in small solids volume fraction ϕ or, equivalently, high permeability, reducing the determination of the nonlinear average to a boundary-value problem involving a single grain. In the local or long-time dispersion problem treated in Koch & Brady (1985) we saw that this closure scheme allowed us to capture the basic physical processes leading to dispersion in all porous media, even those of high solids volume fraction.

In Koch & Brady (1985) we found that at high Péclet number – the regime in which the effective diffusivity differs most dramatically from the molecular diffusivity – the solid influences the average mass transport by three mechanisms which we have termed mechanical, boundary-layer and holdup dispersion. In this paper we shall treat mechanical dispersion, which results from the fluid velocity disturbance induced in the bulk fluid by the solid grains. This mechanism is termed mechanical dispersion because molecular diffusion plays no role in it at high Péclet numbers. The non-mechanical, boundary-layer and holdup mechanisms are investigated in a separate study (Koch & Brady 1987*a*).

It is shown in Koch & Brady (1985) that the long-range nature of velocity fluctuations in a highly permeable porous medium permits the leading mechanical-dispersion contribution to the transport properties to be calculated by treating the solid particles as points – allowing the velocity disturbance induced by a particle to be that of a point force and neglecting any effects of the variation in the solubility and molecular diffusivity of the solute due to the presence of the solid phase. The latter approximation allows us to use the simple form (2.13) of the transport properties, and to write the equation (2.9*b*) for the transition probability as

$$\frac{\partial P}{\partial t}+\boldsymbol{u}\cdot\nabla P-D_{\mathrm{f}}\nabla^2 P=\delta(\boldsymbol{x}-\boldsymbol{x}_1)\,\delta(t-t_1), \tag{3.3}$$

where D_{f} is the molecular diffusivity of the solute in the fluid. In this approximation the equilibrium distribution is $P_{\mathrm{eq}}=1$ and the ensemble-average molecular diffusivity and solute average velocity are $\langle DP_{\mathrm{eq}}\rangle\approx D_{\mathrm{f}}$ and $\boldsymbol{V}\approx\langle\boldsymbol{u}\rangle\equiv\boldsymbol{U}$.

The second ensemble average in (2.13*c*) may be evaluated by relating it to a conditional ensemble average with one grain held fixed. Thus, using the definition of the ensemble average (2.13*c*) may be written

$$\mathbf{D}=D_{\mathrm{f}}\,\mathbf{I}\,\delta(\boldsymbol{x}-\boldsymbol{x}_1)\,\delta(t-t_1)+\int \mathrm{d}\boldsymbol{r}_1\, g(\boldsymbol{r}_1)\langle \boldsymbol{u}'(\boldsymbol{x},\boldsymbol{r}_1)\,P(\boldsymbol{x}-\boldsymbol{x}_1,t-t_1,\boldsymbol{r}_1)\,\boldsymbol{u}'(\boldsymbol{x}_1,\boldsymbol{r}_1)\rangle_1, \tag{3.4}$$

where $\langle\;\rangle_1$ denotes the conditional ensemble average with a grain fixed at $\boldsymbol{r}_1$, and $g(\boldsymbol{r}_1)=\phi/\frac{4}{3}\pi a^3$ is the number density of grains. In the asymptotic limit of low solids volume fraction two-grain correlations may be neglected, and (3.4) becomes

$$\mathbf{D}\approx D_{\mathrm{f}}\,\mathbf{I}\,\delta(\boldsymbol{x}-\boldsymbol{x}_1)\,\delta(t-t_1)+\frac{\phi}{\frac{4}{3}\pi a^3}\int \mathrm{d}\boldsymbol{r}_1\langle \boldsymbol{u}'(\boldsymbol{x}-\boldsymbol{r}_1)\rangle_1\langle P(\boldsymbol{x}-\boldsymbol{x}_1,t-t_1,\boldsymbol{r}_1)\rangle_1\langle \boldsymbol{u}'(\boldsymbol{x}_1-\boldsymbol{r}_1)\rangle_1, \tag{3.5}$$

where the errors in (3.5) can be shown to be small in the limit $\phi\rightarrow 0$.

Equations for the conditionally averaged velocity and transition probability may be derived by conditionally averaging (3.1) and (3.3) to give Brinkman's equation (Hinch 1977)

$$-\mu\nabla^2\langle\boldsymbol{u}\rangle_1+\nabla\langle p\rangle_1+\frac{\mu}{k}\langle\boldsymbol{u}\rangle_1=O(\phi), \tag{3.6a}$$

$$\nabla\cdot\langle\boldsymbol{u}\rangle_1=0, \tag{3.6b}$$

where the permeability $k = \frac{2}{9}\phi^{-1}a^{-2}$, and the advection–diffusion equation (Koch & Brady 1985; Acrivos, Hinch & Jeffrey 1980)

$$\frac{\partial\langle P\rangle}{\partial t}+\langle \boldsymbol{u}\rangle_1\cdot\boldsymbol{\nabla}\langle P\rangle_1-D_{\mathrm{f}}\nabla^2\langle P\rangle_1-\delta(\boldsymbol{x}-\boldsymbol{x}_1)\,\delta(t-t_1)=O(\phi). \tag{3.7}$$

The small $O(\phi)$ terms on the right-hand sides of (3.6a) and (3.7), which represent the influence of grain interactions on the one-grain conditional average velocity and transition probability, are written out fully in the references cited above. With a single exception the effects of grain interactions may be neglected. The drag exerted by the fixed solid leading to the porous-medium term $(\mu/k)\,\boldsymbol{u}$ must be included in the momentum conservation equation (3.6a) even in the low ϕ limit. Although this term is proportional to the small volume fraction ϕ, it has a large influence on the fluid velocity far from the fixed grain where the Laplacian of the velocity is small.

The solution of (3.6) with a point force at $\boldsymbol{r}_1$ when the unconditional or bulk velocity is $\boldsymbol{U}$ is

$$\langle \boldsymbol{u}'\rangle_1=\frac{-3\epsilon}{2R^3}\,\boldsymbol{U}(1+R+R^2)\,\mathrm{e}^{-R}-\epsilon\boldsymbol{X}(\boldsymbol{X}\cdot\boldsymbol{U})\,\frac{9}{R^5}(3+3R+R^2)\,\mathrm{e}^{-R}, \tag{3.8a}$$

and its Fourier transform is

$$\langle \hat{\boldsymbol{u}}'\rangle=\frac{-6\pi\epsilon[\mathbf{I}-\boldsymbol{\xi}\boldsymbol{\xi}/\xi^2]\cdot\boldsymbol{U}}{\xi^2+1}, \tag{3.8b}$$

where $\boldsymbol{X}=k^{-\frac{1}{2}}(\boldsymbol{x}-\boldsymbol{r}_1)$ is the position relative to the grain at $\boldsymbol{r}_1$, non-dimensionalized with the Brinkman screening length $k^{\frac{1}{2}}, R\equiv|\boldsymbol{X}|, \epsilon\equiv ak^{-\frac{1}{2}}=(3/\surd 2)\,\phi^{\frac{1}{2}}$ is a small parameter at low volume fraction ϕ, and $\boldsymbol{\xi}$ is the Fourier transform variable corresponding to $\boldsymbol{X}$. The velocity disturbance (3.8) caused by a point particle in a highly permeable porous medium is the same as that in Stokes flow – decaying as ϵ/R – near the particle $R\ll 1$, but it is screened by hydrodynamic interactions and decays as ϵ/R^3 at distances $R\sim O(1)$. At radial distances $R\sim O(1)$, where the dominant contribution to the integral in (3.5) occurs, the velocity disturbance is small and the transition probability is nearly the same as the free-space transition probability. The Fourier transform of the free-space transition probability is

$$\langle \hat{P}\rangle_1=\frac{1}{\mathrm{i}\omega+\mathrm{i}\boldsymbol{U}\cdot\boldsymbol{\xi}+(1/Pe)\,\xi^2}+O(\epsilon), \tag{3.9}$$

where $Pe=Uk^{\frac{1}{2}}/D_{\mathrm{f}}$ is the Péclet number based on the screening length $k^{\frac{1}{2}}$.

Note that at the present level of approximation, the transition probability and equilibrium distribution are independent of the position of the grain. If we also stipulate that the source be independent of position relative to the grain, i.e. it is injected uniformly in the fluid phase, then the properties $\boldsymbol{w}$ and $\boldsymbol{\sigma}$ in (2.13a,b) are equal to each other and, being proportional to $\boldsymbol{u}'$, are small $O(\epsilon)$. In §4 we shall see that under these circumstances the contributions to the average mass flux from $\boldsymbol{w}$ and $\boldsymbol{\sigma}$ in (2.10a) are small compared to those from $\mathbf{D}$ and may be neglected, i.e. in a weak fluctuation expansion, $\epsilon\ll 1$, the dominant effect comes from $\mathbf{D}$.

The equation (3.5) for the diffusivity written in terms of the non-dimensionalized coordinates is

$$\mathbf{D}=\frac{1}{Pe}\,\mathbf{I}\delta(\boldsymbol{X}-\boldsymbol{X}_1)\,\delta(\tau-\tau_1)+\mathbf{D}^{\mathrm{c}}, \tag{3.10a}$$

where $$\mathbf{D}^{\mathrm{c}}=\frac{\phi}{\frac{4}{3}\pi\epsilon^3}\int \mathrm{d}\boldsymbol{R}_1\langle \boldsymbol{u}'(\boldsymbol{X}-\boldsymbol{R}_1)\rangle_1\langle P(\boldsymbol{X}-\boldsymbol{X}_1,\tau-\tau_1)\rangle_1\langle \boldsymbol{u}'(\boldsymbol{X}_1-\boldsymbol{R}_1)\rangle_1, \tag{3.10b}$$

$\tau = tUk^{-\frac{1}{2}}$, and $\boldsymbol{R}_1 = k^{-\frac{1}{2}}\boldsymbol{r}_1$. Substituting the Fourier inverses of the second velocity disturbance and the transition probability in (3.10*b*) and integrating in $\boldsymbol{R}_1$, the Fourier transform of the diffusivity is

$$\hat{\mathbf{D}} = \frac{1}{Pe}\mathbf{I} + \hat{\mathbf{D}}^{\mathrm{c}}, \tag{3.11a}$$

where
$$\hat{\mathbf{D}}^{\mathrm{c}}(\boldsymbol{\xi}, \omega) = \frac{\phi}{\frac{4}{3}\pi(2\pi)^3\epsilon^3}\int \mathrm{d}\boldsymbol{\xi}' \langle \hat{\boldsymbol{u}}'(-\boldsymbol{\xi}')\rangle_1 \langle \hat{P}(\boldsymbol{\xi}+\boldsymbol{\xi}', \omega)\rangle_1 \langle \hat{\boldsymbol{u}}'(\boldsymbol{\xi}')\rangle_1. \tag{3.11b}$$

Substituting (3.8*b*) and (3.9) for the transformed velocity disturbance and transition probability and using $\phi = \frac{2}{9}\epsilon^2$, (3.11*b*) becomes in dimensional form,

$$\hat{\mathbf{D}}^{\mathrm{c}} = \frac{3Ua}{(2\pi)^2}\int \mathrm{d}\boldsymbol{\xi}' \frac{((\mathbf{I}-\boldsymbol{\xi}'\boldsymbol{\xi}'/\xi'^2)\cdot\mathbf{1}_z)^2}{(\xi'^2+1)^2[\mathrm{i}\omega+\mathrm{i}(\boldsymbol{\xi}'+\boldsymbol{\xi})\cdot\mathbf{1}_z+(1/Pe)(\boldsymbol{\xi}'+\boldsymbol{\xi})\cdot(\boldsymbol{\xi}'+\boldsymbol{\xi})]}, \tag{3.11c}$$

where $\mathbf{1}_z$ is the unit vector in the direction of the bulk flow.

The retention of the diffusive term in the denominator of (3.11*c*) is necessary in order to satisfy causality and make the integral well-defined. However, in the limit $Pe \rightarrow \infty$ the integral is independent of Pe. Any small positive number δ may be used in place of this term and letting $\delta \rightarrow 0$ causality is satisfied and the result is independent of δ (cf. the discussion in §4.1 of Koch & Brady 1985). Thus, in the limit $Pe \rightarrow \infty$, the result for the effective diffusivity is independent of the molecular diffusivity, and is given by

$$\hat{\mathbf{D}}^{\mathrm{c}} = \hat{D}^{\mathrm{c}}_{\parallel}\mathbf{1}_z\mathbf{1}_z + \hat{D}^{\mathrm{c}}_{\perp}(\mathbf{I}-\mathbf{1}_z\mathbf{1}_z), \tag{3.12a}$$

where
$$\hat{D}^{\mathrm{c}}_{\parallel} = Ua(\tfrac{3}{4} - 2\mathrm{i}\alpha + \tfrac{3}{2}\alpha^2 - 3\mathrm{i}\alpha^3 + \tfrac{3}{2}(\alpha^2+\alpha^4)[2\mathrm{i}\tan^{-1}(\alpha^{-1}) - \ln(1+\alpha^{-2})]), \tag{3.12b}$$

$$\hat{D}^{\mathrm{c}}_{\perp} = Ua(\tfrac{1}{2}\mathrm{i}\alpha - 3\alpha^2 + 3\mathrm{i}\alpha^3 + (3\alpha^4 + \tfrac{3}{2}\alpha^2)[\ln(1+\alpha^{-2}) - \mathrm{i}\tan^{-1}(\alpha^{-1})]), \tag{3.12c}$$

and
$$\alpha \equiv \omega + \boldsymbol{\xi}\cdot\mathbf{1}_z.$$

In the limit of low-frequency ω and small wavenumber $\boldsymbol{\xi}$, corresponding to long time and large lengths, this non-local diffusivity (3.12) reduces to the local diffusivity we derived previously (equation (4.8) of Koch & Brady 1985), i.e.

$$\left.\begin{aligned} \hat{D}^{\mathrm{c}}_{\parallel} &\sim [\tfrac{3}{4} - 2\mathrm{i}\alpha]\,Ua \qquad (3.13a)\\ \hat{D}^{\mathrm{c}}_{\perp} &\sim [0 + \tfrac{1}{2}\mathrm{i}\alpha]\,Ua \qquad (3.13b)\end{aligned}\right\} \text{ as } \alpha \rightarrow 0.$$

As a result of the fore–aft symmetry of the streamlines around a spherical grain, there is no contribution to the local transverse diffusivity from the one-sphere, purely mechanical problem. As shown previously (Koch & Brady 1985) it is necessary to include the effects of two-grain interactions, molecular diffusion, or to consider non-spherical grains, in order to obtain the leading behaviour of the transverse diffusivity at long times. The transient, mechanical, one-sphere solution (3.12*c*) gives the correct behaviour of the non-local transverse diffusivity except at long times (low frequencies, $\alpha \sim \phi^{\frac{1}{2}}$).

In the limit of high frequency α the non-local diffusivity is

$$\left.\begin{aligned} \hat{D}^{\mathrm{c}}_{\parallel} &\sim [\tfrac{2}{5}(\mathrm{i}\alpha)^{-1} + \tfrac{1}{4}\alpha^{-2}]\,Ua \qquad (3.14a)\\ \hat{D}^{\mathrm{c}}_{\perp} &\sim [\tfrac{1}{10}(\mathrm{i}\alpha)^{-1} + \tfrac{1}{4}\alpha^{-2}]\,Ua \qquad (3.14b)\end{aligned}\right\} \text{ as } \alpha \rightarrow \infty.$$

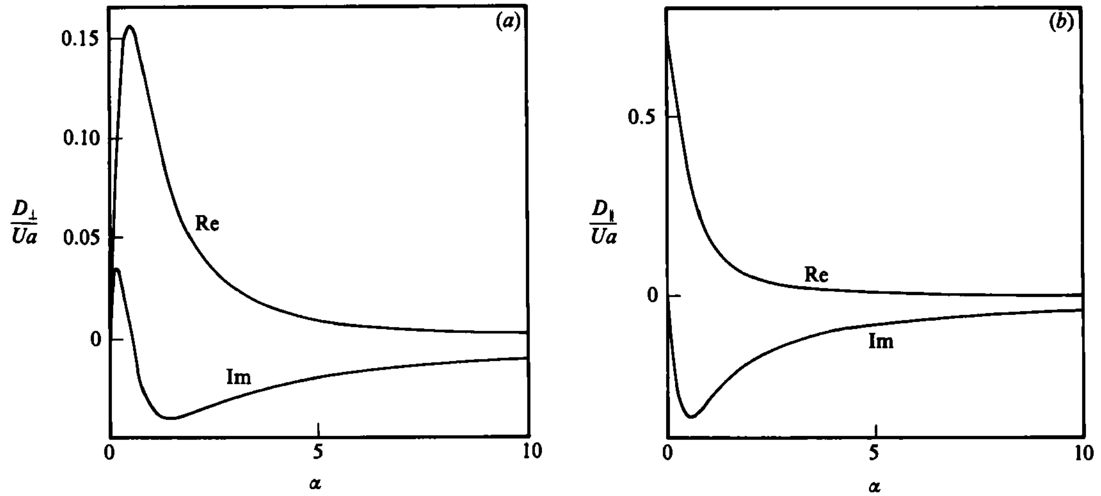

FIGURE 1. The real and imaginary parts of the hydrodynamic contributions to the wavelength-dependent longitudinal $\hat{D}^c_\parallel$ and transverse $\hat{D}^c_\perp$ effective diffusivity (cf. (3.12)) as a function of the temporal–spatial wavelength $\alpha = \omega + \boldsymbol{\xi}\cdot\mathbf{1}_z$. ($\mathbf{1}_z$ is a unit vector in the direction of the bulk flow.) The low and high α asymptotic forms are given in (3.13) and (3.14), respectively. In the limit $\alpha \rightarrow \infty$, corresponding to short times and small wavelengths, the hydrodynamic contributions $\hat{D}^c_\parallel$ and $\hat{D}^c_\perp$ are zero, and the effective diffusivity reduces to the molecular diffusivity (cf. equation (3.11*a*)).

As $\alpha \rightarrow \infty$, the hydrodynamic contributions $\mathbf{D}^c$ to the diffusivity go to zero, and we recover molecular diffusion in the limit of very small distances (large wavenumber $\boldsymbol{\xi}$) and short times (high-frequency ω). The real and imaginary parts of $\hat{D}^c_\parallel$ and $\hat{D}^c_\perp$ are plotted as a function of α in figure 1.

4. The average concentration profile – residence–time distributions in porous media

The average concentration response to an arbitrary source may in general be calculated using (2.14). In the present case, however, a simpler relation may be used to approximate the average concentration field. The transform of the average mass conservation equation (2.2) with (2.10) is

$$i\omega\langle\hat{c}\rangle + i\boldsymbol{\xi}\cdot\langle\hat{\boldsymbol{q}}\rangle = \langle\hat{S}\rangle, \tag{4.1a}$$

$$\langle\hat{\boldsymbol{q}}\rangle = \boldsymbol{V}\langle\hat{c}\rangle - i\hat{\mathbf{D}}\cdot\boldsymbol{\xi}\langle\hat{c}\rangle - \hat{\boldsymbol{w}}(i\omega + i\boldsymbol{\xi}\cdot\boldsymbol{V})\langle\hat{c}\rangle + \hat{\boldsymbol{\sigma}}\langle\hat{S}\rangle. \tag{4.1b}$$

Substituting from (4.1*a*) for the source $\langle\hat{S}\rangle$ in (4.1*b*), using the relation $\hat{\boldsymbol{w}} = \hat{\boldsymbol{\sigma}}$, and noting that $\hat{\mathbf{D}} \sim O(\epsilon)$ and $\hat{\boldsymbol{w}} \sim O(\epsilon)$, the mass flux may be approximated by

$$\langle\hat{\boldsymbol{q}}\rangle = \boldsymbol{V}\langle\hat{c}\rangle - i\hat{\mathbf{D}}\cdot\boldsymbol{\xi}\langle\hat{c}\rangle + O(\epsilon^2). \tag{4.2}$$

Although $\hat{\boldsymbol{w}}$ and $\hat{\mathbf{D}}$ are both $O(\epsilon)$, the net contribution to the mass flux from $\hat{\boldsymbol{w}}$ and $\hat{\boldsymbol{\sigma}}$ is $O(\epsilon^2)$ when $\hat{\boldsymbol{w}} = \hat{\boldsymbol{\sigma}}$. Finally, solving (4.1*a*) and (4.2), the average concentration is simply

$$\langle\hat{c}\rangle = \frac{\langle\hat{S}\rangle}{i\omega + i\boldsymbol{\xi}\cdot\boldsymbol{V} + \boldsymbol{\xi}\cdot\hat{\mathbf{D}}\cdot\boldsymbol{\xi}}. \tag{4.3}$$

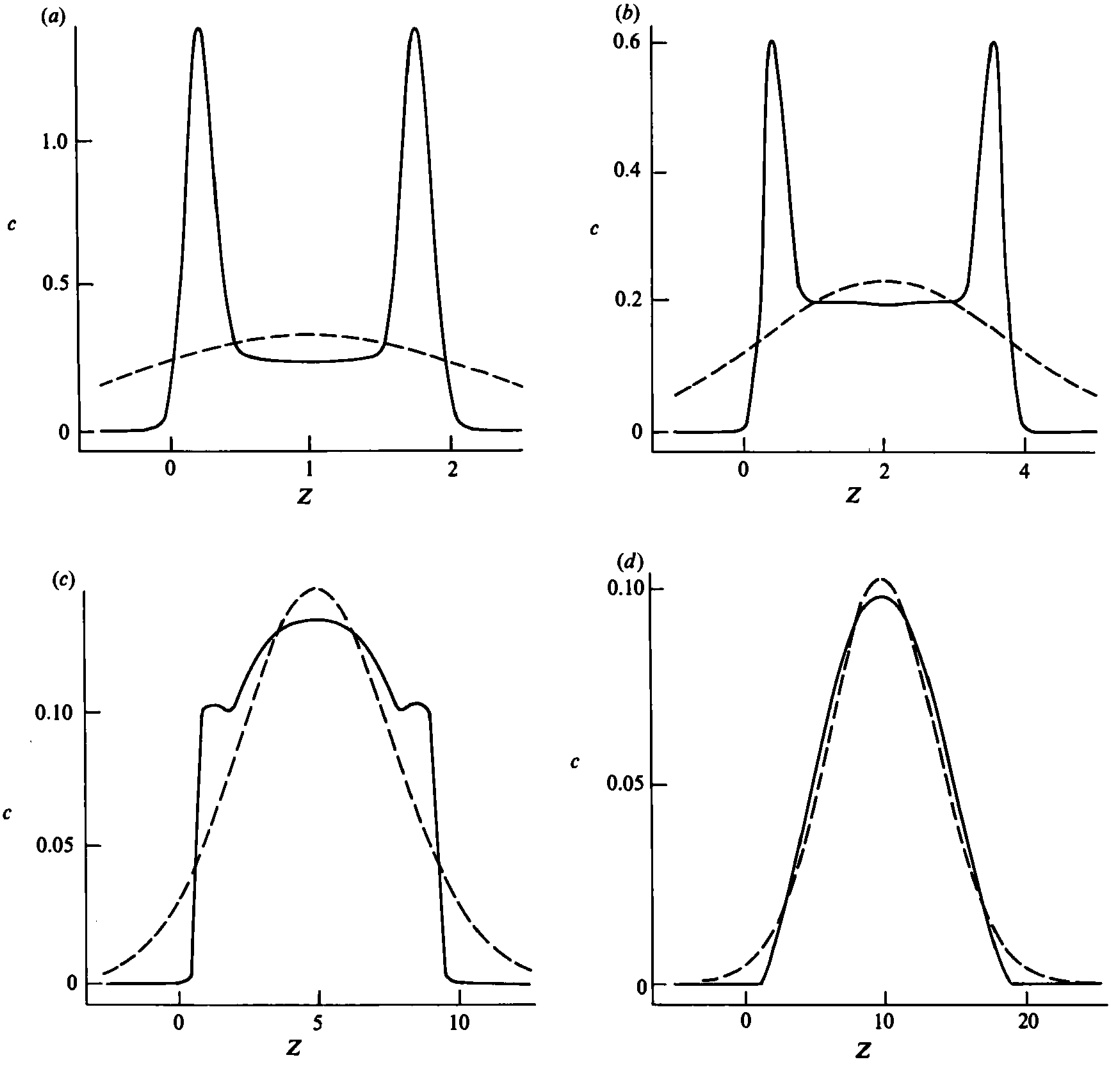

FIGURE 2. The average concentration response c to a pulse source $\delta(\tau)\,\delta(Z)$ in a plane perpendicular to the flow is plotted as a function of position $Z = zk^{-\frac{1}{2}}$ non-dimensionalized by the screening length $k^{\frac{1}{2}}$ at various times $\tau = tUk^{-\frac{1}{2}}$: (a) $\tau = 1$; (b) $\tau = 2$; (c) $\tau = 5$; (d) $\tau = 10$. The calculation is for a Péclet number $Pe = Uk^{-\frac{1}{2}}/D_{\mathrm{f}} = 100$. The dashed curves correspond to the profiles obtained by using the long-time or Fickian diffusivity $D_{\parallel} = \frac{3}{4}Ua$, and are the profiles that would be predicted by ignoring the non-local nature of the transport processes.

The preceding argument may be applied to any problem in which the magnitude of the fluctuations in the velocity field is small and the equilibrium distribution and source are uniform (independent of the position relative to the microstructure).

Equation (4.3) may be used to predict the concentration response to any source. We shall consider an impulse source $\delta(Z)\,\delta(\tau)$, i.e. a source introduced at one instant in time in one plane, $Z = 0$, perpendicular to the direction of flow. In this case an Ergodic hypothesis may be invoked to equate the ensemble-average concentration to the area average over a large area of the (x, y)-plane, i.e. the cross-sectional

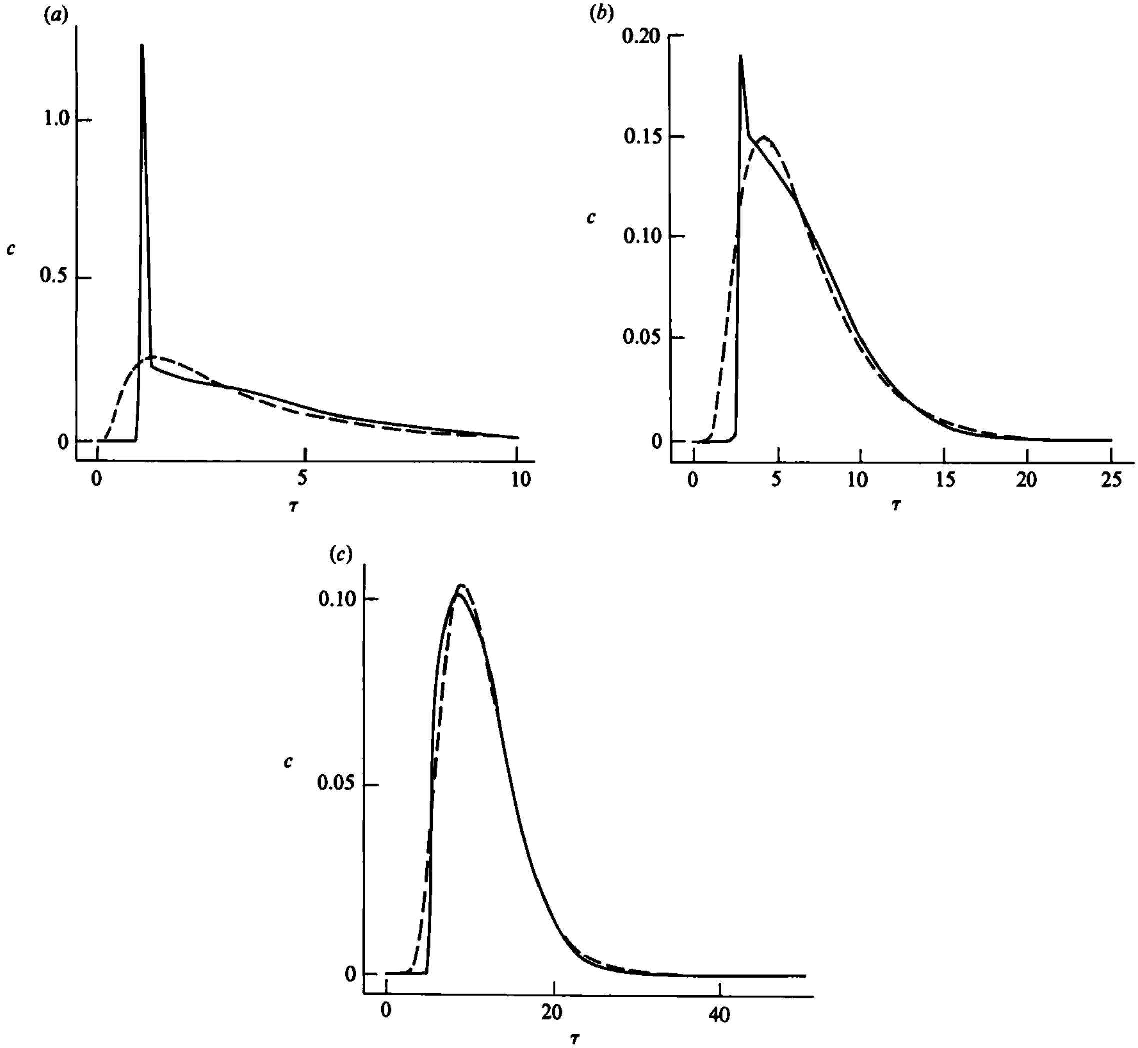

FIGURE 3. The average concentration c is plotted as a function of time τ at various axial positions: (a) $Z = 2$; (b) $Z = 5$; (c) $Z = 10$. The calculation is for an impulse source $\delta(Z)\,\delta(\tau)$ and a Péclet number of 100, and corresponds to the residence–time distributions one would observe at these axial locations. The dashed curves correspond to the profiles obtained by using the long-time or Fickian diffusivity $D_{\parallel} = \frac{3}{4}Ua$, and are the profiles that would be predicted by ignoring the non-local nature of the transport processes.

averaged concentration one normally measures in residence–time distribution studies. Figure 2 shows the concentration as a function of axial position at four points in time $\tau = 1$, 2, 5, and 10. In figure 3 the concentration is plotted as a function of time at three different positions in the bed, $Z = 2$, 5, and 10. This is the response one would measure experimentally with a probe placed at a given set position, i.e. the residence–time distribution. $Z = zk^{-\frac{1}{2}}$ and $\tau = tUk^{-\frac{1}{2}}$ are the coordinate measured parallel to the bulk flow and the time non-dimensionalized with the screening length $k^{\frac{1}{2}}$ and the fluid velocity U. (Recall that k is the permeability.) A volume fraction $\phi = 0.5$ has been used in these calculations. In both figures the dashed curves correspond to the concentration profiles one would predict using the long-time (low-frequency) limit of the diffusivity (3.13), i.e. assuming a local, Fickian behaviour for all time and space.

In the limit of short times (high frequencies $\alpha \rightarrow \infty$), the longitudinal hydrodynamic contribution to the diffusivity from (3.14*a*) is $\hat{D}_{\parallel}^{\mathrm{c}} = \frac{2}{5}(\mathrm{i}\alpha)^{-1}$. Using this high-frequency limit of the longitudinal diffusivity in the absence of molecular diffusion gives a concentration field that consists of two delta functions of equal magnitude travelling with velocities $(1 \pm \sqrt{\frac{2}{5}})\,U$. In this limit the motion is purely advective, and the mean-square displacement grows in proportion to τ^2 because a tracer's velocity is completely correlated with its initial value; the portion of the tracer initially moving faster than the average continues to do so, and likewise for the tracer injected into slower moving fluid. If we include the effects of molecular diffusion at short times $\tau = 1, 2$, the concentration is sharply bimodal with the two peaks being smoothed only by the relatively small molecular diffusion (see figure 2*a*, *b*).

The presence of two peaks travelling with velocities $(1 \pm \sqrt{\frac{2}{5}})\,U$ can be understood by examining the real-space–time counterpart of the equation that gives rise to $\langle \hat{c} \rangle$ in the short-time or high α limit. From (4.3) with (3.14*a*) for $\hat{D}_{\parallel}^{\mathrm{c}}$ we have

$$\langle \hat{c} \rangle = \frac{1}{\mathrm{i}\alpha + \frac{2}{5}\xi^2(\mathrm{i}\alpha)^{-1}} = \frac{\mathrm{i}\alpha}{(\mathrm{i}\alpha)^2 + \frac{2}{5}\xi^2}. \tag{4.4}$$

In real space–time this concentration profile is the solution of the wave equation

$$\frac{\partial^2 \langle c \rangle}{\partial t^2} - \frac{2}{5}\frac{\partial^2 \langle c \rangle}{\partial \eta^2} = \delta(\eta)\,\delta'(t), \tag{4.5}$$

where $\eta = z - |U|t$. The real space–time solution is

$$\langle c \rangle = \tfrac{1}{2}H(t)\,\delta(\eta - \sqrt{\tfrac{2}{5}}t) + \tfrac{1}{2}H(t)\,\delta(\eta + \sqrt{\tfrac{2}{5}}t), \tag{4.6}$$

corresponding to two travelling waves. The $\delta'(t)$ source in (4.5) resulting from the $\mathrm{i}\alpha$ in the numerator of (4.4) is necessary to ensure causality and have no disturbance for $t < 0$. $H(t)$ is the Heaviside step function.

It should be noted here that the results (4.4) and (3.14) are not strictly valid in the limit $t \rightarrow 0$ owing to the small ϵ (small ϕ or weak fluctuation) expansion. At times $t \not\gg \epsilon$, additional terms in the expansion for $\langle \hat{P} \rangle_1$, and therefore in $\hat{\mathbf{D}}$, $\hat{\boldsymbol{w}}$ and $\hat{\boldsymbol{\sigma}}$ are needed to resolve the precise short-time behaviour. The same is true for short spatial distances $|\boldsymbol{x}| \not\gg \epsilon$ if the source distribution $S(\boldsymbol{x}, t)$ varies on scales small compared with ϵ. It is also a consequence of the small ϵ expansion that the concentration profile is strictly symmetric and bimodal as $t \rightarrow 0$. At very short times, $t < \epsilon$, where advection dominates (high Péclet numbers) the initial pulse will spread convectively with a range of speeds, not just two as predicted here. Thus, our results and the profiles in figures 2 and 3 are only valid for t, $|\boldsymbol{x}| \gg \epsilon$.

At longer times $\tau = 5$ and 10 (figure 2*c*, *d*), the tracer is advected past several different grains (or regions of approximately independent velocity fluctuation) and its velocity becomes uncorrelated with its original value. The two peaks merge into a single peak that becomes a Gaussian profile as $\tau \rightarrow \infty$, because the tracer's displacement has then been influenced by many randomly distributed grains. The concentration profile predicted by the non-local theory is seen to be nearly identical to that predicted by the local theory for times τ or positions $Z \geqslant 10$. We see then that a dimensionless time and/or position of $O(10)$ is needed in order to reach the 'long-time' limit for dispersion in the fluid-phase of a porous medium. Note that τ has been non-dimensionalized by the advective timescale $k^{\frac{1}{2}}/U$, and thus the long time is reached after about 10 advective timescales.

The concentration field plotted as a function of position (figure 2) is symmetric about the mean position for a uniform source in the limit of small volume fraction and large Péclet number. The concentration profile resulting from lower-Péclet-number flows may be determined by retaining the full form (3.11*c*) of the non-local diffusivity rather than just its high *Pe* behaviour (3.12).

In a separate publication (Koch & Brady 1987*a*) the non-mechanical mechanisms of dispersion are treated. These non-mechanical mechanisms arise in the grains and near their surfaces, and require a diffusive time to reach their long-time behaviours. Their contributions to the transport properties are of lower order in small volume fraction than the mechanical dispersion contribution considered here. They grow faster with the Péclet number, however, and must be included in the limit of large Péclet number.

5. Conclusions

The non-local dispersion theory we have developed may be used to obtain the average concentration response in a heterogeneous medium to any source regardless of its lengthscale or timescale. The theory gives the full concentration profile at all times following the release of the source. In contrast, a moments expansion (Gill & Sankarasubramanian 1970; Chatwin 1970; Smith 1981; Pagitsas *et al.* 1986) generally only allows one to calculate the first few moments and is not adequate at short times. Note that the sharply bimodal concentration profiles (figure 2*a*, *b*) obtained for the short-time transport behaviour in a porous medium would not be well approximated by the first few moments. As indicated at the end of §2, however, the moments approach can be recovered from our analysis by simply expanding the transform of the flux (equation (2.10)) about $\omega = 0$ and $\xi = 0$.

The example of hydrodynamic dispersion in porous media treated in §§3 and 4 provides a simple illustration of mechanical dispersion in a stochastic velocity field. The results obtained for this case may be indicative of the type of behaviour observed in other stochastic velocity fields – for example, those found in free suspensions and turbulent flows. In particular, note that the effective diffusivity is equal to the molecular diffusivity in the limit of high spatial and/or temporal frequency (small distances and short times); this must hold in general so that molecular diffusion is recovered for transport on the molecular level.

The observation that the effective diffusivity grows with decreasing frequency (increasing wavelength) indicates how micromixing limitations arise. Large-scale concentration fluctuations (those larger than the characteristic length of the velocity fluctuations) are dissipated in the relatively short-time characteristic of advection due to the effects of mechanical dispersion. On the other hand, small-scale concentration fluctuations are not dissipated by mechanical dispersion, but only by molecular diffusion, so they decay in a characteristic diffusive time. If the Péclet number is large the advective time is much shorter than the diffusive time and macromixing occurs much faster than micromixing.

The non-local theory we have developed allows one to examine a whole class of transport processes that exhibit non-Fickian behaviour. In many cases the observed non-Fickian behaviour of transport processes in heterogeneous media has led to the abandonment of attempts to describe these processes as caused by dispersion. For example, chemical reactor engineers have introduced the concepts of channelling and bypassing to explain non-Gaussian residence–time distributions in chemical reactors. Similarly, transport processes in ground-water flows are generally described in terms of capacitance models. The non-local dispersion theory allows us to recognize these non-Fickian processes as simply dispersion processes which have not yet achieved their asymptotic long-temporal- and large-spatial-wavelength, 'diffusive' behaviours, and to identify the fundamental microscale transport processes that are causing the non-diffusive behaviour (Koch & Brady 1987*a*, *c*). In a similar way, the non-local theory provides a convenient setting in which to study transport in macroscopically heterogeneous systems (Koch & Brady 1987*b*).

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