Anomalous diffusion in heterogeneous porous media

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The dispersion of a passive tracer resulting from flow through heterogeneous porous media is studied. When the correlation length for the permeability fluctuations is finite, a normal diffusive process, with the mean-square displacement of the tracer growing linearly with time, is obtained at long times. However, it is shown that, when the correlation length diverges, *anomalous* diffusion occurs in which the mean-square displacement grows *faster* than linearly with time. The space-time evolution of the tracer's concentration is calculated and shown to be universal—uniquely related to the covariance of the permeability field—in the anomalous regime.

I. INTRODUCTION

Naturally occurring porous media such as oil reservoirs and aquifers exhibit variations in permeability over a range of length scales that may extend from the size of the individual grains or pores to the size of the field or reservoir. When a fluid flows through such a heterogeneous medium, the fluctuations in permeability induce fluctuations in the velocity about its mean value, leading to a dispersion or spreading of the concentration of a solute or other scalar species. Dispersion measurements taken on small core samples in the laboratory cannot be used to predict the effect of such large-scale heterogeneities on the dispersion obtained in the field.

In this paper we present a method for predicting the dispersion resulting from flow through heterogeneous porous media based on knowledge of the statistics of the permeability field. The dispersion is expected to be non-Fickian in general, because the permeability fluctuations may extend over length scales comparable to the length scale of the transport process (for example, the well spacing). These non-Fickian effects may be calculated using the nonlocal transport theory developed in an earlier paper¹ and presented briefly in Sec. II of this paper. The nonlocal transport properties are related to the statistics of the permeability field.

Because the permeability varies over a wide range of length scales, the transport may not be Fickian even for average concentration gradients that vary slowly in time and space. In this case (treated in Sec. III) “anomalous diffusion” prevails and a local description of dispersion, in which the mean-square displacement grows linearly with time, is not adequate even at long times. However, the nonlocal theory allows us to develop a simple criterion for the existence of anomalous diffusion and to calculate the concentration field that arises from such an anomalous transport process.

Most previous analyses predicting anomalous diffusion have focused on random walks on lattices.²⁻⁴ In these cases the anomalous behavior arises because certain lattice sites bind the tracer particle very strongly. In general, if the distribution of waiting times for hopping from site to site has a very long tail, such that a mean waiting time does not exist, anomalous diffusion with the mean-square displacement

growing more slowly than linearly with time will occur. In contrast, we predict anomalous diffusion using a *continuum* description of a heterogeneous medium. In this example, anomalous diffusion arises because of long-range velocity correlations in cases in which a mean correlation length for the permeability fluctuations (and thus for the velocity fluctuations) does not exist, and the mean-square displacement grows *faster* than linearly with time.

Recently, hydrologists have focused considerable interest on the dispersion resulting from variations in the permeability of groundwater reservoirs. The problem of determining the Fickian dispersivity tensor describing the long-time dispersion caused by permeability fluctuations with a single length scale has been addressed from both Eulerian^{5,6} and Lagrangian⁷ viewpoints. In a recent review⁸ Dagan compares the Lagrangian and Eulerian approaches. A Lagrangian approach is generally preferred for modeling the dispersion resulting from turbulent flows.⁹ In the latter case, it is argued that neither the Eulerian nor Lagrangian velocity correlations are known with precision, so that either approach requires “modeling” of the velocity correlations. It is further suggested that since the turbulent eddies, as well as the tracer particles, are advected, it is more straightforward to estimate on physical grounds properties of the Lagrangian correlations. Such an argument is not appropriate for flows through porous media, however. Here, the velocity field is a time-independent function of spatial position determined by the permeability field and it is most straightforward to calculate the Eulerian velocity correlations. Thus we believe that an Eulerian approach to dispersion in porous media is most appropriate.

It is becoming widely recognized that a classical Fickian description of mass transport in heterogeneous porous media is often not adequate. In a detailed field experiment of the dispersion of a nonreactive tracer in a sand aquifer, Freyburg¹⁰ found that the tracer's mean-square displacement grew faster than linearly with time and the spatial concentration profiles were non-Gaussian throughout the 1038 day long experiment. A recent review¹¹ of the current state of the hydrology field emphasized the need for a theoretical understanding of non-Fickian dispersion.

Adopting a Lagrangian approach, Dagan⁷ studied the non-Fickian transient dispersion behavior in a porous medium with smooth, Gaussian-distributed, weak permeability fluctuations occurring on a single length scale a_0 . In this case a Fickian diffusion behavior was achieved, when the tracer's residence time was long compared with a_0/U , where U is the mean fluid velocity in the medium. At shorter tracer residence times the dispersion was non-Fickian, i.e., the mean-square displacement grew faster than linearly with time. Nonetheless, for the special case treated by Dagan the spatial concentration profiles were Gaussian even in the non-Fickian, transient dispersion regime. It will be argued in Sec. III that non-Gaussian, bimodal concentration profiles such as those observed in Freyburg's experiments¹⁰ and those predicted here are more typical.

The primary focus of the present investigation is anomalous diffusion, i.e., a dispersive behavior that is non-Fickian even at asymptotically long tracer residence times. Such an anomalous behavior may be expected to exist in fractured media, which contain fractures whose lengths span a wide range. Ross¹² presented some simple scaling arguments, which suggest that the mean-square displacement of a tracer may grow faster than linearly with time in such a fractal, fractured medium. However, Ross did not actually solve for either the velocity or concentration field, and so no definitive conclusions can be drawn from his discussion. A more systematic study of mass transport in fractal pore networks had been presented earlier by Adler.¹³ This analysis was based on the assumptions that the tracer underwent Taylor dispersion in each pore and was perfectly mixed at the nodes. Adler did solve for the velocity field throughout the fractal networks. Results for the asymptotic dispersive behavior at long tracer residence times were obtained only for a simple tree in which each pore bifurcates into two pores. For this class of networks it was found that normal Fickian diffusion resulted when the pore area available for flow was independent of the spatial coordinate measured parallel to the bulk flow direction. When the pore area varied, it was found that the temporal evolution of both the first and second moments of the tracer displacement were anomalous. Such an anomalous growth of the first moment with time at a rate faster or slower than linear has also been obtained in other studies of transport on lattices,² but the possibility of such a behavior was not considered in Ross' study.¹²

In contrast to such fractal networks, we shall consider media in which there is an upper cutoff to the linear size of the grains and/or pores. Thus the momentum conservation in these media may be described by Darcy's law on a sufficiently large length scale. However, we shall be particularly interested in cases in which the permeability fluctuates over a wide range of length scales. Phillip¹⁴ showed that a Lagrangian velocity correlation function that decays sufficiently slowly with time leads to an anomalous diffusion in which the mean-square displacement grows faster than linearly with time. However, Phillip did not attempt to relate these results to the Eulerian velocity field or to the permeability variations. In this paper we shall adopt the Eulerian viewpoint and predict not only the mean-square tracer displacement but also the average tracer concentration profile in me-

dia exhibiting anomalous diffusion caused by long range permeability fluctuations.

II. NONLOCAL TRANSPORT DUE TO VARIATIONS IN PERMEABILITY

We consider a porous medium with heterogeneities that are large compared to the grain size of the medium that is taken to be isotropic on the grain scale, so that Darcy's law,

$$\mu R \mathbf{u} = -\nabla p, \quad (1)$$

$$\nabla \cdot \mathbf{u} = 0, \quad (2)$$

may be used to compute the fluid velocity $\mathbf{u}$. Here p is the dynamic pressure, μ is the fluid viscosity, and the resistivity $R = k^{-1}$ is the reciprocal of the permeability k . Both p and $\mathbf{u}$ refer to quantities averaged over a volume large compared to the grain size; Darcy's law applies to these averaged quantities.

The resistivity of naturally occurring porous media generally varies in an irregular manner, so a statistical description is appropriate. Thus we consider an ensemble of different media, each member with a different detailed resistivity field, and so define the mean and covariance of the resistivity field as ensemble averages, denoted by $\langle \rangle$. Alternatively, if we are only interested in the dispersion in a limited region of a reservoir, we could form an ensemble of such regions within a single reservoir. The ergodic hypothesis usually used to equate the ensemble average to an average over a sufficiently large volume of a single member of the ensemble cannot be invoked in problems of anomalous diffusion such as the present one because there is no upper cutoff for the length scale of the velocity fluctuations. Dagan⁷ showed that the variance of the concentration field in the transient dispersion regime was of the same order of magnitude as the square of the ensemble-average concentration, indicating that the ensemble average gives only the order of magnitude and not the precise value of concentration in a single member of the ensemble. The same difficulty arises in the anomalous diffusion treated here. Nonetheless, the ensemble-average concentration is the best estimate of the concentration with the limited (statistical) information on the permeability field. It is hoped that the mean concentration will embody the important qualitative features of the concentration field in any individual medium.

To obtain quantitative results, we choose a simple model medium consisting of a base uniform resistivity $\langle R \rangle$ upon which are superimposed fluctuations $\langle R' \rangle_1$ of small amplitude ϵ , where

$$\langle R' \rangle_1 = \langle R \rangle_1 - \langle R \rangle = \pm \epsilon \langle R \rangle g(\mathbf{x} - \mathbf{r}_1). \quad (3)$$

Here, $\langle \rangle_1$ denotes an ensemble average at the field point $\mathbf{x}$ conditioned on the presence of a fluctuation centered at position $\mathbf{r}_1$. The medium contains equal numbers of positive and negative fluctuations so that the average resistivity is $\langle R \rangle$. The spatial profile g may be chosen in accord with the available statistics of the resistivity field. If only the covariance is known and is isotropic, we may use a simple isotropic profile: $g = \exp\{-a^{-1}|\mathbf{x} - \mathbf{r}_1|\}$, whose Fourier transform is $\hat{g}(\xi) = 8\pi a^3/(\xi^2 a^2 + 1)^2$, where $\hat{}$ indicates the transform and ξ is the transform variable corresponding to $\mathbf{x} - \mathbf{r}_1$.

The variance of the resistivity field may be written as

$$\begin{aligned} \langle [R'(\mathbf{x})]^2 \rangle &\equiv \int da d\mathbf{r}_1 N(a, \mathbf{r}_1) \langle [R'(\mathbf{x})]^2 \rangle_1 \\ &= \epsilon^2 \langle R \rangle^2 \int da \int d\mathbf{r}_1 N(a, \mathbf{r}_1) \\ &\quad \times g(\mathbf{x} - \mathbf{r}_1, a) g(\mathbf{x} - \mathbf{r}_1, a), \end{aligned} \quad (4)$$

where $N(a, \mathbf{r}_1)$ is the number density of fluctuations of size a at position $\mathbf{r}_1$, which is independent of position if, as we shall assume, the fluctuations are distributed in a statistically homogeneous manner. The variance of the resistivity depends only on correlations involving a single fluctuation because the fluctuations are taken to be independently distributed. Equation (4) may be used to relate the magnitude ϵ of the fluctuations to the measured resistivity variance. Note that despite the fact that the amplitude of each fluctuation is small $O(\epsilon)$, a large resistivity variance may be achieved by superimposing many overlapping resistivity fluctuations.

Similarly the covariance of the resistivity is

$$\begin{aligned} \langle R'(\mathbf{x}) R'(\mathbf{x}_1) \rangle \\ = \epsilon^2 \langle R \rangle^2 \int da \int d\mathbf{r}_1 N(a, \mathbf{r}_1) g(\mathbf{x} - \mathbf{r}_1, a) g(\mathbf{x}_1 - \mathbf{r}_1, a). \end{aligned} \quad (5)$$

The measured covariance, which is a function of $\mathbf{x} - \mathbf{x}_1$, may be used to determine the number density N . In particular, if the covariance decays as a power law $k_2 r^{-\gamma}$ as the radial separation $r = |\mathbf{x} - \mathbf{x}_1|$ tends to infinity, then the number density decays as $k_1 a^{-4-\gamma}$ as the size of the fluctuations $a \rightarrow \infty$, and the constant coefficients are related by

$$k_1 = [\gamma/4\pi\Gamma(3+\gamma)] k_2; \quad (6)$$

with $\Gamma(\)$ denoting the gamma function. Our interest here in relating the mass transport behavior in a heterogeneous porous medium to the statistics of the permeability should not be interpreted as indicating that the latter are themselves easy to obtain. Some of the difficulties encountered in obtaining such statistics for the permeability in a real aquifer are discussed by Sudicky.¹⁵

The fluctuations in the resistivity of the heterogeneous porous medium give rise to fluctuations in the velocity of the fluid. On average the velocity fluctuations that result from all of the randomly distributed resistivity fluctuations cause a tracer species to spread. The fluctuation $\langle \mathbf{u}' \rangle_1 \equiv \langle \mathbf{u} \rangle_1 - \mathbf{U}$ in the fluid velocity caused by a resistivity fluctuation satisfies an equation obtained by subtracting the unconditionally averaged from the conditionally averaged momentum equation to give

$$\begin{aligned} \langle R \rangle_1 \langle \mathbf{u}' \rangle_1 + \langle R' \rangle_1 \mathbf{U} + \nabla \langle p' \rangle_1 \\ = - \int d\mathbf{r}_2 N(a_2, \mathbf{r}_2 | a, \mathbf{r}_1) [\langle R \mathbf{u} \rangle_1 - \langle R \rangle_1 \langle \mathbf{u} \rangle_1], \end{aligned} \quad (7)$$

where $N(a_2, \mathbf{r}_2 | a, \mathbf{r}_1)$ is the number density of fluctuations of size a_2 at position $\mathbf{r}_2$ given that there is a fluctuation of size a at $\mathbf{r}_1$, and $\mathbf{U} \equiv \langle \mathbf{u} \rangle$ in the average velocity. The term on the right-hand side of (7) arising because of two resistivity-fluctuation interactions in the velocity field is small $O(\epsilon)$ for weak permeability fluctuations $\epsilon \ll 1$, and may be neglected.

We may also replace the conditionally averaged resistivity $\langle R \rangle_1$ in the first term on the left-hand side of (7) with the unconditional average $\langle R \rangle$ with a small $O(\epsilon)$ error. Finally, taking the Fourier transform and solving for the velocity fluctuation, we obtain

$$\langle \hat{\mathbf{u}}' \rangle_1 = -\mathbf{U} \cdot (\mathbf{I} - \xi \xi / \xi^2) \langle \hat{R}' \rangle_1. \quad (8)$$

The concentration c of a tracer species averaged over a volume large compared with the grains of a porous medium satisfies the conservation equation

$$\frac{\partial c}{\partial t} + \nabla \cdot \mathbf{q} = S, \quad (9)$$

where

$$\mathbf{q} = \mathbf{U}c - \mathbf{D}_g \cdot \nabla c, \quad (10)$$

when the concentration variation is nearly linear over lengths comparable with the grain size a_g . Here, S is the source of mass of tracer, which is taken to be independent of c . Initial value problems in concentration may be treated by choosing $S(\mathbf{x}, t) = \delta(t)f(\mathbf{x})$. The grain-scale effective diffusivity $\mathbf{D}_g$ includes the effects of convection and diffusion around the grains that make up the porous medium. In a previous publication¹⁶ we studied this grain-scale dispersion and showed that the effective diffusivity is given by

$$\begin{aligned} \mathbf{D}_g = Ua_g \{ (\mathbf{U}\mathbf{U}/U^2) [(A_1 \text{Pe}_g \\ + A_2 \ln(\text{Pe}_g) + A_3)] + \mathbf{I}A_4 \} \end{aligned} \quad (11)$$

in the limit of high grain-scale Peclet number $\text{Pe}_g \equiv Ua_g/D_f$, where D_f is the molecular diffusivity of the tracer in the fluid. The factors A_1, A_2, A_3 , and A_4 are generally functions of the volume fraction of solids, the grain geometry, and the ratios of the solubilities and diffusivities of the tracer in the two phases. The term proportional to Pe_g in (11) arises because of holdup of the tracer in the solids and in stagnant and recirculating fluid; this term may be zero if the tracer is not absorbed into the solid and no stagnant or recirculating regions exist. The term proportional to $\ln(\text{Pe}_g)$ arises from mass-transfer boundary layers near the solid surfaces and the constant terms from purely hydrodynamic dispersion in the bulk fluid.

For simplicity we shall stipulate that the grain-scale effective diffusivity remains constant, despite the resistivity fluctuations in the heterogeneous medium. Provided that the Peclet number $\text{Pe} = Ua/|\mathbf{D}_g|$, based on the size a of the permeability fluctuations and the magnitude of the grain-scale diffusivity, is large, the fluid velocity fluctuations have a larger effect than fluctuations in $\mathbf{D}_g$ on the spreading of the tracer.¹ This high Peclet number requirement is met if the size of the resistivity fluctuations is sufficiently large— $a \gg a_g \text{Pe}_g$ and $a \gg a_g \ln(\text{Pe}_g)$ in the presence and absence of holdup, respectively.

The ensemble-averaged equation of mass conservation is then

$$\frac{\partial \langle c \rangle}{\partial t} + \nabla \cdot \langle \mathbf{q} \rangle = \langle S \rangle, \quad (12)$$

where

$$\langle \mathbf{q} \rangle = \mathbf{U} \langle c \rangle + \langle \mathbf{u}' c' \rangle - \mathbf{D}_g \cdot \nabla \langle c \rangle. \quad (13)$$

The first and third terms in (13) simply indicate that the

tracer is convected with the average fluid velocity and spreads due to the grain-scale dispersion. The second term, involving the correlation of the velocity and concentration fluctuations, $\mathbf{u}' \equiv \mathbf{u} - \langle \mathbf{u} \rangle$ and $c' \equiv c - \langle c \rangle$, gives the effects of the resistivity heterogeneities on tracer transport.

An equation for the concentration fluctuation may be obtained by substituting the definition $c' \equiv c - \langle c \rangle$ into (9) and (10) and using (12) and (13) to give

$$\frac{\partial c'}{\partial t} + \nabla \cdot [\mathbf{U}c' - \mathbf{D}_g \cdot \nabla c' + \mathbf{u}'c'] = -\mathbf{u}' \cdot \nabla \langle c \rangle + \nabla \cdot \langle \mathbf{u}'c' \rangle. \quad (14)$$

In deriving (14) we have taken the source to be uncorrelated with the resistivity fluctuations, $S = \langle S \rangle$. In general, the average concentration field will be different if the tracer is preferentially injected into regions of high or low permeability. In the anomalous diffusion regime, this effect will persist for all times. The influence of such a maldistribution of the source on the average concentration may be investigated using the nonlocal dispersion theory.¹ The concentration fluctuations driven by the small $O(\epsilon)$ velocity fluctuations are also small $O(\epsilon)$. Neglecting the $O(\epsilon^2)$ nonlinear terms in (14) the solution for the concentration fluctuation is

$$c' = - \int d\mathbf{x}_1 \int_{-\infty}^t dt_1 P(\mathbf{x} - \mathbf{x}_1, t - t_1) \mathbf{u}'(\mathbf{x}_1) \cdot \nabla_1 \langle c \rangle, \quad (15)$$

where the transition probability P is the probability of finding a tracer particle at position $\mathbf{x}$ at time t given that it was at $\mathbf{x}_1$ at time t_1 . Because the permeability fluctuations are small $O(\epsilon)$, the transition probability is to leading order in ϵ the free-stream transition probability, which satisfies

$$\frac{\partial P}{\partial t} + \nabla \cdot [\mathbf{U}P - \mathbf{D}_g \cdot \nabla P] = \delta(\mathbf{x} - \mathbf{x}_1) \delta(t - t_1). \quad (16)$$

Substituting (15) and (16) for the concentration disturbance in (13) the average flux is

$$\langle \mathbf{q} \rangle = \langle \mathbf{U} \rangle \langle c \rangle - \int d\mathbf{x}_1 \int_{-\infty}^t dt_1 \times \mathbf{D}(\mathbf{x} - \mathbf{x}_1, t - t_1) \cdot \nabla_1 \langle c(\mathbf{x}_1, t_1) \rangle, \quad (17)$$

$$\mathbf{d}(a\alpha, a\xi) = \frac{8}{\pi} \int d\xi' \frac{[(\mathbf{I} - \xi'\xi'/\xi'^2) \cdot \mathbf{1}_z]^2}{(\xi'^2 + 1)^4 [i\xi' \cdot \mathbf{1}_z + i\alpha\alpha + (a\xi + \xi') \cdot \mathbf{D}_g \cdot (a\xi + \xi')]} \quad (23)$$

and

$$\alpha = \xi \cdot \mathbf{1}_z + \omega U^{-1}.$$

Here, $\mathbf{1}_z$ is a unit vector in the direction of the bulk flow. The transform of the average concentration may be obtained by solving the transform of (12) and (17), giving

$$\langle \hat{c} \rangle = \langle \hat{S} \rangle / (i\omega + i\xi \cdot \mathbf{U} + \xi \cdot \hat{\mathbf{D}} \cdot \xi). \quad (24)$$

Equation (24) with (23) may be used to calculate the average concentration response to any source for all times and all spatial positions. In general, this concentration field differs from that predicted from Fick's law, because the dispersion process is nonlocal, i.e., $\hat{\mathbf{D}}$ is a function of temporal and spa-

where the nonlocal effective diffusivity that includes the dispersive effects of the resistivity fluctuations is

$$\mathbf{D} \equiv \mathbf{D}_g \delta(\mathbf{x} - \mathbf{x}_1) \delta(t - t_1) + \langle \mathbf{u}'(\mathbf{x}) P(\mathbf{x} - \mathbf{x}_1, t - t_1) \mathbf{u}'(\mathbf{x}_1) \rangle. \quad (18)$$

Equations (17) and (18) have a form analogous to that for the perhaps more familiar dispersion of electromagnetic radiation in dielectric media.¹⁷ A nonlocal transport theory that allows for fluctuations in the diffusivity $\mathbf{D}_g$ and large fluctuations in the fluid velocity has been presented in a previous publication.¹

Neglecting the $O(\epsilon^3)$ correlations between the velocity disturbance caused by two different resistivity fluctuations the effective diffusivity may be expressed in terms of the one resistivity-fluctuation velocity disturbance

$$\mathbf{D} = \mathbf{D}_g \delta(\mathbf{x} - \mathbf{x}_1) \delta(t - t_1) + \int da \int d\mathbf{r}_1 N(a, \mathbf{r}_1) \times \langle \mathbf{u}'(\mathbf{x} - \mathbf{r}_1, a) \rangle_1 P(\mathbf{x} - \mathbf{x}_1, t - t_1) \langle \mathbf{u}'(\mathbf{x}_1 - \mathbf{r}_1, a) \rangle_1. \quad (19)$$

Using the convolution theorem the Fourier transform of the effective diffusivity may be written as

$$\hat{\mathbf{D}}(\xi, \omega) = \mathbf{D}_g + \int_0^\infty da N(a) \frac{1}{(2\pi)^3} \int d\xi' \langle \hat{\mathbf{u}}'(-\xi'; a) \rangle_1 \times \hat{P}(\xi + \xi', \omega; a) \langle \hat{\mathbf{u}}'(\xi'; a) \rangle_1, \quad (20)$$

where the Fourier transform of the transition probability is

$$\hat{P} = 1/(i\omega + i\xi \cdot \mathbf{U} + \xi \cdot \mathbf{D}_g \cdot \xi), \quad (21)$$

and ω is the transform variable corresponding to $t - t_1$. Substituting (8) and (21) into (20) and nondimensionalizing ξ' with a^{-1} , the diffusivity may be written as

$$\hat{\mathbf{D}}(\xi, \omega) = \mathbf{D}_g + U\epsilon^2 \int_0^\infty da N(a) a^4 \mathbf{d}(a\alpha, a\xi), \quad (22)$$

where the dimensionless quantity $\mathbf{d}$ is given by

tial wavelength. One usually expects to recover classical, Fickian diffusion at long times following the introduction of a source. In the next section, however, we shall see that under certain conditions classical diffusion is not obtained even at long time.

III. ANOMALOUS DIFFUSION

A. The nonlocal diffusivity

In a classical-diffusion process one observes that at a sufficiently long time after the release of a tracer its mean-square displacement grows in proportion with time. Because the fluctuations in naturally occurring media extend over a

wide range of length scales, however, one may not observe a classical-diffusion behavior even a very long time after the tracer's release. In this section we shall examine the long-time behavior of the concentration field (24) with (22) and (23), determining the conditions under which the concentration may be predicted by a local Fick's law expression at long times. Finally, we shall examine the concentration fields that arise in cases where Fick's law is not applicable at long times.

When the concentration gradient is nearly constant the mass flux (13) is given by the local conservation equation

$$\langle \mathbf{q} \rangle = U \langle c \rangle - \mathbf{D}_L \cdot \nabla \langle c \rangle, \quad (25)$$

where

$$\mathbf{D}_L = \int d\mathbf{x} \int_{-\infty}^t dt_1 \mathbf{D}(\mathbf{x} - \mathbf{x}_1, t - t_1) = \hat{\mathbf{D}}(\xi = 0, \omega = 0). \quad (26)$$

This local description of dispersion is possible only if the local diffusivity $\mathbf{D}_L$ exists.

Thus classical diffusion results if the transformed diffusivity approaches a constant in the limit of low spatial and temporal frequency, i.e., $\xi \rightarrow 0$ and $\omega \rightarrow 0$. This criterion is met if we can replace $\mathbf{d}$ in (22) by its small-frequency limit. In this case the integral in

$$\hat{\mathbf{D}} = \mathbf{D}_g + U\epsilon^2 \mathbf{d}(0,0) \int_0^\infty da N(a) a^4 \quad (27)$$

is convergent. Equation (27) gives a convergent result if the number density decays faster than a^{-5} as the fluctuation size a tends to infinity. This condition in turn corresponds to the requirement that the covariance of the resistivity decays faster than r^{-1} as the radial separation r tends to infinity [cf. Eqs. (5) and (6)].

This simple criterion for classical diffusion based solely on resistivity measurements corresponds to the requirement that a correlation length for the resistivity field exist. This correlation length η is defined as the integral of the covariance with respect to radial separation, i.e.,

$$\eta \equiv \langle [R'(\mathbf{x})]^2 \rangle^{-1} \int_0^\infty dr \langle R'(\mathbf{x}) R'(\mathbf{x}_1) \rangle, \quad (28)$$

where $r = |\mathbf{x} - \mathbf{x}_1|$.⁸ The first to recognize the importance of the correlation length for the velocity fluctuations, albeit in a very special and restricted case, were Matheron and de Marsily.¹⁸ In general, in an anisotropic medium the correlation length η is a function of angle relative to the bulk flow.

The physical significance of this criterion can be explained in terms of the transport of a single tracer particle. A classical-diffusion process is obtained when we have allowed sufficient time for a tracer to experience all values of the fluctuating velocity field by sampling the entire microstructure. If the correlation length for the resistivity field diverges, however, the tracer cannot sample the entire microstructure in a finite time period. This is true whether the sampling is convective or by molecular diffusion or grain-scale dispersion. Instead, the tracer continues to experience the effects of ever longer range resistivity fluctuations with increasing time, and the transport process never attains a long-time classical-diffusion limit. Such processes give rise

to "anomalous diffusion" in which the mean-square displacement grows more rapidly than linearly with time.

In order to complete the specification of the effective diffusivity $\hat{\mathbf{D}}$ in (27), we must evaluate the low-frequency limit of $\mathbf{d}$. Performing the integration in (23) in the limit of high Peclet number $Pe = U\eta/|\mathbf{D}_g|$ based on the correlation length η , we obtain $\mathbf{d}(0,0) = \mathbf{1}_z \mathbf{1}_z 8\pi/3$, indicating that the longitudinal dispersion caused by the permeability variations is independent of the grain-scale diffusion. In order to obtain a nonzero result for the low-frequency transverse diffusivity, one must include the effects of nonspherical permeability fluctuations, two-fluctuation interactions, or grain-scale dispersion.¹⁶ In considering only spatial permeability fluctuation profiles $g(\mathbf{x} - \mathbf{r})$ that are spherically symmetric, we have made an unduly restrictive choice. Even an isotropic medium will, in general, contain individual permeability fluctuations that are not spherically symmetric, subject only to the restriction that the probability of finding a nonspherical fluctuation is independent of its orientation. In a previous study of dispersion in a fixed fibrous bed,¹⁹ we highlighted the crucial role of the fore-aft symmetry of streamlines in determining the nature of the transverse dispersion. The streamlines for flow past a nonspherical permeability fluctuation do not possess fore-aft symmetry, leading to a long-time, "mechanical" transverse diffusivity that is independent of grain-scale dispersion. Previous studies^{5,6} of dispersion in heterogeneous porous media have considered model media in which all the permeability fluctuations had the same spatial profile, leading to the incorrect conclusion that no purely mechanical transverse dispersion can occur in an isotropic medium.

We shall now calculate the low-frequency behavior of the diffusivity in cases of "anomalous diffusion." The effect of grain-scale diffusion on the transition probability (21) is small at low frequencies. If the covariance decays as r^{-1} as radial separation tends to infinite, $r \rightarrow \infty$, so that the number density N decays as a^{-5} , the integral in (27) is conditionally convergent in the limit of high-fluctuation size a . It is then necessary to retain the full functional form of $\mathbf{d}$ in (22) and integrate to obtain

$$\hat{\mathbf{D}} = \mathbf{D}_g + \mathbf{1}_z \mathbf{1}_z U\epsilon^2 k_1 [- (8\pi/3) \ln(ik_1 \alpha) + b_0], \quad \alpha \rightarrow 0, \quad (29)$$

where k_1 is the dimensional constant (of dimension length) defined by (6), and the nondimensional constant b_0 depends on the finite a behavior of the number density. When the number density is $N = k_1 a^{-2} (a^2 + k_1^2)^{-1}$ and the Peclet number $Uk_1/|\mathbf{D}_g|$ based on the length k_1 is large, this constant is $b_0 = -2\pi$.

If the covariance decays slower than r^{-1} so that the number density decays slower than a^{-5} , the integral in (27) is absolutely divergent in the limit of large fluctuation size a . However, the leading behavior of the diffusivity at small frequency may be easily obtained from (22), giving

$$\hat{\mathbf{D}} = \mathbf{D}_g + \mathbf{1}_z \mathbf{1}_z U\epsilon^2 [b_2 (i\alpha)^{r-1} + b_1], \quad (30)$$

where

$$b_2 = \int_0^\infty d\beta \mathbf{1}_z \cdot \mathbf{d}(\beta, 0) \cdot \mathbf{1}_z \beta^{-\gamma}$$

$$= 2k_1 \frac{\pi}{\sin(-\gamma\pi)} \left(\frac{1}{1-\gamma} - \frac{2}{3-\gamma} + \frac{1}{5-\gamma} \right)$$

$$\times (1-\gamma) \left[\frac{5}{2} - (2-\gamma) \left(\frac{\gamma}{6} + 1 \right) \right] \quad (31)$$

depends only on the high-fluctuation size behavior of the number density, and

$$b_1 = \int_0^\infty da \mathbf{1}_z \cdot \mathbf{d}(a\alpha, a\xi) \cdot \mathbf{1}_z [N(a) - k_1 a^{-4-\gamma}] a^4 \quad (32)$$

depends on the full form of the number density $N(a)$. The constant b_2 is independent of grain-scale dispersion (and independent of $a\xi$), because it results from the high-fluctuation size limit in which convection dominates over grain-scale dispersion. The constant b_1 is independent of grain-scale dispersion if a Peclet number based on a length characteristic of the fluctuation sizes that contribute to the integral in (32) is large.

B. The moments of the average concentration field

The concentration field response at long times for an arbitrary source may be calculated using (24) together with (30). We shall consider the long-time response to an impulse source introduced in the plane $z = 0$ (which is perpendicular to the flow direction) at time $t = 0$. The concentration cannot be written in closed analytic form, but its moments,

$$\int dz (z - Ut)^n \langle c \rangle$$

$$= n! \left[\Gamma \left(\frac{n}{2} (2 - \gamma) + 1 \right) \right]^{-1}$$

$$\times (b_2 \epsilon^2 (Ut)^2 - \gamma^{n/2}), \quad \text{if } n \text{ is even,}$$

$$= 0, \quad \text{if } n \text{ is odd,} \quad (33)$$

for $0 < \gamma < 1$, are easily obtained by expanding (24) in powers of $\xi \cdot \mathbf{1}_z$. Note that the second moment or mean-square displacement grows as $t^{2-\gamma}$. In the special case of a conditionally convergent resistivity covariance, i.e., $\gamma = 1$, the mean-square displacement grows as

$$\int dz (z - Ut)^2 \langle c \rangle$$

$$= (16\pi/3) k_1 Ut \ln(Ut/k_1)$$

$$+ 2(b_0 k_1 U + \mathbf{1}_z \cdot \mathbf{D}_g \cdot \mathbf{1}_z) t. \quad (34)$$

Anomalous diffusion processes such as the present one in which the mean-square displacement grows faster than linearly with time may be termed "persistent." A simple example of a "persistent" diffusive process is a random walk on a one-dimensional lattice in which there is a correlation between the direction a tracer moves in one time step and the direction it moved in the preceding time step.²⁰ Similarly, in our process there is a strong correlation of the tracer velocity with its previous values because of the influence of long-range permeability fluctuations. The "persistent" diffusion process may be viewed as intermediate between a classical-diffusion process in which there is no long-range correlation

of a tracer's velocity and the mean-square displacement grows as t , and a purely convective spreading in which there is a perfect correlation between the tracer's velocity and its initial value and the mean-square displacement grows as t^2 .

Matheron and de Marsily⁸ investigated the special case of flow through a heterogeneous medium that is perfectly stratified, i.e., it exhibits permeability variations in one direction only (say the x direction). They found that for flow parallel to the strata (in the z direction), classical diffusion is almost never obtained at long times. Classical diffusion occurs only if the integral over all x of the covariance of the permeability is zero—a much more restrictive condition than that obtained here for nonstratified media.

For most permeability profiles in perfectly stratified porous media Matheron and de Marsily⁸ found that the mean-square displacement in the direction of flow grew as $t^{3/2}$. This peculiar result occurs because in the case of flow parallel to the strata of a stratified porous medium the tracer can sample the various possible values of the velocity field only by transverse diffusion, and diffusion is a relatively ineffective way of sampling an unbounded medium. If the medium is bounded in the x direction, and has permeability fluctuations only in this direction, the long time transport will be diffusive, with an effective diffusivity proportional to $U^2 a^2 / |\mathbf{D}_g|$, corresponding to Taylor dispersion.

The anomalous diffusion found in stratified media by Matheron and de Marsily may be rationalized in the following way. Consider a permeability disturbance that extends only over the region $|x| < 1$, and is uniform in this region. If the tracer is injected at $x = 0$ at $t = 0$, the probability that the tracer is still in the region $|x| < 1$ at time t is proportional to $t^{-1/2}$. As long as the tracer is within the region $|x| < 1$ its mean-square displacement grows convectively, i.e., as t^2 . Only a $t^{-1/2}$ portion of the tracer is within this region, so the overall mean-square displacement grows as $t^{3/2}$. This peculiar behavior occurs only when the flow is strictly parallel to the strata of a perfectly stratified medium, so that the permeability field is sampled only by diffusion.

C. Average concentration profiles

In a classical-diffusion process the concentration response to an impulse initial condition has a Gaussian profile at long times. As can be seen in (31), however, the long-time concentration profiles are not Gaussian in cases of anomalous diffusion. The non-Gaussian profiles resulting from anomalous diffusion for decay exponents $\gamma = \frac{1}{2}$, $\frac{1}{3}$, and $\frac{2}{3}$ are plotted in Fig. 1 together with the Gaussian profile obtained in classical diffusion, i.e., $\gamma > 1$.

The non-Gaussian profiles in Fig. 1 as well as those in Figs. 2 and 3 exhibit discontinuities in slope at the position $z = Ut$, cf. (40). These discontinuities are consequences of the small amplitude and small grain-scale dispersion approximations used in estimating the effective diffusivity. The limit $z \rightarrow Ut$ in real space corresponds to the limit $\xi \rightarrow \infty$ in Fourier space; it is clear from (23) that the effects of grain-scale dispersion on the effective diffusivity cannot in general be neglected in this limit. The inclusion of grain-scale dispersion or finite permeability fluctuation amplitude is expected

FIG. 1. The universal concentration profiles for classical diffusion $\gamma > 1$, and for three cases of anomalous diffusion $\gamma = \frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$. The abscissa and ordinate are stretched so that the zeroth and second moments of each profile are the same, i.e., $\bar{c} \equiv c[2\epsilon^2 b_2 t^{2-\gamma/\Gamma(3-\gamma)}]^{1/2}$ and $\eta \equiv (z - Ut)/[2\epsilon^2 b_2 t^{2-\gamma/\Gamma(3-\gamma)}]^{1/2}$. These profiles are the long-time response to an impulse $\delta(z)\delta(t)$.

to lead to a smooth change of slope over a small distance, $(|D_g|t)^{1/2}$ or ϵUt , respectively.

The profiles in Fig. 1 are universal in the sense that any perturbation in the average concentration field, regardless of its initial shape, will evolve into the profile corresponding to the specific anomalous diffusion process, i.e., corresponding to the appropriate covariance decay exponent γ . This behavior is illustrated in Fig. 2, where an initially Gaussian profile is seen to deform into the bimodal profile characteristic of the anomalous-diffusion process.

The observation that the concentration profiles arising from anomalous diffusion are non-Gaussian is not surpris-

FIG. 2. The concentration response to an initially Gaussian source is plotted as a function of position z measured parallel to the direction of flow for various times t . The response shown is that of a medium with a resistivity covariance decay exponent $\gamma = \frac{1}{4}$. Here the position is nondimensionalized with $\epsilon^4 b_2^2$ and the time with $\epsilon^4 b_2^2 U^{-1}$.

ing. Such non-Gaussian profiles have been observed in previous studies of transient dispersion such as in the classical problem of Taylor dispersion in a tube.²¹ Perhaps it is more surprising, however, that these profiles are bimodal. We note that bimodal concentration profiles qualitatively similar to those predicted here have been observed in field experiments.¹⁰

The bimodal nature of the anomalous diffusion profiles in Figs. 1 and 2 may be viewed as a consequence of the wave-like nature of the mass conservation equation. The transform of the average concentration response to an impulse source in cases of anomalous diffusion is, using (24) and (30),

$$\langle \hat{c} \rangle = 1/[i\alpha + b_2(i\alpha)^{\gamma-1}\xi^2], \quad 0 \leq \gamma < 1. \quad (35)$$

When $\gamma = 0$, the most anomalous case, the average mass conservation equation is simply a wave equation. In this case the real space equivalent of Eq. (35) is

FIG. 3. The residence-time distribution—the concentration response to an impulse source $\delta(z)\delta(t)$ plotted as a function of time t —is given for various distances z downstream from the source. The media's resistivity covariance has decay exponents (a) $\gamma = 0.5$, and (b) $\gamma = 0.25$. The position is nondimensionalized with $(\epsilon^2 b_2)^{1/\gamma}$ and the time with $(\epsilon^2 b_2)^{1/\gamma} U^{-1}$.

$$\frac{\partial^2 \langle c \rangle}{\partial \xi^2} + b_2 \frac{\partial^2 \langle c \rangle}{\partial z^2} = \delta(z) \delta'(\xi), \quad \gamma = 0, \quad (36)$$

where $\xi = z - Ut$. The general anomalous diffusion behavior $0 < \gamma < 1$ may be viewed as intermediate between a classical-diffusion behavior and the purely wavelike behavior attained in the extreme case $\gamma = 0$ in which the resistivity covariance does not decay with radial separation.

In the weak permeability fluctuation limit treated here, the average concentration profiles result from the effects of many independent permeability fluctuations each of which individually has a small influence on the concentration field. The wavelike nature of the anomalous diffusion may be understood in terms of the coupling between the dispersive effects of a single permeability fluctuation and those of all the other permeability fluctuations. This coupling appears in the analysis as a coupling between the concentration disturbance c' due to a permeability fluctuation and the average concentration $\langle c \rangle$. In the limit of small permeability fluctuation amplitude and neglecting grain-scale dispersion the concentration disturbance is given by, cf. (14),

$$\frac{\partial c'}{\partial t} + \mathbf{U} \cdot \nabla c' = -\mathbf{u}' \cdot \nabla \langle c \rangle, \quad (37)$$

indicating that the temporal growth in the concentration disturbance is driven by the average concentration gradient. The temporal changes in the average concentration are in turn driven by spatial gradients in the concentration disturbance, as may be seen by combining (12) and (13) neglecting grain-scale diffusion to give

$$\frac{\partial \langle c \rangle}{\partial t} + \mathbf{U} \cdot \nabla \langle c \rangle = -\nabla \cdot \langle \mathbf{u}' c' \rangle + \langle S \rangle. \quad (38)$$

When the resistivity covariance does not decay with radial separation, i.e., when $\gamma = 0$, the permeability fluctuations are so long-ranged that the tracer does not experience significant variations in $\mathbf{u}'$. In this case we may combine (37) and (38) neglecting spatial variations in $\mathbf{u}'$ to give

$$\left(\frac{\partial}{\partial t} + \mathbf{U} \cdot \nabla \right)^2 \langle c \rangle = \nabla \cdot \langle \mathbf{u}' \mathbf{u}' \rangle \cdot \nabla \langle c \rangle + \left(\frac{\partial}{\partial t} + \mathbf{U} \cdot \nabla \right) \langle S \rangle, \quad (39)$$

which is a wave equation equivalent to (36) if we take

$$\langle S \rangle = \delta(z) \delta(t), \quad \nabla \langle c \rangle = \mathbf{1}_z \frac{\partial \langle c \rangle}{\partial z},$$

$$b_2 = \mathbf{1}_z \cdot \langle \mathbf{u}' \mathbf{u}' \rangle \cdot \mathbf{1}_z.$$

The precise form of the averaged concentration equation (35) and thus the particular shapes of the concentration profiles in Figs. 1 and 2 are consequences of the small permeability fluctuation approximation. The averaged mass conservation equation in heterogeneous porous media with large permeability fluctuations may be obtained using the general nonlocal theory.¹ However, in general this conservation equation will be more complicated than the one developed here for a weakly inhomogeneous medium.

In contrast to our results, Dagan⁷ obtained Gaussian average concentration profiles in his application of a method developed by Phythian²² to the treatment of transient dispersion in a heterogeneous porous medium. Phythian²² had

adapted a Lagrangian method for determining the transient dispersion of a tracer to applications involving Gaussian distributed random velocity fields. The method involves an expansion valid in the limit in which the amplitude of the velocity fluctuations is small. It was shown that such an expansion was possible provided that the velocity fluctuations were sufficiently smooth, i.e., they occurred only over a limited, finite range of length scales. Dagan⁷ applied Phythian's expansion to determine the transient dispersion resulting from flow through a medium with a weakly fluctuating, smooth, Gaussian random permeability field with a single correlation length a_0 . A surprising result of Dagan's analysis is that the tracer concentration profiles were found to be Gaussian even when the dispersion was non-Fickian. The leading-order estimate of the random tracer displacement in the Lagrangian expansion was linearly related to the Gaussian random velocity field, so a Gaussian tracer concentration profile resulted. Phythian²² showed that the inclusion of higher-order nonlinear terms in the expansion leads to non-Gaussian concentration profiles, although he did actually compute these profiles.

Although the theory developed here relies on a small amplitude expansion, it captures at leading order certain aspects of the coupling between the tracer's present and past motions, which arise only in the higher-order, nonlinear terms of the Lagrangian expansion. This coupling, which appears in the analysis in the form of an interdependence of the bulk concentration and the concentration fluctuations, accounts for the non-Gaussian nature of the concentration profiles in Fig. 1. While both the present model and that of Dagan are clearly idealizations of a naturally occurring heterogeneous porous media, we believe the present model exhibits the most important physical processes leading to non-Fickian dispersion.

Field measurements are often in the form of concentration as a function of time at a fixed position, rather than spatial profiles such as those illustrated in Figs. 1 and 2. The bimodal nature of the concentration field may not be as clearly evident, when it is plotted as a function of time rather than as a function of space. In Fig. 3 we plot the concentration as a function of time for various fixed positions downstream from an impulse source of mass $\delta(z) \delta(t)$. Because the concentration is continuously spreading with time, the second peak is much broader than the first by the time it arrives at the fixed position. Thus, depending on the values of z and γ , the residence-time distribution (the concentration plotted as a function of time) may contain two distinct peaks or a single peak followed by a long tail.

In order to determine under what conditions the temporal concentration profile is bimodal, we shall examine the slope of the profile at the nondimensional position $z = t$. This may be accomplished by taking the inverse Fourier transform of (35) with respect to ξ , expanding the resultant expression in a Taylor series about the position $z = t$, and taking the inverse transform in α to give

$$c = \frac{1}{2} \left(\frac{t^{\gamma/2-1}}{\Gamma(\gamma/2)} - \frac{(1-\gamma)t^{\gamma-2}}{\Gamma(\gamma)} |z-t| + O(|z-t|^2) \right). \quad (40)$$

The discontinuity in the concentration profiles at $z = t$ discussed above results from the factor $|z - t|$ in (40). The slope of the temporal concentration profile is always negative as t approaches z from below. The point $z = t$ represents a minimum in the temporal concentration profile indicating that the profile is bimodal if the slope is positive as t approaches z from above. From (40), the criterion for the slope to be positive at $z = t$ is

$$\lim_{z \rightarrow t+} \frac{\partial c}{\partial t} = \frac{1}{2} \left(\frac{(1 - \gamma)z^{\gamma-2}}{\Gamma(\gamma)} - \frac{(1 - \gamma/2)z^{\gamma/2-2}}{\Gamma(\gamma/2)} \right) > 0, \quad (41)$$

or

$$z > \left(\frac{(1 - \gamma/2)\Gamma(\gamma)}{(1 - \gamma)\Gamma(\gamma/2)} \right)^{2/\gamma}. \quad (42)$$

The temporal concentration profile is bimodal, then, for sufficiently large distances downstream from the source. In Fig. 3(a) the profiles are illustrated for $\gamma = 0.5$ and $z = 0.2891$ —the longest distance downstream for which the profile is not bimodal and for $z = 0.6$. Decreasing γ , which increases the range of the permeability fluctuations, results in a slight increase in the height of the second peak; this may be seen by comparing the profiles for $z = 0.6$ and $\gamma = 0.5$ and 0.25 in Figs. 3(a) and 3(b). However, in general the second peak in the temporal profiles is low and broad and may appear more like a long-time tail than a distinct second peak.

“Persistent” anomalous diffusion processes similar to those obtained here are expected in other convective sys-

tems, such as turbulent flows, in which velocity fluctuations occur on all length scales. The transport behavior of these and other systems may be analyzed using the general nonlocal theory employed here.¹

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