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# The effect of morphological disorder on hydrodynamic dispersion in flow through porous media

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**Abstract.** We study hydrodynamic dispersion in flow through a disordered porous medium. The main goals of the paper are to investigate the condition(s) under which a convective-diffusion equation (CDE) *cannot* describe dispersion processes and to investigate the effect of the disordered morphology of the pore space on dispersion processes. We first use simple models of porous media and study dispersion processes analytically and compare the results with the predictions of the CDE. The results show that the morphology of the porous medium can strongly affect dispersion processes. We then use a Monte Carlo simulation approach to study dispersion processes in random network models of porous media which are made of interconnected capillary tubes with distributed effective radii. A percolation network is used as a prototype of porous media with disordered topology. We show that, as the percolation threshold  $X_c$  of the network is approached, there exists an anomalous and length-dependent dispersion regime that cannot be described by the CDE. We propose a generalisation of the Gaussian distribution to describe dispersion in the anomalous regime, and confirm it by Monte Carlo simulations. We also derive the appropriate scaling laws that relate dispersion coefficients to the length of the system and show that, for large systems near  $X_c$ , dispersion coefficients obey universal scaling laws. These scaling laws are derived and confirmed by our Monte Carlo simulations. We then extend the simulations to dispersion in the flow of two immiscible fluids in porous media and discuss the applicability of percolation processes to describe two-phase flow and dispersion in porous media. We argue that percolation processes can be used to describe multiphase flow and dispersion in porous media, contrary to the recent claim of Thompson *et al.* The implication of the results for macroscopically heterogeneous porous media is also briefly discussed.

## 1. Introduction

When two miscible fluids are brought into contact, with an initially sharp interface, a transition zone develops across the initial interface and the two fluids slowly diffuse into one another. As time passes, the original interface becomes a diffused mixed zone, the composition of which changes from one pure fluid to the other. This mixed zone arises because of diffusion of the molecules of the two fluids. During this process there is no equilibrium except that of one fluid uniformly distributed throughout the other. If one assumes that the volume of the two fluids do not change upon this mixing process, then the net transport of one of the fluids across any arbitrary plane can be represented by Fick's second law of diffusion

$$\partial C / \partial t = D \nabla^2 C. \quad (1)$$

Here  $C$  is the concentration,  $t$  is the time and  $D$  is the molecular diffusion coefficient. The mixing process described above takes place whether or not the two fluids are being

convected through the medium. However, if the fluids are flowing, then there may be some additional mixing of a different sort: convective mixing. This mixing process, which is caused by a non-uniform velocity field, which in turn may be caused by the morphology of the medium, the fluid flow condition and chemical or physical interactions with the solid surface of the medium, is called hydrodynamic dispersion. This phenomenon is important for a wide variety of processes and has witnessed considerable research activity during the past several decades. Some examples where dispersion phenomena are important are enhanced recovery of oil, salt water intrusion in coastal aquifers, *in situ* study of the characteristics of an aquifer and the pollution of surface waters because of industrial wastes. Dispersion phenomena also occur in flow in packed-bed chemical reactors; this has been studied extensively by chemical engineers for a long time (see, e.g., Aris and Amundson 1957).

Dispersion processes are sensitive to the structure of the medium in which the transport and mixing processes take place. Dispersion in a single capillary tube of constant or varying cross section behaves very differently from that in a disordered porous medium. In a disordered porous medium, the variation in the orientations of flow passages and the coordination of the junctions, which result in wide variations in the length of the streamlines, together with the variations in the geometry (shapes and sizes) of pores and the local pressure gradients, force a chaotic nature on the pore-level velocity field of the flowing fluid, whereas the velocity field within a single tube is not chaotic at all. Therefore, a collection of dynamically neutral fluid particles, which is being mixed with a flowing fluid, is convected across the porous medium with a broad distribution of transit times, i.e. the times that the particles spend to travel throughout the medium. Moreover, if the medium is poorly connected, e.g. if the medium can be represented by a percolation cluster (Staffer 1985) slightly above the percolation threshold  $X_c$ , its topology (connectedness) can greatly affect the distribution of transit times, because in a percolation cluster near  $X_c$  there are many slow paths that the particles can take. Consequently, if we characterise hydrodynamic dispersion with a distribution of transit times, the structure of the distribution and its different moments can yield information on both the morphology of the medium and the mixing process. One goal of this paper is to study the effect of the morphology of a porous medium on the basic dispersion processes and the associated distribution of transit times and its various properties. We study dispersion processes in various systems with different microstructures, ranging from a single capillary tube to a random network of interconnected pores near its percolation threshold, and investigate the effect of various structural parameters, such as the length of the medium and its state of connectivity, on hydrodynamic dispersion. In particular, we will study dispersion phenomena in flow through a random network near the percolation threshold  $X_c$ . According to percolation theory, transport properties of disordered media obey universal scaling laws near the percolation threshold. These scaling laws are often independent of the microstructure of the media. Thus, we shall investigate the possible universal scaling laws that may describe dispersion near  $X_c$ .

Macroscopic modelling of dispersion processes in disordered and isotropic porous media is usually (see, e.g., Whitaker 1986 and references therein) based on the convective-diffusion equation (CDE)

$$\frac{\partial C_m}{\partial t} + V_a \cdot \nabla C_m = D_L \frac{\partial^2 C_m}{\partial x^2} + D_T \nabla^2 C_m \quad (2)$$

where  $V_a$  is the macroscopic mean velocity,  $C_m$  is the macroscopic mean concentration

and  $\nabla_2^2$  is the Laplacian in transverse (perpendicular to the mean flow) directions. Thus the basic idea is to model dispersion processes as anisotropic diffusional spreading of concentration, the diffusivity being the longitudinal dispersion coefficient  $D_L$  (in the direction of mean flow) and the transverse dispersion coefficient  $D_T$ . Another goal of this paper is to investigate the conditions under which dispersion processes *cannot* be represented by the CDE.

Dispersion is said to be macroscopically diffusive if it obeys the CDE. If a particle population is injected into the medium at the point  $\xi_0 = (x_0, y_0, z_0)$  at  $t = 0$ , for macroscopically diffusive dispersion the probability density  $P(\xi, t)$  obeys the Gaussian distribution

$$P(\xi, t) = (8\pi^3 D_L D_T^2 t)^{-3/2} \exp\left(-\frac{(x-x_0-V_a t)^2}{4D_L t} - \frac{(y-y_0)^2}{4D_T t} - \frac{(z-z_0)^2}{4D_T t}\right) \quad (3)$$

where  $P(\xi, t) d\xi$  is the probability that a particle is in a plane between  $\xi$  and  $\xi + d\xi$  at time  $t$ , where  $\xi = (x, y, z)$ .  $P(\xi, t)$  is proportional to  $C/C_0$ , where  $C_0$  is the concentration at  $t = 0$  and, therefore, equation (3) represents a solution of equation (2). If one defines  $Q(\zeta - \zeta_0, t) dt$  as the probability that a particle beginning in the plane at  $\zeta_0$  will cross, for the first time, a plane at  $\zeta$  between  $t$  and  $t + dt$ , then, from equation (3), one can easily obtain (Sahimi *et al* 1986b)

$$Q(\zeta - \zeta_0, t) = |\zeta - \zeta_0| (4\pi D_\zeta t^3)^{-1/2} \exp[-(\zeta - \zeta_0 - V_\zeta t)^2 / 4D_\zeta t] \quad (4)$$

where  $D_\zeta$  and  $V_\zeta$  are the dispersion coefficient and the mean flow velocity in the  $\zeta$  direction, respectively. Various moments of  $Q$ , the first passage time distribution (FPTD), yield information about the flow field and the dispersion processes. For example,

$$\langle t \rangle = L / V_\zeta \quad (5)$$

and

$$\langle t^2 \rangle = \langle t \rangle^2 (1 + 2D_\zeta / LV_\zeta) \quad (6)$$

where  $L = \zeta - \zeta_0$ . In general, we can easily show that  $\langle t \rangle$  and  $\langle t^n \rangle$  are related, where  $n > 1$  is any integer number and, to the leading order, one has  $\langle t^n \rangle \sim \langle t \rangle^n$ . Of course, this is true if the CDE is applicable and, therefore, one way of showing that the CDE may not describe dispersion processes in a certain medium is to show (Koplik *et al* 1988) that  $\langle t^n \rangle$  is *not* simply related to  $\langle t \rangle$  and one needs to have more information to describe various moments of the FPTD. This will be discussed later in § 4.

Many authors have studied dispersion processes in porous media using a wide variety of techniques and certain models of pore space (for a review see Fried and Combarous (1971) and Sahimi (1984a)). For example, Brenner (1980) developed a general theory for determining the dispersion coefficients in spatially periodic porous media and showed that in the limit of long times the dispersion of tracer particles obeys a CDE. Carbonell and Whitaker (1983) presented a volume average approach for calculating the dispersion coefficients and carried out certain computations for a two-dimensional spatially periodic porous medium (Eidsath *et al* 1983). However, most real porous media do not have a spatially periodic structure and, although the results of Brenner (1980) and Carbonell and Whitaker (1983) are in agreement with some experimental data for dispersion in spatially periodic porous media (see, e.g., Gunn and Pryce 1969), their general applicability is limited. For example, the results of Eidsath *et al* (1983) for the transverse dispersion coefficient are much smaller than

the experimental data, while the predicted longitudinal dispersion coefficient is somewhat too large. This is not surprising, as in spatially periodic porous media no streamlines meander more than a unit cell transverse to the flow direction, so that transverse dispersion is little affected by flow, while longitudinal dispersion resembles that for dispersion in a capillary tube. Thus  $D_T$  is underestimated, while  $D_L$  is overestimated.

Saffman (1959) represented the microstructure of a porous medium as a network of interconnected capillary tubes. If we define a Péclet number by  $Pe = V_a d / D$ , where  $d$  is a characteristic length in the medium (e.g. a grain size), then Saffman showed that at high  $Pe$  and at very long times,  $D_L/D$  grows as  $Pe \ln Pe$ . This agrees with many sets of experimental data (see Perkins and Johnston 1963) for dispersion in consolidated porous media, for which a network of capillary tubes provides a reasonable model (see the discussion below). However, Saffman's approach is a mean-field treatment of the problem and is not appropriate for percolation networks. We shall show in this paper that, if a porous medium is near its percolation threshold,  $D_L/D$  would grow as  $Pe^2$ . This quadratic dependence arises because of the existence of many dead-end branches in which there is no flowing fluid, and from which a tracer particle can escape only by molecular diffusion. Koch and Brady (1985) have shown that a quadratic dependence of  $D_L/D$  on  $Pe$  can also arise in consolidated porous media, if there are regions of pore space in which the velocity field vanishes. However, the approach of Koch and Brady (1985) cannot be used for percolating systems that are of interest here, because it cannot predict correctly the non-analytical behaviour of dispersion coefficients and transport properties of porous media such as diffusivity and permeability near  $X_c$  (see below).

This paper is organised as follows. In § 2 we study analytically dispersion processes in systems with relatively simple microstructures to gain insight about the effect of the microstructure of the system on the mixing process. In particular, we use statistical methods to derive the FPTD of the mixing process. The deviation between this FPTD and that predicted by the CDE, equation (4), is a measure of the departure of the dispersion process from that described by the CDE. In § 3 we describe a Monte Carlo (MC) simulation method which we use for studying dispersion processes in disordered porous media. We represent the porous medium by a square or a simple cubic network of interconnected cylindrical tubes, the effective radii of which are distributed according to a probability density function (PDF)  $f(R)$ . Section 4 contains the results of Monte Carlo simulations of dispersion processes in the random networks. In particular, we study dispersion processes near the percolation threshold of the networks and obtain the appropriate scaling laws for dispersion coefficients and their dependence on the mean flow velocity and the Péclet number. We also study the effect of topological and geometrical disorder on the dispersion process, and investigate the effect of the size of the system on dispersion coefficients. Section 5 extends the simulations to dispersion in flow of two immiscible fluids (e.g. oil and water) in a porous medium. The paper is summarised in § 6 where we also discuss dispersion processes in more complex systems.

## 2. Dispersion in systems with simple microstructure

The simplest system in which one can have a non-uniform velocity field, and in which dispersion processes can be studied, is a straight tube of length  $b$ . If we assume that

the flow is laminar, then the velocity field is given by

$$V = 2V_a[1 - (r/R)^2] \quad (7)$$

where  $R$  is the radius of the tube and  $r$  is the radial position. We now inject into the tube a population of dynamically neutral particles which are miscible with the flowing fluid in the tube. However, the injection is not uniform across the cross section of the tube, since it results in an infinite mean transit time for exiting the tube (because  $V = 0$  on the wall). Rather, although the flux is constant, the position of a streamline on which a particle is placed is weighted with the speed of the streamline. Thus the travel time for a particle is  $b/V$ . Since the fraction of the area between  $r$  and  $r + dr$  is  $r dr/R^2$ , then the probability that a particle is on a streamline between  $r$  and  $r + dr$  is  $(2V/V_a)(r dr/R^2)$ . Thus, if  $Q(b, t)$  is the distribution of transit times, we have

$$Q(b, t) = b^2/2V_a^2 t^3 \quad (8)$$

which is valid for  $t \geq b/2V_a$ . Clearly,  $Q(b, t)$  is very different from equation (4), which means that this type of convective mixing cannot be described by the CDE. Note that, while the first two moments of  $Q(b, t)$  exist, they are not directly related to one another. We now define the dispersion coefficient  $D_L$  by

$$D_L = \int \frac{(b - V_a t)^2}{2t} Q(b, t) dt \quad (9)$$

i.e.  $D_L$  is the temporal average of the ratio of the squared deviations of the mean particle position (which is  $V_a t$ ) from its position at time  $t$  which is fixed at  $b$ , and the time (see, e.g., Hill 1977). We then obtain

$$D_L = \frac{1}{6} b V_a \quad (10)$$

and, therefore,  $D_L \rightarrow \infty$  as  $b \rightarrow \infty$ . Note that  $D_L$  is linearly dependent on  $V_a$ . Although this is a very simple example of dispersion due to convective mixing, we shall show in § 4 that the analysis is equally applicable to dispersion in flow through certain networks of interconnected tubes.

In practice, there is always some molecular diffusion which transfers the particles from one streamline to another and, therefore, the mixing of the particles with the flowing fluid is the result of the competition between convective mixing and molecular diffusion. This problem was first studied by Taylor (1953) and Aris (1956). Starting from the CDE, they showed that  $D_L$  is given by

$$D_L = D_a + R^2 V_a^2 / 48 D_r \quad (11)$$

where the subscripts  $a$  and  $r$  signify the fact that  $D_a$  and  $D_r$  are the contributions of axial and radial molecular diffusion, respectively (of course,  $D_a = D_r = D$ ). If we define a Péclet number  $Pe$  by  $Pe = R V_a / D$ , equation (11) can be written as

$$D_L / D = 1 + \frac{1}{48} Pe^2 \quad (12)$$

Note that in Taylor-Aris dispersion  $D_L$  depends quadratically on  $V_a$ . The first passage time distribution for Taylor-Aris dispersion in capillary tubes is given by equation (4), since Taylor and Aris showed that if the length of the tube is long enough, at large times  $C_m$ , the mean concentration over the cross section of the tube obeys a diffusion equation

$$\frac{\partial C_m}{\partial t} = D_L \frac{\partial^2 C_m}{\partial x_1^2} \quad (13)$$

where  $x_1 = x - V_a t$ . Thus, as discussed above, one may identify  $D_L$  as an effective diffusion coefficient. We may reinterpret equation (11) and rewrite it as

$$D_L = \text{longitudinal (axial) mixing} + \text{axial convection/transverse mixing.} \quad (14)$$

Therefore, axial convection and longitudinal mixing (which, in this case, is molecular diffusion) *enhance* dispersion, whereas transverse mixing (in this case, radial molecular diffusion) *reduces* it. This is true about any system. For example, in a porous medium where transverse mixing is present,  $D_L$  may be reduced as compared with its value in a single capillary tube where transverse dispersion does not exist at all.

Diffusion processes in a given system are often equivalent to random walks of some particles in the same system, with the probability of finding a particle at a point of the system at a given time being proportional to the concentration of the diffusing material at that point. Since dispersion processes such as those studied by Taylor and Aris can sometimes be described by a diffusion equation, it may be instructive to develop a random walk model which can describe these processes. This would help one to understand more easily the conditions under which  $D_L$  may have a specific dependence on  $V_a$  or  $Pe$ . In particular, we may understand the condition(s) under which  $D_L$  may no longer depend quadratically on  $V_a$ . In general, the essence of dispersion processes is the existence of a velocity distribution and the competition between this distribution and molecular diffusion. If a fluid particle is travelling with the speed  $V_1$  along a streamline which is very close to the solid surface of a pore, it may be transferred (by molecular diffusion) to another streamline with speed  $V_2$  (where  $V_2 > V_1$ ), because it takes less time to diffuse to that streamline than to be convected a certain distance. If  $r_D$  is the radial distance between the two streamlines, the diffusion timescale is  $t_D = r_D^2/2D$ . Alternatively, we may imagine that, instead of diffusing to the streamline with speed  $V_2$  in a time  $t_D$ , the particle waits for the time  $t_D$  after which it instantaneously jumps to the streamline of speed  $V_2$ . Therefore, dispersion processes may be formulated in terms of the random walk of a dynamically neutral fluid particle which is being convected along streamlines with speeds  $V_1, V_2, \dots$ , and is making instantaneous jumps between the streamlines, with  $t_D$  being the time between successive transitions. We assume that  $t_D$  is a distributed quantity with a PDF  $\phi(t)$ . This randomness may be due to the fact that each time the particle makes a transition between two streamlines, the distance between the two streamlines may be random and different from that of the previous transition. Such random walks in which the walker waits for a time  $t$  (where  $t$  is a distributed quantity), before it makes an instantaneous transition to another point, are called continuous-time random walks (CTRW) (Scher and Lax 1973) and were first developed for modelling of transport processes in disordered solids. Thus, in what follows we present a CTRW formulation of dispersion processes. Our result is *not* restricted to dispersion in a capillary tube and is valid for *any* system which follows the physics of the process considered here. Indeed, we shall show in § 4 that this analysis is equally applicable to dispersion in flow through certain random networks of interconnected tubes. Moreover, this CTRW formulation enables us to investigate the conditions under which equation (11) may be violated. As we show below, our formulation can also reproduce the dependence of  $D_L/D$  on  $Pe$  that was derived by Saffman (1959). However, our CTRW formulation is in principle exact, provided that the waiting time distribution can be specified, whereas Saffman's formulation involves several approximations.

For simplicity, we consider only two streamlines with speeds  $V_1$  and  $V_2$ ; the generalisation of the technique to many streamlines is also possible, but it is much

more complex and will be briefly discussed below. Suppose that  $T_n$  is the time at which the  $n$ th jump of the particle from one streamline to the other takes place and that its position at that time is  $x_n$ . Obviously

$$x_n = (t_1 - t_0)V_1 + (t_2 - t_1)V_2 + (t_3 - t_2)V_1 \dots \tag{15}$$

and, therefore, if  $n$  is even (since we are considering the limit of very large  $n$ , this assumption is of no significance and is only for convenience), we have

$$x_n = V_1 \sum_{i=1}^n t_i^{(\alpha)} + V_2 \sum_{i=1}^n t_i^{(\beta)} \tag{16}$$

where  $t_i^{(\alpha)}$  and  $t_i^{(\beta)}$  are two independent and identically distributed random variables with a common PDF  $\phi(t)$ . (Note that the waiting time before each transition is  $t_1 - t_0$ ,  $t_2 - t_1$  and so on.) If we let

$$T_n^{(\alpha)} = \sum_{i=1}^n t_i^{(\alpha)} \tag{17}$$

and

$$T_n^{(\beta)} = \sum_{i=1}^n t_i^{(\beta)} \tag{18}$$

then we can calculate all of the statistics of interest from equations (15)–(17). In particular, the average velocity is given by

$$V_a = \left\langle \frac{V_1 T_n^{(\alpha)} + V_2 T_n^{(\beta)}}{T_n^{(\alpha)} + T_n^{(\beta)}} \right\rangle \tag{19}$$

while the dispersion coefficient is given by

$$D_L = \langle (x_n - V_a T_n)^2 / 2 T_n \rangle \tag{20}$$

where  $\langle \dots \rangle$  denotes an averaging over the distributions of  $T_n^{(\alpha)}$  and  $T_n^{(\beta)}$ . Thus, we need to find the PDF  $\psi(t)$  for  $T_n^{(\alpha)}$  and  $T_n^{(\beta)}$ . If  $\hat{\phi}(\lambda)$  is the Laplace transform of  $\phi(t)$  (where  $\lambda$  is the Laplace transform variable conjugate to  $t$ ), then  $\hat{\psi}(\lambda)$ , the Laplace transform of  $\psi(t)$ , is given by (Feller 1971)

$$\hat{\psi}(\lambda) = [\hat{\phi}(\lambda)]^n. \tag{21}$$

We assume that  $\phi(t)$  is not long-tailed (i.e. the first two moments  $\langle t \rangle$  and  $\langle t^2 \rangle$  are finite) so that  $\hat{\phi}(\lambda)$  can be written as

$$\hat{\phi}(\lambda) = 1 - \langle t \rangle \lambda + \langle t^2 \rangle \lambda^2 / 2 + \text{higher-order terms} \tag{22}$$

where  $\langle t \rangle$  is the mean waiting time (the mean time between jumps). If one combines (20) and (21), one obtains

$$\hat{\psi}(\lambda) = (1 - \langle t \rangle \lambda + \dots)^n. \tag{23}$$

Note that both  $T_n^{(\alpha)}$  and  $T_n^{(\beta)}$  have a common PDF  $\psi(t)$ . Equation (19) can now be written as

$$V_a = \int_0^\infty \int_0^\infty \left( \frac{V_1 t_1 + V_2 t_2}{t_1 + t_2} \right) \psi(t_1) \psi(t_2) dt_1 dt_2 \tag{24}$$

which, subject to (23), yields

$$V_a = (V_1 + V_2) / 2 \tag{25}$$



which is expected. However, we should note that we have only required that the first two moments of  $\phi(t)$  be finite (in fact, we only need to have a finite  $\langle t \rangle$  in order to have a finite  $V_a$ ) and we have not specified any particular form for  $\phi(t)$ . It is easy to show that equation (25) is valid for any  $\phi(t)$  for which the mean waiting time  $\langle t \rangle$  is finite. If we have  $n$  streamlines with speeds  $V_1, V_2, \dots$ , it would be easy to show that a generalisation of equation (24) would yield,  $V_a = (1/n) \sum_{i=1}^n V_i$ .

In a similar fashion, the dispersion coefficient  $D_L$  can be written as

$$D_L = \int_0^\infty \int_0^\infty \frac{[V_1 t_1 + V_2 t_2 - (t_1 + t_2) V_a]^2}{2(t_1 + t_2)} \psi(t_1) \psi(t_2) dt_1 dt_2 \tag{26}$$

which, in the limit  $n \rightarrow \infty$  and after many tedious manipulations, yields

$$D_L = U^2 \sigma^2 / 8 \langle t \rangle \tag{27}$$

where  $\sigma^2 = \langle t^2 \rangle - \langle t \rangle^2$ . Here  $U = (V_1 - V_2)/2$ , so that  $U$  is some kind of characteristic velocity. In equation (27), in addition to the right-hand side, several other terms also arise. But such terms are very small in the limit  $n \rightarrow \infty$  and do not contribute significantly, as long as  $\langle t \rangle$  and  $\langle t^2 \rangle$  are finite. Since  $\langle t \rangle / \sigma^2$  is a measure of the diffusion coefficient that characterises the diffusive transition from one streamline to the other (Scher and Lax 1973), i.e.  $\langle t \rangle / \sigma^2 \sim D$ , equation (27) is essentially equivalent to the Taylor-Aris result. In our derivation, we have ignored diffusion of the fluid particle *along* the streamlines. If we do not ignore this diffusion, a term which is similar to a diffusion coefficient would be added to the right-hand side of (27), so that equation (11) would be exactly reproduced.

The derivation of equation (27), based on a CTRW formulation of the problem, enables us to investigate the conditions under which it (or, equivalently, equation (11)) may break down. For example, if  $\langle t \rangle$  is finite but  $\langle t^2 \rangle$  is infinite, a situation that may be realised if

$$\hat{\psi}(\lambda) = 1 - c_1 \langle t \rangle \lambda + c_2 \lambda^{1+\gamma} + \dots \tag{28}$$

where  $\gamma, c_1$  and  $c_2$  are constant and  $0 < \gamma \leq 1$ , we find that  $D_L$  *diverges* unless a large-time cutoff is introduced into the problem to make the integral in equation (26) finite. A careful analysis of this situation shows that, e.g. for  $\gamma = 1$ , we obtain

$$D_L \sim U \ln U \tag{29}$$

which is a strong departure from the Taylor-Aris dispersion theory, but it is similar to Saffman's result mentioned above. Moreover, one may view the exponent  $\gamma$  as a tunable parameter by which one can change the dependence of  $D_L$  on  $U$  (i.e.  $D_L$  depends on  $U$  according to a power law in which the exponent depends on  $\gamma$ ). Since waiting time distributions for which  $\langle t^2 \rangle$  is infinite are characteristics of processes which are very slow, equation (28) may mean that, if the mixing process takes place in a medium which contains very slowly moving or stagnant regions, the dependence of  $D_L$  on the flow velocity may vary anywhere from equation (29) to (27). Note that, according to equation (21), the transit time distribution (i.e. the distribution of  $T_n$ ) can be different from (4) (i.e. the mixing process cannot be described by the CDE) and may depend on the form of  $\phi(t)$ , but equation (27) would still be valid. This means that a quadratic dependence of  $D_L$  on  $V_a$  is *not* restricted to Taylor-Aris dispersion, which is described by a CDE, and may also arise in other systems (see below).

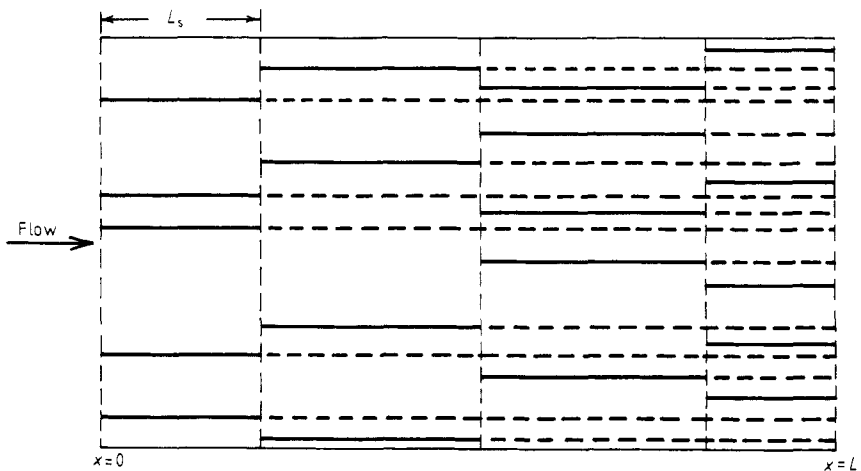
Another possible approach for determining the dependence of  $D_L$  on the flow velocity is to allow, in our CTRW formulation, the streamline speeds  $V_1, V_2, \dots$ , to be

independent and identically distributed quantities with a common PDF  $F(V)$ . Assuming that these speeds are distributed quantities is realistic, as the flow field in a real porous medium is chaotic and essentially random and, therefore, the streamline speeds may be expected to be random variables. The PDF  $F(V)$  can, in principle, be computed if the morphology of the porous medium and the flow regime (laminar, turbulent, etc) are known. The computation of  $F(V)$  is complex and is beyond the scope of the present paper and will be discussed elsewhere, but it suffices to mention that the dependence of  $D_L$  on the flow velocity depends crucially on the behaviour of  $F(V)$  near  $V=0$ . If

$$F_{-1} = \int_0^\infty \frac{F(V)}{V} dV \quad (30)$$

is finite, one finds that  $D_L$  depends linearly on the flow velocity. On the other hand, if  $F_{-1}$  is divergent, i.e. there are many extremely slow streamlines or there are stagnant regions of the pore space where the velocity field vanishes (e.g. if  $F(V) \sim V^{-\gamma}$ , where  $0 < \gamma \leq 1$ ), one finds that  $D_L$  depends non-linearly on the flow velocity,  $D_L \sim V_a^\alpha (\ln V_a)^\beta$ , where  $\alpha$  and  $\beta$  are constants that depend on the flow regime and the strength of molecular diffusion, and  $0 < \alpha \leq 2$  and  $0 \leq \beta \leq 1$ .

We now consider dispersion processes in a system with a microstructure which is more complex than a capillary tube, but simpler than a real porous medium. Because dispersion processes in this system are amenable to exact calculations, their study can help us understand the conditions under which the CDE may not describe dispersion processes. We consider a one-dimensional system of length  $L$  ( $L$  is large) which is made of many sections of length  $L_s$  (see figure 1). Within each section there are  $n$  randomly located streamtubes or ducts, where  $n$  is a randomly distributed quantity with a PDF  $N(n)$ . The width of the medium is assumed to be finite which, for convenience and without lack of generality, is taken to be unity. Creeping (Stokes) flow is assumed within each streamtube and it is also assumed that fluid particles in each tube (duct) move with the mean velocity of the streamtube. Thus, the fluid velocity  $V$  is proportional to  $w^2$  ( $R^2$ ), where  $w$  ( $R$ ) is the width (radius) of the duct



**Figure 1.** One-dimensional idealisation of a porous medium for studying variations in transit times of tracer particles.

(streamtube). There is very little interchange between the tubes. As such, the model is somewhat similar to a stratified porous medium, where the permeability of each stratum is a random variable and there is no appreciable exchange between two neighbouring strata. We now inject into the medium a population of dynamically neutral fluid particles, miscible with the flowing fluid inside the medium, and ask the following question: is this mixing process diffusive, i.e. can it be described by a CDE?

To answer this question, we calculate the transit time distribution  $Q(L, t)$  of the injected fluid particles and compare it with equation (4), which is the prediction of the CDE. Since the medium has been partitioned into  $m = n - 1$  ducts in  $(0, 1)$ , we require the PDF for the width of the duct (the radius of a streamtube), if a given point lies in that duct (streamtube). Because of the partitioning of the unit interval, we have  $m$  independent random variables  $x_i$  with  $i = 1, 2, \dots, m$ , which have a common PDF  $H(x)$  which is concentrated on the unit interval  $(0, 1)$ . We then define an order statistics (Feller 1971) such that

$$0 < x_{(1)} < x_{(2)} < \dots < x_{(m)} < 1. \tag{31}$$

The  $i$ th interval is defined by  $[x_{(i)}, x_{(i+1)}]$ . The PDF  $H_{(k)}$  for  $x_{(k)}$  is given by

$$H_{(k)} = H(x) m \binom{m-2}{k-1} \left( \int_0^x H(y) dy \right)^{k-1} \left( \int_x^1 H(y) dy \right)^{m-k-1}. \tag{32}$$

Equation (32) is a generalisation of a result given by Feller (1971). His result was derived for an exponential or uniform  $H(x)$ , whereas (32) is valid for any  $H(x)$ . In the simplest case in which we have a uniform distribution for  $x_1, x_2, \dots$ , the widths  $w$  of the ducts (or the radii of the tubes) induced by the partition have a common distribution

$$Y(w > w_0) = (1 - w)^{n-1} \tag{33}$$

and thus their PDF is given by  $y(w) = -(\partial/\partial w) Y(w > w_0) = (n - 1)(1 - w)^{n-2}$ . If  $n$  is a random variable which is distributed according to a PDF  $N(n)$ , the joint PDF for  $w$  and  $n$  is given by  $Z(w, n) = y(w)N(n)$ .

We can now calculate the distribution of transit times  $Q(T_j)$ . With  $L_s$  being the length of a section (we have assumed that  $L_s$  is constant, but we can easily generalise the derivation of the results to the case where  $L_s$  is a distributed quantity), the transit time is given by  $t = L_s/V(w)$ . For the  $i$ th section one has  $Q_i(t) dt = Z(w, n) dw$ , and if we assume that  $V_a = aw^2$ , where  $a$  is a constant, we obtain

$$Q_i(t) = \frac{1}{2} \frac{L_s}{t^2} \left( \frac{L_s}{t} \right)^{-1/2} (n - 1) N(n) \left[ 1 - \left( \frac{L_s}{at} \right)^{-1/2} \right]^{n-2}. \tag{34}$$

The total transit time  $T_j$  is given by  $T_j = \sum_{i=1}^j t_i$  where  $j = L/L_s$  and  $t_i = L_s/V_a(w_i)$ . Then, if  $\hat{Q}(\lambda)$  is the Laplace transform of  $Q(T_j)$ , we have

$$\hat{Q}(\lambda) = [\hat{Q}_i(\lambda)]^j. \tag{35}$$

Although the form of  $Q(T_j)$ , in the limit  $j \rightarrow \infty$ , depends on the distribution  $N(n)$ , it is straightforward to show that, for a wide class of  $N(n)$ , the distribution  $Q(T_j)$  would not converge to (4), so that the mixing process is not diffusive.

In the system we just studied, we assumed that there is only convective mixing within each tube (duct) and there is very little exchange between the neighbouring tubes. More generally, we may consider a problem in which a CDE describes dispersion within each tube (duct) and there is a finite exchange of mass between the neighbouring

tubes. The radius (width) of the tubes (ducts) can be a distributed quantity. This problem was studied by Matheron and de Marsily (1980). These authors used an approximate method and asymptotic analysis to show that, as long as the total width of the system is infinite, at long times the mixing process is almost never governed by a macroscopic CDE and the dispersion coefficients will be time-dependent quantities. From these examples, we may conclude that the morphological properties of a medium strongly affect the transport and mixing processes, and the validity of a CDE for describing the process depends on the microstructure of the medium and the interaction between microscopic events (i.e. convection, diffusion, etc) that govern the transport and mixing processes.

### 3. Monte Carlo simulation method for dispersion in porous media

In the previous section, we studied dispersion processes in flows through systems whose microstructures were simple enough to afford an analytical solution for the problem. Our primary strategy was to calculate the distribution of transit times in order to test the validity of the CDE for describing dispersion processes. We now turn our attention to dispersion in flow through a porous medium and study the effect of morphological properties of the medium on dispersion processes.

Dispersion processes in a porous medium are usually different from those in flow through a capillary tube and similar simple systems. Most of dispersion in a porous medium can come from the meandering of the streamtubes through the complex structure of the medium. In the whole porous medium, one may expect that molecular diffusion reduces the concentration difference between streamtubes which, because of the geometrical structure of the medium, happen to occur near each other. But one must be aware that diffusional mixing which results from contact between streamtubes at pore junctions is different from that due purely to a deformation of the displacing fluid front with different velocities, i.e. convective mixing, which may exist without any molecular diffusion because variable pore diameters and tortuous paths of fluid particles create a purely mechanical mixing which is totally independent of molecular diffusion.

Because of the chaotic nature of the flow passages and the streamlines they enforce, statistical models of dispersion are natural. However, the success of such statistical models depends strongly on the models of pore space that are employed. Any porous medium can, in principle, be rigorously mapped onto an equivalent network of bonds which are connected to each other at sites or nodes of the network. The bonds can have any shape but, for convenience, are assumed to be cylindrical tubes. The geometrical characteristics of the medium can be incorporated into the structure of the network by assigning random radii to the network bonds and/or sites. These are selected from a pore size distribution that can, in principle, be measured by porosimetry or automated serial sectioning of the porous medium. The details of such a mapping are given by Mohanty (1981) and Lin and Cohen (1982). Usually, the resulting network has a random topology, i.e. its local coordination number, which is the number of bonds connected to a site, is a random variable. However, recent studies (see Jerauld *et al* (1984) and references therein) show that, as long as the average coordination number of the topologically disordered network is equal to the coordination number of a regular network, transport and many other properties of the two networks are, for all practical purposes, identical. Therefore, we employ a regular structure in the

form of a square network or a simple cubic network in this study. Since we are interested in the effect of connectivity of the pore space on dispersion processes, the concepts of percolation theory (Stauffer 1985) are also relevant. The applicability of percolation theory to modelling of flow and mixing processes in porous media is well established (Larson *et al* 1977, Chandler *et al* 1982, Heiba *et al* 1982, Sahimi *et al* 1983, Thompson *et al* 1987; see also below).

We assume that only a fraction  $X$  of bonds is open to flow where  $X_c \leq X \leq 1$ , where  $X_c$  is the percolation threshold. The open bonds are either selected completely at random (as in a simple percolation process) or, as we shall discuss in § 5 of this paper (where we discuss dispersion in flow of two immiscible fluids), are selected according to a special criterion. We either assign the same effective radius  $R$  to all open bonds, or select their  $R$  from a PDF  $f(R)$  which, in the present paper, is taken to be  $f(R) = 2R \exp(-R^2)$ . The shape of this particular  $f(R)$  mimics qualitatively the measured pore size distributions of many porous media (see, e.g., Chatzis and Dullien 1985). Creeping flow in each open bond is assumed, so that the hydraulic conductance  $g$  of each bond is proportional to the fourth power of its effective radius (as in Hagen-Poiseuille flow). Thus the volumetric flow rate  $q_i$  of the bond  $i$  is given by

$$q_i = g_i \Delta p_i \quad (36)$$

where  $\Delta p_i$  is the pressure difference between the nodes of the bond. We then calculate the steady-state pressure distribution in the entire network. This is done by solving a standard Kirchhoff law formulation in which the flow rate  $q_i$  in each bond is as in (36). The Kirchhoff law formulation of the problem yields a set of linear equations in nodal pressures, which we solve it by a modified Gauss elimination method. The boundary conditions are unit pressure gradient which is either applied at  $45^\circ$  to the two (or three) bond directions, or is applied in the  $x$  direction, so that bonds in the  $y$  and  $z$  directions are perpendicular to the macroscopic pressure gradient. Cyclic (periodic) conditions on the opposed faces in the  $y$  and  $z$  directions are also assumed. From the pressure distribution and the effective radii of the bonds we can calculate the velocity distribution and the flow rate in each bond.

To study dispersion in flow through the random network one can use one of several available approaches. In one of them one assumes that the distribution of the concentration of the fluid particles in every tube is described by a one-dimensional CDE, in which  $D_L$  is replaced by the molecular diffusivity  $D$ . One also assumes that there is perfect mixing at the nodes of the network, so that each bond can 'see' the rest of the network only through the tracer concentration at its two nodes. Thus, one needs only to solve for the concentration of the tracer particles at the nodes of the network. This yields, in the Laplace transform space, a set of linear equations for the (Laplace-transformed) nodal concentrations, from which the quantities of interest can be computed. Various versions of this method have been employed recently (de Arcangelis *et al* 1986, Koplik *et al* 1988, Roux *et al* 1986), with essentially equivalent results. The efficiency of these methods depends crucially on the structure of the model of pore space that is used. For example, the method of de Arcangelis *et al* (1986) becomes highly inefficient and time consuming if it is applied to dispersion in percolating systems which is of interest here.

In the present paper we use a MC simulation method which is an extension and modification of a MC method that we developed earlier (Sahimi *et al* 1983, 1986a, b) for the purely convective limit. We inject into the network a population of dynamically neutral fluid particles, at the plane  $x = 0$ , and monitor their motion. This corresponds

to the injection of an initially sharp concentration front. Intuitively, one may expect that the tracers should be distributed over the inlet plane, with a probability which is proportional to the fluxes of the bonds that cross the inlet plane. However, we select the injection points at random, because this leads to somewhat overweighting of low-flux branches of the network which help the tracers to sample slow fluid paths more efficiently. Such paths play a dominant role, as discussed below. The random selection of the initial point is also convenient from a computational point of view. However, this choice does not affect the essential features of the results. The path along which a particle travels depends not only on the morphology of the network, but also on the microscopic events within bonds and nodes of the network. In the present paper dispersion processes in two distinct cases are studied: in the first case, velocity distribution within each bond is neglected. Thus the tracer particles are assumed to move as in the plug flow. In the second case the velocity distribution within each bond is not neglected and the tracer particles are allowed to diffuse from one streamline to another according to the criterion described below.

We assume that, if the velocity distribution within a bond is neglected, converging streams are completely mixed at the nodes and a particle leaves a node into one of the attached bonds that carry flow *away* from that node (i.e. longitudinal diffusion *against* local flow is not allowed). If the Péclet number is very small, diffusion against local flow may become important, but this possibility is ignored here. The probability of selecting a tube is assumed to be proportional to its flow rate (this law of transition probabilities can in fact be derived from the CDE; see de Arcangelis *et al* (1986)). Within each tube, the particles move with the mean flow velocity  $V_a$  of the tube. If the network is well connected (i.e.  $X \approx 1$ ), this model is perhaps not totally satisfactory, because the regions of slowly moving fluid near the pore walls are not sampled very efficiently. However, since all bonds have the same radius and we mostly use networks in which the macroscopic pressure gradient is imposed at  $45^\circ$  to the two (or three) pore directions (so that there is essentially no difference between various bonds and there are very few, if any, tubes that carry very little flow), and because this model is primarily used for studying dispersion processes near the percolation threshold  $X_c$ , it is expected that the results would contain the essential physics of the process, because near  $X_c$  the dominant transport mechanisms are convection and diffusion over length scales that are of the order of the percolation correlation length  $\xi_p$ . The correlation length  $\xi_p$  diverges as  $X_c$  is approached:

$$\xi_p \sim (X - X_c)^{-\nu} \quad (37)$$

where  $\nu = \frac{4}{3}$  for two-dimensional systems, while  $\nu \approx 0.88$  for three-dimensional ones. The physical significance of  $\xi_p$  is that it is only for length scales  $L \gg \xi_p$ , that the system is macroscopically homogeneous and the description of transport processes by continuum equations of diffusion or the CDE is valid. Thus  $\xi_p$  is the dominant (and the only) length scale in the system and, since  $\xi_p$  is very large near  $X_c$ , microscopic events that take place over length scales smaller than  $\xi_p$  do not contribute significantly. We point out that an approach similar to that we just described has recently been used to study deep bed filtration and the reduction of the permeability of a porous medium as a result of pore plugging by large particles (Imdakh and Sahimi 1987). The result was found to be consistent with the experimental data.

When the velocity distribution within a tube is not neglected, we assume equation (7) holds within each tube. Thus, after selecting at random an injection point on the inlet plane at  $x = 0$ , we also select at random a streamline along which the particle

may be convected with the speed  $V$  given by equation (7). However, if the effective radii of the tubes are distributed according to a PDF  $f(R)$ , the network may contain tubes of very slow moving fluid. Then, as discussed by de Josselin de Jong (1958) and Saffman (1959), one finds that the mean convective time  $\langle t_c \rangle$  in a tube, where  $t_c = b/V$ , remains finite, but  $\langle t_c^2 \rangle$  is divergent. In this case, molecular diffusion intervenes and transfers the fluid particle from a slow streamline near the tube wall to another streamline which is closer to the centre of the tube. The fluid particle is then convected along this new streamline. This is essentially the mechanism that gives rise to the  $D_L/D \sim Pe \ln Pe$  relation. To take this effect into account in our MC simulations, we adopted a method which is similar to that of de Josselin de Jong (1958) and Saffman (1959). For a tracer particle on any streamline, the convection time  $t_c$  is computed. If  $t_c < t_D$ , where  $t_D$  is a diffusion timescale, the particle continues its motion along the streamline and exits the tube and the travel time  $t$  is equal to  $t_c$ . Here,  $t_D = r_D^2/2D$ , where  $r_D$  is the radial distance between the particle's streamline and another streamline along which  $V = V_a$ . However, if  $t_c > t_D$ , we allow the tracer particle to diffuse to the streamline with speed  $V_a$  and continue its motion along this streamline. In this case the total travel time  $t$  in the tube is given by  $t = t_c + t_D$ .

Once the fluid particle arrives at a node, the selection of the next tube becomes important. If, as in the case of the network of equal size tubes which was discussed above, the particle selects the next tube with a probability proportional to the flow rate in that tube, the tubes which contain very slowly moving fluid (i.e. those with very small  $q$ ) would not be sampled sufficiently and dispersion coefficients are underestimated. Thus a prescription must be given for tube-to-tube transfer. If the tracer particles move close to the walls of the tube with incoming flow (see figure 2), then they are more likely to move into the tubes that are adjacent to these walls (the vertical tubes in figure 2). This suggests the introduction of a geometric and deterministic transition of the tracers from one tube to another. First, we assign boundaries for splitting the flow into independent bundles which are separated by hypothetical boundaries. To determine the position of these boundaries, we equate the total flow rate in the vertical tubes to the flow rate that can fill a sector of the horizontal tube, the distance of which from the centre of the cross section of the tube is  $(R - d_1)$  or  $(R - d_2)$ , where  $R$  is the tube radius. Then, in transition from one tube to another, a tracer particle simply follows its own streamline. This intuitive method has been rigorously confirmed by the calculation of Jerauld (1985) who used a finite-element

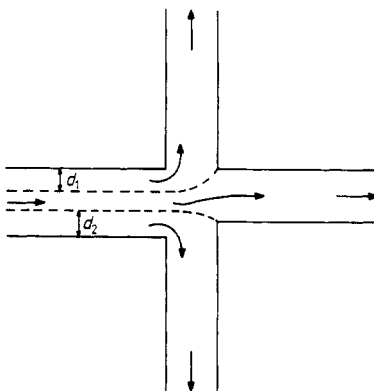


Figure 2. The splitting of the flow rate in a channel into neighbouring channels.

method to compute the distribution and the paths of streamlines in a network of capillary tubes.

Near the percolation threshold  $X_c$ , a large fraction of the bonds in the sample-spanning cluster of open bonds do not carry any fluid and the velocity field vanishes in these tubes. These bonds are the analogue of the dead-end pores in a real porous medium. The rest of the sample-spanning cluster which carries fluid is called the backbone of the cluster. As  $X_c$  is approached, the fraction  $X^B$  of the bonds in the backbone vanishes according to the following power law:

$$X^B \sim (X - X_c)^{\beta_B} \quad (38)$$

where (Sahimi 1984b)  $\beta_B = \frac{39}{72}$  and  $\beta_B \approx 0.95$  for two- and three-dimensional networks, respectively. The total fraction  $X^A$  of bonds that are in the sample-spanning cluster vanishes as

$$X^A \sim (X - X_c)^\beta \quad (39)$$

where  $\beta = \frac{5}{36}$  and  $\beta \approx 0.43$  for two- and three-dimensional networks, respectively. A tracer particle which is travelling with the flow field in a percolation network near  $X_c$  can communicate with the dead-end bonds only by molecular diffusion. Since near  $X_c$  a large fraction of tubes are dead-end, they can have an important effect on the dispersion process, because mixing in such tubes can take place only by molecular diffusion. To account for this effect, we allow the tracer particles to diffuse into the dead-end bonds with a probability proportional to the molecular diffusivity. Alternatively (and, perhaps, more accurately), we may allow the tracer particle to diffuse into the dead-end bonds with a probability proportional to the inverse of the local Péclet number (i.e. based on the local velocities). This rule would allow us to account for the competition between the local flow field and molecular diffusion more realistically, but we found that the results do not change appreciably. The travel time in a dead-end tube is given by  $t_D = b^2/2D$ . If a tracer particle arrives at a node to which only dead-end tubes are connected, it selects one of the tubes at random and continues its motion by molecular diffusion. Diffusion of the tracer particle in a dead-end branch of the network is continued until it joins the backbone of the cluster again and continues its journey with the flow field. Since near  $X_c$  the dead-end branches can be very long, diffusion of the tracer particles in such branches can take a long time, if the molecular diffusivity is small. This makes the distribution of transit times very broad. As a result, we expect dispersion coefficients to increase as  $X_c$  is approached (see below).

A tracer particle, which is injected into the network at the position  $x=0$ , would be at the location  $V_a t$  if there were no dispersion. With dispersion, the actual location of the particle is not at  $V_a t$ . Thus, in analogy with equation (20), we can compute a longitudinal dispersion coefficient  $D_L$  by

$$D_L = \langle (L - V_a t)^2 / 2t \rangle \quad (40)$$

where  $L$  is the length of the network and  $t$  is the time at which the particle crosses the network at  $x=L$  for the first time. Here  $\langle \dots \rangle$  indicates an average over the transit time distribution of a population of tracer particles. The mean flow velocity  $V_a$  is given by  $V_a = L/\langle t \rangle$ . In a similar way, we can calculate the transverse dispersion coefficient  $D_T$ :

$$D_T = \langle L_t^2 / 2t \rangle \quad (41)$$



where  $L_t$  is a (fixed) vertical distance from the starting location at  $t=0$  and  $t$  is the time at which the tracer reaches  $L_t$  for the first time (note that, for unidirectional flow,  $V_a=0$  for the transverse directions). Calculating dispersion coefficients by temporal averaging is consistent with the experimental determination of dispersion coefficients by monitoring at some downstream position the concentration in an emerging concentration front versus time since it was injected. To test the validity of the CDE, we also calculate  $D_L$  and  $D_T$  by using equation (6). If the CDE can describe the dispersion processes studied here, the two estimates of dispersion coefficients must be equal.

For each realisation of the network we injected up to 10 000 tracer particles into the network and calculated the averages of the quantities of interest. We then made several independent realisations of the network and computed the average quantities, where the averaging was done over the population of the independent realisations of the network. The number of independent realisations was dependent upon the network size. For the square network and for network lengths up to  $L=40$ , we used 40 different realisations of the network, whereas for  $40 < L \leq 100$ , we used 30 independent realisations. Up to 100 different realisations were used for the simple cubic network for which we used network lengths up to  $L=20$ .

#### 4. Results of Monte Carlo simulations

In this section we present the results of MC simulations of dispersion processes in square and simple cubic networks. We have carried out MC simulations of dispersion processes both in the backbone of the network alone (i.e. diffusion into the dead-end pores was ignored) and in the entire sample-spanning cluster (i.e. diffusion into the dead-end bonds was included). This would help us to understand the role of dead-end pores and their effect on dispersion processes. In both cases we have simulated dispersion in networks in which the effective radii of the bonds are distributed according to the PDF  $f(R)$ , or they all have the same size. We also consider the Péclet number dependence of dispersion coefficients over a wide range of the values of  $Pe$ . In what follows we first discuss dispersion processes in random networks in the limit of  $Pe \rightarrow 0$  and in fully connected networks for various values of  $Pe$ . We then discuss dispersion on the backbone of the networks. We shall then discuss our results for dispersion processes in flow through the entire sample-spanning cluster and investigate the behaviour of dispersion coefficients near the percolation threshold.

##### 4.1. Dispersion in random networks in the limit $Pe \rightarrow 0$

Let us first consider the limit of vanishing flow such that  $Pe \rightarrow 0$ . In the absence of convection dispersion is only due to molecular diffusion, and both dispersion coefficients  $D_L$  and  $D_T$  are equal to the macroscopic molecular diffusivity  $D_p$  of a tracer particle which is diffusing in the network. According to the well known Einstein relation,  $D_p$  is proportional to the effective conductivity  $K$  of the network. Near  $X_c$ ,  $K$  obeys the following scaling law:

$$K \sim (X - X_c)^\mu \quad (42)$$

where  $\mu \approx 1.3$  for two-dimensional networks (see, e.g., Zabolitzky 1984) while  $\mu \approx 2$  for three-dimensional networks (see, e.g., Pandey and Stauffer 1983). Since molecular diffusion takes place on the sample-spanning cluster of the network, then we have

$D_p \sim K/X^\alpha$ , which means that

$$D_p \sim (X - X_c)^{\mu - \beta} \tag{43}$$

which, in view of equation (37), can be written as

$$D_p \sim \xi_p^{-\theta} \tag{44}$$

where  $\theta = (\mu - \beta)/\nu$ . If we assume that diffusion takes place only on the backbone of the network, then clearly

$$D_p \sim \xi_p^{-\theta_B} \tag{45}$$

where  $\theta_B = (\mu - \beta_B)/\nu$ . In a finite network,  $\xi_p$  cannot exceed  $L$ , the total length of the network. Thus, as Gefen *et al* (1983) have shown, for any length scale  $\zeta < \xi_p$ , one should replace  $\xi_p$  with  $\zeta$  in equations (44) and (45). Thus, for example,

$$D_p \sim \zeta^{-\theta} \tag{46}$$

for diffusion on the sample-spanning cluster. The physical interpretation of (46) is that, for length scales  $\zeta < \xi_p$ , the macroscopic molecular diffusivity of the network and, thus, the dispersion coefficients in the limit  $Pe \rightarrow 0$ , are length-dependent quantities and are *not* constant. We call this anomalous dispersion. Dispersion in this regime *cannot* be described by a CDE. If  $\zeta > \xi_p$ , then dispersion is described by a CDE in the limit  $V_a = 0$ , i.e. a standard diffusion equation. The significance of equation (46) for the interpretation of experimental data is that it indicates that one can use a CDE only if the length of the system is larger than some characteristic length (e.g.  $\xi_p$  in the present case). Because of the well known relation,  $d\zeta^2/dt \sim$  diffusivity, and in view of (46) one obtains

$$\zeta^2 \sim t^{2/d_w} \tag{47}$$

where  $d_w$  is the fractal dimension of diffusing particles. For normal diffusion,  $d_w = 2$ , while for length-dependent diffusion (equation (46))  $d_w = 2 + \theta$ . (For diffusion on the backbone,  $d_w = 2 + \theta_B$ .) Because  $\theta > 0$ , the growth of  $\zeta^2$  with time is slower than linear. If equation (46) holds, one can no longer use a CDE to describe the mixing process and, therefore, equation (3) (in the limit  $V_a = 0$ ) can no longer be used. For this case, Guyer (1985) has proposed that

$$P(\xi, t) \sim At^{-\frac{1}{2}d_s} \exp[-(|\xi|/t^{1/d_w})^{\nu_p}]. \tag{48}$$

Here  $\nu_p = d_w/(d_w - 1)$ ,  $A$  is a constant which is obtained from the normalisation of  $P(\xi, t)$ , and  $\xi$  is the distance from the origin. The quantity  $d_s = 2d_f/d_w$  is the usual spectral dimensionality, where  $d_f$  is the fractal dimension of the infinite percolation cluster and  $d_f = \frac{91}{48} \approx 1.896$  for two-dimensional networks, while  $d_f \approx 2.5$  for three-dimensional ones. Clearly, if equation (48) holds, the FPTD for this mixing process is *not* given by equation (4) but, in the limit of long times, it can be computed (numerically) from (48), since (Sahimi *et al* 1986b)

$$Q(\xi, t) = \mathcal{L}^{-1}[\hat{P}(\xi, \lambda)/\hat{P}(0, \lambda)] \tag{49}$$

where  $\hat{P}(\xi, \lambda)$  is the Laplace transform of  $P(\xi, t)$  and  $\mathcal{L}^{-1}$  denotes the inverse Laplace transform. We shall return to equation (48) to propose a generalisation of it which would be valid for  $V_a \neq 0$ . Note that, in this case, the only timescale in the problem

is  $L^2/D_p$  and, therefore,  $\langle t^n \rangle \sim (L^2/D_p)^n$ . Thus, for the anomalous dispersion regime one has

$$\langle t^n \rangle \sim L^{n(2+\theta)} \sim \langle t \rangle^n. \quad (50)$$

For dispersion on the backbone,  $\beta$  is replaced by  $\beta_B$ .

#### 4.2. Dispersion in fully connected networks

We first consider dispersion processes in fully connected networks in which all bonds are open to flow and have the same effective radius. Consider a square or simple cubic network in which the bonds are either parallel or perpendicular to the mean flow direction. If the velocity distribution within each bond and molecular diffusion are totally neglected (i.e. the limit  $Pe \rightarrow \infty$ ), then there would be no dispersion since the convection time is the same for all tracer particles and the FPTD is of the form  $\delta(t - t_c)$ , where  $t_c = L/V_a$ . However, if the velocity distribution within each bond is not neglected, then there will be some dispersion due to convective mixing even in the absence of molecular diffusion. In this case the longitudinal dispersion coefficient is given by equation (10) in which  $b$  must be replaced by  $L$ , the total length of the network. Therefore, as discussed above, dispersion *cannot* be described by a CDE and  $D_L$  depends linearly on  $L$  and  $V_a$ . Because molecular diffusion has been totally neglected, there can be no transverse mixing and thus  $D_T = 0$ .

However, if molecular diffusion is not neglected, then the situation can drastically change. First, consider the case in which molecular diffusion *between* streamlines is not negligible, but we neglect molecular diffusion into the bonds that are perpendicular to the mean flow direction and carry no flow, because all bonds have the same effective radius. Such bonds are similar to dead-end bonds. Thus, the system is reduced to a bundle of parallel capillary tubes, in each of which Taylor-Aris dispersion is operative. If the network is long enough then, since there is no interaction between the parallel tubes, equation (11) is applicable to each long tube (made of  $L/b$  elementary tubes). Thus  $D_L/D$  depends quadratically on  $Pe$ . The transverse dispersion coefficient  $D_T$  is still zero, because there is no interaction between the parallel tubes.

Next, we assume that diffusion into the vertical bonds cannot be neglected, but there is only convective dispersion in the horizontal bonds. Thus, dispersion is caused by convection in a bundle of parallel long capillary tubes, with molecular diffusion transferring the tracer particles from one long tube to another via the vertical bonds in which there is no flowing fluid. However, the precise dependence of  $D_L$  on the Péclet number depends on the strength of the flow field and that of molecular diffusion in the vertical bonds. If the timescale  $t_{DE}$  for diffusion is much smaller than the convective time  $t_c$  to cross the network at  $x = L$ , we may neglect convection and dispersion coefficients will essentially be equal to the molecular diffusivity  $D_p$ . For an  $L^d$  cubic network  $t_{DE}$  is given by  $t_{DE} = Mb^2/2D$ , where  $M = (d-1)L^2 + (L-1)^2$  and  $t_c = L/V_a$ . Thus, if one defines a macroscopic Péclet number by  $Pe = LV_a/D$ , the condition  $t_{DE} \ll t_c$  leads to  $Pe \ll 2L^2/(Mb^2)$ . Therefore, for a finite network of a given size, we can determine the limiting  $Pe$  below which diffusion dominates the mixing process. On the other hand, for  $Pe \gg 2L^2/(Mb^2)$ , convection and diffusion are both important and both  $D_L/D$  and  $D_T/D$  are quadratically dependent on  $Pe$ .

The intermediate regime in which there is molecular diffusion between the streamlines in the horizontal bonds is even more interesting. Now, one has Taylor-Aris dispersion in long parallel tubes with molecular diffusion carrying the fluid particles

from one long tube to another (via the vertical bonds). This problem is similar to that studied by Aris (1959) who considered Taylor-Aris dispersion in long tubes to which are connected tubes of varying lengths and in which there is no flowing fluid. Thus, the side tubes communicate with the main tube only by molecular diffusion (similar to dead-end bonds). Aris (1959) derived an expression for the longitudinal dispersion coefficient which, for the present problem, simplifies to

$$D_L = D + f_v \frac{R^2 V_a^2}{D} + \frac{v^2 V_a^2}{3D(1+v)^2} \quad (51)$$

where  $v$  is the volume of the vertical bonds per unit volume of the long tubes. Here  $f_v$  is a numerical factor and is given by

$$f_v = \frac{1+6v+11v^2}{48(1+v)^2} \quad (52)$$

so that, for  $v=0$ , equation (51) reduces to (11) as it must. One immediate result of equation (51) is that diffusion into dead-end bonds *increases* dispersion coefficients. This is reasonable, because in this network dispersion is caused only by the fluid particles spending time in the slowly moving regions (since no structural disorder or a chaotic velocity field exists in this network). The second conclusion that one can draw from equation (51) is that, if there are dead-end bonds in the network and molecular diffusion is slow (but cannot be neglected),  $D_L/D$  is proportional to  $Pe^2$ . As we shall show below, for dispersion near the percolation threshold, where there is a large fraction of dead-end bonds,  $D_L/D$  is still proportional to  $Pe^2$ . Thus, dispersion in the ordered networks considered here can help us understand dispersion in a disordered percolation network near  $X_c$ , which is a totally different and far more complicated system. It is clear that in the present system  $D_T/D$  is also proportional to  $Pe^2$ .

Consider now the case in which the network is very weakly disordered. For example, consider a network in which only a few vertical bonds have different effective radii, with the radii of the rest of the tubes being the same. If we consider the  $i$ th row (or plane) of the tubes that are in the direction of macroscopic flow (i.e. the  $x$  direction), the flow field in all of these tubes is essentially the same. We denote by  $V_{ai}$  the mean velocity in these tubes. It is obvious that the mean velocity  $V_{aj}$  of the tubes in the  $j$ th row is not equal to  $V_{ai}$  (although the difference may be small) because of the presence of those few vertical bonds, the effective radii of which are different from the rest. Therefore, the network is essentially made of a bundle of long tubes in which the mean speeds are  $V_{a1}, V_{a2}, \dots$ . These tubes interact with one another via the vertical tubes in which there is very little, if any, flowing fluid. A tracer particle that is injected into this network travels with the mean speed  $V_{a1}$ , then diffuses into one of the vertical bonds until it reaches another tube with the mean speed  $V_{a2}$  and continues its journey until it diffuses into another vertical tube, and so on. Thus, the problem is exactly similar to that analysed in § 2 by a CTBW formulation, where the diffusion times in the vertical tubes correspond to the waiting times. In a sense, each long horizontal tube serves as an effective streamline. Therefore, we expect  $D_L/D$  to depend quadratically on  $Pe$  and our computer simulations support this. If the network is totally disordered in the sense that the effective radii of the tubes are distributed according to a PDF  $f(R)$ , then dispersion is dominated by the slowest tubes. This case is studied in § 4.3 and will not be discussed here any further.

We now consider dispersion in fully connected networks in which the macroscopic pressure gradient is applied at  $45^\circ$  to the two (or three) pore directions. Dispersion in such networks is similar to that we investigated above, except that there are no pores that carry no flow. Thus, most of our discussion above is equally applicable to dispersion in such networks. In the next sub-section, we investigate dispersion in the backbone of the networks. All of our results that are presented in §§ 4.3, 4.4 and 5 are for dispersion in networks in which the macroscopic pressure gradient is applied at  $45^\circ$  to the two (or three) pore directions.

#### 4.3. Dispersion in the backbone of random networks

At the outset we can dispose of the question of how the longitudinal dispersion coefficient  $D_L$  depends on the axial position in the porous medium. There have been many experimental measurements of  $D_L$  in packed beds and in porous media (e.g. Harleman and Rumer 1963, Edwards and Richardson 1968, Salter and Mohanty 1982, Delshad *et al* 1985). Implicit in these experimental studies is the assumption that  $D_L$  is constant and depends only on Reynolds number and Péclet number and is independent of position in the porous medium. However, as we showed in §§ 2 and 4 for dispersion in capillary tubes and in networks,  $D_L$  can be strongly dependent on the length of the system (see equation (10)) and, in their work on convective diffusion in capillary tubes, Taylor (1953) and Aris (1956) pointed out carefully that their result would be valid if the length of the tube is long enough and only after a sufficiently long time has passed. More recently, Han *et al* (1985) measured  $D_L$  (and  $D_T$ ) at various axial positions in a packed bed and found that, unless the dispersion length satisfies a certain constraint, which was found to depend on Péclet number,  $D_L$  would be strongly dependent on the axial position in the bed.

We simulated dispersion in the square and simple cubic networks with distributed pore sizes. We then computed  $D_L$  at various (longitudinal) positions in the network. All of the results in this paper are dimensionless (see Sahimi *et al* (1986b) for converting the dimensionless quantities to dimensional ones). Figure 3 presents our results for the square network. At short distances  $D_L$  rises sharply, but the rate of increase falls

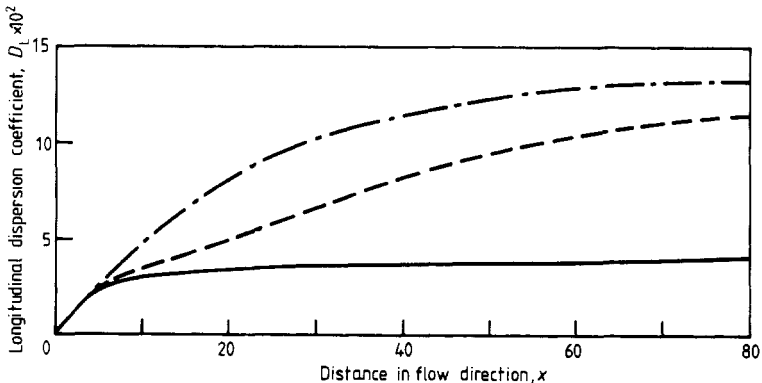
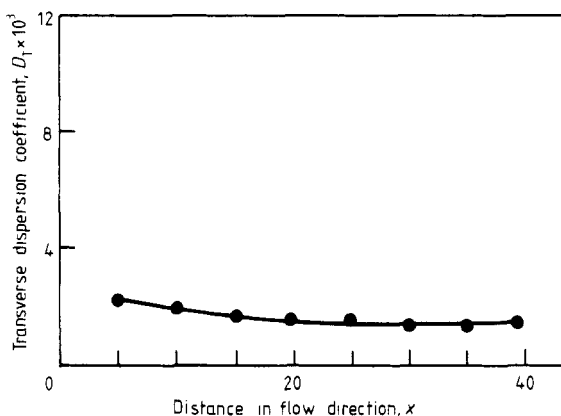


Figure 3. The variations of  $D_L$  with position in the direction of macroscopic flow in the square network. (—) denotes  $D_L$  based on the random walk model with the transition probabilities proportional to the local pore fluxes, (---) denotes  $D_L$  in which the transition probabilities are equal in all directions, while (-·-) denotes  $D_L$  in which diffusion between streamlines has been taken into account.

off rapidly and, consequently, for large distances  $D_L$  increases with position very slowly if at all. This figure is in good qualitative agreement with the experimental results of Han *et al* (1985). This agreement is an indication of the validity of our MC approach. Moreover, the values of  $D_L$  which were computed by using equations (6) and (40) were in total agreement with each other. This means that the dispersion process simulated here can be described by a macroscopic CDE. Similar results were found for dispersion in simple cubic networks. On the other hand, the transverse dispersion coefficient  $D_T$  showed very little variation with position in the network, as demonstrated in figure 4, where we present the results for dispersion in the simple cubic network. This is also in qualitative agreement with the experimental results of Han *et al* (1985). To make the agreement quantitative, one needs to have detailed information about the morphology of the porous medium, which is not available to us.



**Figure 4.** The variations of  $D_T$  with position in the direction of macroscopic flow in the cubic network.

To demonstrate the significance of the slow pores that carry very little flow, we also simulated dispersion in networks in which the velocity distribution within each bond was neglected and the particles were moved with the mean velocity of each bond. Perfect nodal mixing was also assumed, as discussed above. We then simulated two distinct cases. In the first case, a tracer particle selects a bond with a probability proportional to the flow rate in that bond. In the second case, a tracer particle selects a bond at random (i.e. if there are  $z$  bonds that carry flow away from a node, the particle selects one of them with the probability  $1/z$ ). Thus, in these cases, molecular diffusion within a bond is totally absent and dispersion is only the result of convective mixing. The results are also shown in figure 3. As can be seen,  $D_L$  attains its smallest value when perfect nodal mixing is assumed and a bond is selected with a probability proportional to its flow rate. However,  $D_L$  increases when a bond is selected at random. Finally,  $D_L$  attains its largest value when velocity distribution within bonds and diffusion between streamlines in the slowest bonds are not ignored. This is of course because of the fact that, in the third case, the bonds that carry very little flow (i.e. the bonds with the largest transit times) are sampled very efficiently and, therefore,  $D_L$  attains its maximum value, whereas they are not sampled sufficiently in the first case and thus  $D_L$  is minimum.

Next, we determined the dependence of dispersion coefficients on the Péclet number  $Pe$ . To vary  $Pe$ , one can vary molecular diffusivity  $D$  or the mean flow velocity by changing the macroscopic pressure gradient that is imposed on the network in the  $x$  direction. Parabolic velocity profile within each tube (whose effective radius is selected from PDF  $f(R)$ ) and molecular diffusion between streamlines were assumed, as described above. The results for  $D_L$  and  $D_T$  are presented in figures 5 and 6, respectively. (The results shown are the average values over many realisations. However, the variations of the values  $D_L$  and  $D_T$  for different realisations were somewhat large.) If one assumes that  $D_L/D \sim Pe^{\beta_L}$  and  $D_T/D \sim Pe^{\beta_T}$ , then a fit of the curves to such power laws yields

$$\beta_L \approx 1.2 \pm 0.1 \tag{53}$$

$$\beta_T \approx 0.95 \pm 0.05. \tag{54}$$

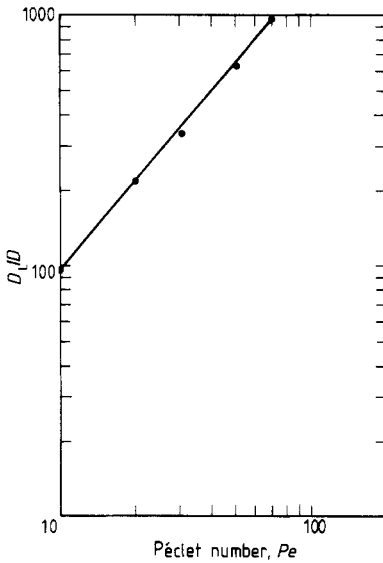


Figure 5. The dependence of  $D_L/D$  on the Péclet number  $Pe$ .

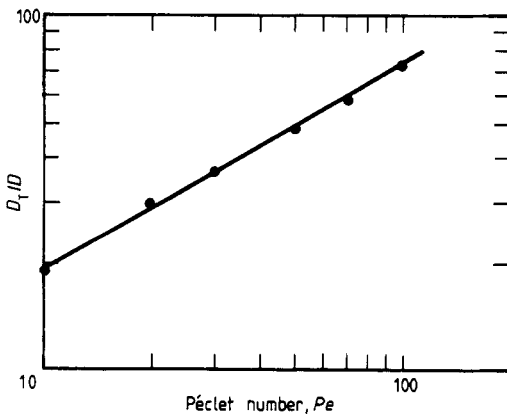


Figure 6. The dependence of  $D_T/D$  on the Péclet number  $Pe$ .

These results are in good agreement with the available experimental data which are mostly in the ranges  $1.15 \leq \beta_L \leq 1.25$  and  $0.9 \leq \beta_T \leq 1$ . They are also consistent with the more rigorous computations of Jerauld (1985). On the other hand, if we assume that  $D_L/D \sim Pe \ln Pe$ , the results of figure 5 can also be fitted to this equation with a high degree of accuracy. This is in agreement with the theoretical predictions of de Josselin de Jong (1958), Saffman (1959) and Koch and Brady (1985). These authors have predicted that, if there are regions of the pore space in which the fluid is moving very slowly (such as a boundary layer close to solid surfaces of the pores, or pores that are nearly perpendicular to the macroscopic pressure gradient),  $D_L/D$  will grow with  $Pe$  as

$$D_L/D \sim Pe \ln Pe. \quad (55)$$

Equation (55) is often valid if  $5 \leq Pe \leq 100$ .

The dispersion process investigated above is caused by the random geometry (sizes of the pores) of the pore space and its interaction with molecular diffusion. We now examine the effect of varying the topology of the pore space. To this end, we investigate dispersion processes on the backbone of a percolation cluster. Thus, each bond is assumed to be open to flow with the probability  $X$  (i.e. the fraction of open bonds is  $X$ ). The open bonds either have the same effective radius or their radii are distributed according to PDF  $f(R)$ . The computed values of  $D_L$  for the simple cubic network are shown in figure 7. As the percolation threshold  $X_c$  is approached, the longitudinal dispersion coefficient  $D_L$  increases. However,  $D_L$  appears to attain a maximum at a point close to  $X_c$  and ultimately vanishes at  $X_c$ , whereas for the square network  $D_L$  appears to diverge without bounds (see figure 12 below).

To understand the results of figures 7 and 12, we develop a scaling theory for  $D_L$  near  $X_c$ . The volume fraction of the fluid flowing in the backbone is proportional to

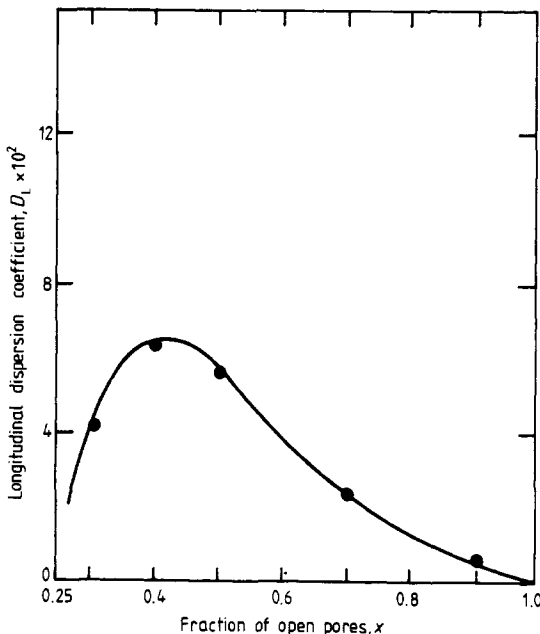


Figure 7. The variations of  $D_L$  with the fraction of open pores in a simple cubic network.



$X^B$ . Thus, because the mean velocity of fluid particles is proportional to  $K/X^B$ , we obtain

$$V_a \sim (X - X_c)^{\mu - \beta_B} \quad (56)$$

which is similar to equation (43). Consider now the purely convective limit in which  $D_L$  depends linearly on  $V_a$  and, therefore,  $D_L \sim L_\xi V_a$ , where  $L_\xi$  is a characteristic length which is often called dispersivity.  $L_\xi$  may depend on the structure of the porous medium, direction relative to mean flow and the flow field. Since in a percolating system the only relevant length scale, aside from the length of the bonds, is the correlation length  $\xi_p$ , we must have  $D_L \sim \xi_p V_a$ . If we combine this equation with equations (37) and (56), we obtain

$$D_L \sim \xi_p^{1 - (\mu - \beta_B)/\nu}. \quad (57)$$

In a finite network of length  $L$ ,  $\xi_p$  cannot exceed  $L$ . Thus, by an argument similar to that used for equation (46), we must have

$$D_L \sim L^{1 - \theta_B} \quad (58)$$

which is valid for  $L < \xi_p$ . Equation (58) implies that one has anomalous length-dependent dispersion. (Compare equation (58) with  $D_L \sim L^{-\theta_B}$ , which holds in the limit  $Pe \rightarrow 0$ .) Therefore, if we substitute the estimates of  $\beta_B$ ,  $\mu$  and  $\nu$  in equation (58), we find that  $D_L \sim L^{0.42}$  for two-dimensional networks, whereas  $D_L \sim L^{-0.19}$  for three-dimensional ones. Note that, according to our scaling theory,  $D_L$  vanishes in three dimensions whereas it diverges in two-dimensional networks. This is presumably caused by the structure of the backbone. The backbone is made of tortuous flow paths involving links and blobs. Links are the bonds that connect the blobs and the remaining multiply connected bonds aggregate together in blobs. The blobs are very dense in two dimensions, providing a wide variety of paths for the fluid particles with a broad FPTD. Because of this,  $D_L$  appears to diverge in two-dimensional networks. However, the blobs are not very dense in three-dimensional networks and the FPTD is not very broad. As a result,  $D_L$  appears to vanish in three dimensions. Note also that an equation such as (57) or (58) cannot be predicted by a CDE and, therefore, an approach such as that of Koch and Brady (1985) cannot be used to predict the power-law dependence of dispersion coefficients on  $L$  or  $(X - X_c)$  at or near  $X_c$ . If we do not neglect molecular diffusion between streamlines in the slowest regions of the backbone (but neglect diffusion into the dead-end bonds) then, according to equation (55), equations (57) and (58) would be modified by a logarithmic term, which is usually ignored in scaling theories of transport processes, because it does not change the form of a power law, since the logarithmic vanishing or divergence of a quantity is slower than any power law. To check the validity of equation (58), we simulated dispersion in the backbone of the square and simple cubic networks at  $X = X_c$ . The results for the square and cubic networks are presented, in log-log plots, in figures 8 and 9. The slopes of the straight line agree very well with the prediction of equation (58), confirming its validity. We also simulated the same process at  $X = X_c$ , but took into account diffusion, in the slowest tube, between the streamlines. Although our results showed large scatter, we found that for the square network  $D_L \sim L^{0.55}$ , somewhat larger than that predicted by equation (58). This is, of course, caused by the logarithmic corrections discussed above.

The behaviour of the transverse dispersion coefficient  $D_T$  in flow through the backbone of the simple cubic network is shown in figure 10. Similar to  $D_L$ , the

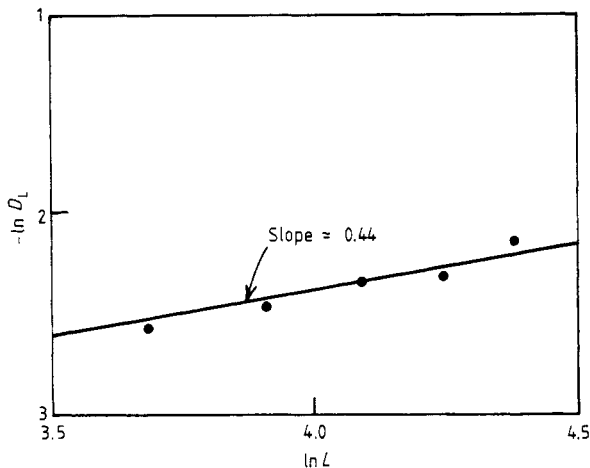


Figure 8. The dependence of  $D_L$  on the length  $L$  of the square network (for flow through the backbone) at  $X_c$ .

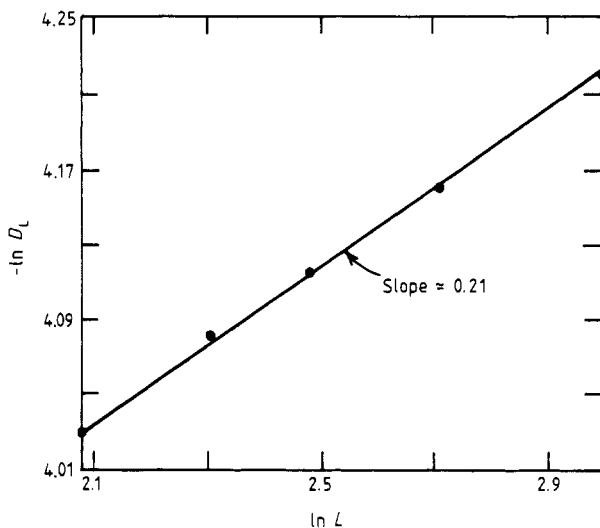


Figure 9. The dependence of  $D_L$  on the length  $L$  of the simple cubic network (for flow through the backbone) at  $X_c$ .

transverse dispersion coefficient appears to vanish at  $X_c$ . Since, from a macroscopic point of view, transverse dispersion is similar to a purely diffusion process and it is not driven by a macroscopic flow field (since the mean flow velocity is zero in the transverse directions), it is not surprising that  $D_T$  vanishes at  $X_c$ , since the diffusivity of a percolating network vanishes at  $X_c$ . Moreover, one may argue that near  $X_c$  the paths that the particles take are so tortuous that the particles cannot distinguish between longitudinal and transverse directions, so that an equation similar to (58) may also hold for  $D_T$ , albeit with a different prefactor that is implied by the right-hand side of equation (58).

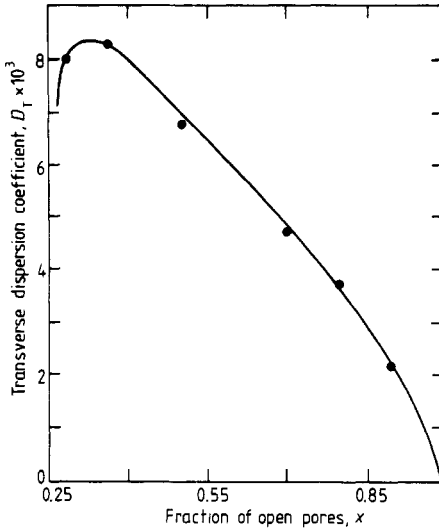


Figure 10. The variations of  $D_T$  with the fraction of open pores in flow through the backbone of the simple cubic network.

From equation (58) we can obtain the fractal dimension of the tracer particles for the anomalous dispersion regime. In equation (58), similar to equation (46), the length  $L$  can also be the mean distance  $\zeta$  from the origin of motion that the fluid particles have travelled at time  $t$ . Therefore, we can rewrite equation (58) as  $d\zeta^2/dt \sim \zeta^{1-\theta_B}$  which, after integration, yields  $\zeta^2 \sim t^{2/(1+\theta_B)}$ . This means that the fractal dimension  $d_w$  is given by

$$d_w = 1 + \theta_B. \tag{59}$$

Equation (59) should be compared with the corresponding fractal dimensions of the fluid particles in the limit  $Pe \rightarrow 0$ . In these cases, for dispersion in the backbone we had  $d_w = 2 + \theta_B$ , whereas for dispersion in the sample-spanning cluster we had  $d_w = 2 + \theta$ , as discussed above. Both of these are larger than the fractal dimension given by equation (59), which means that the movement (and thus mixing) of the tracer particles, in the limit  $Pe \rightarrow 0$ , is slower than linear. This is not totally surprising as the flow field (when  $Pe > 0$ ) generates a net bias on the backbone of the cluster, which makes it easier for the fluid particles to get away from the origin of their motion. We also propose that for the present case  $P(\xi, t)$  is given by (see also Sahimi 1987)

$$P(\xi, t) \sim A_1 t^{-\frac{1}{2}d_s} \exp \left[ -\alpha_1 \left( \frac{|x - x_0 - \langle x \rangle|}{t^{\nu_d}} \right)^{\nu_p} - \alpha_2 \left( \frac{|y - y_0|}{t^{\nu_d}} \right)^{\nu_p} - \alpha_3 \left( \frac{|z - z_0|}{t^{\nu_d}} \right)^{\nu_p} \right]. \tag{60}$$

Here  $\nu_p = d_w / (d_w - 1)$ ,  $\nu_d = 2d_w^{-1}$ ,  $d_s = d_B / d_w$ ,  $\alpha_1, \alpha_2$  and  $\alpha_3$  are constant and  $d_B = d - \beta_B / \nu$  is the fractal dimension of the backbone and thus  $d_B = \frac{153}{96} \approx 1.6$  in two dimensions and  $d_B \approx 1.91$  in three dimensions. Equation (60) reduces to (3) for macroscopically diffusive dispersion (with  $d_s = 3$  and  $\nu_d = \nu_p = 2$ ). We point out that, according to equation (59),  $d_w (d = 2) \approx 1.57$ , which implies that  $\zeta^2 \sim t^{1.3}$ , i.e. mixing of fluid particles in two-dimensional media is faster than is predicted by a CDE and a Gaussian distribution, whereas it is slower in three dimensions since  $d_w (d = 3) \approx 2.19$  and  $\zeta^2 \sim t^{0.9}$ . Equation (3) predicts that  $\zeta^2 \sim t$  in both two and three dimensions. To check the validity of (60), we performed MC simulations in the square network and

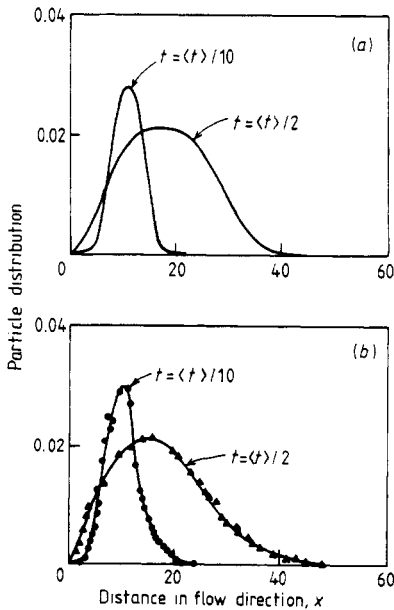
computed  $P(\xi, t)$ . The results are shown in figure 11, where we present the simulation results (for the  $x$  direction) together with the predictions of equation (60). The constants  $A_1$  and  $\alpha_1$  were determined by using two data points from the simulation data. The agreement is very good, giving strong support to the validity of equation (60). Note that the form of equation (60) suggests that the governing equation of dispersion, of which equation (60) is presumably the solution, has a far more complicated form than a CDE. The work of Guyer (1985), who proposed equation (48), indicates that the governing equation of diffusion in the anomalous regime may involve integrals over both space and time, and we may anticipate the same phenomenon for anomalous dispersion. On the other hand, with the aid of equation (6), it is easy to show that for the anomalous (length-dependent) dispersion, we have

$$\langle t^n \rangle \sim L^{1+n\theta_B} \quad (61)$$

which means that the scaling with  $L$  of  $\langle t^n \rangle$  ( $n > 1$ ) cannot be obtained from that related to that of  $\langle t \rangle$ , in contrast with the limit  $Pe \rightarrow 0$  (equation (50)).

#### 4.4. Dispersion in the sample-spanning cluster of random networks

We now discuss dispersion in flow through random networks in which diffusion into the dead-end bonds is also allowed. The presence of dead-end bonds introduces into the problem a new timescale  $t_{DE}$ , which is the time that a fluid particle spends in a dead-end branch of the network. If molecular diffusion in a dead-end branch is relatively fast, the dead-end branches cannot have much effect and, therefore, dispersion follows essentially the same laws as those in the backbone which we discussed above. Therefore, we only discuss the case of slow molecular diffusion. As the percolation threshold is approached, many dead-end bonds and branches appear which, in case



**Figure 11.** The probability density  $P(\xi, t)$  for flow through the backbone of the square network. (a) The predictions of equation (60), (b) the simulation data.

of slow molecular diffusion into such branches and bonds, cause an increase in dispersion coefficients, as discussed in § 4.2. This is illustrated in figure 12, where we present the results of the longitudinal dispersion coefficient in the square network. As can be seen, near  $X_c$  the values of  $D_L$  are larger than those for dispersion in the backbone of the network, and again  $D_L$  appears to diverge as  $X_c$  is approached. However, it is the largest dead-end branch that dominates the dispersion process and short dead-end branches cannot have a significant effect. This can also be inferred from the results of Aris (1959) discussed above. In his formulation of the problem, the length of the dead-end tubes is a distributed quantity. However, from his general formula for  $D_L$  (equation (28) of his paper) it can be easily seen that the longest tube has a dominant role. Near  $X_c$  diffusion in a dead-end branch is anomalous, because the length of this branch is smaller than  $\xi_p$  (Ohtsuki and Keyes 1984). Therefore the diffusivity in this branch obeys equation (46) and the timescale  $t_{DE}$  is given by  $t_{DE} \sim L^2/D_p \sim L^2/L^{-\theta}$  or

$$t_{DE} \sim L^{2+\theta} \tag{62}$$

which must be valid for any  $L < \xi_p$ . For  $L \gg \xi_p$ , equation (62) becomes  $t_{DE} \sim \xi_p^{2+\theta} \sim \xi_p^2/D_p$ . de Gennes (1983) has suggested that  $D_L$  diverges as  $X_c$  is approached according to the following formula:

$$D_L \sim (V_a \xi_p)^2 / D_p \tag{63}$$

which is similar to Taylor-Aris dispersion in which the radius  $R$  and the microscopic diffusivity  $D$  have been replaced by the correlation length and the macroscopic diffusivity  $D_p$ , respectively. We offer here a simple derivation of the result of de Gennes (1983). From the work of Aris (1959) we know that  $D_L \sim V_a^2$ , and from dimensional

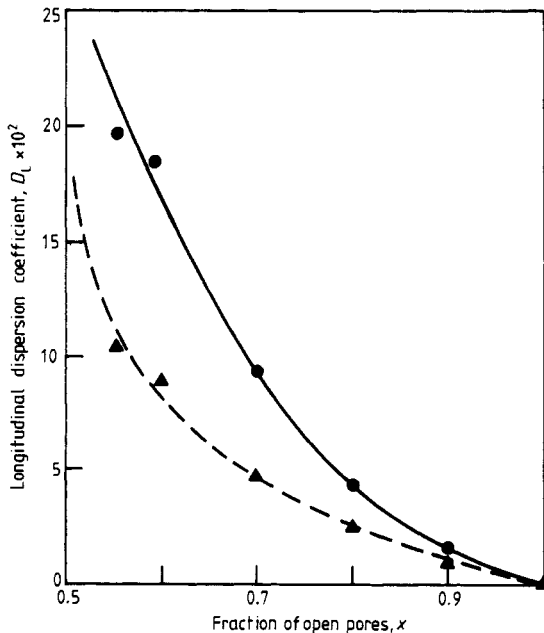


Figure 12. The dependence of  $D_L$  on the fraction of open pores of the square network. ●, with dead ends; ▲, without dead-ends.

analysis we are led to write  $D_L \sim V_a^2 \tau$ , where  $\tau$  is a characteristic timescale. Since, in the present case, the timescale  $t_{DE}$  for diffusion into a dead-end branch is supposed to be the dominant timescale (because  $D_L$  is dominated by the contributions from dead-end branches), one must have  $\tau \sim t_{DE}$  and, therefore,  $D_L \sim V_a^2 \xi_p^{2+\theta} \sim V_a^2 \xi_p^2 / D_p$ , which is identical with equation (63). Note that if diffusion into the dead-end bonds is included, then the mean flow velocity  $V_a$  is proportional to  $K/X^A$  (and not  $K/X^B$ ), which means that  $V_a \sim \xi_p^{-\theta}$ . If we combine this with equations (46) and (63), we obtain  $D_L \sim \xi_p^{2-\theta}$ . Thus, for any length scale  $L < \xi_p$ , we have

$$D_L \sim L^{2-\theta} \tag{64}$$

Equation (64) implies again that for any  $L < \xi_p$  we have anomalous length-dependent dispersion which *cannot* be described by a CDE. Since  $\theta < 2$  for two- and three-dimensional systems, equation (64) implies that  $D_L$  diverges with  $L$ , whereas both equations (46) and (58) indicate that  $D_L$  vanishes with  $L$  in three-dimensional systems. If we substitute the values of  $\theta$  in equation (64), we obtain  $D_L \sim L^{1.1}$  and  $D_L \sim L^{0.2}$  for two- and three-dimensional networks, respectively. To test these predictions, we have carried out extensive MC simulations at the percolation threshold of the square and simple cubic networks. The results are presented in figures 13 and 14, respectively, and they are in good agreement with the theoretical predictions.

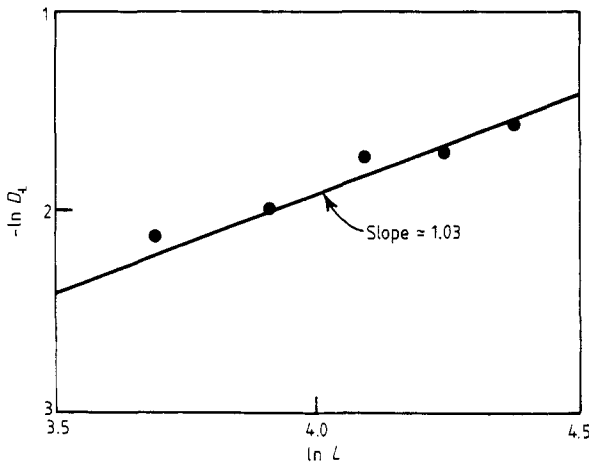


Figure 13. The dependence of  $D_L$  on the length  $L$  of the square network at  $X_c$ , in which diffusion into the dead-end pores has been taken into account.

Several new results are immediately obtained from equation (64). If we employ the same method that we used to derive equation (59), then for any length scale  $\zeta < \xi_p$  we may write  $d\zeta^2/dt \sim \zeta^{2-\theta}$  and obtain  $\zeta^2 \sim t^{2/\theta}$ , which means that

$$d_w = \theta \tag{65}$$

which should be compared with equation (59) and with  $d_w = 2 + \theta$ , which is the fractal dimension of the fluid particles in the limit  $Pe \rightarrow 0$ . Thus equation (65) implies that  $\zeta^2 \sim t^{2.3}$  and  $\zeta^2 \sim t^{1.1}$ , in two- and three-dimensional systems, different from  $\zeta^2 \sim t$  which is predicted by the CDE and equation (3). It also implies that the spectral dimension of the tracer particles is larger than two (Sahimi 1987), in contrast with the limit  $Pe \rightarrow 0$ . Equation (63) also has some implications for the moments  $\langle t^n \rangle$  of the FPTD. If we

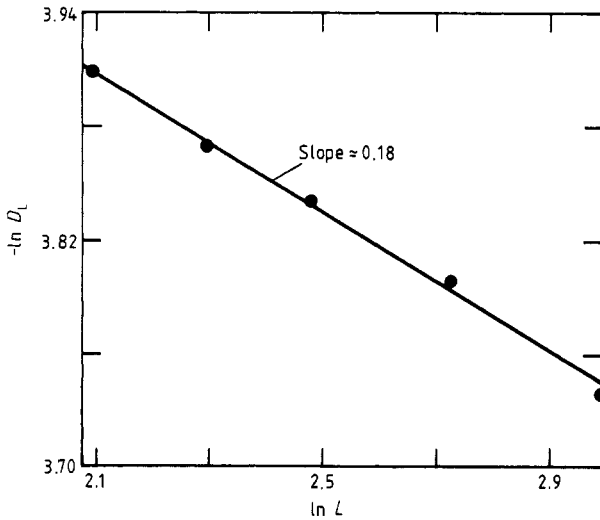


Figure 14. The dependence of  $D_L$  on the length of the simple cubic network at  $X_c$ , in which diffusion into the dead-end pores has been taken into account.

neglect  $\langle t \rangle^2$  in equation (6) (which is supported by our simulations shown in figure 15), we can rewrite it as  $\langle t^2 \rangle \sim LD_L / V_a^3$  which, in view of equation (63), yields

$$\langle t^2 \rangle \sim L^{3+2\theta} \tag{66}$$

which is in agreement with the results of Koplik *et al* (1988). These authors have derived a general formula for  $\langle t^n \rangle$ , which is given by

$$\langle t^n \rangle \sim L^{n(\theta+2)-1}. \tag{67}$$

Therefore equation (67) predicts that  $\langle t \rangle \sim L^{\theta+1}$ , which can also be obtained directly from equation (5). Note that, according to these formulae, the scaling of  $\langle t^n \rangle$  ( $n > 1$ ) with  $L$  is *not* directly related to  $\langle t \rangle$  (i.e.  $\langle t^n \rangle \neq \langle t \rangle^n$ ) which, as was mentioned in the introduction (see also Koplik *et al* 1988), is characteristic of anomalous dispersion

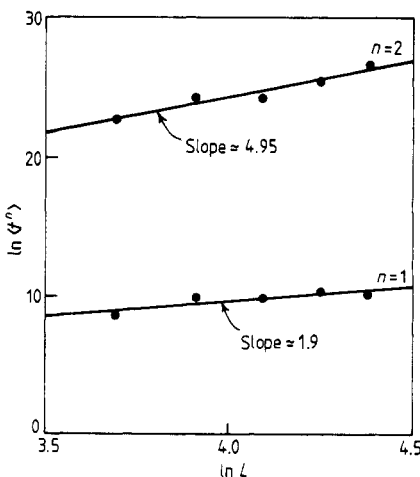
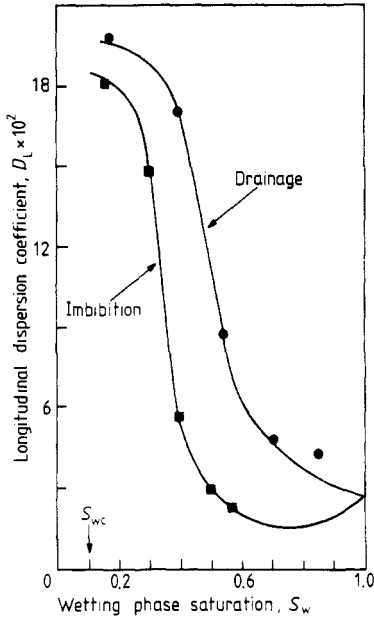


Figure 15. The dependence of  $\langle t^n \rangle$  on the length  $L$  of the square network at  $X_c$ .

(compare equations (50), (61) and (67)). If we use  $\theta \approx 0.87$  for two-dimensional networks, we obtain  $\langle t \rangle \sim L^{1.87}$  and  $\langle t^2 \rangle \sim L^{4.75}$ , which indicate a large difference between the two moments of the FPTD. To test these formulae, we present in figure 15 the moments  $\langle t \rangle$  and  $\langle t^2 \rangle$  and the results appear to be consistent with the predictions. Similar results were obtained for the simple cubic network (for which  $\langle t \rangle \sim L^{1.78}$  and  $\langle t^2 \rangle \sim L^{6.55}$ ) and thus are not shown here.



**Figure 16.** Longitudinal dispersion coefficient  $D_L$  in the wetting phase in flow through the cubic network.

Finally, we propose that an equation similar to (60) should be valid for any  $|\xi| < \xi_p$ , if we use  $d_s = 2d_f/d_w$ ,  $\nu_p = d_w/(d_w - 1)$  and  $\nu_d = d_w^{-1} = \theta^{-1}$ , where  $d_f$  is the usual fractal dimension of the sample-spanning cluster. Our computer simulations support the validity of such a generalisation of equation (60), and since the agreement between simulations and the predictions is essentially as good as that shown in figure 11, they are not presented here.

## 5. Dispersion in two-phase flow through porous media

In the previous section, we studied dispersion in single-phase flow in porous media and investigated the effect of the disordered morphology of the pore space on dispersion. We now turn our attention to dispersion in flow of two immiscible fluids (e.g. oil and water) in a porous medium. Dispersion in multiphase flow depends strongly on the distribution of the immiscible phases in the pore space. As the saturation of a phase, i.e. the volume fraction of the pore space occupied by the phase, decreases that phase may ultimately lose its connectivity because of disconnections brought about by capillary instability. Once a fluid phase loses its macroscopic connectivity, it occupies only isolated clusters of pores and its saturation falls below a percolation threshold.



Thus the process of displacing and disconnecting a fluid phase is essentially a percolation phenomenon. However, in contrast with random percolation in which a pore is selected at random and is disconnected from the sample-spanning cluster, a given phase does not lose its connectivity by a totally random process. In slow flow of two immiscible fluids, the velocity, capillarity and pore space morphology determine what space is occupied by a given phase and how this fluid phase loses its connectivity, if the porous medium is invaded by another immiscible fluid.

A porous medium is strongly wet if the pore surfaces have a distinct preference for one of the fluids, the wetting fluid, to the other. In such a porous medium, the contact angle on the solid surface as measured through the wetting phase would be zero or nearly so. For intermediately wet porous media this contact angle is between  $50^\circ$  and  $140^\circ$  (Morrow and McCaffery 1978). A mixed-wet porous medium is one in which some of the pores are strongly wet by one fluid and the other pores are strongly wet by the other fluid. The pressures  $P_i$  and  $P_j$  of phases  $i$  and  $j$  are related to their saturation  $S_i$  by capillary pressure  $P_c(S_i)$ , where  $P_c(S_i) = P_i - P_j$ . The capillary pressure  $P_c$  is generally not zero because the interfacial tension exerts a pressure increase across the curved interface. The distribution of phases, the relative permeabilities and  $P_c$  depend on the saturation of each phase, saturation history (i.e. the process by which that saturation has been reached), the morphology and wettability of the porous medium. In strongly wet media, if the saturation of the non-wetting phase increases because of its displacing the wetting phase, a process that is usually called drainage, it preferentially invades the larger pores that are accessible to it. On the other hand, if the saturation of the wetting phase increases because of its displacing the non-wetting phase, a process that is usually called imbibition, the wetting phase invades the smaller pores that are accessible to it. In intermediately wet porous media, the invading phase always occupies the largest accessible pores. These matters have been fully discussed by Heiba (1985).

The above discussion indicates that, before dispersion in multiphase flow can be investigated, the two fluid distributions and the subset of pore space accessible to and occupied by a given phase must be determined. Two different procedures have been developed to accomplish this task. The first one is the so-called invasion percolation model (Chandler *et al* 1982, Wilkinson and Willemsen 1983). In this model each site of a network is assigned a random number (which represents the resistance to flow), selected from a given PDF, and at each time step the site on the interface with the smallest random number is invaded by the invading fluid. This simulates the drainage process discussed above, because the largest pores offer the least resistance to an invading fluid. The process continues until the invading phase displaces enough fluid from the porous medium to reach the opposite surface of the medium. At this point and beyond one obtains the macroscopic distribution of the two immiscible fluids, both of which are flowing through the porous medium. One can then study dispersion in each of the fluid phases. As may be clear, invasion percolation is an inherently dynamical process. The second method, which was developed by Heiba (1985) (see also Heiba *et al* 1982), uses the concepts of random percolation processes to model the distribution of immiscible fluids in porous media. Since random percolation processes are usually static phenomena, the model of Heiba (1985) is also a static one. We have used both methods and have obtained different results, which are discussed below.

In the percolation theory of Heiba *et al* (1982) the key parameter defining the displacement in both drainage and imbibition is the capillary pressure. As drainage

proceeds, the current value of  $P_c$  determines the minimum effective bond radius  $R_d$  of pores into which non-wetting fluid can penetrate. If we consider a strongly wet porous medium, then the total fraction  $X_d$  of bonds that are allowed to the non-wetting phase is given by

$$X_d = \int_{R_d}^{\infty} f(R) dR \quad (68)$$

and the distribution of the radii of the bonds that are allowed to the non-wetting phase is

$$f_{nw,d}(R) = \begin{cases} f(R)/X_d & R \geq R_d \\ 0 & R < R_d. \end{cases} \quad (69)$$

Similarly, the fraction of bonds that are invaded by the wetting phase during imbibition is given by

$$X_i = \int_0^{R_i} f(R) dR \quad (70)$$

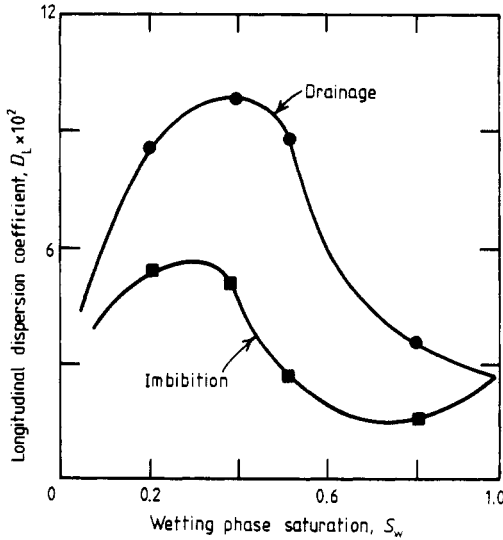
where  $R_i$  is the effective radius of the largest bond that is penetrated by the wetting phase. Therefore, in imbibition the distribution of the radii of bonds that are open to the wetting phase is

$$f_{w,i}(R) = \begin{cases} f(R)/X_i & R < R_i \\ 0 & R \geq R_i. \end{cases} \quad (71)$$

Thus, the procedure to simulate dispersion in two-phase flow is as follows. We first distribute the effective radii of *all* bonds according to the distribution  $f(R)$ . We then identify all bonds, the effective radii of which are larger (smaller) than  $R_d$  ( $R_i$ ), and set the effective radii of the remaining bonds to be zero. This creates the sample-spanning cluster of bonds that are occupied by the non-wetting (wetting) phase during drainage (imbibition). We then determine the flow field and perform our MC experiments of dispersion processes. Heiba (1985) gives formulae for the distributions of the effective radii of bonds that are occupied by different phases for intermediately wet and mixed-wet media, which can be used for MC simulations.

In figure 16 we present the predicted longitudinal dispersion coefficient in the wetting phase during imbibition and drainage. We neglected the possibility of partitioning of the tracer particles between phases, i.e. we allowed no mass transfer between the two phases. However, diffusion into the dead-end bonds and between the streamlines in the smallest bonds was allowed. As can be seen, as the residual saturation  $S_{wc}$  is approached, i.e. as the saturation at which the wetting phase loses its macroscopic connectivity is neared, the longitudinal dispersion coefficient appears to diverge. This is in agreement with the prediction of equation (63), which is expected because near  $S_{wc}$  a relatively large number of bonds in the sample-spanning cluster are dead-end and, thus, according to equation (63),  $D_L$  must diverge. In these simulations we neglected the thin films of the wetting fluid that can coat the surfaces of the pores occupied by the non-wetting phase. We found that, if we do not neglect such thin films, the behaviour of the longitudinal dispersion coefficient is different from that shown in figure 16. To take the effect of such thin films into account, we assumed that the surfaces of the pores that were occupied by the non-wetting phase are coated with a thin film of the wetting phase and we assigned a hydraulic conductance to such thin films in each pore that was small compared to the total hydraulic conductance of the

pore. One immediate effect of such thin films is that the wetting phase never loses its macroscopic connectivity and its apparent residual saturation  $S_{wc}$  is essentially zero. We then observed that the longitudinal dispersion coefficient reaches a maximum at a wetting phase saturation  $S_w \approx 0.4$  and then decreases and becomes very small as  $S_w \rightarrow 0$ . This is shown in figure 17. However, the contribution of such thin films to the hydraulic conductivity of the phase is very small. Therefore, the wettability characteristics of a porous medium and the presence of thin films can strongly affect dispersion processes in two-phase flow in porous media. Figure 17 is in qualitative agreement with some experimental data (e.g. Salter and Mohanty 1982) for porous media in which thin films were apparently important.



**Figure 17.** Longitudinal dispersion coefficient  $D_L$  in the wetting phase, in the cubic network, in which the effect of thin films has been taken into account.

As can be seen in figures 16 and 17, there is hysteresis in the values of  $D_L$ . The reason for this is that the sets of pores that are occupied by the wetting phase during imbibition and drainage are different. Thus, one should expect different transit times and, therefore, different dispersion coefficients. Because of hysteresis in dispersion coefficients, the scaling laws for the dependence of dispersion coefficients on phase saturations near the residual saturations can be different from those derived in § 4, which are in terms of the fraction  $X$  of open bonds, and they can also be different for each fluid phase during imbibition and drainage processes. Here, we develop scaling laws for the longitudinal dispersion coefficient. We derive the analogue of equation (63) for  $D_L$  in two-phase flow through strongly wet porous media. For porous media with other types of wettability characteristics, one can use our method and develop the appropriate scaling laws.

The main problem in deriving such scaling laws is to express the saturation of a given phase in terms of the fraction  $X$  of the open bonds. We first consider the drainage process and relate the saturation of the non-wetting phase  $S_{nw}$  to  $X$ . To do this, we simply note that  $S_{nw}$  is the product of two factors. The first one is the ratio of the fraction of pores occupied by the non-wetting phase and the fraction of all pores that are allowed to this phase (i.e. those pores with a radius larger than  $R_d$ ).

The second factor is the ratio of the volume of the pores that can be occupied by the non-wetting phase and the total volume of all pores in the porous medium. The first factor is clearly  $X^A/X_d$  (since  $X^A$  is the fraction of the bonds in the sample-spanning clusters, i.e. the fraction of bonds that are invaded and occupied by the non-wetting phase). The second factor is  $\int_{R_d}^{\infty} v(R)f(R) dR / \int_0^{\infty} v(R)f(R) dR$ , where  $v$  is the volume of a pore. It is often approximately true that the volume of a pore is independent of its effective radius. Under this assumption, the second factor is simply  $X_d$ . (Even if we do not make this assumption, it can be easily shown that the final result would be unchanged.) Therefore, we obtain

$$S_{nw} \sim X^A \tag{72}$$

which, when combined with equation (39), yields,  $X - X_c \sim S_{nw}^{1/\beta}$ . Since equation (63) is equivalent to  $D_L \sim (X - X_c)^{\mu - \beta - 2\nu}$ , we obtain the following result for the longitudinal dispersion coefficient in the non-wetting phase during drainage:

$$D_L \sim S_{nw}^{(\mu - \beta - 2\nu)/\beta} \tag{73}$$

which, for three-dimensional systems, is simplified to  $D_L \sim S_{nw}^{-0.44}$ . The drainage process continues until the wetting phase saturation reaches its residual value  $S_{wc}$ , at which point the wetting phase becomes disconnected. Since  $S_w + S_{nw} = 1$ , it is easy to see that  $S_w - S_{wc} \sim X - X_c$  and therefore

$$D_L \sim (S_w - S_{wc})^{\mu - \beta - 2\nu} \tag{74}$$

for the longitudinal dispersion coefficient in the wetting phase during drainage. For three-dimensional systems, equation (74) is simplified to  $D_L \sim (S_w - S_{wc})^{-0.19}$ . In a similar fashion, we find that during imbibition one has

$$S_w - S_{wc} \sim (X - X_c)^{1+\beta} \tag{75}$$

which means that the longitudinal dispersion coefficient in the wetting phase during imbibition scales as

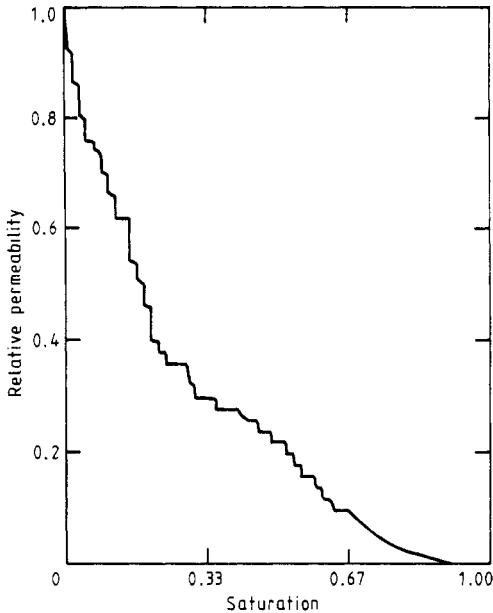
$$D_L \sim (S_w - S_{wc})^{(\mu - \beta - 2\nu)/(1+\beta)} \tag{76}$$

For three-dimensional systems, equation (76) reduces to  $D_L \sim (S_w - S_{wc})^{-0.13}$ , which is almost identical to the corresponding expression for the drainage process. The corresponding expression for the longitudinal dispersion coefficient in the non-wetting phase during imbibition becomes

$$D_L \sim (S_{nw} - S_{nwc})^{\mu - \beta - 2\nu} \tag{77}$$

where  $S_{nwc}$  is the residual saturation of the non-wetting phase; for three-dimensional systems, equation (77) reduces to  $D_L \sim (S_{nw} - S_{nwc})^{-0.19}$ , which is totally different from its corresponding expression for the drainage process. This weak divergence of  $D_L$  is in agreement with some experimental data (e.g., Delshad *et al* 1985) for porous media in which thin films were apparently not important.

However, when we generated the fluid distributions according to the invasion percolation model, the relative permeability  $K$  appeared to decrease discontinuously (i.e. in a stepwise manner), except near the residual saturation (percolation threshold), where the permeability curve appears to become smooth, in contrast with the permeability of large percolation networks which decreases continuously. This is shown in figure 18, where we present the relative permeability to the wetting phase during drainage. The pore size distribution used is  $f(R) = 2R \exp(-R^2)$  and the results are for a single realisation of a  $10 \times 10 \times 15$  simple cubic network. This is in contrast with almost all of the available experimental data which show a continuous reduction of  $K$  as the residual saturation is approached. However, Thompson *et al* (1987) argued, by highly



**Figure 18.** Relative permeability to the wetting phase during drainage as a function of the wetting phase saturation.

precise measurements, that mercury injection into a porous medium (which is essentially a two-phase flow problem similar to what is discussed here) and permeability of the sample during this process *do not* follow a usual percolation process, even though the shape and the topology of the cluster of pores that are occupied by mercury *can* be described by percolation statistics. They have argued that mercury injection near the residual saturation is a kind of first-order phase transition, as opposed to the usual percolation processes which are second-order phase transitions. They have also proposed that the same type of phenomenon should occur for the permeabilities near the residual saturations (i.e.  $K$  must vanish discontinuously), so that one cannot write down a scaling law for  $K$ . Their measurements are consistent with what we have observed in our simulations with the invasion percolation model with small networks. However, since our conductivity curve becomes smooth near the percolation threshold, we argue that this process is still a second-order phase transition and the usual scaling laws of percolation still apply. The stepwise reduction in the permeability is presumably caused by the finite size of the sample and we expect that, as the size of the sample increases, the permeability curve should become smooth. Work is currently in progress to further investigate this and we shall report our results in a future paper (Siddiqui and Sahimi 1988).

## 6. Summary and discussion

We have investigated dispersion in flow through disordered porous media. We have found that the disordered morphology of the porous medium can strongly affect dispersion processes. Moreover, depending on the strength of molecular diffusion and the existence of stagnant regions in which the flow field vanishes, the dependence of

dispersion coefficients on mean flow velocity  $V_a$  can vary anywhere from  $V_a$  to  $V_a^2$ . We have found a length-dependent dispersion regime that cannot be described by a macroscopic convective-diffusion equation with constant dispersion coefficients. If the disordered topology of the porous media can be represented by percolation statistics, we can derive the appropriate scaling laws that relate dispersion coefficients to the length of the system. We have also proposed a generalisation of the Gaussian distribution for describing dispersion in porous media, the length of which is less than a characteristic length. In such media the mean first passage time is less than a characteristic time that the tracer particles need to sample the microstructure of the media. Therefore, the convective-diffusion equation cannot adequately describe dispersion. Equation (60) may be valid for dispersion in such porous media, provided that the proper values of the fractal dimension  $d_w$  of the particles, which may not necessarily be identical with those for percolation systems discussed here, are used.

In this paper we have studied dispersion processes in macroscopically homogeneous, microscopically disordered, porous media. An important problem is dispersion in porous media in which there are macroscopic heterogeneities in permeabilities and dispersion is caused by the chaotic velocity field which is a result of the contrast between permeabilities of different regions. Length-dependent dispersion coefficients have been observed in such porous media (see, e.g., Molz *et al* 1983, Arya *et al* 1985). For example, Arya *et al* (1985) have reported that

$$D_L \sim L^{1.75} \quad (78)$$

where  $L$  is the length of the porous medium. Equation (78) is similar to anomalous dispersion that we find in percolation systems near  $X_c$ . Moreover, the correlation length for permeability heterogeneities plays a role similar to the correlation length of percolation. Thus, we may expect dispersion coefficients in such porous media to increase with time *faster* than linearly, similar to our results for percolation systems. Although the topology of the porous media that can give rise to a dispersion coefficient that is given by (78) is not similar to that of a percolation cluster, equation (78) does indicate the possibility that some of the ideas developed in this paper may be applicable to the study of dispersion in heterogeneous porous media. We hope to report the results of such a study in a future paper.

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