Hydrodynamic dispersion near the percolation threshold: scaling and probability densities

## LETTER TO THE EDITOR

# Hydrodynamic dispersion near the percolation threshold: scaling and probability densities

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**Abstract.** Hydrodynamic dispersion in random network models of porous media near the percolation threshold is investigated. This is done by studying the random walk of a particle in flow through the random network. Various scaling regimes (which depend on the Peclet number which is the ratio of diffusion and convection times) are identified, and the scaling relations for the mean-square displacement of the walk, both in the direction of macroscopic flow and in directions perpendicular to the macroscopic flow, are derived and related to those of anomalous diffusion on percolation clusters. It is shown that dispersion can give rise to *superdiffusion* in which the mean-square displacements of the random walk grow with time faster than linearly, while the spectral dimension of such random walks can be significantly larger than two, which is the critical dimension for diffusion on fractal systems. We propose a new equation for the probability density of finding the random walker at a point at a given time and discuss a method by which the probability density for first passage times of the walker can be determined.

Hydrodynamic dispersion is unsteady mixing of two immiscible fluids displacing one another in a porous medium. This mixing process is caused by a chaotic velocity field in the porous medium, which in turn is caused by the morphology of the pore space, the fluid flow condition, and chemical and physical interactions with the solid surface of the pores. Dispersion can be modified by molecular diffusion and the subtle interplay between diffusion and the chaotic velocity field gives rise to a phenomenon which is considerably more complex, but richer, than that of diffusion alone. Dispersion is important to a wide variety of processes ranging from enhanced recovery of oil from underground reservoirs and salt-water intrusion in coastal aquifers, to the pollution of surface waters by industrial wastes, and heat and mass transfer in packed-bed chemical reactors. Because of its significance, dispersion has been studied for a long time (see Scheidegger (1974) and Sahimi (1984) for reviews of dispersion phenomena).

Macroscopic modelling of dispersion processes in disordered and isotropic porous media is usually based on the convective-diffusion equation (CDE)

$$\frac{\partial C}{\partial t} + V_a \cdot \nabla C = D_L \frac{\partial^2 C}{\partial x^2} + D_T \nabla_2^2 C \tag{1}$$

where $C$ is the macroscopic mean concentration, $t$ the time, $V_a$ the mean flow velocity and $\nabla_2^2$ the Laplacian in transverse (perpendicular to the mean flow) directions. Thus the basic idea is to model dispersion as an anisotropic diffusion process, the diffusivity being the longitudinal dispersion coefficient $D_L$ (in the direction of mean flow which

is assumed to be the $x$ direction) and the transverse dispersion coefficient $D_T$. Dispersion is said to be *macroscopically diffusive* if it obeys a CDE, in which case $C$ obeys a Gaussian (normal) distribution which is the solution of equation (1) with proper initial and boundary conditions (see below). However, an approach based on the CDE is purely phenomenological and provides no insight into how $D_L$ and $D_T$ depend on the morphology of the pore space.

More recently, dispersion has been studied in random network models of porous media. Sahimi *et al* (1982, 1983, 1986a, b) were the first to undertake such a study. They developed a Monte Carlo method by which dispersion is studied by the random walk of tracer particles in the flow field. The flow field induces a bias in the network in the direction of a macroscopic pressure gradient, so that the motion of the particles is a biased random walk. However, the bias is dynamical (since it is flow induced) and therefore this bias random walk is significantly different from the previous models of biased random walks (see, e.g., Pandey 1984, Stauffer 1985, Michel 1986). In these models, it is typically assumed that there is a uniform (and fixed) bias *everywhere*, including the dead-end branches of the network, whereas in our model bias exists only on the *backbone* (the flow-carrying part) of the network. A variety of other methods have also been developed for studying dispersion, including the transfer-matrix algorithm (Roux *et al* 1986), probability-propagation algorithm (de Arcangelis *et al* 1986) and the direct solution of the CDE at the pore level (Koplik *et al* 1987). The efficiency of these methods depends on the structure of the network. For example, the probability-propagation algorithm is very inefficient for dispersion in a percolating network.

In this letter we study the scaling properties of dispersion coefficients $D_L$ and $D_T$ in a random network near the percolation threshold $p_c$, which is relevant to the study of dispersion in two-phase flow. As the fraction $p$ of conducting bonds (i.e., bonds that are open to flow) approaches $p_c$, the percolation correlation length $\xi_p$ diverges as $(p - p_c)^{-\nu}$. The fraction $X^A$ of bonds in the infinite cluster vanishes as $X^A \sim (p - p_c)^\beta$, the fraction $X^B$ of bonds in the backbone vanishes as $X^B \sim (p - p_c)^{\beta_B}$, and the conductivity $K$ of the network vanishes as $K \sim (p - p_c)^\mu$. In analogy with diffusion near $p_c$ (Gefen *et al* 1983) we may expect the scaling of $D_L$ and $D_T$ to depend on the length scale $L$ over which dispersion is studied. Thus, depending on whether $L < \xi_p$ or $L > \xi_p$, we may expect different scaling regimes for $D_L$ and $D_T$.

We first define a Peclet number $Pe$ by $Pe = V_a l / D_m$, where $l$ is a characteristic length scale of the medium and $D_m$ the molecular diffusivity. We may interpret $Pe$ as the ratio of the diffusion time $l^2 / D_m$ and the convection time $l / V_a$. Near $p_c$ a large fraction of bonds in the infinite cluster are dead-end and the tracer particles can communicate with such bonds only by molecular diffusion. If molecular diffusion is slow enough, the tracer particles can spend a long time in the dead-end branches and dispersion is dominated by the time that is spent in the dead-end branches. This also affects the scaling of $V_a$ near $p_c$. If diffusion into the dead-end branches is ignored then one has $V_a \sim K / X^B \sim (p - p_c)^{\mu - \beta_B} \sim \xi_p^{-\theta_B}$, where $\theta_B = (\mu - \beta_B)/\nu$. On the other hand, if molecular diffusion in the dead-end branches is the dominating factor, then, $V_a \sim K / X^A \sim (p - p_c)^{\mu - \beta} \sim \xi_p^{-\theta}$, where $\theta = (\mu - \beta)/\nu$ is the same as the anomalous diffusion exponent introduced by Gefen *et al* (1983). Near $p_c$ the only relevant length scale (aside from the length of the bonds) is $\xi_p$. Moreover, over the length scale $\xi_p$ the molecular diffusivity $D_m$ is proportional to $D_p$, the diffusivity of the tracer particles in the *absence of the flow field*, which is given by $D_p \sim \xi_p^{-\theta}$. Therefore, the *macroscopic* Peclet number is rewritten as $Pe = V_a \xi_p / D_p$. For length scales $L \ll \xi_p$, we should replace

$\xi_p$ with $L$ and write $Pe = V_a L / D_p$, in which case $V_a \sim L^{-\theta}$ (or $V_a \sim L^{-\theta_B}$ for the backbone) and $D_p \sim L^{-\theta}$ (or $D_p \sim L^{-\theta_B}$ if diffusion is restricted to the backbone). We also introduce two random walk fractal dimensions which are given by

$$\langle \Delta x^2 \rangle \sim t^{2/d_w^l} \tag{2}$$

for longitudinal dispersion, and

$$\langle y^2 \rangle = \langle z^2 \rangle \sim t^{2/d_w^t} \tag{3}$$

for transverse dispersion. Here $\langle \; \rangle$ denotes an averaging over the ensemble of all initial positions of the particles, and $\langle \Delta x^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$. We have assumed that the particles start their motion at the origin of the coordinates. For diffusion on percolation clusters $d_w^l = d_w^t = d_w$, where $d_w = 2$ for normal diffusion and $d_w = 2 + \theta$ for anomalous (i.e. length-dependent) diffusion. Similarly, for macroscopically diffusive dispersion $d_w^l = d_w^t = 2$; one goal of our paper is to derive the relations for $d_w^l$ and $d_w^t$ for the anomalous dispersion, which *cannot* be described and predicted by the CDE. Note that one has $\mathrm{d}\langle x \rangle / \mathrm{d}t \sim V_a$, $\mathrm{d}\langle \Delta x^2 \rangle / \mathrm{d}t \sim D_L$ and $\mathrm{d}\langle y^2 \rangle / \mathrm{d}t \sim D_T$. The scaling properties of $D_L$ and $D_T$ near $p_c$ and the relations for $d_w^l$ and $d_w^t$ depend on the value of $Pe$ and are given below.

(i) Let us first consider the limit $Pe \to 0$, i.e. the limit of vanishing flow. In this regime mixing is caused by only molecular diffusion and $D_L = D_T = D_p \sim (p - p_c)^{\mu - \beta}$ for $L \gg \xi_p$, and $D_L = D_T = D_p \sim L^{-\theta}$ and $d_w^l = d_w^t = d_w = 2 + \theta$ for $L \ll \xi_p$. Moreover, $\langle x^2 \rangle \sim \langle x \rangle^2$.

(ii) Consider now the opposite limit, namely, the limit of very large $Pe$. In this regime dispersion is caused only by convection and $D_L$ and $D_T$ are independent of molecular diffusion. Hence, mixing takes place only in flow through the backbone of the infinite cluster (since diffusion, which transfers the particles to the dead-end branches, does not exist). Therefore, $D_L$ and $D_T$ are linearly dependent on $V_a$ (Sahimi *et al* 1986a, b) and we may write $D_L \sim L_1 V_a$ and $D_T \sim L_2 V_a$, where $L_1$ and $L_2$ are two characteristic length scales. Near $p_c$ the only relevant length scale is $\xi_p$ and, thus, $L_1 \sim L_2 \sim \xi_p$ and hence $D_L \sim D_T \sim \xi_p^{1 - \theta_B}$. Therefore, for length scales $L \ll \xi_p$ we have $D_L \sim D_T \sim L^{1 - \theta_B}$. We may rewrite these as $\mathrm{d}\langle \Delta x^2 \rangle / \mathrm{d}t \sim L^{1 - \theta_B}$ and $\mathrm{d}\langle y^2 \rangle / \mathrm{d}t \sim L^{1 - \theta_B}$, which after integration yield $\langle \Delta x^2 \rangle \sim t^{2/(1 + \theta_B)}$ and $\langle y^2 \rangle = \langle z^2 \rangle \sim t^{2/(1 + \theta_B)}$, which mean that

$$d_w^l = d_w^t = 1 + \theta_B. \tag{4}$$

Moreover, because $\mathrm{d}\langle x \rangle / \mathrm{d}t \sim V_a$, we obtain $\langle x \rangle^2 \sim \langle x^2 \rangle$. In two dimensions, $\mu \simeq 1.3$, $\beta_B \simeq 0.53$ and $\nu = \frac{4}{3}$ and, thus, $d_w^l = d_w^t \simeq 1.58$. On the other hand, for three-dimensional networks $\mu \simeq 2$, $\beta_B \simeq 0.95$, $\nu \simeq 0.88$ and, therefore, $d_w^l = d_w^t \simeq 2.2$. Therefore, at high Peclet numbers and in two-dimensional networks, hydrodynamic dispersion gives rise to *superdiffusion*, i.e. the mean-square displacements grow with time faster than linearly (because $d_w^l = d_w^t < 2$), which is similar to turbulent diffusion (Grossman *et al* 1985) for which $d_w = \frac{3}{2}$ (in fact dispersion in this limit and turbulent diffusion are very similar). In contrast, for anomalous diffusion on percolating clusters we have $d_w(d = 2) \simeq 2.87$ and $d_w(d = 3) \simeq 3.78$. On the other hand, for $d \geq 6$, we have $d_w^l = d_w^t = 3$. We remark that Ohtsuki and Keyes (1987) have also studied dispersion in the convective limit, using a renormalisation group method, and have argued that $V_a \sim \xi_p^{-\theta_B/2}$. They have argued that $V_a$ varies in the same way as a sound velocity and thus $V_a \sim (K/X^B)^{1/2}$. However, this is not supported by numerical simulations (Sahimi and Imdakm 1988) and thus their proposed relation $d_w^l = 1 + \theta_B/2$ may not be correct.

(iii) For relatively high values of *Pe* convection still dominates but the contribution of diffusion cannot be neglected. For example, if the porous medium contains regions of very slowly moving fluid (e.g., a boundary layer very close to the pore walls, or pores that are nearly perpendicular to the macroscopic pressure gradient) the tracer particles can escape such regions only by a combination of molecular diffusion and convection. In this limit, with no molecular diffusion, the mean transit time $\langle t \rangle$ of the particles is finite (since $\langle t \rangle \sim V_a^{-1}$) but $\langle t^2 \rangle$ is divergent, and $D_L \to \infty$. Introduction of molecular diffusion provides an effective cut-off and forces $\langle t^2 \rangle$ to remain finite. In this case, as the works of Saffman (1959) and Koch and Brady (1985) have shown, $D_L/D_m \sim Pe \ln Pe$ and $D_T/D_m \sim Pe$. Therefore, as far as scaling near $p_c$ is concerned, equations (4) are still valid, although there are logarithmic corrections to $D_L$ and $\langle \Delta x^2 \rangle$.

(iv) If the tracer particles spend a long time in the dead-end branches of the network then molecular diffusion becomes the dominating factor. Molecular diffusion in the dead-end branches also causes the velocity fluctuations experienced by the particles to become uncorrelated. For this case de Gennes (1983) has suggested that $D_L \sim (V_a \xi_p)^2/D_p \sim \xi_p^{2-\theta}$. Here we offer a very simple derivation of de Gennes's result. From the work of Aris (1959) (who studied dispersion in long capillary tubes to which capillary tubes of various lengths, which contained stagnant fluids, were connected) we know that $D_L \sim V_a^2$. Dimensional analysis then leads us to write $D_L \sim V_a^2 \tau$, where $\tau$ is a characteristic timescale in the dispersion process. Since diffusion into the dead-end branches is assumed to be dominant, $\tau$ must be the characteristic time for exploring a dead-end branch which is given by $\tau \sim \xi_p^2/D_p \sim \xi_p^{2+\theta}$, which yields $D_L \sim \xi_p^{2-\theta}$. For $L \ll \xi_p$ we can write $d\langle \Delta x^2 \rangle/dt \sim L^{2-\theta}$ and $d\langle y^2 \rangle/dt = d\langle z^2 \rangle/dt \sim L^{2-\theta}$ (since $D_L$ and $D_T$ have the same kind of dependence on *Pe*) which, after integration, yields $\langle \Delta x^2 \rangle \sim t^{2/\theta}$ and $\langle y^2 \rangle = \langle z^2 \rangle \sim t^{2/\theta}$, which means that

$$d_w^l = d_w^t = \theta. \tag{5}$$

Since $\theta(d=2) \simeq 0.87$ and $\theta(d=3) \simeq 1.78$, equations (5) predict that one has super-diffusion in *both* two and three dimensions.

Equations (4) and (5) have an interesting consequence for the spectral dimension $d_s$. The spectral dimension of a random walk process on a fractal is defined (Alexander and Orbach 1982) as $d_s = 2d_f/d_w$, where $d_f$ is the fractal dimension of the system. Since for percolations clusters $d_f(d=2) = 91/48$ and $d_f(d=3) \simeq 2.5$, and for the backbone $d_B(d=2) \simeq 1.6$ and $d_B(d=3) \simeq 1.9$, the spectral dimension for case (iv) is $d_s(d=2) \simeq 4.34$, $d_s(d=3) \simeq 2.82$ and $d_s(d \geq 6) = 2$, whereas for cases (ii) and (iii) we have $d_s(d=2) = 2d_B/d_w^l \simeq 2.02$, $d_s(d=3) \simeq 1.74$ and $d_s(d \geq 6) = \frac{4}{3}$, while for case (i) we have $d_s \simeq \frac{4}{3}$ at all *dimensions*. Thus in contrast with anomalous diffusion for which $1 \leq d_s \leq 2$, hydrodynamic dispersion can give rise to phenomena with $d_s > 2$. The inequality $d_s > 2$ means that $d_w^l = d_w^t < d_f$, which implies that the random walk of the particles is *not recurrent*. To the best of our knowledge, hydrodynamic dispersion studied here is the first physical example of a phenomenon with $d_s > 2$.

Two important quantities in diffusion and dispersion processes are $P(x, y, z, t)$, the probability that a tracer particle is at the position $\mathbf{r} = (x, y, z)$ at time $t$ and $Q(\mathbf{r}, t)$, the first-passage time distribution (FPTD), which is the probability that a particle reaches $\mathbf{r}$ *for the first time* at time $t$. For macroscopically diffusive dispersion $P(x, y, z, t)$ obeys a Gaussian distribution and the mean concentration $C$ is proportional to $P$. The FPTD is given by (Sahimi *et al* 1986b)

$$Q(\mathbf{r}, t) = L^{-1}[\hat{P}(\mathbf{r}, \lambda)/\hat{P}(\mathbf{0}, \lambda)] \tag{6}$$

where $\hat{P}(r, \lambda)$ is the Laplace transform of $P$, $\lambda$ is the Laplace transform variable conjugate to $t$ and $L^{-1}$ denotes the inverse Laplace transform. However, for anomalous diffusion and dispersion $P$ is not Gaussian and a CDE (or the diffusion equation) cannot properly describe these processes. For anomalous diffusion Guyer (1985) has suggested that

$$P(r, t) \sim t^{-d_s/2} \exp[-a(|r|/t^{1/d_w})^{\nu_p}] \tag{7}$$

where $\nu_p = d_w(d_w - 1)^{-1}$ and $a$ is a constant. Banavar and Willemsen (1984) and O'Shaughnessy and Procaccia (1985) have suggested another expression for $P$, but their expression is not supported by numerical simulations for percolation clusters (see e.g. Havlin *et al* 1985). We propose that for anomalous dispersion, which cannot be described by a CDE, $P$ is given by

$$P(x, y, z, t) \sim t^{-d_s/2} \exp\left[ -\alpha \left( \frac{|x - \langle x \rangle|}{t^{1/d_w^l}} \right)^{\nu_p^l} - \delta \left( \frac{|y|}{t^{1/d_w^l}} \right)^{\nu_p^l} - \gamma \left( \frac{|z|}{t^{1/d_w^l}} \right)^{\nu_p^t} \right] \tag{8}$$

where $\alpha$, $\delta$ and $\gamma$ are constant. Here $\nu_p^l = d_w^l(d_w^l - 1)^{-1}$ and $\nu_p^t = d_w^t(d_w^t - 1)^{-1}$. Equation (8), which reduces to a Gaussian distribution for macroscopically diffusive dispersion (with $d_s = d = 3$ and $\nu_p^l = \nu_p^t = 2$), should be valid for dispersion in cases (ii)-(iv), provided that the appropriate random walk fractal dimensions (equations (4) and (5)) and the spectral dimension are used. On the other hand, equation (6) is supposed to be valid for translationally invariant structures. For length scales $L \ll \xi_p$, the largest percolation cluster lacks translational invariance and is a fractal object. In this case, equation (6) does not hold for large $\lambda$ (small $t$). However, we may expect that for large times the probability of being at a point at a given time will no longer depend on the origin of the walk (and this is especially true if there is diffusion into the dead-end branches) in which case equation (6) should hold. Thus equation (8) together with equations (6) and (7) can be used to determine $Q(r, t)$ for both anomalous diffusion and dispersion processes, although this has to be done numerically, since it seems difficult to derive an analytical expression for $Q(r, t)$.

Finally, we must emphasise that equations (4), (5) and (8) are supposed to be valid in the anomalous regime. This regime is defined by a timescale $\tau_a$, such that for $t \gg \tau_a$ one should have macroscopically diffusive dispersion. The timescale $\tau_a$ is given by $\tau_a \sim \xi_p^2/D_L$. Therefore, $\tau_a \sim \xi_p^{2+\theta}$ for case (i), $\tau_a \sim \xi_p^{1+\theta_B}$ for cases (ii) and (iii) and $\tau_a \sim \xi_p^\theta$ for case (iv). In a future paper, we will report the results of Monte Carlo simulations of hydrodynamic dispersion near $p_c$ to test the validity of our predictions.

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