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Hydrodynamic dispersion in unsaturated porous media

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We consider a porous solid, partially filled with a non-wetting fluid, just above the injection threshold: the injected regions have the topology of the infinite cluster in a percolation problem, and they split into a 'backbone' part plus 'dead ends'. Under a steady Darcy flow, a dye molecule moves by convection on the backbone, and by molecular diffusion on the dead ends. The process has some similarity with solute transport in chromatographic columns. However, because the 'dead ends' have a broad distribution of sizes, special singularities may occur, which are reminiscent of non-Gaussian transport for charge carriers in amorphous semiconductors.

We ultimately predict the existence of a well-defined diffusion coefficient $D_{\parallel}$ for motion parallel to the average flow, in the limit of slow molecular diffusion. We find $D_{\parallel} \approx (\bar{U}\xi)^2/D_a$, where ξ is the percolation correlation length, $\bar{U}$ the macroscopic flow velocity and D_a the diffusion coefficient of an 'ant' on the infinite cluster (i.e. the macroscopic diffusion constant measured in the absence of flow).

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1. Stagnation effects

Consider first a *saturated* porous medium with a reasonably narrow distribution of pore sizes (pore diameter d). Let us then impose an average drift velocity U on the fluid, and investigate the spreading of a dye injected at one point. The average drift of the dye during a time t is $\langle x\rangle = Ut$. The mean-square deviation (for a macroscopic interval t) is

$$\Delta x^2 = \langle x^2\rangle - \langle x\rangle^2 = 2D_{\parallel}\,t. \qquad (1.1)$$

At very low U, $D_{\parallel} = D_1$ is the molecular diffusivity of the dye. At higher Péclet numbers ($Pe = dU/D_1$) we reach a regime where

$$D_{\parallel} = \text{const} \times dU \quad (Pe \gg 1). \qquad (1.2)$$

Similarly, for motions normal to the average flow, we have another diffusion coefficient $D_{\perp}$. At high Péclet numbers $D_{\perp} = \text{const} \times D_{\parallel}$. A detailed discussion of these coefficients can be found for instance in Bear (1972).

These relatively simple features can be upset, however, by *stagnation effects*.

(1) A simple example (de Jong 1958) is based on a capillary model for the pores, where the capillaries are oriented at random. Then the dye particles located in a capillary which is nearly *normal to the flow* drift very slowly; this leads to logarithmic singularities in $D_{\parallel}$, which are weak and rather difficult to detect.

(2) Another, stronger, example of stagnation effects is found in *liquid–liquid chromatography* (see e.g. Aris 1959; Rosset, Caude & Jardy 1982): here we deal with a two-scale system: porous grains (inside which the flow velocity is negligible) and interstices (with a finite flow velocity U). A solute (or dye) particle is convected in the interstices, and then trapped in a grain. The distribution of release times from

one grain leads to a dispersion Δx, and the associated diffusion coefficient has the structure

$$D_{\parallel} = \text{const} \times U^2 \tau, \tag{1.3}$$

where the numerical factor depends on the partition coefficient for the dye, between grains and interstices. τ is an average lifetime for one dye molecule in one grain. The contribution (1.3) is essential in all discussions on the optimization of a chromatographic column.

(3) A third example can be found in a very different field of physics: namely with the drift of electrical carriers in an amorphous semiconductor: the carriers are trapped by various defects, and the distribution of release rates W from the traps extends to very slow rates. This has been analysed by Scher & Montroll (1975). They discuss in particular a distribution $p(W)$ of release rates of the form

$$p(W) = \text{const} \times W^{\alpha-1} \quad (W \to 0), \tag{1.4}$$

where $0 < \alpha < 1$. This form is physically meaningful (it can be achieved commonly when W involves an activation energy) and it leads to very extreme effects of stagnation. The average drift is not linear in time, but is

$$\langle x(t) \rangle = \text{const} \times U t^{\alpha}, \tag{1.5}$$

where U is the drift velocity without traps. Also the width Δx is comparable to $\langle x \rangle$. One cannot define a diffusion coefficient for this case. These pathological features are related to the fact that the slowest traps (with $W < 1/t$) dominate the behaviour.

2. Stagnation near a percolation threshold

2.1. *Partial saturation of a porous medium*

Our aim in the present paper is to study another example of stagnation effects. We consider a porous medium, again with a relatively narrow distribution of pore sizes a. We fill a certain fraction of the pores by a non-wetting fluid. As discussed in particular by Dullien (1979) and by de Gennes & Guyon (1978), we then expect to encounter a percolation transition: a macroscopic sample is penetrated only when the pressure p is above a threshold p_c. For $p > p_c$ we generate an infinite cluster of fluid in the sample. The volume fraction of fluid $S_\infty(p)$ is a steeply rising function of $p - p_c = \Delta p$:

$$S_\infty(p) = \text{const} \times \left(\frac{\Delta p}{p_c}\right)^{\beta}, \tag{2.1}$$

with $\beta = 0.39$ in 3 dimensions. We are interested only in the region $\Delta p / p_c \ll 1$ where this infinite cluster is not very dense. More precisely the mesh size of the cluster (the so-called correlation length ξ) must be much larger than a pore size: we then expect a universal type of behaviour, independent of the details of the pore statistics. The scaling formula for ξ is

$$\xi = \text{const} \times d \left(\frac{\Delta p}{p_c}\right)^{-\nu}, \tag{2.2}$$

where $\nu = 0.9$ in 3 dimensions. The general structure of the impregnated regions is represented on figures 1 and 2.

2.2. *Steady flow conditions*

We now apply a pressure gradient $-f$ to our sample. This will induce a certain flow Q (volume/cm^2/s) given by Darcy's law

$$Q = k \eta^{-1} f, \tag{2.3}$$

where k is the permeability of the partly saturated medium, and η the liquid viscosity.

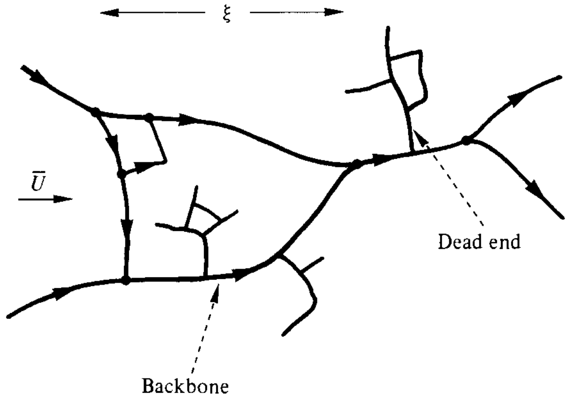

FIGURE 1. Qualitative structure of the impregnated regions just above threshold. The only pores represented are those which are invaded by the fluid. The pores are drawn as thin lines: near threshold, the pore diameter d is negligible in comparison with the correlation length ξ.

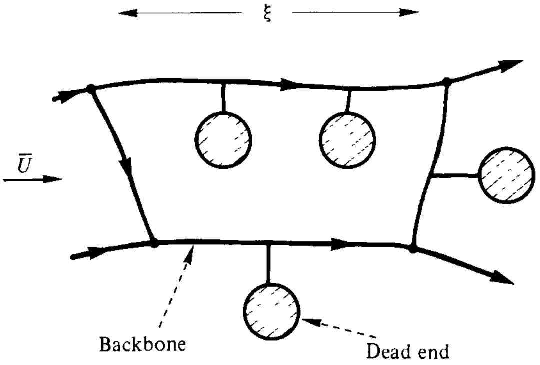

FIGURE 2. Simplified representation of the cluster structure. The size of the largest loops in the backbone is the correlation length ξ. ξ is also the size of the largest dead ends.

Near the percolation threshold, we expect a scaling law for the permeability of the form

$$k = \text{const} \times P_0 d^2 \left(\frac{\Delta p}{P_c}\right)^{\tilde{t}}, \tag{2.4}$$

where $\tilde{t}$ (~ 1.7) is the same exponent that appears in the conductance of an electrical network, and P_0 is the porosity. Reviews discussing the exponent $\tilde{t}$ have been given (among others) by Stauffer (1979) and Kirkpatrick (1979).

Thus the average velocity of a fluid particle is

$$\overline{U} = \frac{Q}{S_\infty} = Kf\left(\frac{\Delta p}{p_c}\right)^{\tilde{t}-\beta}. \tag{2.5}$$

We assume that $\overline{U}$ is not too high, so that the flow does not perturb the geography of the infinite cluster.

This resistance to deformation and drag is conditioned by the surface tension γ of the liquid: we expect all interfaces to be locked in permanent positions provided that the local velocities U are smaller than γ/η: this condition is well-achieved in most cases.

2.3. '*Dead ends*' and '*backbone*'

As shown qualitatively on figure 1, the infinite cluster may be split into two distinct portions: a 'backbone' plus 'dead ends'. There is no hydrodynamic flow in the dead ends. There is flow in all the backbone (except for accidental stagnations of the de Jong type). Thus the backbone is the analogue of the interstices in chromatography, while the dead ends are the analogue of the porous grains.

We know the relative weight of backbone versus dead ends. The probability S_B of belonging to the backbone has been studied numerically on percolation networks, and is of the form

$$S_B = \text{const} \times \left(\frac{\Delta p}{p_c}\right)^{\beta_B}, \tag{2.6}$$

where the exponent β_B is larger than β ($\beta_B \approx 0.9$ in 3 dimensions) (Stauffer 1979; Kirkpatrick 1979). Thus, at small Δp, the relative probability $\bar{\mu}$ of being located on the backbone is small,

$$\bar{\mu} = \frac{S_B}{S_\infty} = \text{const} \times \left(\frac{\Delta p}{p_c}\right)^{\beta_B - \beta}. \tag{2.7}$$

Having defined these weights, it is immediately important to realize that there exist, not one, but *two average velocities* of importance:

(*a*) if we average over all sites on the infinite cluster we obtain the velocity $\bar{U}$ of (2.5);

(*b*) however, we know that only the backbone sites are experiencing a flow. Let us define an average velocity $\bar{U}_B$ *on the backbone*

$$\bar{U}_B = \frac{Q}{S_B} = \frac{\bar{U}}{\bar{\mu}}. \tag{2.8}$$

We see that $\bar{U}_B$ is much larger than $\bar{U}$. If we inject our dye at one point in the backbone, it will first drift at a velocity $\sim \bar{U}_B$; later, by molecular diffusion into the dead ends, it will slow down and reach an average velocity $\bar{U}$.

2.4. *Diffusion coefficients*

We have already mentioned that our problem is somewhat related to the question of solute transport in a liquid–liquid chromatographic column. However, there is one important difference. In the chromatographic example, the grains are relatively monodisperse: the distribution of release times has no special singularity. But in the partly saturated system, just above threshold, the distribution of dead ends is very polydisperse: some are small, some are large. From that standpoint, we might expect certain similarities with the problem of electron drift in the presence of deep traps in an amorphous solid, discussed by Scher & Montroll (1975). Our analysis of the spread Δx is thus conceptually related to that of Scher & Montroll (1975) and Pfister & Scher (1978). But our distribution of the release frequencies W is different. We have a cutoff at low W.

The maximum size of the dead ends is the correlation length ξ, and the minimum escape rate (by molecular diffusion inside the dead end) is a certain $1/\tau_\xi$, which has been analysed recently by Gefen, Aharony & Alexander (1983):

$$\tau_\xi = \xi^2/D_a, \tag{2.9}$$

where ξ is the correlation length defined in (2.2), and D_a is the diffusion constant for an 'ant in a labyrinth' (de Gennes 1976; Mitescu, Ottavi & Roussenq 1979; Straley

1980; Havlin & Avraham (to be published); Angles d'Auriac, Benoît & Rammal (to be published). More precisely, D_{a} is the macroscopic diffusion which can be measured on the same, partly saturated, porous sample in the absence of flow ($f = 0$). The coefficient D_{a} is much smaller than the molecular diffusivity D_1 of the dye, because (for small Δp) only a rather weak backbone allows for macroscopic transport. The scaling structure of D_{a} is (Gefen *et al.* 1983)

$$D_{\mathrm{a}} = D_1 \left(\frac{\Delta p}{p_{\mathrm{c}}}\right)^{\bar{t}-\beta}. \tag{2.10}$$

Thus the detailed structure of the 'maximum residence time' τ_ξ is

$$\tau_\xi = a^2 D_1^{-1} \left(\frac{\Delta p}{p_{\mathrm{c}}}\right)^{-2\nu-\bar{t}+\beta}. \tag{2.11}$$

Having defined τ_ξ, let us return to the problem of $\bar{U} \neq 0$, i.e. of hydrodynamic dispersion. In analogy with (2.3) we may guess that the diffusivity, at high Péclet numbers, will be of the form:

$$D_\parallel = U^2 \tau_\xi, \tag{2.12}$$

where U is a certain average velocity.

The main problem, to be discussed in the following sections, is to find out *what average is relevant*: is it $\bar{U}$, or is it U_{B}, or is it a combination of the two? We show that $\bar{U}$ is the correct average to be used. The complete proof is given in §§3 and 4. But, because this central point was not fully understood by some of our early readers, we sketch it now briefly here. In terms of velocity correlation functions we have

$$D_\parallel = \int_0^\infty \langle [v(t) - \bar{U}]\,[v(t) - \bar{U}] \rangle \mathrm{d}t \tag{2.13}$$

and $v(t) = \mu(t)\, U_{\mathrm{B}}(t)$, where $U_{\mathrm{B}}(t)$ is a local backbone velocity, and $\mu(t)$ is equal to 1 on the backbone and to 0 on the dead ends. There are then many terms in (2.13). The dominant one is obtained by neglecting the fluctuations of U_{B}:

$$D_\parallel = \int \langle [\mu(t) - \bar{\mu}]\,[\mu(0) - \bar{\mu}] \rangle\, U_{\mathrm{B}}^2\, \mathrm{d}t. \tag{2.14}$$

The $\mu\mu$ correlation function

$$F(t) = \langle (\mu(t) - \bar{\mu})\,(\mu(0) - \bar{\mu}) \rangle \tag{2.15}$$

starts from a value $\bar{\mu}(1 - \bar{\mu})$ at $t = 0$ and has a time integral

$$\int F(t)\, \mathrm{d}t = \bar{\mu}^2 \tau_\xi. \tag{2.16}$$

This ultimately leads to (2.12). But the proof of (2.16) is not obvious, and requires the full analysis of §4.

It is important to notice that $D_\parallel$ involves certain convective parameters ($\bar{U}$), but also depends on the molecular diffusivity (through τ_ξ). Thus (as is the case for many transport problems) $D_\parallel$ is really a complex admixture of hydrodynamic and molecular parameters.

We conclude this section by a remark on the domain of applicability of the present calculation.

(*a*) We want to be in a slow-flow regime (immobile menisci) and this requires

$$U_{\mathrm{B}} \ll \frac{\gamma}{\eta}. \tag{2.17}$$

(*b*) Hydrodynamic dispersion is important only if the velocities are not too slow, so that $D_{\parallel} \gg D_{\mathrm{a}}$. Using (2.12) with $U = \bar{U}$, this leads to

$$\bar{U} > D_{\mathrm{a}}/\xi. \tag{2.18}$$

Now $\bar{U}$ and U_{B} are related by (2.8). Thus to satisfy both conditions (2.13, 2.14) we must have

$$\frac{\gamma}{\eta} > \frac{D_{\mathrm{a}}}{\xi\mu}, \tag{2.19}$$

or explicitly

$$\frac{\gamma d}{\eta D_1} \gg \left(\frac{\Delta p}{p_{\mathrm{c}}}\right)^{t-\beta_{\mathrm{B}}+\nu}$$

In 3 dimensions the exponent on the right-hand side is very close to zero, and the condition reduces practically to $\gamma d/\eta D_1 \gg 1$ or

$$d \gg a, \quad a = \frac{D_1 \eta}{\gamma}. \tag{2.20}$$

The length a is comparable to a molecular diameter, and the condition (2.16) is amply satisfied.

3. Diffusion and correlation functions

Let us assume that a solute particle (a dye) has been injected at time $t = 0$ at one point, and look at its displacement $x_{\alpha}(t)$ after a long time interval ($t \gg \tau_{\xi}$). We restrict our attention to an isotropic porous medium: there are then two separate components of interest $x_{\parallel}(t)$ parallel to the average flow $\bar{U}$ and $x_{\perp}(t)$ (normal to $\bar{U}$). In what follows we shall be mainly concerned with $x_{\parallel}(t)$. We can write the displacement x_{α} in terms of an instantaneous velocity v_{α}:

$$x_{\alpha}(t) = \int_0^t \mathrm{d}t'\, v_{\alpha}(t'). \tag{3.1}$$

For our discussion at macroscopic scales ($t > \tau_{\xi}$, $x \gg \xi$) we may factorize v_{α} as follows:

$$v_{\alpha}(t) = U_{\mathrm{B}\alpha}(t)\,\mu(t) \quad (t \gg \tau_{\xi}), \tag{3.2}$$

where $\mu(t) = 1$ if the particle is on the backbone, and $\mu(t) = 0$ if the particle is in a dead end, while $U_{\mathrm{B}}(t)$ is the local (Eulerian) flow velocity on the backbone. Equation (3.2) ignores the displacements occurring on the dead ends. This is justified at large times t, for the following reason: if a dye molecule enters a dead end at a certain point A, it will move inside this dead end by Brownian motion; but, when it leaves the dead end, this must occur again at point A: thus the displacements inside each dead end integrate to zero. (On the other hand, (3.2) would not be adequate to discuss $x_{\alpha}(t)$ at times $t < \tau_{\xi}$, where our particle need not have returned to A during the available time.)

Inserting (3.2) into (3.1) and taking averages, we recover (2.8) in the form

$$\langle x_{\parallel}(t)\rangle = \bar{\mu}\bar{U}_{\mathrm{B}}\,t = \bar{U}t. \tag{3.3}$$

But our real interest here lies in the deviations from the mean, so define d as

$$\Delta x_{\alpha}^2(t) = \langle x_{\alpha}^2(t) - \langle x_{\alpha}(t)\rangle^2\rangle = 2D_{\alpha}t \quad (t \gg \tau_{\xi}). \tag{3.4}$$

Inserting (3.1) into (3.4) and performing classical manipulations (Bear 1972) we can relate D_α to the velocity correlations

$$D_\alpha = \int_0^\infty \mathrm{d}t \, \langle \delta v_\alpha(0) \, \delta v_\alpha(t) \rangle, \tag{3.5}$$

$$\delta v_\parallel = v_\parallel - \overline{U}, \quad \delta v_\perp = v_\perp. \tag{3.6}$$

The simple form (3.4) is valid if and only if the integral (3.5) converges at large times: we shall see later that this is indeed the case here.

We shall now *assume* that the variables $\mu(t)$ and $U_\mathrm{B}(t)$ are decoupled:

$$\langle U_{\mathrm{B}\alpha}(0) \, U_{\mathrm{B}\alpha}(t) \, \mu(0) \, \mu(t) \rangle \rightarrow \langle U_{\mathrm{B}\alpha}(0) \, U_{\mathrm{B}\alpha}(t) \rangle \, \langle \mu(0) \, \mu(t) \rangle. \tag{3.7}$$

(*a*) The correlation function $\langle U_\alpha U_\alpha \rangle$ decays to its asymptotic value $(\langle U_\alpha \rangle^2)$ in a time θ_U. In a *saturated* porous medium the classical estimate for θ_U is $^{(1)}$

$$\theta_U \sim a/U_\mathrm{B}. \tag{3.8}$$

This means that all velocity correlations are out after moving from one pore to the next. In our *weakly saturated* medium (where any arc on the backbone is not a simple random walk) the structure of the function $\langle UU \rangle$ is more complex. But θ_U is still a rapidly decreasing function of the flow velocities.

(*b*) The correlation function $\langle \mu\mu \rangle$ decays towards its asymptotic value $(\overline{\mu}^2)$ in a time θ_μ, which is essentially controlled by molecular diffusion, and thus independent of the flow velocities.

In the present paper we restrict our attention to the limit $\theta_U \ll \theta_\mu$. This means that convective effects are dominant; the ratio θ_μ/θ_U is somewhat similar to a Péclet number, and we investigate only the limit of high Péclet numbers. We shall also be concerned mainly by motions *parallel to the average flow* $(x_\parallel)$. Then the correlation function (3.7) may be simplified into

$$\langle v_\parallel(0) \, v_\parallel(t) \rangle \rightarrow \overline{U}_\mathrm{B}^2 \langle \mu(0) \, \mu(t) \rangle \quad (\theta_U \ll \theta_\mathrm{B}), \tag{3.9}$$

and the coefficient of hydrodynamic dispersion (3.5) becomes

$$D_\parallel = \overline{U}_\mathrm{B}^2 \int_0^\infty \mathrm{d}t \, \langle \mu(0) \, \mu(t) - \overline{\mu}^2 \rangle. \tag{3.10}$$

Equation (3.10) is our starting point. The main task is to construct a form of the $\langle \mu\mu \rangle$ correlation allowing for capture into a polydisperse ensemble of dead ends.

4. Exchanges between backbone and dead ends

4.1. *Memory function for one dead end*

Let us assume that the solute molecule is inside one particular dead end at time $t = 0$, and ask for the probability $\Gamma(t)$ that it be still in the same dead end at time t. We call $\Gamma(t)$ the memory function. It has the following limiting values:

$$\Gamma(t = 0) = 1, \quad \Gamma(t = \infty) = 0. \tag{4.1}$$

Three representations will be useful for $\Gamma(t)$.

(*a*) One of them is purely formal, but makes contact with the discussions concerning traps in amorphous semiconductors by Noolandi, Scher, and others. It amounts to writing

$$\Gamma(t) = \sum_i f_i \mathrm{e}^{-W_i t} \rightarrow \int_0^\infty p(W) \, \mathrm{e}^{-Wt} \, \mathrm{d}W, \tag{4.2}$$

where the sum Σ_i is over all types of traps, f_i is the corresponding weight, and W_i the associated release rate. In the second form we have introduced a probability distribution for the release rates $p(W)$.

(*b*) The second representation for $\Gamma(t)$ is based on our present knowledge of percolation clusters (Stauffer 1979; Kirkpatrick 1979; Gefen *et al.* (to be published) together with certain specific assumptions.

Consider an 'ant' moving by Brownian motion on a percolation cluster of n sites (the word 'site' refers to a lattice model for percolation (Stauffer 1979; Kirkpatrick 1979); more generally nd^3 would be the volume of fluid in the cluster). We know that, for large n, the number of sites explored by the ant in a time t is

$$s(t) \approx (W_1 t)^{\frac{1}{2}\tilde{d}} \quad (s < n), \tag{4.3}$$

where $W_1 = D_1 d^{-2}$ is the unit of frequency (the molecular diffusion rate over one pore) and $\tilde{d}$ is the so-called *spectral dimensionality* of the percolation lattice introduced by Alexander & Orbach (1982) and discussed later by Rammal & Toulouse (1983):

$$\tilde{d} = 2\frac{\beta+\gamma}{\bar{t}-\beta+2\nu}$$

($\tilde{d} \approx \frac{4}{3}$ for all known percolating systems). Let us call $\Gamma_n(t)$ the memory function for our cluster of n sites. We may then propose the scaling form

$$\Gamma_n(t) = g\left(\frac{s(t)}{n}\right), \tag{4.4}$$

with $g(0) = 1$ and $g(\infty) = 0$. In practice $g(x)$ will have a rather sharp cutoff at $x \sim 1$. We may then construct the overall memory function as a weighted average:

$$\Gamma(t) = \sum_n \phi_n \Gamma_n(t), \tag{4.5}$$

where ϕ_n is the probability for one site to belong to a dead end of n sites. We shall *assume* that this distribution is qualitatively similar to the Stauffer distribution for finite clusters (Stauffer 1979; Kirkpatrick 1979), namely

$$\phi_n = \mathrm{const} \times n^{-(1+\epsilon)} \quad (n < N^*), \tag{4.6}$$

with $\epsilon = \beta/(\beta+\gamma)$, where β is defined in (2.1) while $\gamma = \nu d_s - 2\beta$ is another exponent, discussed in Stauffer (1979) and Kirkpatrick (1979) (d_s is the dimensionality of space). Numerically $\gamma \approx 1.8$ in 3 dimensions, and $\epsilon \approx 0.18$. The distribution (4.6) is cut off at a certain maximum value $n = N^*$ and the scaling law for N^* is (Stauffer 1979; Kirkpatrick 1979)

$$N^* = \left(\frac{\Delta p}{p_c}\right)^{-(\beta+\gamma)}. \tag{4.7}$$

It is of importance to note the following properties:

$$N^* = s(\tau_\xi), \tag{4.8}$$

$$(N^*)^\epsilon = S_\infty^{-1}, \tag{4.9}$$

which may be checked on (2.1), (2.11) and (4.3) (keeping in mind the value of $\tilde{d}$ quoted after (4.3)). Equation (4.8) shows that τ_ξ is the time required to explore the largest clusters (or, here, the largest dead ends).

We can now construct the scaling form of $\Gamma(t)$ using (4.5). This is easy to visualize if we replace the function $g(x)$ by a sharp cutoff at $x = 1$, giving

$$\Gamma(t) = \sum_{n > s(t)}^{N^*} n^{-(1+\epsilon)}$$

$$= \text{const} \times \frac{1}{s^{\epsilon}(t)}. \tag{4.10}$$

Equation (4.10) holds when $s(t) < N^*$, or equivalently when $t < \tau_\xi$. In the opposite case ($t > \tau_\xi$) we expect $\Gamma(t)$ to decay rapidly, as in any diffusion problem within a bounded domain containing a sink.

(*c*) It will be useful for us to work with Laplace transforms, setting

$$\tilde{\Gamma}(P) = \int_0^\infty \Gamma(t)\, \mathrm{e}^{-Pt}\, \mathrm{d}t.$$

For the macroscopic properties discussed in the present paper, we shall need only to know the limit of $\tilde{\Gamma}(P)$ at low P (low frequencies). Making use of (4.10) (together with the existence of a cutoff in $\Gamma(t)$ at $t \sim \tau_\xi$), we arrive at the following properties:

$$\tilde{\Gamma}(P) = \frac{\tau_\xi}{(N^*)^{\epsilon}}(1 - A\tau_\xi P) \tag{4.11}$$

$$= S_\infty \tau_\xi (1 - A\tau_\xi P), \tag{4.12}$$

where A is an unknown numerical constant, depending on the detailed structure of the cutoff functions. Equation (4.12) will be our basic tool for the study of hydrodynamic dispersion. It is important to appreciate the difference between our case (described by (4.12) and the Montroll–Scher problem, where $p(W) \sim W^{-1+\alpha}$ and $\tilde{\Gamma}(P) \sim P^{-1+\alpha}$ is singular at $P = 0$. Physically, in the Montroll–Scher case, some traps are infinitely slow, while, in our problem, the slowest traps have a finite release time $\sim \tau_\xi$.

4.2. *The backbone response function*

4.2.1. *Definition*

Let us assume that we have injected our dye molecule at an arbitrary point on the backbone, at time $t = 0$. We introduce a 'response function' $R(t)$ defined as the probability (at a later time t) of finding the molecule again on the backbone. The limiting behaviours of $R(t)$ are

$$R(0) = 1, \quad R(t \to \infty) = \bar{\mu}. \tag{4.13}$$

As usual, the response $R(t)$ is directly proportional to the corresponding correlation function

$$\langle \mu(0)\, \mu(t) \rangle - \bar{\mu}^2 = \bar{\mu}\,[R(t) - \bar{\mu}]. \tag{4.14}$$

We can check the normalization in (4.14) at time $t = 0$; since $\mu = 0$ or 1 we have $\langle \mu^2 \rangle = \langle \mu \rangle \equiv \bar{\mu}$ and (4.13) and (4.14) are compatible.

4.2.2. *Relation between response function and memory function*

We shall now construct this relation, using a detailed kinetic model with traps, following Montroll, Scher & Noolandi. Let us call $\sigma_i(t)$ the probability of being on a trap of type (i) at time t. The rate equation for $T(t)$ is

$$\frac{\partial R(t)}{\partial t} = -\omega R(t) + \sum_i \sigma_i(t)\, W_i f_i + \delta(t - 0_+). \tag{4.15}$$

The first term describes capture with a rate ω, which will be specified below. The second term describes a release from the traps. The third term accounts for the injection of the dye at $t = 0_+$. The rate equation for the traps is

$$\frac{\partial \sigma_i}{\partial t} = -W_i \sigma_i + \omega R. \tag{4.16}$$

Going to Laplace transforms, we may write (4.16) in the form

$$\tilde{\sigma}_i(P) = \frac{\omega}{W_i + P} \tilde{R}(P), \tag{4.17}$$

and, returning to (4.15),

$$[\tilde{R}(P)]^{-1} = P[1 + \omega \tilde{\Gamma}(P)]. \tag{4.18}$$

Two limits are of especial interest in (4.18). First let us take $P \to \infty$. The known structure of $\Gamma(t)$ ((4.1), (4.10)) shows that $\tilde{\Gamma}(P) \to 0$ and thus $\tilde{R}(P) \to P^{-1}$. Inserting this, we check that $R(t \to 0) = 1$ as expected from (4.13). The second limit is $P \to 0$, corresponding to

$$\tilde{R}(P) \to P^{-1}[1 + \omega \tilde{\Gamma}(0)]^{-1} \tag{4.19}$$

or to

$$R(t \to \infty) = [1 + \omega \tilde{\Gamma}(0)]^{-1}. \tag{4.20}$$

Comparing this with (4.13), we conclude that

$$\omega \tilde{\Gamma}(0) = -1 + (\bar{\mu})^{-1} \approx (\bar{\mu})^{-1}, \tag{4.21}$$

or (inserting (4.12) for $\tilde{\Gamma}(0)$ and (2.7) for $\bar{\mu}$)

$$\omega = (\bar{\mu} S_\infty \tau_\xi)^{-1} = (S_{\mathrm{B}} \tau_\xi)^{-1}. \tag{4.22}$$

Notice again the difference with the Montroll–Scher problem, where $\tilde{\Gamma}(P = 0) = \infty$. In their case, the probability $\bar{\mu}$ of finding a free carrier vanishes and this modifies the physics very deeply.

Having now specified the capture rate ω, we can go back to (4.18) and write the full relation between memory function and response function in the form

$$[\tilde{R}(P)]^{-1} = P[1 + (S_{\mathrm{B}} \tau_\xi)^{-1} \tilde{\Gamma}(p)] \tag{4.23}$$

$$\to P[1 + (\bar{\mu})^{-1}(1 - A\tau_\xi P)], \tag{4.24}$$

the latter form being valid for $P\tau_\xi < 1$.

4.3. *Longitudinal-diffusion coefficient*

We can now return to the basic equation for $D_\parallel$ (3.11) and replace the $\langle \mu\mu \rangle$ correlation by the response function using (4.14). The result is

$$D_\parallel = \int_0^\infty \mathrm{d}t\, \bar{U}_{\mathrm{B}}^2 \bar{\mu}[R(t) - \bar{\mu}]$$

$$= \bar{\mu} U_{\mathrm{B}}^2 \lim_{P \to 0} [R(P) - \bar{m} P^{-1}]. \tag{4.25}$$

Inserting (4.24) into (4.25), we arrive at the central result

$$D_\parallel = A\tau_\xi \bar{\mu}^2 U_{\mathrm{B}}^2 = A\tau_\xi \bar{U}^2 \tag{4.26}$$

$$= \mathrm{const} \times (\bar{U}\xi)^2 / D_{\mathrm{a}}, \tag{4.27}$$

where we have expressed τ_ξ in terms of the ant diffusivity D_{a} as explained in (2.9).

5. Discussion

The formula (4.26) for the diffusivity may appear trivial at first sight, because of its similarity with classical results for liquid–liquid chromatography (e.g. Rosset *et al.* 1982). However, as pointed out in §2, the proper choice of velocity average ($\bar{U}$) in (4.25) is rather delicate, and its justification required the (relatively) heavy artillery of §4. More precisely, for a given pressure $p_c + \Delta p$ and a given driving force f the predicted scaling law is

$$D_{\parallel} = (U_0 d)^2 D_1^{-1} \left(\frac{\Delta p}{p_c}\right)^{\bar{t}-\beta-2\nu}, \tag{5.1}$$

where U_0 is the drift velocity in a totally saturated medium under the same driving force f, and where we have used (2.5), (2.10) and (2.11). The exponent $\bar{t}-\beta-2\nu$ is of order -0.5. This value cumulates the uncertainties in three percolation exponents and may be rather imprecise, but the sign is probably meaningful.

When we have a very weakly saturated medium, the flow velocities $\bar{U}$ become small, but the dead ends become very large, and create a very broad distribution of retardation times. The latter effect dominates, and $D_{\parallel}$ diverges at $p = p_c$.

The same conclusion holds in two dimensions ($\bar{t} = 1.2$, $\beta = 0.14$, $\nu = 1.35$). On the other hand, if we could go to higher dimensionalities d, we should find a drastic change in behaviour: for $d = 6$, where the percolation statistics becomes simple we have $t = 3$, $\beta = 1$, $\nu = 0.5$ and $t-\beta-2\nu = +1$. Thus, in this hypothetical case, $D_{\parallel}$ would vanish at $p = p_c$.

We do not know of any existing experiments giving $D_{\parallel}$ for weakly saturated media, impregnated with a non-wetting fluid.† We should especially need to have data on *large samples* (to avoid spurious end affects near the threshold) taken at small, variable Δp, just above threshold. As already mentioned, these experiments could be performed not only in 3 dimensions, but also in 2 dimensions, where some interesting model systems are available (Lenormand & Bories 1980; Lenormand 1981; Lenormand, Zarcone & Sarr (to be published).

Our discussion has been restricted to longitudinal dispersion ($D_{\parallel}$). The structure of the transverse-diffusion coefficient $D_{\perp}$ is completely different. Returning to (3.5), we see that $D_{\perp}$ is dominated by the fast velocity fluctuations on the backbone

$$D_{\perp} = \int \langle U_{B\perp}(0)\, U_{B\perp}(t)\rangle \, \mathrm{d}t \, \langle \mu^2 \rangle, \tag{5.2}$$

where $\langle \mu^2 \rangle = \bar{\mu}$ (since $\mu^2 \equiv \mu$ at any point, because $\mu = 0$ or 1). As pointed out in §2, if the flowline was following a simple random walk, we might argue that the correlation time for $\langle U_B\, U_B \rangle$ is simply $a\bar{U}_B^{-1}$, giving $D_{\perp} = \bar{U}a$. But we are dealing with backbone paths that (i) deviate from ideal random walks and (ii) are branched. Thus it may be that the $\langle UU \rangle$ correlation has a relatively slow (power-law) decay in time (up to certain cutoff related to the correlation length ξ): this would complicate seriously the structure of $D_{\perp}$.

Another important question for future work is the structure of the dye distribution at earlier times ($t < \tau_{\xi}$) which may well be probed experimentally in the 'semilocal' range of distances r ($a \ll r \ll \xi$) provided that one is close enough to threshold ($\xi \gg a$). Here, as mentioned in §3, the whole formalism must be revised: the displacements inside each dead end must be taken into account, and (3.2) does not hold.

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† The case of a fluid that wets completely the solid/air interface is clearly more complex. All our discussion assumes well-defined clusters and this, in turn, requires that the contact angle between fluid and solid be finite.

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