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Diffusion of a passive impurity through a porous media: fractal model in an unsaturated medium

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The theory of fractal sets is used to describe convective diffusion of a passive impurity in a partly-saturated porous medium.

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Fluid flows through a porous medium have attracted much attention due to its importance in several technological processes (e.g., filtration, catalysis, chromatography, spread of hazardous waste, petroleum exploration, and recovery, etc. [1,2]). The study of the diffusion of a passive impurity being transported by a liquid or gas in a porous medium is one of the main approaches used to investigate flows in porous materials. By a neutral indicator such as radioactive isotopes, one can obtain a large quantity of information on the motion and mixing of the fluid. Besides isotopes, the neutral indicator may be a pigment or even temperature if the investigator is interested in processes involving convective heat transfer. Helium is often used as the indicator in the study of transport processes in gases.

It is particularly interesting to study convective diffusion in a partly saturated medium, since in this case one can obtain information not only on the flow itself, but also on the geometric characteristics of the regions occupied by a single phase. It is understood that diffusion becomes anomalous in an unsaturated medium and differs appreciably from both normal molecular diffusion and convective diffusion in a completely saturated porous medium, because the diffusion coefficient depends not only on the dynamic characteristics of the flow (as in the case of complete saturation) but also on the geometric characteristics of the one-phase region.

It is assumed hereafter that we are studying the diffusion of a natural impurity in a liquid while its gas (or another liquid) is being forced into a porous medium. Diffusion in the gas will be ignored.

As is known [3], a displacement such as that being studied here can be formulated in terms of percolation (flow) theory [4,5], and in this case the beginning of filtration of the liquid through the gas-saturated sample is equivalent to the formation of an infinite liquid cluster permeating the sample. An infinite cluster exists at $p > p_c$, where p is displacement pressure and p_c is breakthrough pressure (or percolation threshold). On the contrary, the volume fraction of liquid (or saturation coefficient) c_∞ near the percolation threshold, i.e., at small $\Delta p = p - p_c > 0$, exhibits the following scale behaviour: $c_\infty \sim (\Delta p/p_c)^\beta$ and $\beta \cong 0.39$ at $d = 3$, where β is a universal exponent dependent on the dimension of the space d. Similar scaling behaviour is described by certain other characteristics of the infinite cluster, such as the correlation length $l_c = l_0(\Delta p/p_c)^{-\nu}$ and the permeability coefficient $k \sim m l_0^2 (\Delta p/p)^{\bar{t}}$, where l_0 is characteristic dimension of a pore-space capillary and m is porosity. The universal exponents $\bar{t}$ and υ in the three dimensional space take the value $\bar{t} = 1.7$, $\nu \cong 0.9$ [4–6].

It follows from above formulas that $c_\infty \sim (l_c/l_0)^{-\beta/\nu}$. The geometric structure of the liquid cluster near the percolation threshold is extremely complex and cannot be adequately described by the methods of conventional Euclidean geometry. However, it turns out that at distances $l_0 \ll l \ll l_c$, the structure of the cluster can be satisfactorily expressed within the framework of the theory of fractals – sets of fractional dimensionality.

A set of F (enclosed in a Euclidean space of the dimension d) is called a fractal if its fractal dimension d_f is not a whole number (in particular, does not coincide with d or with the natural topological dimension F) and if F satisfies the property of self-similarity. Self-similarity means local invariance of F relative to a discrete half-group dilatations. The fractal dimension is given by

$$d_f = \lim_{\varepsilon \to 0} \frac{\ln N(\varepsilon)}{\ln(1/\varepsilon)},$$

where $N(\varepsilon)$ is the minimum number of d-dimensional cubes of the dimension ε covering the set F: it is understood that F is compact. It is obvious that $d_f \leqslant d$. Along with geometric (regular) fractals, frequent use is also made of stochastic fractals (nearly all natural fractals are stochastic fractals). The properties of stochastic fractals are fully analogous to the properties of geometric fractals if we interpret them only in terms of their mean value. For example, in the formula for d_f, instead $N(\varepsilon)$ we write $\langle N(\varepsilon)\rangle$ for a stochastic fractal, where $\langle \bullet \rangle$ denotes averaging over all possible realizations. Numerous examples of fractal sets and the corresponding definitions can be found in [7,8].

A percolating cluster near the percolation threshold is a typical example of a stochastic fractal. It can be shown that the fractal dimension of the cluster $d_f = d - \beta/\nu$. Thus, at $d = 3$, we have $d_f = 2.56$.

In this study the fractal model is employed to investigate real physical processes. We observe followings:

- (i) a fractal satisfying the property of self-similarity for all length scales is a mathematical object,
- (ii) the use of fractal models to describe natural processes can be valid only with certain limitations on the scale of the phenomena being investigated.

In the subject being examined here, there are actually two length scales: the microscale from the characteristic dimension of a pore-space capillary l_0 to the correlation l_c; the microscale characterizing the nonuniformity of the physical fields in the problem such as the pressure field. The microscale is determined by the dimensions of the sample and depends on external parameters in relation to the problem being considered, while the microscale depends on l_c and thus, on Δp. Here the fractal approach is used only in microscale, i.e., for $l_0 < l < l_c$. All of the power laws governing self-similarity without anomalous exponents are also valid only in this region. The problem is averaged with the transition to the microscale, and fractal internal structure of the liquid cluster disappears. In the microscale, all of the geometric parameters of the cluster and the percolation processes are characterised by the normal dimension $d = 3$. Thus, in regard to actual physical object such as the liquid cluster being examined here, the asymptote in the direction of the fractal dimension d_f should be interpreted not as an actual mathematical limit but only as a transition to the lengths $\varepsilon \sim l_0$, i.e., to the lower boundary of the microscale.

Let us examine the case of steady-state filtration in a partly saturated porous medium at $p_c < p$, $p \cong p_c$. The mean rate of filtration is assumed to be constant within the above-mentioned scales and to be low enough so that the flow has no effect on the geometry of the liquid cluster. Besides, since the scales in question are appreciably greater than the size of the capillary, it can be assumed as a first approximation that Darcy's law is valid for mean filtration velocity:

$$U = -\frac{k}{u}\, q,$$

where k is permeability, u is viscosity, and q pressure gradient. Darcy's law is usually used to describe flow on the macroscopic scale, and it may not be satisfied for each specific cluster at the microscopic level. However, in our case, we are dealing with the average flow velocity for the cluster present. As a result, Darcy's law can be used in this case.

The structure of the cluster is fairly complex and, along with the channels comprising its skeleton (and through which, of course, flow takes place), it contains a substantial number of blind channels so-called dead ends through which liquid does not flow and which participate only in normal molecular (not convective) diffusion. Calculations and numerous experiments [4–6,9] demonstrate that the skeleton of the cluster near the percolation threshold can also be regarded as a fractal. Here, the probability of the cluster c_1 being associated with the skeleton obeys the scaling law $c_1 \sim (\Delta p/p_c)^{\beta_1}$, where $\beta_1 > \beta$. In three dimensional space, $\beta_1 \cong 0.9$. It follows from this fact that the fractal dimension of the cluster is greater than the fractal dimension of the skeleton $d_{1f} = d - (\beta_1/\nu) < d_f$, while mean flow velocity $U_1 \sim U/c_1$ is significantly greater than that which could be expected if an evaluation was made only on the basis of the saturation coefficient.

Since the motion of a single impurity particle does not possess universality, we are going to examine the relative motion of two impurity particles. We designate $r_i(t)$ as the position of the ith particle ($i = 1, 2$) at the moment of time t,

$\xi(t) = r_1(t) - r_2(t) = \xi(0) + \int_0^t V(\tau)\mathrm{d}\tau$, where $V(t)$ is relative coordinate of particle at the moment of time t. Since $\langle V(t)\rangle = 0$, we have $\langle \xi(t)\rangle = \langle \xi(0)\rangle$. This equality means that

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle \xi(t)\rangle = 0,$$

but at the same time

$$\xi = \left\langle \left|\xi(t)\right|^2 \right\rangle^{1/2}, \qquad \frac{\mathrm{d}}{\mathrm{d}t}\left\langle \left|\frac{\mathrm{d}}{\mathrm{d}t}\xi(t)\right|^2 \right\rangle$$

may be nonvanishing. It is evident for these quantities that

$$\left\langle \left|\frac{\mathrm{d}}{\mathrm{d}t}\xi(t)\right|^2 \right\rangle = \langle V(t)V(t)\rangle, \tag{1}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\xi^2 = 2\int_0^t \langle V(t)V(\tau)\rangle \mathrm{d}\tau. \tag{2}$$

The quantity (1) is easily calculated, since it is a simultaneous correlation function and equal to the mean of the square of the difference in velocities at the points $r_1(t)$ and $r_2(t) = r_1(t) + \xi(t)$. Thus

$$\langle V(t)V(t)\rangle = \left\langle \left|V\big(r_1(t)\big) - V\big(r_1(t) + \xi(t)\big)\right|^2 \right\rangle \sim U_\mathrm{c}^2 f_0(U_\mathrm{c}, \xi, l_\mathrm{c}, \eta),$$

where U_c is the mean velocity of the impurity particle; $f_0 = f_0(U_\mathrm{c}, \xi, l_\mathrm{c}, \eta)$ is a weight factor associated with the fractal structure of the cluster: η is the kinematical viscosity.

In view of the self-similarity of the liquid cluster, the function f_0 can be regarded as relatively invariant with respect to the scale transformations $x \to \alpha x, t \to bt$. This leads to the following equation

$$f_0\left(\frac{a}{b}U_\mathrm{c}, a\xi, al_\mathrm{c}, \frac{a^2}{b}\eta\right) = f_0(U_\mathrm{c}, \xi, l_\mathrm{c}, \eta).$$

Therefore, $f_0(U_\mathrm{c}, \xi, l_\mathrm{c}, \eta) = f(\mathrm{Re}_\mathrm{c}, \xi/l_\mathrm{c})$, where $\mathrm{Re}_\mathrm{c} = U_\mathrm{c} l_\mathrm{c}/\eta$.

In the fractal region, f determines the probability that points separated by the distance $\xi(t)$ belong to the active flow region, i.e., to the liquid cluster.

For scales $l_0 \ll \xi \ll l_\mathrm{c}$, we have

$$f(\mathrm{Re}_\mathrm{c}, \xi/l_\mathrm{c}) \sim c_\infty \frac{(\xi/l_0)^{d_\mathrm{f}-1}}{(\xi/l_0)^{d-1}} \sim c_\infty^2 (\xi/l_0)^{-\delta},$$

where $\delta = d - d_\mathrm{f}$, while the coefficient in the above asymptote f may be depend on Re_c. Accordingly, in the regularity region $\xi \geqslant l_\mathrm{c}$, we have $f(\mathrm{Re}_\mathrm{c}, \xi/l_\mathrm{c}) \sim c_\infty^2$. The specific form of the function f in the transitional region $\xi \sim l_\mathrm{c}$ is fairly complex and depends on the geometric properties of the porous medium.

An impurity particle to come into the flow participates in two types of motion:

(i) it is transported by the liquid over the skeleton of the cluster at the velocity U_1,

(ii) having entered a dead end, the particle is slowed and moves only as a result of molecular diffusion.

It leaves the blind channel after the characteristic drift time $\tau_1 \sim l_c^2/D_1$, where the diffusion coefficient in a partly saturated medium $D_1 \cong D_0(\Delta p/p_c)^{\bar{t}-\beta}$ and D_0 is that of molecule [9]. The mean drift velocity U_2 is evaluated by the quantity $l_c/\tau_c \cong D_1/l_c$, where τ_1 represents time of particle drift from the dead end, and τ_c correlation time. Taking into account that the relative probability of the cluster being associated with the skeleton is approximately c_1/c_∞, we have

$$U_c \sim \frac{c_1}{c_\infty}U_1 + \left(1 - \frac{c_1}{c_\infty}\right)U_2 \sim \frac{U}{c_\infty} + U_2.$$

Since $U_2 \cong (\Delta p/p_c)^{\bar{t}+\nu-\beta}$ and $U/c_\infty \cong (\Delta p/p_c)^{\bar{t}-\beta}$ at small Δp, U_c is assumed to be U/c_∞.

To calculate equation (2), we assume that

$$\langle V(t)V(\tau)\rangle = \langle V(t)V(t)\rangle g\left(\frac{t-\tau}{\tau_c}\right),$$

where g is a correlation function, as well as that $g(0) = 1$ and that, with x going to infinity, $g(x)$ decreases more rapidly than any power of x. Here $\tau_c \sim l_c/U_c$.

Equation (2) can be rewritten in the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\xi^2 \sim U_c^2 f(\mathrm{Re}, \xi/l_c)\tau_c \int_0^{t/\tau_c} g(x)\,\mathrm{d}x. \tag{3}$$

In the case of $\xi \ll l_c$ and $t \ll \tau_c$, the integral in equation (3) can be replaced by the quantity $g(0)t/\tau_c$. Thus

$$\frac{\mathrm{d}}{\mathrm{d}t}\xi^2 \sim 2U_c^2\left(\frac{\xi}{l_c}\right)^{-\delta} t c_\infty^2.$$

Under the condition of $\xi_0 = \xi(0)$ we have

$$\xi^{2+\delta} - \xi_0^{2+\delta} \sim U_c^2 l_c^\delta t^2 c_\infty^2.$$

Assuming that $\xi \gg \xi_0 \sim 0$, we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\xi^2 \sim c_\infty^{2\alpha} U_c^{2\alpha} t^{2\alpha-1} l_c^{\alpha\delta}, \quad \alpha = \frac{2}{2+\delta} \leqslant 1.$$

At $t \geqslant \tau_c$, we find that $f(\mathrm{Re}_c, \xi/l_c) \sim c_\infty^2$. Thus, equation (3) takes the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\xi^2 \sim 2U_c^2\tau_c c_\infty^2 \sim 2U\lambda, \quad \lambda = c_\infty l_c.$$

Since the diffusion coefficient $D_\mathrm{c} \sim (1/2)(\mathrm{d}/\mathrm{d}t)\xi^2$, we find that in the fractal region ($\xi \ll l_c$)

$$D_\mathrm{c} \sim c_\infty^{-\alpha\delta} U^{2\alpha} t^{2\alpha-1} \lambda^{\alpha\delta}, \tag{4}$$

while outside this region ($\xi \geqslant l_\mathrm{c}$)

$$D_\mathrm{c} \sim U\lambda. \tag{5}$$

Equations (4,5) can have a somewhat different form. At $\left(\xi \ll l_\mathrm{c}\right)$, we have

$$D_\mathrm{c} \sim \left(\frac{\Delta p}{p_0}\right)^{\alpha_1} t^{v_1},$$

where $\alpha_1 = \alpha(2\bar{t} - \beta) \cong 2.47$, $v_1 = 2\alpha - 1 \cong 0.64$, while at $\xi \geqslant l_c$

$$D_\mathrm{c} \sim \left(\frac{\Delta p}{p_\mathrm{c}}\right)^{\alpha_2},$$

where $\alpha_2 = \bar{t} + \beta - v \cong 1.19$. Thus, we differentiate two diffusion regimes – an anomalous region in the fractal and the normal convective region outside.

In summary, we used numerical values of the critical percolation indices obtained for network models. Since percolation is important in a number of critical phenomena, these indices have the property of universality, i.e., they are nearly independent of type of network. However, they may also depend on its dimensionality. In the case of porous materials with the pore space having the structure of a fractal, this may be significant. Consequently, the numerical values of the above-cited indices α_1 and v_1 might change. The index α_2 corresponds to the diffusion coefficient outside fractal region and in this case should be fairly universal. There has been considerably less study of percolation theory on fractal sets than on regular network, so it is not yet possible to obtain sufficiently reliable values of the critical percolation in relation to the dimensions of fractal sets. We believe that the above estimates are definitely valid when the porous materials have a sufficiently regular structure or a high porosity and the pore space is not fractal.

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