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Some aspects of diffusion: fluctuations in reaction diffusion, and geometric influences in nonuniform media

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Summary. We deal with two diffusion problems: Space-integrated conserved entities characterizing very fast - diffusion - controlled reactions, such as time lags, etc. are universal. They are given by relationships which do not reflect the failure of the mean field hydrodynamic equations. We present another application which does not reflect this failure, for determining the surface flux via a diffusion controlled reaction producing a colored product. Another anomalous diffusion process we considered is transport through cellular materials whose cell sizes are highly nonuniform. We have analyzed the effects of extreme nonuniformity by considering fractal-like models of cellular solids. The diffusion current through these models can exhibit anomalous time-dependencies which are not predicted by the diffusion equation. In particular, it is shown that the initial diffusion current can be characterized by a power-law dependence on the time. Furthermore, the exponent of the power law is given in terms of the distribution of cell sizes in the fractal-like cellular solid.

Key words: Diffusion-reaction – Transport – Time lag – Fractal foams – Low density microcellular materials

Recently our interests have been engaged in two areas of diffusion in which the honoree, Steven Prager, has made notable contributions: (a) diffusion-controlled reactions, and (b) diffusion in inhomogeneous media.

Diffusion limited, very fast reactions have attracted considerable interest in recent years [1–3]. In very fast reactions, diffusion dominates the dynamics and the large concentration fluctuations resulting from the tendency of the particles to react mostly with their immediate neighbors. These slower kinetics are in general no longer described by the mean field hydrodynamic equations with large deviations – particularly for lower than three-dimensional diffusion. A recent investigation based on numerical simulation of one dimensional diffusion limited permeation in a reacting membrane of species 1, 2 reacting according to:

$$1 + 2 \rightarrow \text{inert}$$

showed though, that when one focused only a gross variable such as the total flow up to time t, $Q(t)$, out of the membrane, the hydrodynamic equations gave an excellent approximation even in the diffusion-limited regime [4]. Denoting by $u_i(x, t)$ the concentration of species $i = 1, 2$ in the membrane (and taking 2 to be immobile or essentially attached to the membrane, i.e., $D_2 = 0$) the mean field, hydrodynamic equations are:

$$\begin{aligned} \partial u_1/\partial t &= D_1\, \partial^2 u_1/\partial x^2 - k u_1 u_2 \\ \partial u_2/\partial t &= -k u_1 u_2 \end{aligned} \tag{1}$$

in $0 < x < l$ with

$$u_1(x, 0) = v_1(x), \qquad u_2(x, 0) = v_2(x) \tag{2}$$

and

$$u_1(0, t) = c_0, \qquad u_1(l, t) = c_1 \quad (c_0 > c_1). \tag{3}$$

Quite independently of whether the mean field equations of Eq. (1) apply, the difference in the number of particles of type 1 over that of type 2 can only change because of the flux of type 1 particles in and out of the membrane. Because of this conservation theorem the steady state flux j_s out of the membrane at $x = l$, $j_x = -D_1(\partial u_1/\partial x)_{x=l}$. The time-lag T is the horizontal asymptote to the time axis (see Fig. 1) which characterizes the long time behavior of $Q(t)$:

$$Q(t) \sim (t - T) j_s \quad \text{as } t \to \infty \tag{4}$$

is still given exactly by the values obtained by integrating Eqs. (1)–(3):

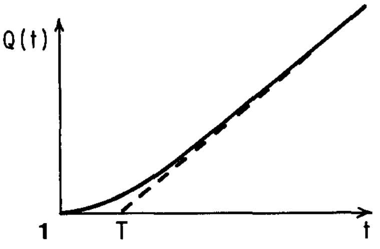
$$j_s = D_1(c_0 - c_1)/l, \tag{5}$$

and

$$T = \int_0^l dx \int_x^l dz[c_0 + (c_1 - c_0)(z/l + v_2(z) - v_1(z))]/D_1(c_0 - c_1). \tag{6}$$

These quantities are measurable and universal, i.e., they depend on the initial and boundary conditions but not on any details of the reaction between particles 1 and 2, and they reflect only the validity of the equation for the difference $(u_1 - u_2)$:

$$\partial(u_1 - u_2)/\partial t = D_1\, \partial^2 u_1/\partial x^2. \tag{7}$$



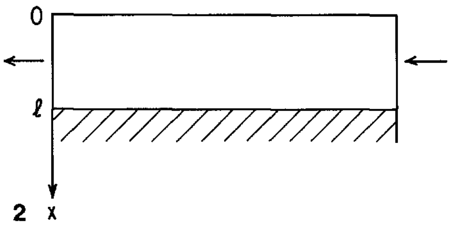


Fig. 1. The total flow per unit area through the membrane, $Q(t)$, as a function of the time t and its linear asymptote which intersects the time axis at the time-lag T

Fig. 2. Colorimetric measurement of the flux F in a membrane of known area and thickness, l. The bounding surface at $x = l$ is impermeable to all species and that at $x = 0$ to the colored species. Light passes through the sample as indicated by the arrows

This holds even if Eq. (1) does not. The simulations of Ref. [4] confirm these results over the whole, large range of k values which was employed, as can be seen from Figs. (1)–(3) of Ref. [4].

One can use a diffusion controlled reaction to study the surface fluxes, $F(t)$, of a reagent of concentration w, into a fixed area of different membranes. The fixed thickness of the membrane is l, and it contains a small amount, but in sufficient excess, of other reagents to react with w to form a new species, of concentration c, which can be identified by its color. This reaction is quasi-first order [5]. The rate constant k_1 of this reaction can be separately determined. The colored species is monitored colorimetrically perpendicularly to the direction of diffusion (cf. Fig. 2). The total color developed up to time t, is directly proportional to:

$$\phi(t) = \int_0^l c(x, t)\, dx, \tag{8}$$

and ϕ need only be measured to obtain the desired fluxes:

$$F(t) = -[D_w(\partial w/\partial x)_{x=0}]. \tag{9}$$

The mean field diffusional boundary value problem is:

$$(\partial w/\partial t) = (\partial/\partial x)[D_w(\partial w/\partial x)] - k_1 w, \tag{10}$$

$$(\partial c/\partial t) = (\partial/\partial x)[D_c(\partial c/\partial x)] - k_1 w, \tag{11}$$

with

$$[D_c(\partial c/\partial x)]_{x=l} = [D_w(\partial w/\partial x)]_{x=l} = 0, \tag{12}$$

$$[D_c(\partial c/\partial x)]_{x=0} = 0 \tag{13}$$

and the upper surface is maintained at fixed concentration:

$$w(0, t) = w_0, \text{ a constant}, \tag{14}$$

and initially the membrane is free of reagent:

$$w(x, 0) = c(x, 0) = 0. \tag{15}$$

Even if these hydrodynamic equations do not apply, their space integrated versions reflect the conservation of species except for what enters at $x = 0$. Thus integrating Eqs. (10) and (11) over x from 0 to l and eliminating $d\phi/dt$ one finds the desired flux:

$$F(t) = d\phi/dt + 1/k_1(d^2\phi/dt^2). \tag{16}$$

Thus by differentiating the measured $\phi(t)$, knowing k_1, $F(t)$ is determined.

Transport through foams and fractal-like cellular solids also can deviate from what is expected from Fick's and Fourier's law of transport of mass and heat in a homogeneous medium. We have considered the nature of gas diffusion through rigid polyurethane foams blown by, say, water vapor rather than chloro-fluorocarbons. Such foams have a highly non-uniform distribution of cell sizes. Foams belong to the upper linear dimension limits of a class of materials with certain anomalous physical properties called "low density microcellular materials" (LDMM), which have been recently reviewed [6]. We studied gas diffusion through one- and three-dimensional, regular fractal models of these foams [7].

In considering this diffusion, we assume gas concentrations are sufficiently small that nonlinear effects are not important. This means the gas flowing through a cell boundary is proportional to the difference in gas concentrations across the boundary. It also means the structural integrity of the foam is not compromised: gas pressure differences are assumed to be so small that no cell walls are bent or broken.

Our previous results can be summarized as follows:

(1) Diffusion through fractal-like foams cannot be accurately described by a diffusion equation.

(2) The characteristics of the diffusion depend sensitively on both the distribution of the cell sizes, and on the wall thicknesses which separate the cells.

(3) If the surface of an initially empty foam is brought into contact with a gas at a time $t = 0$, the transient current surge has an anomalous time dependence. In many cases, the time derivative of this current diverges as $t \to 0$, and then decays like $t^{-\alpha}$, where the value of α depends on the structure of the foam.

(4) The long-time diffusion characteristics of the diffusion in foams are also anomalous, and in some cases the rate at which gas escapes from the foam can be very slow.

Here we present a simple illustration of the anomalous transient time dependence of the transient gas diffusion into (or out of) a fractal-like foam in which all cell walls are assumed to have the same thickness. Our earlier work was based on a specific fractal model (the Sierpinski gasket), and considered a systematic variation in cell-wall thicknesses. The results derived here are more general in the sense that we obtain the anomalous transient current surge using only the distribution of cell sizes which lie at the foam surface. We characterize this distribution by $N(v)$, where v is the cell volume.

For sufficiently short times, gas diffusion does not penetrate deeply into the foam, so the transient current involves primarily those foam cells which make up the surface. As the cells fill with gas, the current into the ith cell is of the form:

$$J_i(t) \sim \sigma a_i \exp[-\sigma(\gamma_i a_i t/v_i)] \quad \text{for small } t, \tag{17}$$

where the index i labels the cells bordering the surface, v_i is the cell volume, a_i is the cell area on the foam surface, and γ_i is a number of order unity. This equation simply notes that the initial current is proportional to the cell area exposed to the gas, but the current decreases in time. This time decrease is associated with the filling of the cell. The rate at which gas concentration in the cell increases is inversely proportional to the cell volume, and linearly related to the cell area. The extra factor γ_i is inserted because the filling rate also depends on the rate at which gas "leaks" out into other cells deeper in the foam. This extra current is also proportional to a cell area, so the correction has the same characteristic dependence on area and volume. In other words, if the γ_i for cells in a narrow volume range were averaged, to give $\gamma(c)$, this average should not vary significantly with the v.

The total current into the foam is:

$$j(t) = \sum_i J_i(t). \tag{18}$$

The sum can be simplified by assuming that, on average, cell areas are proportional to cell volumes to the 2/3 power, and the γ_i are independent of volume:

$$a_i \sim (v_i)^{2/3} \quad \text{and} \quad \gamma_i \sim \gamma. \tag{19}$$

Then

$$J(t) \sim \int N(v) v^{2/3} \exp[-(Ct/v^{1/3})]\, dv, \tag{20}$$

where C is a constant. This integral is finite for all t, since at $t = 0$ the integral is proportional to the surface area of the foam, which is finite. However, the time derivative of the current:

$$(d/dt)\, J(t) \sim \int N(v) v^{1/3} \exp[-(Ct/v^{1/3})]\, dv \tag{21}$$

is not necessarily finite. If the foam is fractal-like, with cells of arbitrarily small size, then:

$$(d/dt)\, J(0) \sim \int_0^\infty N(v) v^{1/3}\, dv \tag{22}$$

is proportional to the average radius of a cell at the surface, and this quantity may be divergent. For example, in the Sierpinski gasket a smoothed distribution function of the cell sizes is:

$$N(v)_s \sim (1/v)^\beta \quad \text{with } \beta = 1 + \ln(3)/3\ln(2), \tag{23}$$

and this gives a divergent time derivative for $J(t)$ as $t \to 0$.

When $N(v)$ has the power-law form as described above, the transient current derivative can be evaluated. Setting $x = C(1/v)^{1/3}$:

$$(d/dt)\, J(t) \sim \int_0^\infty x^{(3\beta - 5)} \exp(-xt)\, dx, \tag{24}$$

and letting $y = xt$, so that the integral can be written as a power of t times a dimensionless constant gives:

$$(d/dt)\, J(t) \sim (1/t)^{(3\beta - 4)} \tag{25}$$

for the case of the Sierpinski-gasket type foam, the result:

$$(d/dt)\, J(t) \sim (1/t)^\alpha \quad \text{with } \alpha = (\ln(3/2)/\ln(2)) \tag{26}$$

agrees with the earlier established result.

It is worth noting that gas diffusion is only one of many transport properties that one might consider in fractal-like cellular solids. Heat conduction, for example, is technologically important and theoretically challenging. Heat-transport takes place through convection within cells, radiation across cells, and conduction along the cell-wall and cell-edge network. Which heat transport mechanism is dominant depends on the physical character of the foam and the material contained in the cells. If the cell walls form the primary barrier to heat conduction, our treatments of diffusion could be directly applicable. On the other hand, if the cell wall material is a relatively good heat conductor, the transport is more directly related to the diffusion on fractals which was reviewed by Havlin and Ben-Avraham [8].

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