Kinetics of diffusion-controlled processes in a fractal medium

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The kinetics of diffusion-controlled reactions describable by a Smoluchowski equation in a fractal medium is analyzed. A class of model potentials which make it possible to solve the time-dependent Smoluchowski equation is constructed. Corrections to the standard solution for the fractal geometry of the medium are discussed.

The Smoluchowski equation can be used to advantage to describe the kinetics of diffusion-controlled reactions. Steady-state solutions of this equation can essentially always be found, at least in quadrature form. Time-varying solutions, in contrast, cannot be derived for arbitrary interaction potentials. Studies have accordingly been made[1-3] of the question of constructing model potentials which, on the one hand, would make it possible to find analytic solutions of the time-dependent Smoluchowski equation and which, on the other, might be regarded as "reasonable" approximations of real interaction potentials. The problem of seeking such potentials becomes much more complex if the reaction is occurring in an inhomogeneous medium.

1. Fractal models of amorphous and disordered media have recently been adopted widely.

Fractals differ from Euclidean structures in that they have a fractional spatial dimension, do not conform to a translation group (even locally), and are instead characterized by self-similarity (i.e., a local invariance under scale transformations). For this reason, transport and reaction processes on fractals are "anomalous." For example, for a particle undergoing a random walk along a fractal we have a dependence[4-6]

$$\langle|\mathbf{r}(t)|^2\rangle\propto t^{2/d_w},\quad d_w=2+\theta>2,$$

where d_w is the dimension of the trajectory of the random walk, and $\theta>0$ is an anomalous diffusion exponent. The diffusion coefficient on a fractal thus cannot be regarded as constant and is instead characterized by a scaling behavior[4-6]

$$K(r)\sim K_0r^{-\theta}. \tag{1}$$

Brownian diffusion on a fractal is described by the equation

$$\frac{\partial\psi(r,t)}{\partial t}=r^{1-D}\frac{\partial}{\partial r}\left[K(r)r^{D-1}\frac{\partial\psi(r,t)}{\partial r}\right], \tag{2}$$

where $\psi(r,t)$ is a distribution function (the average probability density for finding the particle at time t at point $\mathbf{r}$ under the condition that at time $t=0$ the particle was at the point $\mathbf{r}=\mathbf{0}$). For simplicity, the equation has been written in spherical coordinates; D is the dimension of the fractal.

A solution of Eq. (2) is well known:[4,6]

$$\psi(r,t)=\frac{d_w}{D\Gamma(D/d_w)}(K_0d_w^2t)^{-D/d_w}\exp\left(-\frac{r^{d_w}}{K_0d_w^2t}\right). \tag{3}$$

It leads to the behavior

$$\langle|\mathbf{r}(t)|^2\rangle=(K_0d_w^2t)^{2/d_w}\Gamma[(D+2)/d_w]/\Gamma(D/d_w),$$

$$\psi(0,t)=\frac{d_w}{D\Gamma(D/d_w)}(K_0d_w^2t)^{-D/d_w}. \tag{4}$$

Expressions (3) and (4) agree well with the results of a numerical simulation of diffusion on fractals and also with the results of renormalization-group calculations for regular fractals (Sierpinski gaskets).[4-6]

The diffusion of interacting particles of diffusion processes in a potential have received much less study, although these processes are of particular interest from the standpoint of reaction kinetics in a fractal medium. To a large extent, the reason for this situation is that the interaction between diffusing particles in a real system is usually fairly complex, containing both a short-range part associated with excluded-volume effects and a long-range component due to, for example, a Coulomb interaction. Incorporating the effect of long-range forces on diffusion characteristics is a rather complex problem even in the Euclidean case.

In the present paper we are interested in the effect of long-range potential forces on diffusion-kinetic processes describable by a Smoluchowski equation in a fractal medium. By analogy with the approach taken in Refs. 1–3, we focus on the construction of a class of model potential which make it possible to find analytic solutions (in quadrature form) of the time-dependent Smoluchowski equation.

2. Using (1), we write a Smoluchowski equation for a particle executing a Brownian motion on a fractal in the field of another particle, which is at the origin of coordinates (for simplicity, we consider the case of spherical symmetry and a potential interaction):

$$\frac{\partial\psi}{\partial t}=r^{1-D}\frac{\partial}{\partial r}\left[K(r)r^{D-1}\left(\frac{\partial\psi}{\partial r}+\beta\frac{\partial V}{\partial r}\psi\right)\right]. \tag{5}$$

Here $\psi(r,t)$ is a distribution function, $\beta^{-1}=kT$, and $V(r)$ is the interaction potential.

In solving Eq. (5), we use the very simple boundary conditions

$$\psi(\rho,t)=0,\quad \psi(\infty,t)=1, \tag{6}$$

where ρ is the radius of the reaction surface. Introducing

$$\tau=K_0t,\quad U=\beta V,\quad x=\frac{1}{\gamma}r^{\gamma},\quad \gamma=\frac{\theta}{2}+1,$$

and introducing the new function $\varphi(x,\tau)$ in accordance with

$$\varphi=\psi e^{v},$$

$$v(x)=\alpha\ln x+u(x),\quad u(x)=\frac{U(x)}{2},\quad \alpha=(D-\gamma)/2\gamma,$$

we can put Eq. (5) and boundary conditions (6) in the form

$$\frac{\partial\varphi}{\partial\tau}=\varphi''+F(x)\varphi, \tag{7}$$

$$\varphi(R,t)=0,\quad \lim x^{-\alpha}\varphi(x,t)=1, \tag{8}$$

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where the primes mean partial derivatives with respect to x, $R = (1/\gamma)\rho^{\gamma}$, and the function $F(x)$ is given by

$$F(x)=u''(x)-[u'(x)]^2+2\alpha x^{-1}u'(x)+\alpha(1-\alpha)x^{-2}.$$

Assuming

$$u(x)=\alpha\ln x-\ln w,\quad U=-2\ln x^{-\alpha}w(x),$$

we find that the function $w(x)$ satisfies the equation

$$w''+F(x)w=0. \tag{9}$$

As was pointed out in Refs. 1–3, this equation can be used to construct model potentials for a given function $F(x)$. Noting that it is frequently possible to use either Laplace transforms or the method of separation of variables to solve time-dependent equation (7), once an eigenvalue problem has been found, we conclude that the question of constructing model potentials is determined by whether it is possible to find an analytic solution of the equation

$$y_\lambda''(x)+(F(x)+\lambda)y_\lambda(x)=0.$$

For $\lambda = 0$, the solution $y_0(x) = w(x)$ must satisfy the boundary condition

$$\lim_{x\to\infty} x^{-\alpha}y_0(x)=1. \tag{10}$$

It is not difficult to see that in contrast with the Euclidean case (with $\alpha = 1$) condition (10) is "nontrivial" in the sense that it is not satisfied by a solution of the equation with $F(x)\equiv 0$. The simplest solution of Eq. (9) which satisfies boundary condition (10) is the "null" solution $w(x) = x^{\alpha}$, which corresponds to $U(x) = 0$. In this case the function $F(x)$ is

$$F(x)=-\alpha(\alpha-1)x^{-2},\quad {}^1/_2<\alpha<1. \tag{11}$$

It is not difficult to seek all solutions of Eq. (9) which correspond to the choice of F in form (11):

$$w(x)=x^{\alpha}+a_0x^{1-\alpha},$$

where a_0 is a parameter.

The corresponding model potentials are

$$U(x)=-2\ln(1+a_0x^{1-2\alpha}). \tag{12}$$

In the Euclidean case ($\alpha = 1$), potential (12) becomes the very simple model potential which was studied in Ref. 1.

From (12) we find that at large r we have

$$V(r)\sim -a_0r^{d_w-D},\quad D-d_w<1.$$

Potential (12) falls off at infinity more slowly than a Coulomb potential, so long-range effects should be more prominent in this model than in the Euclidean case.

3. We turn now to a solution of Eq. (7), (8). As the initial condition we use a Boltzmann distribution

$$\psi(r,0)=e^{-\beta V(r)},\quad \varphi(x,0)=x^{\alpha}e^{-U(x)/2}.$$

It is a simple matter to find a steady-state solution of Eq. (7):

$$\varphi_\infty(x)=x^{\alpha}[1-(x/R)^{1-2\alpha}].$$

We set

$$z(x,\tau)=\varphi(x,\tau)-\varphi_\infty(x).$$

It is not difficult to verify that z satisfies the same equation as is satisfied by φ and also the following boundary and initial conditions:

$$z(R,\tau)=0,\quad \lim_{x\to\infty}x^{-\alpha}z(x,t)=0,$$
$$z(x,0)=(l_0+a_0)x^{1-\alpha},\quad l_0=R^{2\alpha-1}. \tag{13}$$

We are interested below in the reaction rate $k(t)$, which is determined by the following expression according to Ref. 3:

$$k(t)=S_D(\rho)K(\rho)\frac{\partial\psi}{\partial r}\bigg|_{r=\rho},$$

where $S_D(\rho) = S_D(1)\rho^{D-1}$ is the area of the surface of a D-dimensional sphere of radius R, and $S_D(1) = 2\pi^{D/2}/\Gamma(D/2)$.

In the steady state, the reaction rate is

$$k_\infty=S_D(R)K_0(2\alpha-1)\gamma^{2\alpha}R^{2\alpha-1/\gamma}(1+l_0R^{1-2\alpha}).$$

Taking Laplace-Carson transforms of Eq. (7), written for the function z, and of conditions (13), we find

$$p(\tilde z(x,p)-z(x,0))=\tilde z''(x,p)+F(x)\tilde z(x,p), \tag{14}$$

$$\tilde z(R,p)=0,\quad \lim_{x\to\infty}x^{\alpha}\tilde z(x,p)=0, \tag{15}$$

where $\tilde z(x,p)$ is the transform of the function $z(x,t)$.

Setting

$$z_1(x,p)=\tilde z(x,p)-z(x,0),$$

we can rewrite Eq. (14) and boundary conditions (15) as

$$z_1''(x,p)+[-p+\alpha(1-\alpha)x^{-2}]z_1(x,p)=0, \tag{16}$$

$$z_1(R,p)=-(l_0+a_0)R^{1-\alpha},\quad \lim_{x\to\infty}x^{-\alpha}z_1(x,p)=0. \tag{17}$$

Equation (16) is related to the Bessel equation. Its solution can be written in the form

$$z_1(x,p)=C_1(x)^{1/2}I_m(p^{1/2}x)+C_2x^{1/2}K_m(p^{1/2}x),\quad m=\alpha-{}^1/_2>0.$$

Using the second of boundary conditions (17), we find $C_1 = 0$ and thus

$$z_1(x,p)=(l_0+a_0)x^{1-\alpha}\left[1-\left(\frac{x}{R}\right)^m\frac{K_m(p^{1/2}x)}{K_m(p^{1/2}R)}\right]. \tag{18}$$

Using the notation $\Delta k(p) = k_1(p) - k_\infty$, we find

$$\Delta k(p)\infty\frac{\partial z_1(x,p)}{\partial x}\bigg|_{x=R}\propto(l_0+a_0)R^{1-\alpha}\left[p^{1/2}\frac{K_{m-1}(p^{1/2}R)}{K_m(p^{1/2}R)}\right]. \tag{19}$$

4. To find $z(x,t)$ and $k(t)$, we would have to take the inverse transforms of (18) and (19). Unfortunately, this cannot be done exactly. We can, on the other hand, discuss several important asymptotic cases.

A. The large-t limit: $R^2/t,\ x^2/t \ll 1$.

We use the asymptotic expression for the function $K_\nu(z)$ as $z\to 0$ (Ref. 7):

$$K_\nu(z)\approx\frac{1}{2}\Gamma(\nu)\left(\frac{z}{2}\right)^{-\nu}\left[1+\frac{z^2}{4(1-\nu)}\right].$$

From (18) we then find

$$z_1(x,p)\propto(l_0+a_0)x^{1-\alpha}\left(1-\frac{x^2}{R^2}\right)\left[1-\frac{1}{1+R^2p/4(1-m)}\right].$$

We thus have

$$z(x,t) \propto (l_0+a_0)x^{1-\alpha}\left(1-\frac{x^2}{R^2}\right)\exp\left[-\frac{4(1-m)}{R^2}t\right],$$

$$\Delta k(t) \propto 1-\exp\left[-\frac{4(1-m)}{R^2}t\right].$$

B. The small-t limit: R^2/t, $x^2/t \gg 1$.

In this case, using the asymptotic expression $K_m(z) \approx (\pi/2z)^{1/2}e^{-z}$ for $|z| \gg 1$, we can write

$$z_1(x,p) \propto (l_0+a_0)x^{1-\alpha}\left\{1-\left(\frac{x}{R}\right)^{\alpha-1}\exp[-p^{1/2}(x-R)]\right\}.$$

In the small-t limit we thus have

$$z(x,t) \propto (l_0+a_0)x^{1-\alpha}\left\{1-\left(\frac{x}{R}\right)^{\alpha-1}\left[1-\Phi\left(\frac{x-R}{2t^{1/2}}\right)\right]\right\},$$

$$\Delta k(t) \propto \left.\frac{\partial z}{\partial x}\right|_{x=R} \propto (l_0+a_0)R^{1-\alpha}\frac{1}{(\pi t)^{1/2}},$$

where $\Phi(x)$ is the probability integral.

In the Euclidean case ($\alpha = 1$) we have

$$z_e(x,t) \propto (a_0+l_0)\,\Phi\left(\frac{x-R}{2t^{1/2}}\right).$$

The asymptotic behavior at large distances is

$$x/R \gg 1 \quad (R^2/t \ll 1, \quad x^2/t \gg 1).$$

Using the asymptotic expressions above, we find

$$z_1(x,p) \propto (l_0+a_0)x^{1-\alpha}\left[1-\frac{1}{\Gamma(m)}\left(\frac{2\pi}{x}\right)^{1/2}\left(\frac{x}{2}\right)^m \times p^{(\alpha-1)/2}\exp(-p^{1/2}x)\right].$$

Taking inverse transforms, we find

$$z(x,t) \propto (l_0+a_0)x^{1-\alpha}\left[1-\left(\frac{x}{2}\right)^{-\alpha}2^{(2-\alpha)/2}t^{(1-\alpha)/2} \times \frac{\exp(-x^2/8t)}{\Gamma(\alpha-{}^1/_2)}D_{\alpha-2}\left(\frac{x}{2t^{1/2}}\right)\right],$$

where $D_\alpha(z)$ is the Whittaker function.

Using an asymptotic expansion for $D_\alpha(z)$ at $z \gg \alpha$ (Ref. 7),

$$D_\alpha(z) \approx z^\alpha \exp\left(-\frac{z^2}{4}\right),$$

we find

$$z(x,t) \propto (l_0+a_0)x^{1-\alpha}\left[1-\frac{t^{(3-2\alpha)/2}}{x^2}\frac{4}{\Gamma(\alpha-{}^1/_2)}\exp\left(-\frac{x^2}{4t}\right)\right].$$

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