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Kinetics on diffusion-controlled reactions in a fractal medium

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The kinetics are investigated for diffusion-controlled reactions in a fractal medium described by a Smoluchowski equation. A class of model potentials are taken into account so as to solve the time-dependent Smoluchowski equation. Corrections to the standard solution are proposed for the fractal geometry of the medium.

KEY WORDS: fractal, Smoluchowski equation, diffusion-controlled reaction

1. Introduction

The Smoluchowski equation can be used to describe the kinetics of diffusion-controlled reactions. Steady-state solutions of this equation is always found at least in quadratic form. In contrast, time-varying solutions cannot be obtained for arbitrary interaction potentials. Some of studies [1] have been carried out for handling 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 hand, might be considered as reasonable approximations of real interaction potentials. The work on seeking such potentials is getting more complex if the reaction takes place in an inhomogeneous medium. Fractal models of amorphous and disordered media [2,3] have intensively been investigated.

Fractals differ from Euclidian structures in that they have a fractional spatial dimension, do not conform to a translation group (even locally), and are instead characterised 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 work along a fractal the mean-square displacement of a random walker is described as a form [3–5]:

$$\left\langle \left| \boldsymbol{r}(t) \right|^2 \right\rangle \propto t^{2/d_{\mathrm{w}}}, \quad d_{\mathrm{w}} = 2 + \theta > 2,$$

where t is time, d_{w} is the dimension of the trajectory of the random work, and $\theta > 0$ is an anomalous diffusion exponent. The diffusion coefficient on a fractal thus can not be regarded as constant and is instead characterised by a scaling behaviour [3–5]

$$K(r) \sim K_0 r^{-\theta}. \tag{1}$$

Brownian diffusion on a fractal is described by the equation

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

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

A solution of equation (2) is well known [3,4]:

$$\psi(r,t) = \frac{d_\mathrm{w}}{D\Gamma(D/d_\mathrm{w})} \left(K_0 d_\mathrm{w}^2 t\right)^{-D/d_\mathrm{w}} \exp\left\{-\frac{r^{d_\mathrm{w}}}{K_0 d_\mathrm{w}^2 t}\right\}. \tag{3}$$

Here the mean-square displacement has a form:

$$\left\langle \left|\boldsymbol{r}(t)\right|^2 \right\rangle = \frac{(K_0 d_\mathrm{w}^2 t)^{2/d_\mathrm{w}} \Gamma((D+2)/d_\mathrm{w})}{\Gamma(D/d_\mathrm{w})}. \tag{4}$$

Equations (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) [3–5].

The diffusion of interacting particles on diffusion processes in a potential has not been sufficiently investigated, although these processes are of significance from a reaction kinetics point of view in fractal media. The reason for this is that the interaction between diffusing particles in a real system is fairly complex since it contains not only a short-range part associated with excluded volume effects but also a long-range component due to, for example, a Coulomb interaction. Incorporation of the long-range forces into diffusion characteristics is a rather complex problem even in the Euclidean case.

The aim of this paper is to investigate the effect of long-range potential forces on diffusion-kinetic processes described as a Smoluchowski equation in a fractal media. By analogy with the approach in [1], we focus on the construction of a class of model potential which enable us to find analytic solutions (in quadrature form) of time-dependent Smoluchowski equation.

2. Theoretical method on diffusion-controlled kinetics

Using equation (1), we write a Smoluchowski equation for a particle with 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. So as to solve equation (5), we use the simple boundary conditions:

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

where ρ is the radius of the reaction surface. When we assume $\tau = K_0 t$, $U = \beta V$, $x = (1/v)r^\gamma$, $\gamma = (\theta/2) + 1$ and assume the new function $\varphi(x,\tau)$ in accordance with

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

equation (5) and boundary conditions (6) is transformed into the following forms:

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

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

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

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

Taking $u(x) = \alpha \ln x - \ln w$, $U = -2\ln x^{-\alpha} w(x)$, we obtain the function $w(x)$ to satisfy the equation:

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

As mentioned in [1], this equation can be used to represent model potentials for a given function $F(x)$. It is possible to use either Laplace transforms or the method of separation of variables to solve time-dependent equation (7), if it is related to an eigenvalue problem. As a result the question for model potentials is determined by whether it is possible to get an analytic solution of the equation

$$y''_\lambda(x) + \left[F(x) + \lambda\right]y''_\lambda(x) = 0.$$

For $\lambda = 0$, the solution $y_0(x) = w(x)$ has to 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 $\alpha = 1$ equation (10) is nontrivial in the sense that it is not satisfied by a solution of the equation with $F(x) = 0$. The simplest solution of equation (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 given by

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

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

$$w(x) = x^\alpha + a_0 x^{1-\alpha},$$

where a_0 is a parameter. The corresponding model potentials are

$$U(x) = -2\ln\bigl(1 + a_0 x^{1-2\alpha}\bigr). \tag{12}$$

In the Euclidean case ($\alpha = 1$), potential (12) becomes very simple model potential given in [1].

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

$$V(r) \sim -a_0 r^{d_\mathrm{w} - D}, \quad D - d_\mathrm{w} < 1.$$

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

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

$$\psi(r, 0) = \exp\bigl(-\beta V(r)\bigr), \qquad \varphi(x, 0) = x^\alpha \exp\left(\frac{-U(x)}{2}\right).$$

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

$$\varphi_\infty(x) = x^\alpha \left\{1 - \left(\frac{x}{R}\right)^{1-2\alpha}\right\}.$$

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 condition:

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

We are interested below in the reaction rate $k(t)$, which is determined by the following expression [1]:

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

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, the reaction rate is

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

Taking Laplace–Carson transforms of equation (7) with respect to z, and of conditions (13), we find

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

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

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

Setting $z_1(x, p) = \tilde{z}(x, p) - z(x, 0)$, we can rewrite equation (14) and boundary conditions (15) as

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

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

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

$$z_1(x, p) = C_1x^{1/2}I_m\left(p^{1/2}x\right) + C_2x^{1/2}K_m\left(p^{1/2}x\right), \quad m = \alpha - \frac{1}{2} > 0.$$

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

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

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

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

3. Summary

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 $K_v(z)$ as $z \to 0$ [6]:

$$K_v(z) \approx \frac{1}{2}\Gamma(v)\left(\frac{z}{2}\right)^{-v}\left\{1 + \frac{z^2}{4(1-v)}\right\}.$$

From (18) we then find

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

We thus have

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

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

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

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

In the small-t limit we thus have

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

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

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

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

The asymptotic behaviour at large distance is

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

Using the asymptotic expressions above, we find

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

Taking inverse transforms, we find

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

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

Using an asymptotic expansion for $D_\alpha(z)$ at $z \gg \alpha$ [6],

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

we find

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

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