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Intermittent free diffusion in the presence of sparse obstacles: mean obstacle encounter time

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Abstract

Particle diffusion in the presence of sparse obstacles may be considered as a sequence of relatively long intervals, during which the particle diffuses in regions free of obstacles, separated by relatively short intervals during which the particle suffers multiple collisions with an obstacle. The present paper focuses on the mean duration of the short intervals, called mean encounter time, assuming that the obstacles are identical spheres. Based on scaling arguments, one can deduce that this time is proportional to the ratio of the square of the obstacle radius and the particle diffusivity. We derive an expression for the mean encounter time, which shows that the proportionality coefficient is $1/6$.

Keywords

Smoluchowski theory; effective diffusivity; Wiener sausage

1. Introduction

It is well known that the presence of obstacles results in a slowdown of diffusion compared to the obstacle-free case. This happens because every time a diffusing particle meets an obstacle, it wastes some time. When the obstacle volume fraction is small, the particle travels in a region of space free of obstacles for a relatively long time. Then it encounters an obstacle and spends a relatively short time near this obstacle, during which the particle suffers multiple elastic collisions with the obstacle. After that, the particle leaves the obstacle and freely travels again until it meets another obstacle, and the next encounter begins. Thus, particle diffusion in the presence of sparse obstacles is intermittent in nature.

The encounter time is a random variable. The focus of this paper is on the mean encounter time of a diffusing point particle with a static spherical obstacle of radius R . This problem involves two dimensional parameters, the obstacle radius, R , and the intrinsic particle diffusivity in free space, D_0 . The only combination of these two parameters having the

dimensions of time is the ratio R^2/D_0 . Denoting the mean encounter time by τ_{enc} , we can write this quantity as

$$\tau_{\text{enc}} = \alpha \frac{R^2}{D_0}, \quad (1.1)$$

where α is a dimensionless factor. Our aim is to estimate factor α . To do this we derive an expression for the mean encounter time, which shows that $\alpha = 1/6$. This estimate and the approach we use to derive the expression for τ_{enc} are the main results of the present paper.

A quantity playing an important role in our estimate of the mean encounter time is the mean Wiener sausage volume. The Wiener sausage is the region swept by a spherical particle when its center moves along a Wiener trajectory. This mathematical object turns out to be useful in different applications. In particular, as discussed in section 2, it naturally arises in the analysis of the so-called trapping problem which describes the trapping of diffusing particles by perfectly absorbing spherical static traps randomly distributed in space. The trapping problem is a special case of the general theory of diffusion-controlled reactions pioneered by Smoluchowski [1] in his colloid coagulation theory. One can find detailed discussion of different aspects of the theory of diffusion-controlled reactions in [2–5] and references therein.

The outline of this paper is as follows. In the next section we briefly outline the Smoluchowski theory of diffusion-controlled reactions and introduce the concept of the Wiener sausage, which is used in section 3 to estimate the mean encounter time. Some concluding remarks are made in the final section 4.

2. Theory of diffusion-controlled reactions from target to trapping problem

Consider the annihilation of freely diffusing spherical particles A and B of radii R_A and R_B , respectively, which disappear instantly as soon as they touch each other, i.e. when the distance between their centers becomes equal to the contact radius R for the first time, $R = R_A + R_B$. It is assumed that the particles occupy a small volume fraction of the entire system, i.e. $c_A R_A^3 + c_B R_B^3 \ll 1$, where c_A and c_B are the particle concentrations. It is also assumed that $c_A \ll c_B$. This allows one to ignore the decrease of the B particle concentration, $c_B(t) = c_B(0) = c_B$, and to write the time-dependent concentration of the A particles as

$$c_A(t) = c_A(0)S(t), \quad (2.1)$$

where $S(t)$ is the survival probability of an A particle for time t . This survival probability is the focus of this section.

2.1. Smoluchowski theory of diffusion-controlled reactions

Consider a large box of volume V containing one particle A and N particles B , $N = c_B V \gg 1$. Let $S_N(t|r_1, \dots, r_N)$ be the survival probability of particle A on condition that the initial distance from the i th particle B to particle A is equal to r_i , $i = 1, 2, \dots, N$. Let $p(t|r)$ be the survival probability of an isolated reactant pair, initially separated by distance r , for time t . A key step leading to the Smoluchowski expression for the survival probability, $S_{\text{Sm}}(t)$, is the approximation of the survival probability $S_N(t|r_1, \dots, r_N)$ by the product of the pair survival probabilities,

$$S_N(t|r_1, \dots, r_N) = \prod_{i=1}^N p(t|r_i). \quad (2.2)$$

Denote the survival probability $S_N(t|r_1, \dots, r_N)$ averaged over all possible initial positions of the particles B by $S_N(t)$. Taking advantage of the fact that $S_N(t|r_1, \dots, r_N)$ is the product of the survival probabilities of independent pairs, we obtain

$$S_N(t) = \left(\frac{4\pi}{V} \int_{r>R} p(t|r) r^2 dr \right)^N. \quad (2.3)$$

Introducing the annihilation probability of the reactant pair for time t , denoted by $q(t|r)$, $q(t|r) = 1 - p(t|r)$, we can write equation (2.3) as

$$S_N(t) = \left(1 - \frac{4\pi}{V} \int_{r>R} q(t|r) r^2 dr \right)^N. \quad (2.4)$$

Finally, taking the limit $V \rightarrow \infty$, we arrive at the Smoluchowski expression for the survival probability,

$$\lim_{V \rightarrow \infty} S_N(t) = e^{-4\pi c_B \int_{r>R} q(t|r) r^2 dr} = S_{\text{Sm}}(t). \quad (2.5)$$

The annihilation probability $q(t|r)$ can be found by solving the problem for a diffusing point particle trapped by a perfectly absorbing spherical static trap of radius R ; the particle is initially located at distance r from the trap center, $r > R$, and its diffusivity is equal to the relative diffusivity of the particles A and B , given by the sum of their individual diffusivities D_A and D_B , $D = D_A + D_B$. The solution is

$$q(t|r) = \frac{R}{r} \operatorname{erfc} \left(\frac{r - R}{2\sqrt{Dt}} \right), \quad (2.6)$$

where $\text{erfc}(z)$ is the complimentary error function. Substituting $q(t|r)$ in equation (2.6) into equation (2.5) and performing the integration, we obtain

$$S_{\text{Sm}}(t) = e^{-(4\pi R D t + 8\sqrt{\pi} R^2 \sqrt{D t}) c_B}. \quad (2.7)$$

The Smoluchowski rate coefficient, $k_{\text{Sm}}(t)$, is defined in the standard way,

$$k_{\text{Sm}}(t) = - \frac{1}{c_B S_{\text{Sm}}(t)} \frac{dS_{\text{Sm}}(t)}{dt}. \quad (2.8)$$

As follows from equation (2.7),

$$k_{\text{Sm}}(t) = k_{\text{Sm}} \left[1 + \sqrt{R^2 / (\pi D t)} \right], \quad k_{\text{Sm}} = 4\pi R D, \quad (2.9)$$

where k_{Sm} is the Smoluchowski rate constant which is the long-time plateau value of the Smoluchowski rate coefficient.

The expression for $S_{\text{Sm}}(t)$ in equation (2.7) is an exact solution for the survival probability in the so-called target problem where $D_A = 0$ and $D = D_B$ [6, 7]. In the opposite limiting case of $D_B = 0$ and $D = D_A$, which is sometimes referred to as the trapping problem, equation (2.7) provides an estimate for the survival probability from below. The Wiener sausage is a useful tool for studying the annihilation kinetics in this case, where a particle A diffuses among randomly located spherical static traps (particles B) [8, 9]. This annihilation kinetics is discussed in the rest of this section with the aim of introducing the Wiener sausage and to show how it works in the trapping problem.

2.2. Trapping problem and the Wiener sausage

Consider a particle A , the center of which moves along a Wiener trajectory W_t . The survival probability of this particle for time t in the presence of randomly located immobile particles B , denoted by $S(t|W_t)$, is equal to the fraction of the particle B configurations for which the distance from the trajectory to the nearest particle B exceeds the contact radius R . As a consequence, the region swept by a sphere of radius R , whose center moves along the trajectory W_t , for such configurations does not contain centers of particles B . This region is the Wiener sausage associated with the trajectory W_t . Denoting the volume of the Wiener sausage by $v(W_t)$, we can write the survival probability $S(t|W_t)$ as the probability of finding this volume free from centers of particles B . For randomly distributed particles B the latter probability is determined by the Poisson distribution, and hence $S(t|W_t)$ is given by

$$S(t|W_t) = e^{-c_B v(W_t)}. \quad (2.10)$$

The survival probability $S_{\text{trapping}}(t)$ of a particle A , diffusing among immobile particles B , is the survival probability in equation (2.10) averaged over realizations of the Wiener trajectory. Denoting this averaging by the angular brackets, $\langle \dots \rangle$, we can write

$$S_{\text{trapping}}(t) = \langle S(t|W_t) \rangle = \langle e^{-c_B v(W_t)} \rangle. \quad (2.11)$$

The Wiener sausage volume is a random variable. It is convenient to introduce the probability density of this volume at time t , denoted by $\varphi(v|t)$ and defined as $\varphi(v|t) = \langle \delta(v - v(W_t)) \rangle$. Then equation (2.11) can be written as

$$S_{\text{trapping}}(t) = \int_0^\infty e^{-c_B v} \varphi(v|t) dv. \quad (2.12)$$

Thus $S_{\text{trapping}}(t)$ is the Laplace transform of the probability density $\varphi(v|t)$ with respect to the Wiener sausage volume v , with the Laplace parameter equal to the concentration c_B of particles B [8, 9].

In the mean-field (MF) approximation, the exact solution for $S_{\text{trapping}}(t)$ in equation (2.12) reduces to the Smoluchowski solution, $S_{\text{Sm}}(t)$ in equation (2.7) with $D = D_A$. This approximation neglects fluctuations in the Wiener sausage volume and assumes that the probability density $\varphi(v|t)$ can be approximated by a delta-function centered at the mean Wiener sausage volume at time t , $\langle v \rangle_t = \langle v(W_t) \rangle$,

$$\varphi(v|t) \approx \varphi_{\text{MF}}(v|t) = \delta(v - \langle v \rangle_t). \quad (2.13)$$

As a consequence, in this approximation the survival probability in equation (2.12) reduces to $S_{\text{trapping}}^{(\text{MF})}(t)$ given by

$$S_{\text{trapping}}(t) \approx S_{\text{trapping}}^{(\text{MF})}(t) = e^{-c_B \langle v \rangle_t}. \quad (2.14)$$

It can be shown [10] that the mean Wiener sausage volume at time t is

$$\langle v \rangle_t = 4\pi R D t + 8R^2 \sqrt{\pi D t} = \int_0^t k_{\text{Sm}}(t') dt'. \quad (2.15)$$

From this and equation (2.14) it follows that

$$S_{\text{trapping}}^{(\text{MF})}(t) = e^{-c_B \int_0^t k_{\text{Sm}}(t') dt'} = S_{\text{Sm}}(t). \quad (2.16)$$

Comparison of equations (2.11) and (2.14) shows that the mean-field approximation leads to the replacement of the mean value of a negative exponential function of a random variable by the value of this function when its argument equals the mean value of the random variable. The exponential is a concave function. As a consequence, according to Jensen's inequality [11], we have

$$\langle e^{-c_B v(W_t)} \rangle > e^{-c_B \langle v \rangle_t}, \quad (2.17)$$

and, hence,

$$S_{\text{trapping}}(t) > S_{\text{sm}}(t). \quad (2.18)$$

Thus, the Smoluchowski theory provides an estimate of the survival probability $S_{\text{trapping}}(t)$ from below [8, 9].

The slowdown of the annihilation rate in the trapping problem compared to the rate given by the Smoluchowski theory was first demonstrated in the long-time behavior of the survival probability [12–16]. It was shown that at asymptotically long times $S_{\text{trapping}}(t)$ decays as $\exp(-t^{3/5})$, whereas the Smoluchowski theory predicts exponential decay of the survival probability (see equation (2.7)). The long-time behavior of $S_{\text{trapping}}(t)$ can also be obtained from equation (2.12). The probability density $\phi(v|t)$ of the Wiener sausage volume is a bell-shaped function. In the course of time the bell moves towards infinity. As a result, at very long times, the integrand in equation (2.12) has two maxima, one near $v = \langle v \rangle_t$ where the top of the bell is located, and another one at much smaller values of the Wiener sausage volume. The long-time asymptotic behavior of the survival probability $S_{\text{trapping}}(t)$ is determined by the second maximum, located at $v \ll \langle v \rangle_t$ (see the details in [8, 9]).

Thus, we have introduced the Wiener sausage and outlined its application in the analysis of the annihilation kinetics in the trapping problem, which exploits the statistical properties of the Wiener sausage volume discussed in [10]. In the next section we use the mean Wiener sausage volume when estimating the mean encounter time of a diffusing point particle with a static spherical obstacle. One can learn more about the mathematical properties of the Wiener sausage volume from [17, 18]. Statistical properties of this random variable have been studied in Brownian dynamics simulations in [19]. A discussion of statistical properties of the Wiener sausage surface can be found in [20–22].

3. Mean encounter time

Consider a point particle diffusing among static spherical obstacles of radius R randomly distributed in space. It is assumed that the obstacle concentration c_{obst} is low in the sense that the volume fraction $\phi_{\text{obst}} = 4\pi R^3 c_{\text{obst}}/3$, occupied by the obstacles, is much smaller than unity, $\phi_{\text{obst}} \ll 1$. (Of course, R can be a contact radius, i.e. the sum of the obstacle and particle radii.) The long-term behavior of the mean square displacement of the particle in time t , $\overline{r^2(t)}$, is given by

$$\overline{r^2(t)} = 6D_{\text{eff}}t, \quad t \rightarrow \infty, \quad (3.1)$$

where D_{eff} is the particle effective diffusivity, related to its intrinsic diffusivity D_0 and the obstacle volume fraction ϕ_{obst} by the relation [23–25]

$$D_{\text{eff}} = D_0 \left(1 - \frac{\phi_{\text{obst}}}{2} \right), \quad (3.2)$$

which follows from the Maxwell–Garnet [26, 27] formula for the conductivity of composite media.

Substituting D_{eff} in equation (3.2) into equation (3.1), we can write the mean square displacement as

$$\overline{r^2(t)} = 6D_0 t_{\text{eff}}(t), \quad t \rightarrow \infty. \quad (3.3)$$

where $t_{\text{eff}}(t)$ can be interpreted as an effective time of free diffusion of the particle,

$$t_{\text{eff}}(t) = \left(1 - \frac{\phi_{\text{obst}}}{2} \right) t, \quad t \rightarrow \infty. \quad (3.4)$$

The effective time is shorter than the total observation time t since the particle loses some time every time it encounters an obstacle. Introducing the mean number of encounters in time t , $N(t)$, we can write the effective time in terms of $N(t)$ and the mean encounter time, τ_{enc} , as

$$t_{\text{eff}}(t) = t - \tau_{\text{enc}} N(t), \quad t \rightarrow \infty. \quad (3.5)$$

Then the mean encounter time is

$$\tau_{\text{enc}} = \frac{t - t_{\text{eff}}(t)}{N(t)} \Big|_{t \rightarrow \infty} = \frac{\phi_{\text{obst}}}{2\nu}. \quad (3.6)$$

Here we have used the expression for $t_{\text{eff}}(t)$ in equation (3.4) and introduced the encounter frequency ν defined by

$$\nu = \lim_{t \rightarrow \infty} \frac{N(t)}{t}. \quad (3.7)$$

There are two ways to find this frequency. First, we estimate ν by taking advantage of the fact that the number of encounters, $N(t)$, of a point particle diffusing among static spherical obstacles of radius R is equal to the number of encounters of a spherical particle of radius R diffusing among point obstacles. The latter can be estimated using the mean Wiener sausage volume. For a spherical particle of radius R diffusing with the diffusivity D_0 for time $t_{\text{eff}}(t)$, the long-time behavior of this volume, according to equation (2.15), is given by

$$\langle v \rangle_{t_{\text{eff}}(t)} = 4\pi R D_0 t_{\text{eff}}(t), \quad t \rightarrow \infty. \quad (3.8)$$

We use this to estimate the number of encounters in time t , as it is done when estimating the number of collisions in the kinetic theory of gases, i.e. as the product of the swept volume $\langle v \rangle_{t_{\text{eff}}(t)}$ and the obstacle concentration c_{obst} ,

$$N(t) = \langle v \rangle_{t_{\text{eff}}(t)} c_{\text{obst}} = 4\pi R D_0 t_{\text{eff}}(t) c_{\text{obst}}, \quad t \rightarrow \infty. \quad (3.9)$$

Substituting the above estimate into equation (3.7), we obtain

$$\nu = 4\pi R D_0 c_{\text{obst}} \frac{t_{\text{eff}}(t)}{t} \Big|_{t \rightarrow \infty} \approx 4\pi R D_0 c_{\text{obst}}, \quad (3.10)$$

where we have used the fact that, as follows from equation (3.4), the time ratio $t_{\text{eff}}(t)/t$ is close to unity when the obstacle volume fraction is small, $\phi_{\text{obst}} \ll 1$. According to equation (3.10), the encounter frequency is the product of the Smoluchowski rate constant for a point particle diffusing with diffusivity D_0 among static spherical traps of radius R randomly distributed in space (see equation (2.9)) and the obstacle concentration.

Now we derive this result following a different way of reasoning, which exploits the fact that, when $\phi_{\text{obst}} \ll 1$, the mean encounter time, τ , is much shorter than the mean duration of the inter-encounter interval, $1/\nu$. For a freely traveling particle a new encounter begins when it touches one of the obstacles for the first time. With this in mind, we can estimate the mean duration of the inter-encounter interval as the mean lifetime of a point particle freely diffusing with diffusivity D_0 among randomly distributed in space static spherical traps of radius R , the concentration of which is equal to the obstacle concentration c_{obst} . This mean lifetime, denoted by θ , is related to the particle survival probability $S_{\text{trapping}}(t)$ by the relation

$$\theta = \int_0^\infty S_{\text{trapping}}(t) dt. \quad (3.11)$$

The main contribution to this integral comes from not too long times, where the Smoluchowski solution, $S_{\text{Sm}}(t)$, in equation (2.7) with $D = D_0$ and $c_B = c_{\text{obst}}$ provides a

good approximation for $S_{\text{trapping}}(t)$ [8, 9]. Substituting this solution into equation (3.11), we obtain

$$\theta \approx \int_0^\infty S_{\text{sm}}(t) dt = \int_0^\infty e^{-(4\pi R D_0 t + 8\sqrt{\pi} R^2 \sqrt{D_0 t}) c_{\text{obst}}} dt. \quad (3.12)$$

Performing the integration we arrive at

$$\theta = \frac{1}{4\pi R D_0 c} (1 - \sqrt{3\phi_{\text{obst}}} e^{3\phi_{\text{obst}}/\pi} \text{erfc}(\sqrt{3\phi_{\text{obst}}/\pi})). \quad (3.13)$$

In the case under consideration $\phi_{\text{obst}} \ll 1$, and, therefore, $\theta \approx 1/4\pi R D_0 c_{\text{obst}}$. The encounter frequency is the inverse of the mean duration of the inter-encounter interval. Since the latter is equal to the mean lifetime θ , we have $\nu = 1/\theta$. Using this, we recover the expression for the encounter frequency in equation (3.10).

To obtain the desired estimate for the mean encounter time, it remains to substitute the encounter frequency in equation (3.10) into equation (3.6). This leads to

$$\tau_{\text{enc}} = \frac{\phi_{\text{obst}}}{8\pi R D_0 c_{\text{obst}}} = \frac{R^2}{6D_0}, \quad (3.14)$$

which is one of the main results of this work.

4. Concluding remarks

A distinctive feature of particle diffusion in the presence of obstacles whose volume fraction is low, $\phi_{\text{obst}} \ll 1$, is that the process can be viewed as intermittent free diffusion, i.e. a sequence of long inter-encounter intervals during which the particle travels in the space free of obstacles, separated by short encounter intervals. As a consequence, the effective free diffusion time, $t_{\text{eff}}(t)$, is shorter than the total observation time t ,

$$t_{\text{eff}}(t) = \left(1 - \frac{\phi_{\text{obst}}}{2}\right) t = (1 - \nu \tau_{\text{enc}}) t, \quad t \rightarrow \infty, \quad (4.1)$$

where ν and τ_{enc} are the encounter frequency and encounter time, respectively, given in equations (3.10) and (3.14).

The lost time is the product of the mean number of encounters in time t , $N(t) = \nu t$, and the mean encounter time, $\tau_{\text{enc}} = R^2/(6D_0)$. Denoting the lost time by $t_{\text{lost}}(t)$, we can write equation (4.1) as

$$t_{\text{eff}}(t) = t - t_{\text{lost}}(t), \quad t \rightarrow \infty, \quad (4.2)$$

where

$$t_{\text{lost}}(t) = \tau_{\text{enc}} \nu t, \quad t \rightarrow \infty. \quad (4.3)$$

Such presentation of the effective time can be easily generalized to the case of reversible binding of the particle to the obstacles, described by the kinetic scheme

where k_b and k_d are the binding and dissociation rate constants. In this case when the particle meets an obstacle, it may bind to the obstacle, spend some time in the bound state, then dissociate, and continue its journey. Denoting the binding probability for a particle starting from the surface of an obstacle by W_b and the mean particle lifetime in the bound state by τ_b , we can replace the lost time in equation (4.3) by a more general expression

$$t_{\text{lost}}(t) = (\tau_{\text{enc}} + W_b \tau_b) \nu t, \quad t \rightarrow \infty. \quad (4.5)$$

Substituting $t_{\text{lost}}(t)$ in equation (4.2) into equation (4.2), we obtain

$$t_{\text{eff}}(t) = \left[1 - \nu \left(\frac{R^2}{6D_0} + W_b \tau_b \right) \right] t \approx \left(1 - \nu \frac{R^2}{6D_0} \right) (1 - \nu W_b \tau_b) t, \quad t \rightarrow \infty \quad (4.6)$$

Explicit expressions for W_b and τ_b in terms of the two rate constants, k_b and k_d , the obstacle radius, R , and the particle intrinsic diffusivity, D_0 , are given by [2–5]

$$W_b = \frac{k_b}{k_b + 4\pi R D_0}. \quad (4.7)$$

and

$$\tau_b = \frac{1}{(1 - W_b)k_d} = \frac{k_b + 4\pi R D_0}{4\pi R D_0 k_d}. \quad (4.8)$$

From this it follows that the product $\nu W_b \tau_b$ entering into equation (4.6) is

$$\nu W_b \tau_b = \frac{k_b c_{\text{obst}}}{k_d} \approx \frac{k_b c_{\text{obst}}}{k_d + k_b c_{\text{obst}}}. \quad (4.9)$$

Note that the ratio on the right-hand side of equation (4.9) is the equilibrium probability of finding the particle bound to the obstacle. Then $1 - \nu W_b \tau_b$ on the right-hand side of equation (4.6) is the equilibrium probability P_m of finding the particle in the mobile state,

$$P_m = \frac{k_d}{k_d + k_b c_{\text{obst}}}. \quad (4.10)$$

Using P_m , the effective time in equation (4.6) can be written as

$$t_{\text{eff}}(t) = (1 - \nu \tau_{\text{enc}}) P_m t, \quad t \rightarrow \infty. \quad (4.11)$$

This leads to the following expression for the effective diffusivity

$$D_{\text{eff}} = D_0 \left(1 - \frac{\phi_{\text{obst}}}{2} \right) P_m, \quad (4.12)$$

which is a natural generalization of the expression in equation (3.2) to the case of reversible binding of the diffusing particle to the obstacles.

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