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Many-Body Effects in Diffusion-Limited Kinetics

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We review a novel approach to treating many-body effects in diffusion-limited kinetics. The derivation of the general expression for the survival probability of a Brownian particle in the presence of randomly distributed traps is given. The reduction of this expression to both the Smoluchowski solultion and the well-known asymptotic behavior is demonstrated. It is shown that the Smoluchowski solution gives a lower bound for the particle survival probability. The correction to the Smoluchowski solution which takes into account the particle death slowdown in the initial process stage is described. The steady-state rate-constant concentration dependence and the reflection of many-body effects in it are discussed in detail.

KEY WORDS: Many-body effects; diffusion-limited kinetics.

1. INTRODUCTION

The idea of Brownian particles trapped by randomly distributed ideal traps is widely used in theoretical models of different physical and chemical processes, exemplified by diffusion-influenced fluorescence quenching, diffusion-controlled chemical reactions, and so on. All these processes have a common feature, viz., the kinetic behavior is determined by the rate at which reactans approach one another. The rate at which such an approach is made is described in terms of Brownian motion. This is why such processes are termed diffusion-limited processes.

In this paper we discuss the kinetics of Brownian particle death due to reaction with static traps. Smoluchowski was the first to consider this problem in his colloid coagulation theory.[(1)] The characteristic feature of the Smoluchowski theory is that it is based on the one-body approximation. The mutual influence of all traps on particle death on each of

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them, the so-called competition between the traps,[2] is neglected in this approximation. As a result, the difficult many-body problem is reduced to the simpler problem of particle death on a single trap. However, it is the competition between traps which is the origin of a number of many-body effects in the diffusion-limited kinetics.

Numerous attempts have been made to improve the Smoluchowski theory in different directions. For example, investigators have tried to incorporate many-body effects into the theory. Because there are so many papers on the subject, we cite the references to be found in some recent monographs and review articles.[2–9]

The present review paper is devoted to a novel approach to the analysis of many-body effects in diffusion-limited kinetics that have been suggested in our recent papers.[10–13] We also discuss in detail some methodological questions related to the derivation of the Smoluchowski solution, the steady-state rate constant, and its dependence on trap concentration. Such a discussion seems useful, since some of these rather important questions have not been consider in detail in the literature.

2. THE SMOLUCHOWSKI THEORY

One of the basic assumptions in the Smoluchowski theory is the one-body approximation. It allows one to reduce a difficult many-body problem to the problem of particle death on a single trap. This approximation enables us to solve a wider range of problems than just the problem of particle death in the presence of a finite concentration of static traps. The simplification due to Smoluchowski allows us to analyze the particle death problem in the case in which both the particle and traps can have different diffusion constants, by using the relative diffusion coefficient

$$D = D_p + D_{\mathrm{tr}} \tag{2.1}$$

where D_p and D_{tr} are the diffusion coefficients describing the motion of particles and traps, respectively.

We assume that the particle death takes place at the first contact between a particle and a trap, i.e., when a particle approaches within a distance b of the trap. We suppose that the trap concentration is uniform and equal to c_0. In the Smoluchowski theory the parameter of major interest is the rate coefficient, which generally depends on time. This rate coefficient is identified with the flux of traps at time t into an absorbing sphere of radius b. The expression for this flux in d dimensions is

$$k_{\mathrm{Sm}}(t) = \frac{2p^{d/2} D b^{d-1}}{\Gamma(d/2)} \left[\frac{\partial}{\partial r} c(\mathbf{r}, t) \right]_{r=b} \tag{2.2}$$

where $c(\mathbf{r}, t)$ is the concentration of diffusing traps at $\mathbf{r}$ at time t. The concentration $c(\mathbf{r}, t)$ is determined as the solution to a diffusion equation

$$\frac{\partial c}{\partial t} = D \Delta c \tag{2.3}$$

subject to the initial condition $c(r, 0) = c_0$ for $r > b$, and an absorbing boundary condition at the sphere surface.

At this point we derive the Smoluchowski solution, using an analysis given by Tachiya.[14] The object of our calculations is to find the probability of particle survival during the time interval t, $P(t)$. This probability is obtained in terms of the analogous survival probability for a fixed initial trap configuration $P_\alpha(t)$, where α is an index which corresponds to a particular trap configuration. After one calculates this survival probability, the overall survival probability $P(t)$ is found by averaging over all trap configurations. Assuming that both the contacts between particles and traps and the diffusive motion of the particles are independent, we can write the survival probability $P_{\alpha,\mathrm{Sm}}(t)$ as a product of independent probabilities

$$P_{\alpha,\mathrm{Sm}}(t) = \prod_{j=1} p(t \mid \mathbf{R}_{j,\alpha}) \tag{2.4}$$

In this equation $\mathbf{R}_{j,\alpha}$ is the initial position of the jth trap in configuration α, and $p(t \mid \mathbb{R})$ is the survival probability in the presence of a single trap initially at $\mathbf{R}$.

To calculate the survival probability $p(t \mid \mathbf{R})$, it is necessary to solve the one-body problem by finding the Green's function $G(r, t \mid \mathbf{R})$ which satisfies the diffusion equation (2.3) subject to the same initial and boundary conditions. Without loss of generality we solve this problem for an immobile particle whose center is at the origin, and a movable trap whose motion is characterized by the diffusion coefficient in Eq. (2.1). The Green's function is the probability density of finding the trap at point $\mathbf{r}$ at time t, given that is was initially at $\mathbf{R}$, and that it has not been trapped by time t. The survival probability $p(t \mid \mathbf{R})$ is then given by

$$p(t \mid \mathbb{R}) = \int G(r, t \mid \mathbf{R})\, d^d\mathbf{r} \tag{2.5}$$

To obtain the final expression for the survival probability $P(t)$, Eq. (2.4) should be averaged over the initial trap configurations. The Smoluchowski theory is based on the assumption that the mobile particles are uniformly distributed throughout space. To average over configurations, we introduce the auxiliary volume Ω containing N traps, and pass to the limit N, $\Omega \to \infty$, $N/\Omega = c_0$. Thus, we have

$$P_{\text{Sm}}(t) = \langle P_{\alpha,\text{Sm}}(t) \rangle$$

$$\equiv \lim_{N,\Omega \to \infty, N/\Omega = c_0} \frac{1}{\Omega^N} \int \cdots \int \prod_{j=1}^{N} p(t \mid \mathbf{R}_{j,\alpha}) \, d^d\mathbf{R}_{j,\alpha} \tag{2.6}$$

Now let us introduce the probability that the particle is trapped sometime during the time interval $(0, t)$. This will be denoted by $q(t \mid \mathbf{R})$ related to the survival probability by $q(t \mid \mathbf{R}) = 1 - p(t \mid \mathbf{R})$. Introduction of this probability allows us to express the survival probability $P_{\text{Sm}}(t)$ as

$$P_{\text{Sm}}(t) = \lim_{N,\Omega \to \infty, N/\Omega = c_0} \left[1 - \frac{1}{\Omega} \int q(t \mid \mathbf{R}) \, d^d\mathbf{R} \right]^N$$

$$= \exp\left[-c_0 \int q(t \mid \mathbf{R}) \, d^d\mathbf{R} \right] \tag{2.7}$$

To confirm the fact that this expression is really equivalent to the Smoluchowski solution, we calculate the rate coefficient from it,

$$k_{\text{Sm}}(t) \equiv -\frac{1}{P_{\text{Sm}}(t)} \frac{dP_{\text{Sm}}(t)}{dt} = c_0 \int \frac{\partial q(t \mid \mathbf{R})}{\partial t} \, d^d\mathbf{R} \tag{2.8}$$

The derivative $\partial q(t \mid \mathbf{R})/\partial t$ is the flux into the sphere at time t that comes from a diffusing trap initially at $\mathbf{R}$. The right-hand side of Eq. (2.8) gives the sum of all such contributions. It expresses the total flux into the absorbing sphere at time t when the initial concentration of traps is uniform and equal to c_0. Thus, the rate coefficient in Eq. (2.8) is equal to that in Eq. (2.2), and Eq. (2.7) gives the survival probability as calculated in the framework of the Smoluchowski theory.

Let us enumerate once more the main assumptions used in the derivation of Eq. (2.8): (a). A reduction of the initial problem to a pair problem, i.e., the single-body approximation, and (b) an initially uniform distribution of traps. It should be emphasized that these assumptions, which allow us to treat the general case when both particles and traps are mobile, is possible only within the framework of a single-body approximation in which Eq. (2.1) is satisfied. We may expect different kinetic behavior when either assumption is violated. In this paper we consider the deviations that arise due to a violation of the first assumption, i.e., when many-body effects are taken into account.

3. A NEW APPROACH

Equation (2.1) links two limiting cases, viz., the case of static traps and a diffusing particle ($D_{tr} = 0$, $D_p = D \neq 0$) and the case of moveable traps in the presence of an immobile particle ($D_{tr} = D \neq 0$, $D_p = 0$). It should be noted that the single-body solution in Eq. (2.4) is an accurate one in the second case (provided the diffusing traps do not interact) and incorrect in the first. The survival probability of a diffusing particle in the presence of a fixed configuration of static traps $P_\alpha(t)$ is expressed in terms of the Green's function $G_\alpha(_r, t)$ by an equation of the form of Eq. (2.5). The Green's function $G_\alpha(\mathbf{r}, t)$ is found by solving the diffusion equation with absorbing boundary conditions at every trap surface and the initial condition $G_\alpha(\mathbf{r}, 0) = d(\mathbf{r})$ (without loss of generality we may suppose that a particle starts from the origin). It is also possible to recast the mathematical formalism by introducing the effects of the traps into the diffusion equation in the form of a hard-core potential at radius b. The emended version of the diffusion equation then takes the form

$$\frac{\partial G_\alpha}{\partial t} = D \bigtriangleup G_\alpha - \sum_{j=1}^{\infty} U(|r - \mathbf{R}_{j,\alpha}|) G_\alpha \tag{3.1}$$

where

$$U(r) = \begin{cases} \infty & \text{for} \quad r < b \\ 0 & \text{for} \quad r > b \end{cases} \tag{3.2}$$

It is evident that the factorization in Eq. (2.4) can only be valid in the absence of many-body effects.[10,11,14,15]

Finding a solution to Eq. (3.1) clearly poses an extremely difficult problem. This is why a direct method of evaluating the survival probability $P(t)$ based on an intermediate calculation of the survival probability for all fixed configurations and a subsequent averaging over all trap configurations is to be avoided. An alternative approach requires performing a formal average of survival probabilities over all configurations, i.e.,

$$P(t) = \langle P_\alpha(t) \rangle = \int \langle G_\alpha(\mathbf{r}, t) \rangle \, d^d\mathbf{r} \tag{3.3}$$

Different approximate methods have been used for calculating the average $\langle G_\alpha(\mathbf{r}, t) \rangle$. Such techniques include the optimal-fluctuation method, the effective medium theory, and a modified perturbation theory.[16,17]

The optimal-fluctuation method has been used to find the asymptotic behavior of the survival probability $P(t)$. It has been shown that at $t \to \infty$ the particles perish at a considerably slower rate than predicted by the

Smoluchowski theory[18–22] (the so-called particle death fluctuation slowdown effect). We shall discuss this effect in more detail below. Progress is considerably more modest in refining approximations to the behavior of the survival probability $P(t)$. Moreover, several authors have come to the incorrect conclusion that particles perish faster than predicted by the Smoluchowski theory. The error in this assertion will become clear from our later analysis.

Our new approach to the calculation of the survival probability $P(t)$ takes into account some specific features of the problem under study. The point is that the problem of the Brownian point particle death on spherical traps of radius b is equivalent to the problem of the diffusion of a spherical Brownian particle (of radius b) which is removed from the system when it comes into contact with a point trap. If such a particle visits a region of volume v in a space without traps, then its survival probability, in the case when the particle moves along the same Wiener trajectory in a space with point traps, equals the probability that there are no traps in the volume. Because the number of traps in any volume has a Poisson distribution, the probability that there are no traps in a volume v is equal to $\exp(-c_0 v)$. The volume v visited by the Brownian particle in a space without traps is a random variable. Let us introduce its probability density $F_t(v)$, which characterizes the distribution of v at time t. This density satisfies the normalization condition

$$\int F_t(v)\,dv = 1 \tag{3.4}$$

Therefore we may express the survival probability as

$$P(t) = \int \exp(-c_0 v)\,F_t(v)\,dv \tag{3.5}$$

Equation (3.5) for the survival probability is the key formula in our approach. We will now derive it from the general expression in (3.3). To do this we use the Kac–Feynman formula and express the Green's function $G_\alpha(\mathbf{r}, t)$ as a sum over the Wiener trajectories $\mathbf{r}(t')$ $(0 < t' < t)$ for which $\mathbf{r}(0) = 0$ and $\mathbf{r}(t) = \mathbf{r}$,[23,24]

$$G_\alpha(\mathbf{r}, t) = \int_{(0,0)}^{(t,\mathbf{r})} \exp\left\{-\int_0^t \sum_{j=1}^{\infty} U(|\mathbf{r}(t') - \mathbf{R}_{j,\alpha}|)\,dt'\right\} D\mathbf{r}(t') \tag{3.6}$$

From the definition of the potential $U(r)$ in Eq. (3.2), it follows that in Eq. (3.6) the contribution of a trajectory is equal to zero if the trajectory passes within a distance b of a trap center and equals unity if it does not.

Averaging Eq. (3.6) over all trap configurations, we obtain

$$\langle G_\alpha(\mathbf{r}, t)\rangle = \int_{(0,0)}^{(t,\mathbf{r})} \left\langle \exp\left\{ -\int_0^t \sum_{j=1}^{\infty} U(|\mathbf{r}(t') - \mathbf{R}_{j,\alpha}|)\, dt' \right\}\right\rangle D\mathbf{r}(t') \quad (3.7)$$

The contribution from different trajectories to the integral (3.7) is equal to the fraction of such trap configuration in which the b vicinity of the trajectory is free from traps. Because of the Poisson distribution of traps, this fraction is equal to $\exp\{-c_0 v([\mathbf{r}(t')])\}$, where $v([\mathbf{r}(t')])$ is the volume of the b vicinity of trajectory $\mathbf{r}(t')$, and the square brackets indicate that the volume v is a functional of the Wiener trajectory $\mathbf{r}(t')$. Thus, we obtain

$$\langle G_\alpha(\mathbf{r}, t)\rangle = \int_{(0,0)}^{(t,\mathbf{r})} \exp\{-c_0 v([\mathbf{r}(t')])\}\, D\mathbf{r}(t') \quad (3.8)$$

The integration of the Green's function in Eq. (3.8) over $\mathbf{r}$ in Eq. (3.3) is equivalent to the sum over all termination points of the trajectory. Thus, we are able to express the survival probability $P(t)$ as a sum over all Wiener trajectories whose starting point is at the origin. Denoting such a sum by angular brackets $\langle\cdots\rangle_t$, we can write

$$P(t) = \langle \exp\{-c_0 v([\mathbf{r}(t')])\}\rangle_t \quad (3.9)$$

To pass from Eq. (3.9) to Eq. (3.5), one need only introduce a formal definition of the probability density $F_t(v)$, which has the form

$$F_t(v) \equiv \langle d(v - v([\mathbf{r}(t')]))\rangle_t \quad (3.10)$$

In this way we confirm the validity of Eq. (3.5), which was proposed earlier on the basis of a heuristic argument.

Equations (3.5) and (3.9) for the survival probability are the main results of our approach. Below we show how these formulas may be applied. Now we note some interesting consequences of Eq. (3.5). There are two factors responsible for the probabilistic nature of the problem under study, viz., the disorder related to the arrangements of traps and the random Brownian motion of the particle. These factors are represented by the two factors in the integrand of Eq. (3.5). In our approach all difficulties in solving the problem under consideration are transferred to the problem of calculating the probability density $F_t(v)$ characterizing the Brownian motion of a spherical particle in a space free of traps.

One should point out that the volume visited by a spherical particle whose center moves along the Wiener trajectory (the b vicinity of the trajectory) is known in the mathematical literature as the Wiener sausage.[24,25] The function $F_t(v)$ is therefore the probability density of the

Wiener sausage volume. This function, considered as a function of v for a fixed t, has a bell-shaped form. In the course of time the position of the maximum shifts to infinity, and its width increases. In the limit $t \to 0$ the curve tends toward the delta function $d(v - v_0)$, where $v_0 = p^{d/2} b^d / \Gamma(1 + d/2)$ is the volume of a d-dimensional sphere of radius b. An explicit form for the function $F_t(v)$ is known only in one dimension.[12,26] The mean value and dispersion of the Wiener sausage volume have been calculated for spaces of arbitrary dimensionality.[27] The behavior of the function $F_t(v)$ has also been calculated for v much smaller than the mean volume.[10,11] All this information may be used to analyze the behavior of the survival probability $P(t)$.

A comment is in order regarding our general expression for the survival probability. The point is that the survival probability as given in Eq. (3.5) or (3.9) is a product of two probabilities.[28] One of them is the probability that a particle introduced in the space with traps is not trapped initially. This probability is

$$P(t = 0) = \exp(-c_0 v_0) \tag{3.11}$$

It is the second probability that is the particle survival probability. We designate this probability by $P_{\text{srv}}(t)$, where

$$P_{\text{srv}}(t) = P(t)/P(0) = \exp(c_0 v_0)\, P(t) \tag{3.12}$$

In our later discussion we will not distinguish between $P(t)$ and $P_{\text{srv}}(t)$ in order to avoid excessive formalism which might confuse the physical interpretation. If required, the necessary details can be worked out using Eq. (3.12).

4. DISCUSSION OF THE GENERAL EXPRESSION

We begin by showing that our general expression for the survival probability can be reduced to the conventional Smoluchowski solution. To do this, it is necessary to neglect fluctuations in volume of the Wiener sausage. In this approximation the function $F_t(v)$ is

$$F_t(v) = d(v - \langle v \rangle_t) \tag{4.1}$$

where $\langle v \rangle_t$ is the mean Wiener sausage volume at time instant t. In this case Eq. (3.5) takes the form

$$P(t) = \exp(-c_0 \langle v \rangle_t) \tag{4.2}$$

To convince oneself that $\exp(-c_0\langle v\rangle_t)$ is the Smoluchowski solution, one needs to use the formal definition of the Wiener sausage volume. In order to write this definition, we introduce an auxiliary quantity $\varphi(\mathbf{R}, [r(t')])$, which is a function of point $\mathbf{R}$ of a d-dimensional space and a functional of the Wiener trajectory $\mathbf{r}(t')$ $(0<t'<t)$,

$$\varphi(\mathbf{R}, [\mathbf{r}(t')]) = \begin{cases} 1 & \text{if } \min|\mathbf{r}(t') - \mathbf{R}| < b \\ 0 & \text{if } \min|\mathbf{r}(t') - \mathbf{R}| > b \end{cases} \tag{4.3}$$

The definition of the Wiener sausage volume corresponding to the Wiener trajectory $\mathbf{r}(t')$ $(0<t'<t)$ can be written as

$$v([\mathbf{r}(t')]) = \int \varphi(\mathbf{R}, [\mathbf{r}(t')])\, d^d\mathbf{R} \tag{4.4}$$

Having averaged the volume whose expression is Eq. (4.4) over the Wiener trajectories, we obtain

$$\langle v\rangle_t = \langle v([\mathbf{r}(t')])\rangle_t = \int \langle \varphi(\mathbf{R}, [\mathbf{r}(t')])\rangle_t\, d^d\mathbf{R} \tag{4.5}$$

The quantity $\langle \varphi(\mathbf{R}, [\mathbf{r}(t')]\rangle_t$ is the fraction of the trajectories which have visited the b vicinity of point $\mathbf{R}$ during the time interval $(0, t)$ at least once. This quantity is equal to the probability that a point Brownian particle will die during a time interval of duration t, when there is a single trap of radius b placed at distance R from the particle's starting point. So, $\langle \varphi(\mathbf{R}, [\mathbf{r}(t')]\rangle_t = q(t\,|\,\mathbf{R})$ and

$$\langle v\rangle_t = \int q(t\,|\,\mathbf{R})\, d^d\mathbf{R} \tag{4.6}$$

Thus, we obtain the result

$$P_{\mathrm{Sm}}(t) = \exp(-c_0\langle v\rangle_t) \tag{4.7}$$

An explicit form of the time dependence of the mean volume in space of different dimensionalities was calculated in ref. 27. When $\tau = Dt/b^2 \gg 1$ these dependences have the form

$$\begin{aligned} \langle v([\mathbf{r}(t')]\rangle_r &= 2\left(\frac{\tau}{\pi}\right)^{1/2} v_0, && d=1 \\ &= \frac{4\tau}{\ln\tau} v_0, && d=2 \\ &= d(d-2)\,\tau v_0, && d\geqslant 3 \end{aligned} \tag{4.6a}$$

We note that the approximation in Eq. (4.1) is a mean-field approximation in the problem under study since it neglects fluctuations in the volume of the Wiener sausage. Now we show that this approximation leads to a bound on the survival probability estimation from below, i.e., we show that

$$P(t) > P_{\mathrm{Sm}}(t) \tag{4.8}$$

is satisfied for $t > 0$. To prove the correctness of the inequality, we rewrite it using Eqs. (3.9) and (4.7),

$$P(t) = \langle \exp\{-c_0 v([\mathbf{r}(t')])\}\rangle_t > \exp(-c_0 \langle v\rangle_t) = P_{\mathrm{Sm}}(t) \tag{4.9}$$

The validity of this inequality is a consequence of its being a particular case of the more general Jensen inequality, which gives the relationship between the mean value of a function of random variable and the value of this function when its argument equals the mean value of a random variable.[29]

The fact that (4.8) is valid at large times is well known. The effect of the particle death fluctuation slowdown mentioned earlier[18-22] is, in fact a direct consequence of this result. We calculate the asymptotic survival probability in the framework of our approach. Let us introduce the dimensionless variables $u = v/v_0$ and the trap volume fraction $f = c_0 v_0$. In terms of this notation Eq. (3.5) takes the form

$$P(\tau) = \int \exp(-fu)\, F_\tau(yu)\, du \tag{4.10}$$

We define a function $L(\tau)$ which can be written in terms of $P(\tau)$ as

$$L(\tau) = -\ln P(\tau) \qquad \text{or} \qquad P(\tau) = \exp[-L(\tau)] \tag{4.11}$$

In the course of time the maximum of the function $F_\tau(u)$ shifts toward infinity. As a result, the maximum of the integrand in (4.10) is located in the small u region defined by $u \ll \langle u\rangle_\tau$. At very long times the kinetic behavior of the process under consideration is determined by rare fluctuations in the volume of the Wiener sausage which arise because of fluctuations in the arrangement of traps. In the regime defined by $u \ll \langle u\rangle_\tau$ the explicit form of the probability density $F_\tau(u)$ can be written as[10,11]

$$F_\tau(u) \propto \frac{\tau}{u^{(d+2)/d}} \exp\left(-\gamma_d \frac{\tau}{u^{2/d}}\right) \tag{4.12}$$

where γ_d is the square of the first zero of the first-kind Bessel function of order $(d-2)/2$. If we substitute Eq. (4.12) into Eq. (4.10) and calculate the integral by means of Laplace's method, we arrive at the known expression[10, 11, 18–22]

$$L_\infty(\tau) = \frac{d+2}{d}\left[\left(\frac{d}{2}\right)^{2/d} \gamma_d f^{2/d} t\right]^{d/(d+2)} \tag{4.13}$$

which describes the asymptotic kinetics of particle death.

To confirm that this death occurs much slower than predicted by the Smoluchowski theory, one can compare the time dependence shown in Eq. (4.13) with the corresponding result found in the Smoluchowski theory

$$L_{\text{Sm}}(t) = -\ln P_{\text{Sm}}(t) = f\langle u\rangle_t \tag{4.14}$$

For $t \gg 1$ this dependence has the form

$$\begin{aligned} L_{\text{Sm}}(t) &= 2f\left(\frac{t}{p}\right)^{1/2}, \qquad && d=1 \\ &= \frac{4ft}{\ln t}, && d=2 \\ &= d(d-2)\, ft, && d \geqslant 3 \end{aligned} \tag{4.15}$$

The question of the reduction in trapping rate at early times as compared to the prediction of Smoluchowski theory is a much more delicate one. It has been claimed in the literature that in this stage the particles perish faster than predicted by the conventional theory. A detailed discussion of this point is given in ref. 13. The inequality (4.8) shows that this statement is erroneous. To treat this question within the framework of our approach, we take advantage of the fact, that, according to Eq. (4.10), the survival probability $P(t)$ is the Laplace transformation of the probability density $F_t(u)$. This allows us to express the $L(t)$ function as a power series in f:

$$L(t) \equiv \ln P(t) = \sum_{j=1}^{\infty} \frac{(-f)^j}{j!} K_j(t) \tag{4.16}$$

The coefficients $K_j(t)$ in this power series are cumulants of the volume of the Wiener sausage.

If we approximate the series in Eq. (4.16) by its first term, we get the original Smoluchowski approximation, since $K_1(t) \equiv \langle u\rangle_t$. Such an approximation is correct for $f \ll 1$ as long as the time is not too large. At sufficiently short times the second term of the series in Eq. (4.16) gives the next-order correction to the Smoluchowski solution. To make sure that the correction reflects the particle death slowdown, we n ote that the first and second terms have different signs, since $K_2(t) = \sigma^2(t)$ is the variance of the Wiener sausage volume and is therefore positive. Thus, in this approximation the survival probability has the form

$$P(t) \simeq P_{\text{Sm}}(t) \exp[\tfrac{1}{2} f^2 K_2(t)] \tag{4.17}$$

An explicit form of the Wiener sausage volume dispersion time dependence was calculated in ref. 27. This is

$$\begin{aligned} K_2(t) &= \ln 4 - \frac{4}{p}, & d&=1 \\ &= b_2 \frac{t^2}{\ln^4 t}, & d&=2 \\ &= 9t \ln t, & d&=3 \\ &= b_d t, & d&>3 \end{aligned} \tag{4.18}$$

where b_d denotes a constant ($b_2 \simeq 27.18$).

Thus, starting with the general expression for the survival probability in which the many-body effects are taken into account, we find the following results: (a) The one-body Smoluchowski solution. (b) An inequality that shows that the Smoluchowski solution is a lower bound for the survival probability for the more general case of many traps. (c) The asymptotics of the survival probability in the limit $t \to \infty$. (d) The correction to the Smoluchowski solution, which accounts for the initial slowdown in trapping rate.

5. STEADY-STATE RATE CONSTANT

So far, we have discussed the time dependence of the particle survival probability $P(t)$. In the present section we shall consider the so-called steady-state rate constant K_{ss}, which is related to the survival probability by the equation

$$K_{\text{ss}}^{-1} = \int_0^\infty P(t)\, dt \tag{5.1}$$

It should be noted that K_{ss}^{-1} is a mean particle lifetime h derived from the definition

$$h = \int_0^\infty t \left[-\frac{dP(t)}{dt} \right] dt \tag{5.2}$$

Evaluating the integral by parts, one sees that $h = K_{\text{ss}}^{-1}$.

The steady-state rate constant characterizes the particle death rate in the case when particle generation takes place at the same time as one has particle death due to trapping. After a fairly large time, a steady-state concentration is attained, which is to say that the number of particles perishing on traps per unit time equals the number of new particles arising due to generation. If new particles are generated uniformly in space, then the generation intensity I and the steady-state concentration c_{ss} are connected by the relationship[5]

$$I = K_{ss} c_{ss} \tag{5.3}$$

where the product $K_{ss} c_{ss}$ is the trapping rate of particles.

The steady-state rate constant depends on the trap concentration or, equivalently, on the volume fraction of traps $f = c_0 v_0$. There has been some confusion concerning the relation between the rate coefficients K_{ss} and $K(t)$ in a number of papers. To clarify the situation, following ref. 5, we shall discuss this point in greater detail. We restrict ourselves to a consideration of the three-dimensional case only, since it is mainly in this case that calculations of K_{ss} have been made.

We start by considering the results given by the original Smoluchowski theory:

$$K_{\mathrm{Sm}}(t) = 4pbDc_0 \left[1 + \frac{b}{(pDt)^{1/2}} \right] \tag{5.4}$$

This rate coefficient approaches the limiting value $4pbDc_0$ on a time scale that exceeds the characteristic time of diffusional passage through a trap, b^2/D.

On the other hand, the substitution of the Smoluchowski solution $P_{\mathrm{Sm}}(t)$ into the integral in Eq. (5.1) gives the result[5]

$$K_{\mathrm{ss,Sm}} = K_{\mathrm{Sm}}(\infty)[1 - (3f)^{1/2} \exp(3f/\pi) \operatorname{erfc}((3f/\pi)^{1/2})]^{-1} \tag{5.5}$$

where $\operatorname{erfc}(z) = (2/p^{1/2}) \int_z^\infty \exp(-x^2)\, dx$ is the complementary error function.[31] When $f \ll 1$, Eq. (5.5) can be approximated by[5]

$$K_{\mathrm{ss,Sm}} = K_{\mathrm{Sm}}(\infty) \left[1 + (3f)^{1/2} + 3\left(1 - \frac{2}{p}\right) f + \cdots \right] \tag{5.6}$$

It is worth emphasizing that the Smoluchowski steady-state rate constant $K_{\mathrm{ss,Sm}}(f)$ is larger than the rate constant $K_{\mathrm{Sm}}(\infty)$ found from Eq. (5.4). We note that both this fact and the mentioned dependence of the steady-state rate constant of f stem from the fact that very early times $K_{\mathrm{Sm}}(t)$ differs significantly from $K_{\mathrm{Sm}}(\infty)$ make a noticeable contribution to the integral in Eq. (5.1). From the definition of steady-state rate constant in Eq. (5.1) and the inequality in Eq. (4.8) one finds that

$$K_{\mathrm{ss,Sm}}(f) > K_{\mathrm{ss}}(f) \tag{5.7}$$

There are a number of papers that analyze the dependence of K_{ss} on the parameter f. A more detailed bibliography can be found in refs. 5, 6, and 32. Most authors, in calculating $K_{\mathrm{ss}}(f)$ taking into account many-body effects, avoid the straightforward procedure involving the calculation of $P(t)$ and the integral indicated in Eq. (5.1). Instead, the Laplace transform of the survival probability is introduced

$$\hat{P}(s) = \int_0^{\infty} \exp(-st)\, P(t)\, dt = \iint \exp(-ts)\, \langle G_\alpha(\mathbf{r}, t)\rangle\, dt\, d^d\mathbf{r} \tag{5.8}$$

which allows one to express the steady-state rate constant as

$$K_{\mathrm{ss}} = [\hat{P}(s=0)]^{-1} \tag{5.9}$$

A number of approximate methods can be used to calculate $\hat{P}(s)$ using this formalism. A critical discussion of the functional form of the f dependence of $K_{\mathrm{ss}}(f)$ can be found in ref. 32. The authors of that reference state that only three first terms of the $K_{\mathrm{ss}}(f)$ expansion with $f \ll 1$ can be found correctly,

$$K_{\mathrm{ss}}(f) \simeq K_{\mathrm{Sm}}(\infty)[1 + (3f)^{1/2} + \tfrac{3}{2} f \ln 3f] \tag{5.10}$$

We note that the two first terms in the square brackets correspond to the Smoluchowski solution [see Eq. (5.6)] and only the last term relates to many-body effects.

The f dependence of $K_{\mathrm{ss}}(f)$ can be calculated quite straightforwardly by making use of Eq. (5.1). The approximate expression for $P(t)$ given in Eq. (4.17) is used in the simplified form

$$P(t) = P_{\mathrm{Sm}}(t)[1 + \tfrac{1}{2} f^2 K_2(t)] \tag{5.11}$$

Such a simplification is valid, since the main contribution to integral in Eq. (5.1) is made at small times, where the product $f^2 K_2(t)$ is small compared to unity. Our analysis confirms Eq. (5.10). It should be noted that the second term in the square brackets in Eq. (5.11) accounts for many-body effects neglected in the Smoluchowski theory. It is just this term which is responsible for the last term in the square brackets in Eq. (5.10). When $f \ll 1$, this term is negative and hence $K_{\mathrm{ss}}(f)$ as given in Eq. (5.10) satisfies the inequality (5.7).

To summarize this section, we note that the nontrivial dependence of the steady-state rate constant on the trap concentration arises even within the framework of the Smoluchowski theory which neglects the many-body effects.[5] The real value of $K_{ss}(f)$ is always smaller than $K_{ss,Sm}(f)$. When $f \ll 1$ the leading terms in the expansion of $K_{ss}(f)$ taking many-body effects into account are given by Eq. (5.10).

6. CONCLUDING REMARKS

The approach discussed above can be generalized to encompass many variations of the trapping problem. These follow from the generalization of each of two multipliers in the integrand in Eq. (3.5). For example, when the particle is charged and its Brownian motion occurs in an external electric field, one needs to modify the Wiener sausage volume probability density $F_t(v)$ in Eq. (3.5). A similar modification is required in the case of the anisotropic Brownian motion, which takes place in quasi-one-dimensional and layered materials. On the other hand, when the distribution of the number of traps in a given volume differs from the Poisson, then the first multiplier in the integrand in Eq. (3.5) must be modified. One can show that trap repulsion leads to a decrease in the particle survival probability, since it decreases the probability of finding the volume v free of traps. In contrast, an increase in trap attraction leads to an increase in the probability of finding the volume v free of traps and therefore to an increase in the survival probability.[34] It should be noted that the expression in Eq. (3.5) for the survival probability is not correct in general, since the survival probability of a particle moving along a Wiener trajectory depends not only on the Wiener sausage volume corresponding to this trajectory, but also on the Wiener sausage shape and attitude.

Now let us touch briefly on one more question related to many-body effects in diffusion-limited kinetics. So far we have considered the Brownian particle death on static traps and have discussed the deviations from the Smoluchowski theory predictions due to many-body effects, which are ignored in the Smoluchowski theory. At the same time, the Smoluchowski theory gives the exact solution of the problem of static particle death as a result of its collision with one of the moveable traps.[5,10,11,14,15]

Within the framework of the Smoluchowski theory there is no difference between these cases (the trapping and target problems), since only the total diffusion coefficient given in Eq. (2.1) appears in later formulas. In this connection, a very interesting problem arises related to the many-body effect on the reaction rate in the course of transition from the trapping to the target problem. In other words, this is a question of many-body effects with arbitrary mobility of both particles and traps. The first steps in this direction were made in recent papers,[35–37] where the influence of trap mobility on the particle death fluctuation slowdown was analyzed. However, this set of questions generally remains open for further investigation. In conclusion, we note that though some progress has been achieved in constructing a diffusion-limited reaction theory taking many-body effects into account, there remain many unsolved problems in this area awaiting further investigation.

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