Residence time distribution of a Brownian particle

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The residence time of a Brownian particle within a spatial domain is the total time it spends within this domain. It is shown that the residence time distribution can be calculated from the survival probability for a constant trapping rate inside the domain. This isomorphism is exploited to derive explicit relations for the distribution and its moments for a three-dimensional spherical domain. Results are verified by a Brownian dynamics simulation. [S1063-651X(98)08504-3]

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I. INTRODUCTION

Consider a particle which spends all of its lifetime within a prescribed spatial domain. The particle disappears either from the interior of the domain or from its boundary. When the motion of the particle is governed by probabilistic laws, such as, for example, random walk or Brownian motion, one can speak about the particle *mean* lifetime, the first moment of its lifetime distribution [1,2]. The mean lifetime is of fundamental importance for diffusion influenced reactions, as it is a measure for the (reciprocal) reaction rate constant.

In more specific language, suppose that $p(\vec{r},t|\vec{R})$ is the probability density of finding the particle at a point $\vec{r}$ within a domain ω by time t, given that at $t=0$ it was located at point $\vec{R}\in\omega$. Under the above conditions, the survival probability of the particle within the domain is defined by

$$S(t|\vec{R})\equiv\int_{\omega}p(\vec{r},t|\vec{R})d\vec{r}. \tag{1.1}$$

From it, the lifetime distribution may be calculated as

$$F(t|\vec{R})=-\partial S(t|\vec{R})/\partial t. \tag{1.2}$$

The average lifetime, the first moment of the lifetime distribution, is thus given by

$$\overline{\tau}(\vec{R})=-\int_0^{\infty}\frac{\partial S(t|\vec{R})}{\partial t}t\,dt=\int_0^{\infty}S(t|\vec{R})dt. \tag{1.3}$$

The second equality follows from integration by parts, using the fact that under the above-mentioned conditions the survival probability decreases from unity to zero [1,2].

In the usual case when a lifetime distribution can be defined, ω is either an infinite or a finite domain with reflecting or absorbing boundaries. During its lifetime, the diffusing particle never exits from this domain. In the present work we consider a more general case when the particle can exit from and enter into a finite domain an unrestricted number of times. The initial location, $\vec{R}$, is either inside or outside ω. The function $S(t)$, Eq. (1.1), which may be defined for an arbitrary domain ω, does not necessarily decrease to zero at infinitely long times. Moreover, it need not even be monotonic in t.

It is nevertheless meaningful to ask, for a given observation time t, what is the time τ spent by the particle within ω? This quantity, $\tau\leqslant t$, is the ''residence time'' (RT) of the particle in ω up to time t. Starting from the Green function for diffusion, $p(\vec{r},t|\vec{R})$, the mean residence time (MRT) may be defined in a manner analogous to Eq. (1.3), namely,

$$\overline{\tau}_t(\vec{R})=\int_0^t dt'\int_{\omega}d\vec{r}\;p(\vec{r},t'|\vec{R}). \tag{1.4}$$

The MRT for an infinite observation time, $t=\infty$, has found several applications [3–7]. However, the general problem of obtaining the RT distribution has not been discussed in the physics literature. Therefore one goal of the present paper is to survey the RT theory for the physicist.

The ''residence time'' is known in the mathematics literature as the ''occupation time'' [8–14]. (We prefer the less aggressive terminology of ''residence'' times [5]. ''Occupation'' implies that the particle takes possession of the domain and may thus prevent other particles from entering. This is not the case for the problem at hand, in which particles may simultaneously occupy the same domain.) The basic theory has been worked out by Kac [8–11], who has returned to this problem several times during his career [12]. There are two routes for obtaining the RT distribution (Sec. II): The direct route involves a multiple integral for the moments which, if known, gives the distribution in the form of a moment expansion. (We apply this approach in Appendix A). The second route involves solving a partial differential equation for the ''Kac functional'' [11]. In the language of diffusion influenced reactions, this is just the survival probability for a diffusing particle which is scavenged inside ω (Sec. III).

We could not find in the literature explicit expressions for the RT distribution and its moments. (In two dimensions, where the moments diverge, Darling and Kac have derived the long-time asymptotics [9]). Therefore the second goal of our paper is to obtain explicit results for a three-dimensional

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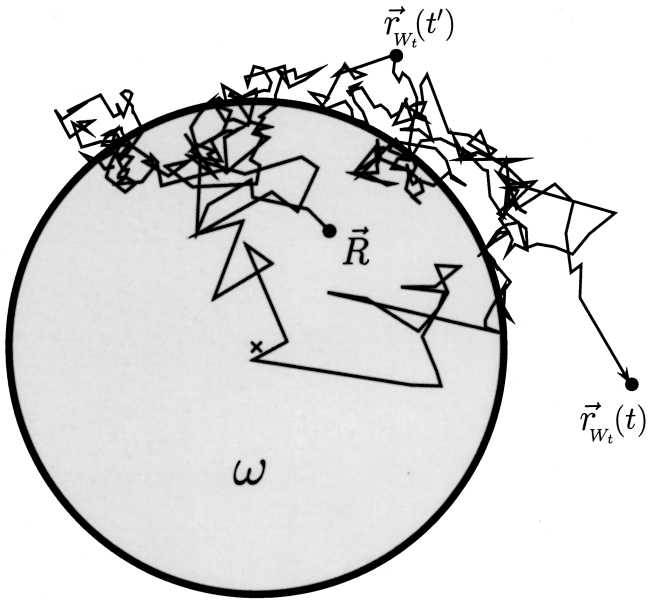

FIG. 1. A domain ω with a Wiener trajectory W_t.

sphere, possibly the only case where the theory can be exemplified analytically. We find two analytic representations for the moments. One is in terms of finite, Euler-like polynomials in the starting position of the random walker (''Euler representation''). The other is in terms of an infinite trigonometrical series (''Fourier representation''). Each of the two routes can yield either representation, as detailed in the text. The distribution function itself also admits several representations, all in terms of infinite series. Some series converge rapidly for short times and others at long times (Sec. III).

The third goal of our exposition is to explain how an accurate Brownian dynamics (BD) algorithm for calculating the RT distribution is constructed (Sec. IV). The results in Sec. IV C show nice agreement between the BD simulations and our analytic expressions for the special case of spherical domains in three-dimensional space. Clearly, for domains of more complex shapes the BD simulation might be the only route for obtaining results.

II. GENERAL RELATIONSHIPS

Let ω be a domain in three-dimensional space, as depicted in Fig. 1. The quantity of our interest is the residence time τ spent by a Brownian particle in ω. This time is a random quantity. It depends on the stochastic Wiener trajectory chosen by the particle. The probability density of the distribution over τ, $F_t(\tau|\vec{R})$, is a function of the particle starting position $\vec{R}$ and the observation time t. As we will see below, it is easy to calculate the MRT $\overline{\tau}_t(\vec{R})$ from the Green function of the free Brownian motion, Eq. (1.4). However, calculation of higher moments or the probability density itself is a more complicated task. Let us begin by introducing the formal definitions of the quantities under study in terms of stochastic trajectories.

A. Residence time of Wiener trajectories

Consider a Brownian particle which moves along the Wiener trajectory W_t which begins at the point $\vec{R}$, the subscript ''t'' indicates the observation time (Fig. 1). The RT $\tau(W_t|\vec{R})$ is the time spent by this particle inside the domain ω [9–14],

$$\tau(W_t|\vec{R}) = \int_0^t \chi_\omega(\vec{r}_{W_t}(t'))dt', \tag{2.1}$$

where $\vec{r}_{W_t}(t')$ is the position of the particle at time instant t', $0 \leqslant t' \leqslant t$, along the specified trajectory, W_t, and $\chi_\omega(\vec{r})$ is the indicator function of ω defined as

$$\chi_\omega(\vec{r}) = \int_\omega \delta(\vec{r}-\vec{r}')d\vec{r}' = \begin{cases} 1 & \text{if } \vec{r} \in \omega \\ 0 & \text{otherwise.} \end{cases} \tag{2.2}$$

Thus in Eq. (2.1) the integrand, Eq. (2.2), is equal to unity when the particle is inside ω and zero when the particle is outside. This is why the integral is equal to the RT. By inserting Eq. (2.2) into Eq. (2.1) and changing the order of integration, one obtains

$$\tau(W_t|\vec{R}) = \int_\omega \varphi_{W_t}(\vec{r},t)d\vec{r}, \tag{2.3}$$

where the random variable

$$\varphi_{W_t}(\vec{r},t) \equiv \int_0^t \delta(\vec{r}_{W_t}(t')-\vec{r})dt' \tag{2.4}$$

is the RT density, also known as the ''local time'' [13].

The probability density of the RT distribution is the ensemble average of the number of trajectories whose RT in ω equals τ. Therefore we set

$$F_t(\tau|\vec{R}) = \langle \delta(\tau - \tau(W_t|\vec{R}))\rangle, \tag{2.5}$$

where $\delta(z)$ is the Dirac δ function, and $\langle\cdots\rangle$ denotes averaging over realizations of Wiener trajectories which start from the point $\vec{R}$. The probability density is normalized to unity,

$$\int_0^t F_t(\tau|\vec{R})d\tau = 1, \tag{2.6}$$

due to the δ-function form of Eq. (2.5).

Using the above definitions, the MRT assumes the forms

$$\begin{aligned}\overline{\tau}_t(\vec{R}) &\equiv \int_0^t \tau F_t(\tau|\vec{R})d\tau = \int_0^t \tau \langle \delta(\tau - \tau(W_t|\vec{R}))\rangle d\tau \\ &= \langle \tau(W_t|\vec{R})\rangle = \int_0^t \langle \chi_\omega(\vec{r}_{W_t}(t'))\rangle dt' \\ &= \int_0^t dt' \int_\omega d\vec{r} \langle \delta(\vec{r}-\vec{r}_{W_t}(t'))\rangle. \end{aligned} \tag{2.7}$$

These equalities admit various interpretations. The average time with respect to $F_t(\tau|\vec{R})$ is the ensemble average of $\tau(W_t|\vec{R})$, Eq. (2.1). The ensemble average of the indicator function, $\langle \chi_\omega(\vec{r}_{W_t}(t))\rangle$, is the fraction of trajectories found within the domain ω at time t. This ''residence probability''

generalizes the notion of ''survival probability'' to partial domains within the diffusion space. Hence the fourth equality in Eq. (2.7) is a generalization of (the second equality in) Eq. (1.3). However, $F_t(\tau|\vec{R})$ is generally not equal to the negative time derivative of the residence probability. Finally, the integrand $\langle \delta(\vec{r}-\vec{r}_{W_t}(t'))\rangle$ is the Green function of the Brownian particle which starts from the point $\vec{R}$ at $t=0$,

$$g(\vec{r},t'|\vec{R}) \equiv \langle \delta(\vec{r}-\vec{r}_{W_t}(t'))\rangle. \tag{2.8}$$

Using this fact we arrive at the relationship (1.4), which expresses the MRT in terms of the Green function of the Brownian particle, in agreement with earlier work [5]. Alternately, the MRT can be expressed using the ensemble average of the ''local time,'' see Eqs. (2.3) and (2.4).

The higher moments can be expressed as repeated convolutions of $g(\vec{r},t|\vec{R})$ with itself [14]. Consider the second RT moment as an example,

$$\begin{aligned}\overline{\tau_t^2}(\vec{R}) &= \int_0^t \tau^2 F_t(\tau|\vec{R})d\tau = \int_0^t \tau^2 \langle \delta(\tau-\tau(W_t|\vec{R}))\rangle d\tau \\ &= \langle \tau^2(W_t|\vec{R})\rangle \\ &= \int_0^t dt_1 \int_0^t dt_2 \langle \chi_\omega(\vec{r}_{W_t}(t_1))\chi_\omega(\vec{r}_{W_t}(t_2))\rangle. \end{aligned} \tag{2.9a}$$

From the Markov property of W_t and the fact that Eq. (2.9a) is symmetric with respect to the interchange of t_1 and t_2, one obtains [14]

$$\begin{aligned}\overline{\tau_t^2}(\vec{R}) &= 2! \int_0^t dt_2 \int_0^{t_2} dt_1 \langle \chi_\omega(\vec{r}_{W_t}(t_1))\rangle \langle \chi_\omega(\vec{r}_{W_t}(t_2))\rangle \\ &= 2! \int_\omega d\vec{r}_2 \int_\omega d\vec{r}_1 \int_0^t dt_2 \int_0^{t_2} dt_1 g(\vec{r}_1,t_1|\vec{R}) \\ &\quad \times g(\vec{r}_2,t_2-t_1|\vec{r}_1). \end{aligned} \tag{2.9b}$$

The nth moment is thus obtained from the n-fold convolution of the diffusion Green function with itself.

For an infinite observation time, change the order of integration to $\int_0^t dt_1 \int_{t_1}^t dt_2$ and set $t_2' = t_2 - t_1$. The upper limit in both time integrals may now be replaced by ∞. For three-dimensional diffusion the Green function is

$$g(\vec{r},t|\vec{R}) = (4\pi t)^{-3/2} \exp[-|\vec{r}-\vec{R}|^2/4t], \tag{2.10}$$

where, for simplicity, we set the diffusion constant to unity (thus t stands for Dt). Inserting into Eq. (2.9b) and performing the temporal integrals analytically, one obtains [[10], Eq. (IV.8.5)]

$$\overline{\tau_\infty^2}(\vec{R}) = \frac{2!}{(4\pi)^2} \int_\omega d\vec{r}_2 \int_\omega d\vec{r}_1 |\vec{r}_1-\vec{R}|^{-1} |\vec{r}_2-\vec{r}_1|^{-1}, \tag{2.11}$$

where $|\vec{r}|$ denotes the norm of the vector $\vec{r}$. The fact that the Coulomb potential appears in the above integral is not at all surprising, since the MRT is the spatial integral of the density, $\varphi(\vec{r}|\vec{R}) \equiv \langle \varphi_{W_t}(\vec{r})\rangle$, see Eq. (2.3). The latter obeys the Poisson equation [4,5]

$$\Delta_{\vec{r}} \varphi(\vec{r}|\vec{R}) = -\delta(\vec{r}-\vec{R}), \tag{2.12}$$

which is obtained by integrating the diffusion equation for $g(\vec{r},t|\vec{R})$ over time ($\Delta_{\vec{r}}$ is the Laplace operator in three dimensions).

For simple geometries, one might hope to perform the ''Coulombic convolution'' integral in Eq. (2.11) analytically. Equation (2.11) indeed simplifies for spherical domains, which can then be used to calculate the moments (see Appendix A). This then allows a moment expansion for the Laplace transform of the RT distribution

$$\begin{aligned}\hat{F}_\infty(k|\vec{R}) &\equiv \int_0^\infty F_\infty(\tau|\vec{R}) \exp(-k\tau)d\tau \\ &= \sum_{n=0}^\infty (-1)^n \overline{\tau_\infty^n}(\vec{R}) k^n/n!, \end{aligned} \tag{2.13a}$$

where the nth moment is given by

$$\overline{\tau_\infty^n}(\vec{R}) = (-1)^n \left[\frac{\partial^n \hat{F}_\infty(k|\vec{R})}{\partial k^n} \right]_{k=0}. \tag{2.13b}$$

The alternative route taken below allows a direct computation of $\hat{F}_\infty(k|\vec{R})$ by noting that it obeys a partial differential equation with a clear physical interpretation.

B. Relationship to the trapping problem

The alternate route to the Laplace transform of the RT density begins with the ''Kac functional'' [11,12]. It can be given physical meaning as follows. The key point is the observation that the integral $\int_0^t F_t(\tau|\vec{R})\exp(-k\tau)d\tau$ is the survival probability $S(t|k|\vec{R})$ of our particle when it may be trapped only within the domain ω, and with a constant trapping rate k. Thus as we argue below

$$S(t|k|\vec{R}) = \int_0^t F_t(\tau|\vec{R}) \exp(-k\tau)d\tau \tag{2.14a}$$

$$= \langle \exp[-k\tau(W_t|\vec{R})]\rangle. \tag{2.14b}$$

The second line follows by using the RT probability density, Eq. (2.5), and interchanging the order of averaging and integration. Thus to find $F_t(\tau|\vec{R})$ one could first solve the diffusional problem for $S(t|k|\vec{R})$ and then invert the integral relation (2.14a).

To derive Eq. (2.14), note first that the survival probability of a stationary particle located at the point $\vec{r}$, where the local trapping rate coefficient is $k(\vec{r})$, is

$$S(t|\vec{r}) = \exp[-k(\vec{r})t]. \tag{2.15}$$

Suppose the particle moves along the trajectory W_t, given by the set of points $\{t',\vec{r}_{W_t}\}$, where $t' \leq t$. The survival probability of the particle becomes

$$S(t|W_t)=\exp\left(-\int_0^t k(\vec{r}_{W_t}(t'))dt'\right). \tag{2.16}$$

Averaging over all trajectories which begin at point $\vec{R}$, one obtains

$$S(t|\vec{R})=\left\langle \exp\left(-\int_0^t k(\vec{r}_{W_t}(t'))dt'\right)\right\rangle. \tag{2.17}$$

This is known in the mathematics literature as the ''Kac functional'' [e.g., Eq. (5.38) in Chap. 15 of Ref. [13]]. In the case of our interest, $k(\vec{r})$ is a nonzero constant only within the domain ω,

$$k(\vec{r})=k\chi_\omega(\vec{r}). \tag{2.18}$$

Substituting this $k(\vec{r})$ into Eq. (2.17) gives the survival probability in the desired form of Eq. (2.14b). We will solve the trapping problem directly, for an infinite observation time, to obtain $S(\infty|k|\vec{R})$.

III. EXPLICIT EXPRESSIONS

To illustrate the general approach presented above, we consider the case when the domain ω is a three-dimensional sphere. In this case the survival probability $S(t|k|\vec{R})$ can be calculated. To avoid too cumbersome expressions we calculate the probability density $F_\infty(\tau|\vec{R})$ as well as the moments for an infinitely long observation time, when Eq. (2.14a) takes the form

$$S(\infty|k|\vec{R})=\hat{F}_\infty(k|\vec{R})\equiv\int_0^\infty F_\infty(\tau|\vec{R})\ \exp(-k\tau)d\tau. \tag{3.1}$$

This means that the survival probability $S(\infty|k|\vec{R})$ is the Laplace transform of the probability density $F_\infty(\tau|\vec{R})$ corresponding to the value of the Laplace parameter equal to the absorption rate constant k.

We calculate the survival probability in Sec. III A. While a similar derivation can be found in a late work of Kac [11], he has not proceeded to obtain explicit expressions for the distribution function and its moments. This is done in Secs. III B and III C below. To our knowledge, this is the only case yielding an analytical solution which, moreover, generates a surprising number of identities.

A. Survival probability

In this subsection we calculate the survival probability of a Brownian particle which may be absorbed inside a spherical domain. We take the center of the sphere as the origin and its radius as a unit of length. We also assume that the diffusion coefficient of the Brownian particle is equal to unity. This sets the distance and time units.

To calculate the survival probability, one first has to find the Green function $g(\vec{r},t|\vec{R})$ by solving a diffusion equation with a sink term [11],

$$\partial g(\vec{r},t|\vec{R})/\partial t=[\Delta_{\vec{r}}-kH(1-|\vec{r}|)]g(\vec{r},t|\vec{R}). \tag{3.2}$$

Here $\Delta_{\vec{r}}$ is the Laplace operator acting on the variable $\vec{r}$ and $H(z)$ is the Heaviside step function, i.e., $H(z)=0$ for $z<0$ and $H(z)=1$ for $z>0$. The initial condition is $g(\vec{r},0|\vec{R})=\delta(\vec{r}-\vec{R})$. As a boundary condition, we use the evident property that $g(\vec{r},t|\vec{R})\to 0$ when $|\vec{r}|\to\infty$.

The survival probability of the Brownian particle is given by

$$S(t|k|\vec{R})=\int g(\vec{r},t|\vec{R})d\vec{r}, \tag{3.3}$$

with integration over the whole space. The survival probability of interest is obtained from $S(t|k|\vec{R})$ by taking the limit $t\to\infty$.

It is convenient to use, instead of Eq. (3.2), the Kolmogorov backward equation [1]

$$\partial g(\vec{r},t|\vec{R})/\partial t=[\Delta_{\vec{R}}-kH(1-|\vec{R}|)]g(\vec{r},t|\vec{R}), \tag{3.4}$$

where $\Delta_{\vec{R}}$ is the Laplace operator acting on the *initial* variable, $\vec{R}$. By integrating Eq. (3.4) over $\vec{r}$, one obtains an analogous equation for the survival probability,

$$\partial S(t|k|\vec{R})/\partial t=[\Delta_{\vec{R}}-kH(1-|\vec{R}|)]S(t|k|\vec{R}), \tag{3.5}$$

subject to the boundary condition that $S(t|k|R)\to 1$ when $R\to\infty$. The initial condition is $S(0|k|R)=1$.

Due to the spherical symmetry, the survival probability depends on a single coordinate, namely, the distance $R=|\vec{R}|$ from the center of the sphere. Thus we write the Laplacian in spherical coordinates. In addition, when $t\to\infty$ the survival probability becomes independent of time and its time derivative vanishes. As a consequence, $S(\infty|k|R)$ satisfies the equation

$$\left[\frac{1}{R^2}\frac{d}{dR}\left(R^2\frac{d}{dR}\right)-kH(1-R)\right]S(\infty|k|R)=0, \tag{3.6}$$

with the corresponding boundary condition.

We seek a solution of Eq. (3.6) in the form $S(\infty|k|R)\equiv f(R)/R$. The function $f(R)$ satisfies the equation

$$\frac{d^2f}{dR^2}-kH(1-R)f=0, \tag{3.7}$$

with the boundary conditions $f(0)=0$ and $R^{-1}f(R)\to 1$ when $R\to\infty$. The former condition is necessary for the finiteness of $S(\infty|k|R)$ at $R=0$. The solution satisfying these boundary conditions reads

$$f(R)=\begin{cases} A\sinh(\sqrt{k}R), & R<1 \\ R+B, & R>1. \end{cases} \tag{3.8}$$

The constants A and B are determined from the continuity of $f(R)$ and its first derivative at $R=1$. As a result, one obtains [11]

$$S(\infty|k|R)=\begin{cases}\dfrac{\sinh(\sqrt{k}R)}{\sqrt{k}R\,\cosh(\sqrt{k})}, & R\leqslant 1\\ 1-\dfrac{1}{R}+\dfrac{1}{\sqrt{k}R}\tanh(\sqrt{k}), & R\geqslant 1.\end{cases} \tag{3.9}$$

We note an alternative form for this survival probability, obtained by a Fourier expansion of $\sinh(\sqrt{k}R)$, using the basis $\sin[\pi(j+1/2)R]$ in the interval $[0,1]$. For $R\leqslant 1$ this gives

$$S(\infty|k|R)=\frac{2}{R}\sum_{j=0}^{\infty}(-1)^j\,\frac{\sin[\pi(j+\frac{1}{2})R]}{[(j+\frac{1}{2})\pi]^2+k}. \tag{3.10}$$

The last result is immediate using the ''direct approach,'' where it is recognized as an eigenvalue expansion in the eigenfunctions of the Kac integral equation, see Appendix A. In the following subsections the above solutions are used to determine the probability density of the RT distribution and its moments.

B. Moment generation

We only need to generate the moments for random walks starting within the sphere: for $R>1$, Eq. (3.9) reads $S(\infty|k|R)=C+S(\infty|k|1)/R$, where C is a k-independent constant. Equation (2.13b) thus implies that for $n\geqslant 1$

$$\overline{\tau_\infty^n}(R)=\overline{\tau_\infty^n}(1)/R. \tag{3.11}$$

The moments of the RT distribution, $\overline{\tau_\infty^n}(R)$, follow directly from Eqs. (3.9) and (3.10), yielding their Euler and Fourier representations, respectively.

1. Euler representation

The Euler form for the moments is based on the connection between the Laplace transform, Eq. (3.9), and the generating function of the Euler polynomials, $E_n(x)$,

$$\frac{2e^{xy}}{e^y+1}=\sum_{n=0}^{\infty}E_n(x)\,\frac{y^n}{n!}, \tag{3.12}$$

see Eq. (23.1.1) in the handbook of Abramowitz and Stegun [15]. Thus we rewrite Eq. (3.9) as

$$\begin{aligned}\hat{F}_\infty(k|\vec{R})&=\frac{1}{2\sqrt{k}R}\left[\frac{2e^{2\sqrt{k}[(R+1)/2]}}{e^{2\sqrt{k}}+1}-\frac{2e^{-2\sqrt{k}[(R+1)/2]}}{e^{-2\sqrt{k}}+1}\right]\\&=\frac{1}{R}\sum_{n=0}^{\infty}[1-(-1)^n]E_n\left(\frac{R+1}{2}\right)\frac{(2\sqrt{k})^{n-1}}{n!},\end{aligned} \tag{3.13}$$

where we have set $y\equiv\pm 2\sqrt{k}$. Comparing with the moment expansion, Eq. (2.13a), one obtains

TABLE I. Moments of the residence time distribution within a unit sphere, $\overline{\tau_\infty^n}(R)$, for two initial starting locations.

n	0	1	2	3
$R=1$	1	1/3	4/15	34/105
$R=0$	1	1/2	5/12	61/120

$$\overline{\tau_\infty^n}(R)=\frac{(-1)^n\,2^{2n+1}n!}{(2n+1)!R}E_{2n+1}\left(\frac{R+1}{2}\right). \tag{3.14}$$

Thus $\overline{\tau_\infty^n}(R)$ are polynomials of degree $2n$ in R.

These polynomials can be written explicitly using the series decomposition of the Euler polynomials [see Eq. (23.1.7) in Ref. [15]]. Denoting the ''Euler numbers'' by $E_n\equiv 2^nE_n(1/2)$, and taking into account the fact that $E_{2n+1}=0$, one obtains

$$\overline{\tau_\infty^n}(R)=(-1)^n\frac{n!}{(2n+1)!}\sum_{k=0}^{n}\binom{2n+1}{2k}E_{2k}\,R^{2(n-k)}. \tag{3.15}$$

Thus all the RT moments are *even* polynomials in the starting point, R.

For the first moment we get

$$\overline{\tau_\infty^1}(R)=\frac{1}{2}-\frac{1}{6}R^2. \tag{3.16a}$$

This result, for $R=0$, has been obtained in Eq. (2.37) of Blumen and Zumofen [3]. Note that $R^2/6$ is the mean lifetime for diffusional motion starting at the origin of a sphere of radius R (i.e., when an absorbing boundary condition is imposed at $r=R$). Thus the MRT starting at $0<R<1$ equals the MRT starting at zero minus the mean lifetime in a sphere of radius R. The analytical form of the second and third moments is

$$\overline{\tau_\infty^2}(R)=\frac{5}{12}-\frac{1}{6}R^2+\frac{1}{60}R^4, \tag{3.16b}$$

$$\overline{\tau_\infty^3}(R)=\frac{61}{120}-\frac{5}{24}R^2+\frac{1}{40}R^4-\frac{1}{840}R^6. \tag{3.16c}$$

For the special cases when the initial condition is in the center or on the surface of the sphere, the moments of the RT are given by

$$\overline{\tau_\infty^n}(0)=(-1)^n\frac{n!}{(2n)!}E_{2n}, \tag{3.17a}$$

$$\overline{\tau_\infty^n}(1)=(-1)^n\frac{n!}{(2n+2)!}\,2^{2n+2}(2^{2n+2}-1)B_{2n+2}, \tag{3.17b}$$

where the B_n's are the Bernoulli numbers, see Eq. (23.1.20) in Ref. [15]. The first few values are summarized in Table I.

2. Fourier representation

The Fourier form of the RT moments (for $R \leqslant 1$) follows by differentiating Eq. (3.10) according to Eq. (2.13b). We find that

$$\overline{\tau_\infty^n}(R) = \frac{2n!}{R} \sum_{j=0}^{\infty} (-1)^j \frac{\sin[\pi(j+\frac{1}{2})R]}{[\pi(j+\frac{1}{2})]^{2(n+1)}}. \quad (3.18)$$

The equivalence with the Euler representation in Eq. (3.14) implies the identity

$$\sum_{j=0}^{\infty} (-1)^j \frac{\sin[(2j+1)\pi x]}{(2j+1)^{2n}} = -\frac{(-1)^n \pi^{2n}}{4(2n-1)!} E_{2n-1}\left(x+\frac{1}{2}\right), \quad (3.19)$$

which can also be obtained by replacing x by $x+1/2$ in the Fourier expansion of the Euler polynomials, Eq. (23.1.17) of Ref. [15].

When $R=0$, Eq. (3.18) simplifies to

$$\overline{\tau_\infty^n}(0) = \frac{2^{2(n+1)} n!}{\pi^{2n+1}} \beta(2n+1), \quad (3.20)$$

where $\beta(m)$ is the series

$$\beta(m) \equiv \sum_{j=0}^{\infty} (-1)^j (2j+1)^{-m}, \quad (3.21)$$

defined in Eq. (23.2.21) of Ref. [15]. Equivalence with the representation in Eq. (3.17a) arises because $2\beta(2n+1) \equiv (\pi/2)^{2n+1} |E_{2n}|/(2n)!$, see Eq. (23.2.22) in Ref. [15].

For $R=1$, Eq. (3.18) simplifies to

$$\overline{\tau_\infty^n}(1) = 2(2/\pi)^{2(n+1)} n! \lambda(2(n+1)), \quad (3.22)$$

where $\lambda(m)$ is defined by Eq. (23.2.20) in Ref. [15],

$$\lambda(m) \equiv \sum_{j=0}^{\infty} (2j+1)^{-m} = (1-2^{-m})\zeta(m), \quad (3.23)$$

and $\zeta(m)$ is the Riemann ζ function [15], $\zeta(m) \equiv \Sigma_{j=1}^{\infty} j^{-m}$. This result is the same as Eq. (3.17b) in view of the identity that $2\zeta(2n) \equiv (2\pi)^{2n} |B_{2n}|/(2n)!$, see Eq. (23.2.16) in Ref. [15].

C. The probability density

With the moments determined, the probability density itself is given by the moment expansion, Eq. (2.13a). However, this expansion does not converge rapidly at long times. We thus proceed to invert the Laplace transforms obtained in Sec. III A. For didactic purposes, let us proceed in order of complexity. Consider first the case when the particle starts at the surface of the sphere, $R=1$, then when it is outside the domain and finally the case $R \leqslant 1$. The different solutions are demonstrated in Fig. 2 and compared with results of Brownian simulations using the algorithm described in Sec. IV below. They are cast in terms of two infinite series, one which converges rapidly for short times and another which converges rapidly for long times.

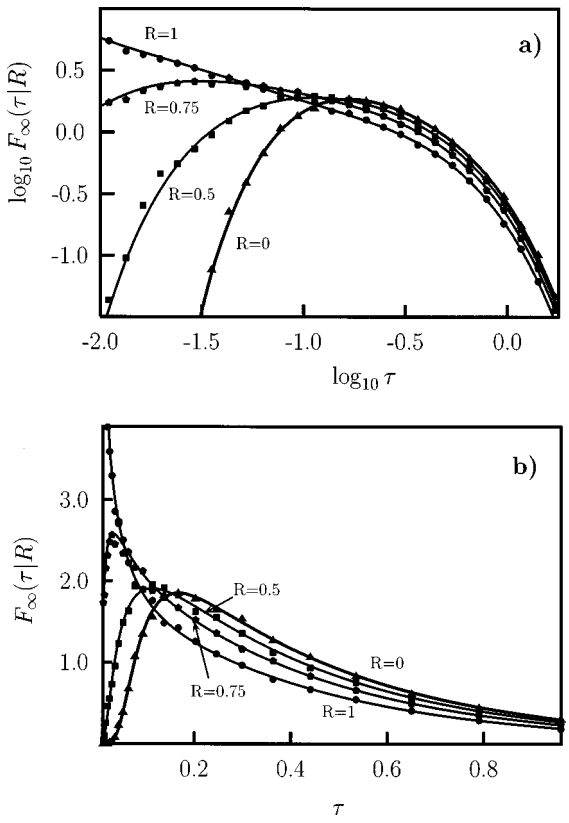

FIG. 2. The residence time probability density: (a) logarithmic scale and (b) linear scale. Full lines are analytic solutions, Eqs. (3.30) and (3.31), or Eqs. (3.25) and (3.26) for $R=1$. Different lines correspond to the different starting positions, as indicated. Symbols are from Brownian dynamics simulations, see Sec. IV C. Sphere radius and diffusion constant are both unity.

1. Initial position on the surface, R=1

The simplest case involves a particle initially at the surface of the sphere. By setting $R=1$ in Eq. (3.9) we obtain

$$S(\infty|k|1) = \frac{1}{\sqrt{k}} \tanh(\sqrt{k}) = \frac{1}{\sqrt{k}} \left(1 + 2\sum_{j=1}^{\infty} (-1)^j \exp(-2j\sqrt{k})\right). \quad (3.24)$$

The second equality is obtained by expanding $1/[1+\exp(-2\sqrt{k})]$ in a Taylor series. Inverting the Laplace transform, $S(\infty|k|1)$, we obtain $F_\infty(\tau|1)$ in the form convenient to analyze the behavior at small values of τ,

$$F_\infty(\tau|1) = \frac{1}{\sqrt{\pi\tau}} \left[1 + 2\sum_{j=1}^{\infty} (-1)^j \exp\left(-\frac{j^2}{\tau}\right)\right], \quad (3.25)$$

see Eq. (29.3.84) in Ref. [15]. An expression which converges rapidly for large τ can be derived in several ways [cf. Eq. (3.31) below],

$$F_\infty(\tau|1) = 2\sum_{j=0}^{\infty} \exp\left(-\frac{\pi^2}{4}(2j+1)^2\tau\right). \quad (3.26)$$

It follows that $F_\infty(\tau|1)$ tends to infinity as $1/\sqrt{\tau}$, when $\tau\to 0$, and to zero as $\exp(-\pi^2\tau/4)$, when $\tau\to\infty$, see Fig. 2.

2. Initial position outside the sphere, R>1

When the particle starts outside the absorbing domain, $R>1$, the desired solution may be related to the above solution for $R=1$. Let us divide the Wiener trajectories into two groups, depending on whether they enter into the domain or not. For a sphere of radius unity, the fraction $\gamma(R)$ of trajectories which reach the surface of the sphere is given by

$$\gamma(R)=1/R. \tag{3.27}$$

This ''trapping probability'' solves Eq. (3.6) with the boundary conditions $\gamma(1)=1$ and $\gamma(\infty)=0$ [1]. The fraction of trajectories which never enter into the spherical domain is $[1-\gamma(R)]$.

A common feature of the trajectories belonging to the fraction $\gamma(R)$ is that at a certain instant they enter into the domain for the first time. Their contribution to $F_\infty(\tau|R)$ is thus $\gamma(R)F_\infty(\tau|1)$. This is why, for $R>1$, Eq. (3.9) has the form

$$S(\infty|k|R)=[1-\gamma(R)]+\gamma(R)S(\infty|k|1). \tag{3.28}$$

Mathematically, both $S(\infty|k|R)$ and $\gamma(R)$ obey the same differential equation, but with different boundary conditions. Consequently, for $R>1$ the RT distribution is

$$F_\infty(\tau|R)=2[1-\gamma(R)]\delta(\tau)+\gamma(R)F_\infty(\tau|1). \tag{3.29}$$

This universal $1/R$ scaling holds only when the particle starts outside the spherical domain.

3. Initial position inside the sphere, R<1

When the particle starts from a point located inside the domain, $R<1$, the dependence on R is not as simple as in the previous cases. Inverting the Laplace transform of the survival probability, Eq. (3.9), gives

$$F_\infty(\tau|R)=\frac{1}{\sqrt{\pi\tau}R}\sum_{j=-\infty}^{\infty}(-1)^j\exp\left(-\frac{(2j+1-R)^2}{4\tau}\right). \tag{3.30}$$

As before, this series converges rapidly for small τ. The probability density $F_\infty(\tau|1)$, Eq. (3.25), is recovered when $R\to 1$.

An expression convenient to analyze the large τ behavior of $F_\infty(\tau|R)$ is obtained by inverting Eq. (3.10), namely,

$$F_\infty(\tau|R)=\frac{2}{R}\sum_{j=0}^{\infty}(-1)^j\sin\left(\frac{\pi}{2}(2j+1)R\right)\times\exp\left(-\frac{\pi^2}{4}(2j+1)^2\tau\right). \tag{3.31}$$

Alternative ways of deriving this result directly from Eq. (3.30) involve the ''Poisson summation formula'' or the procedure discussed in Appendix B. Note that the moments calculated from $\int_0^\infty F_\infty(\tau|R)\tau^n d\tau$ using this expression are given, again, by Eq. (3.18).

For $R=1$, Eq. (3.31) reduces to Eq. (3.26). For $R=0$, it simplifies to

$$F_\infty(\tau|0)=\frac{1}{\sqrt{\pi}\tau^{3/2}}\sum_{j=0}^{\infty}(-1)^j(2j+1)\exp\left(-\frac{(2j+1)^2}{4\tau}\right)=\pi\sum_{j=0}^{\infty}(-1)^j(2j+1)\exp\left(-\frac{\pi^2}{4}(2j+1)^2\tau\right). \tag{3.32}$$

When $\tau\to 0$, $F_\infty(\tau|R)$ with $R<1$ tends to zero because, when the starting point is located inside the domain, the particle surely spends some time there. The short-time behavior is proportional to $\exp[-(1-R)^2/4\tau]$. While the small τ asymptotic behavior of the probability density is qualitatively different when $R>1$ and $R<1$, the large τ asymptotic behavior is the same in both cases. The probability density approaches zero proportional to $\exp(-\pi^2\tau/4)$ when $\tau\to\infty$.

IV. NUMERICAL SIMULATIONS

The goal of our Brownian simulations is to validate the analytical solution for the RT density as obtained in the preceding section. For domains more complicated than spherical, numerical simulations are the sole available route. We limit the computations to spherical domains because their results can be compactly described as a function of the single initial parameter R. In the following subsections, we describe the principles, details, and results of our Brownian dynamics simulations.

A. Principles of Brownian dynamics

Our goal is to run stochastic trajectories of freely diffusing particles (no boundaries, no sinks), and count directly the time epochs spent in a predefined domain. The simplest approach might involve running lattice random walks [14], where at each time step the particle moves with equal probability (1/6) in one of the six canonical directions on a predefined grid. In its simplest form, this approach requires (i) a fine (uniform) grid, on which a sphere is adequately represented; (ii) small and constant time steps; and (iii) a large simulation box (as compared with the radius of the sphere), to allow accurate calculation of the long-time tail of $F_\infty(\tau|\vec{R})$. These demands can make the computation time consuming.

Brownian dynamics is an off-grid method for simulating diffusion processes, which allows taking large and variable time steps and is not restricted to a finite simulation box [16,17]. This results in enhanced computational accuracy and/or reduction in computational time. The isomorphism between the diffusion and Langevin equations implies that, in the absence of interactions (potentials, boundaries, etc.), the particle can be moved using Gaussian random numbers. These are random numbers out of a Gaussian distribution whose width corresponds to the predefined time step.

For the present problem, complications arise near the boundaries of the domain ω, not because these are physical boundaries of any sort, but because we wish to record precisely the fraction of time spent by a particle within ω. Thus for a hop which carries the particle across the boundary, it is

impossible to decide how to divide the corresponding time epoch between the interior and exterior of ω. Hence crossing the boundary must be done with small time steps. The choice of time steps is one consideration in constructing the Brownian dynamics algorithm. Another consideration involves the correct rules for terminating trajectories which have migrated far away from the region of interest. These considerations are discussed below.

B. Technical detail

In a given run, the particle is released from the initial position, $\vec{r}_0=\vec{R}$, and moved through a sequence of points $\{\vec{r}_i\}$, $i=1,2,3,\ldots$. The ith hop occurs during a predefined time interval Δt_i, so that

$$\vec{r}_i=\vec{r}_{i-1}+\sqrt{2\Delta t_i}\vec{G}. \tag{4.1}$$

Here $\vec{G}$ is a vector of Gaussian random numbers with a standard deviation of unity. Thus $\sqrt{2\Delta t_i}$ is the standard deviation of the Brownian particle during the time step. The Gaussian random numbers can be generated by inversion of the error function [17] or the Box-Muller method [18].

The time step is chosen so that the probability of crossing the surface of the domain ω in a single hop is negligibly small. Therefore the minimal distance of the particle, d_i, from the surface of ω is computed before making a new move. Δt_i is then determined from

$$d_i=3\sqrt{2\Delta t_i}, \tag{4.2}$$

so that the root-mean-square displacement is several times smaller than d_i. Thus as the particle approaches the boundary its time step constantly decreases. Since the particle must cross the surface within a finite number of time steps, we require that $\Delta t_i\geqslant\Delta t_{\min}$. In the present implementation, the minimal time step $\Delta t_{\min}$ is chosen smaller than $\Delta\tau_{\min}$, which is the smallest temporal bin introduced below.

An important aspect of the algorithm is how to terminate a trajectory. The termination rules should make a trajectory, generated with a finite number of hops, equivalent to an infinite one. For problems of spherical symmetry this is easy. Suppose after the ith move the particle escaped to a point $\vec{r}_i$ outside the spherical domain ω, namely, $r_i>1$. According to Eq. (3.27), its probability to return to the surface is $\gamma_i=1/r_i$, whereas its escape probability is $1-\gamma_i$. Therefore, given a uniform random number ξ between 0 and 1, the trajectory is terminated if $\xi>\gamma_i$. Otherwise, it is placed back on the surface of the unit sphere. For spherically symmetric problems, the location on the sphere to which the particle returns is immaterial, because the exit points will also be distributed with spherical symmetry.

For a (finite) domain ω of an *arbitrary* shape, one may use the algorithm of Luty *et al.* [19–21]. The domain is enclosed within a virtual ''decision sphere'' of radius b. Whenever $r_i>b$, the trajectory is either terminated or returned to the surface by comparing a uniform random number with $\gamma_i=b/r_i$, as before. However, the return point on the sphere, $\vec{r}_{i+1}$, is selected from the probability density

$$w(\theta,\phi)=\frac{1-\gamma_i^2}{4\pi(1-2\gamma_i\cos\theta+\gamma_i^2)^{3/2}}, \tag{4.3}$$

which is uniform over ϕ and depends on the azimuthal angle θ between the vectors $\vec{r}_i$ and $\vec{r}_{i+1}$. Thus one random number is used to determine θ whereas a second, uniformly distributed random number determines the polar angle ϕ.

For each trajectory $\{\vec{r}_i\}$, the total residence time τ within the domain ω is computed as follows. If the ith move occurred inside the domain, $\vec{r}_{i-1},\vec{r}_i\in\omega$, τ is incremented by Δt_i. If it occurred outside, τ is not incremented. If the particle crossed the surface of ω during the move, τ is incremented by a fraction of Δt_i. This fraction can be taken as 1/2 or better, as the ratio of the distances from $\vec{r}_{i-1}$ and $\vec{r}_i$ to the surface. The exact procedure is immaterial if we insist that surface crossing occurs with a very small time step, $\Delta t_i\approx\Delta t_{\min}$.

The set of RTs thus generated is used to calculate the probability density $F_\infty(\tau|\vec{R})$. The time axis is divided into binning intervals, $\tau_0\equiv\tau_{\min},\ldots,\tau_k,\ldots,\tau_{\max}$. Logarithmic binning is convenient if both the short- and long-time behavior of $F_\infty(\tau|\vec{R})$ is to be calculated. If N_k is the number of trajectories for which $\tau_{k-1}\leqslant\tau\leqslant\tau_k$, the distribution function is computed as

$$F_\infty(\tau=\sqrt{\tau_k\tau_{k-1}}|\vec{R})=N_k/(\Delta\tau_k\,N_{\text{total}}), \tag{4.4}$$

where N_{total} is the total number of released trajectories and $\Delta\tau_k\equiv\tau_k-\tau_{k-1}$.

C. Results

We have calculated the RT probability density for Brownian trajectories of a free particle with unit diffusion coefficient, which starts at four different locations within the unit sphere, $R=0.00$, 0.50, 0.75, and 1.00. A sample trajectory (in two dimensions) is shown in Fig. 1. It demonstrates how the moves are made smaller near the spherical boundary. In the present calculation, we set $\Delta t_{\min}=10^{-3}$ (or 5×10^{-3} for $R=0$). About 18 000 trajectories were run for each value of R (42 500 for $R=0$) and the RTs were collected in 32 bins, starting with $\tau_{\min}=0.01$. Each of the four computations required only 4 min on a 150 MHz SGI Indy R5000 workstation. We have also checked that the results are insensitive to the radius, $b\geqslant1$, of the ''decision sphere'' [19], which can therefore be set to unity for spherically symmetric problems. The Brownian simulations, shown by the symbols in Fig. 2, are in excellent agreement with our theory which is therefore exact for spherical domains.

V. CONCLUSION

The residence time distribution of a particle within a spatial domain is a natural extension of the lifetime (or ''first passage time'') distribution. While the latter can be defined only in cases where the particle does not exit from the domain, the RT distribution is valid in the general case of multiple exits and entries. The concept of mean residence time could find more extensive practical applications in the future. For example, in optical imaging of tissues one monitors dif-

fusive photon migration in turbid media [22]. One is interested in delays to photon migration induced by abnormal regions in the tissue such as tumors. The mean photonic residence time in such regions is directly connected to the signal delay and hence to the possibility of tumor detection by such methods.

The calculation of the RT distribution is equivalent to solving the trapping problem for a constant sink term within the domain. The isomorphism has been used to derive explicit relations, in terms of infinite series, for the RT distribution of a spherical domain in three dimensions with an arbitrary initial location of the particle. The derivation has yielded a surprising number of mathematical identities, such as between the RT moments in their ''Euler'' and ''Fourier'' representations. The present derivation is limited to an infinite observation time. It might be interesting to generalize it to a finite observation epoch, though this will generate more cumbersome expressions.

In parallel, we have developed a Brownian dynamic algorithm which is capable of calculating the RT distribution for an arbitrarily shaped domain. In the case of a spherical domain, we find excellent agreement between the numerical and analytical solutions. In more general cases, one could rely only on the numerical technique. It could be interesting to use it for investigating the effect of the domain shape on the distribution function. It is also straightforward to extend the algorithm to generate the RT distribution for a finite observation time t. In fact, the algorithm in this case is simpler, since one does not have to deal with the trajectory termination problem.

By integrating $\exp(-kt)$ times the numerically generated RT distribution for a given t, one obtains the survival probability for the corresponding trapping problem at time t, for an arbitrary value of the trapping rate constant, k, imposed within the domain [cf. Eq. (2.14a)]. This might prove relevant for analyzing certain diffusion influenced reactions in solution, such as energy transfer and fluorescence quenching [23]. It can also describe biological reactions which, for example, take place only within the interior of certain organelles.

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APPENDIX A: DIRECT APPROACH TO MOMENT CALCULATION

The general formula for the nth moment of the residence time distribution in a three-dimensional domain ω was obtained by Kac in the form of a multiple Coulombic integral [8,10],

$$\overline{\tau_\infty^n}(\vec{R})=\frac{n!}{(4\pi)^n}\int_\omega d\vec{r}_n\cdots\int_\omega d\vec{r}_1\,|\vec{r}_1-\vec{R}|^{-1}\cdots|\vec{r}_n-\vec{r}_{n-1}|^{-1}. \tag{A1}$$

We now show how this integral can be evaluated for a three-dimensional sphere. Performing the integral over orientations

$$\frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi}\frac{1}{|\vec{r}-\vec{R}|}\sin\theta\,d\theta\,d\phi=\frac{1}{\max(R,r)} \tag{A2}$$

gives the following result for the nth moment within a spherical domain of unit radius:

$$\overline{\tau_\infty^n}(R)=n!\int_0^1 r_n^2\,dr_n\cdots\times\int_0^1 r_1^2\,dr_1\,\frac{1}{\max(R,r_1)}\cdots\frac{1}{\max(r_{n-1},r_n)}. \tag{A3}$$

From here, one may continue in two routes. Applying a recursion relation leads naturally to the Euler representation of the moments whereas use of the Kac integral equation leads to their Fourier representation.

1. Recursion relation Euler representation

The integrals (A3) can be evaluated using a recurrence relation that holds for $R\leqslant 1$,

$$\overline{\tau_\infty^n}(R)=n\int_0^1\frac{1}{\max(R,r)}\,\overline{\tau_\infty^{n-1}}(r)r^2dr, \tag{A4}$$

and starting from the condition that $\overline{\tau_\infty^0}(R)=1$.

Let us assume that the general form of the nth moment is

$$\overline{\tau_\infty^n}(R)=(-1)^n\frac{n!}{(2n+1)!}\sum_{k=0}^{n}\binom{2n+1}{2k}A_k^n\,R^{2(n-k)}, \tag{A5}$$

where the A_k^n are coefficients to be determined. Insertion into the recurrence relation, Eq. (A4), gives

$$\begin{aligned}\overline{\tau_\infty^n}(R)&=\frac{n}{R}\int_0^R\overline{\tau_\infty^{n-1}}(r)r^2dr+n\int_R^1\overline{\tau_\infty^{n-1}}(r)rdr\\&=(-1)^n\frac{n!}{(2n+1)!}\left[\sum_{k=0}^{n-1}\binom{2n+1}{2k}A_k^{n-1}R^{2(n-k)}-(2n+1)\sum_{k=0}^{n-1}\binom{2n}{2k}A_k^{n-1}\right].\end{aligned} \tag{A6}$$

Comparing with Eq. (A5), we obtain a recurrence formula for the coefficients A_k^n,

$$A_k^n=A_k^{n-1},$$

$$A_n^n=-\sum_{k=0}^{n-1}\binom{2n}{2k}A_k^{n-1}, \tag{A7}$$

with the initial condition $A_0^0=1$. This means that the A_k^n's are independent of n and obey the recursion relation of the Euler numbers

$$E_{2n}=-\sum_{k=0}^{n-1}\binom{2n}{2k}E_{2k}. \tag{A8}$$

Thus $A_k^n\equiv E_{2k}$ and Eq. (A5) agrees with Eq. (3.15).

2. Integral equation Fourier representation

Kac has suggested evaluating the multiple Coulombic integral, Eq. (A1), using the (square-normalized) eigenfunctions $\psi_j(\vec{r})$ and eigenvalues λ_j of an integral equation

$$\frac{1}{4\pi}\int_\omega d\vec{\rho}\,\frac{\psi(\vec{\rho})}{|\vec{r}-\vec{\rho}|}=\lambda\psi(\vec{r}), \tag{A9}$$

whose kernel is the Coulomb potential [8,10,11]. Since the eigenvalues span the space of the square integrable functions, one may insert the ''decomposition of unity,''

$$1=\sum_{j=0}^{\infty}\psi_j(\vec{r})\int_\omega d\vec{\rho}\,\psi_j(\vec{\rho}), \tag{A10}$$

into Eq. (A1) to obtain (for $\vec{R}\in\omega$) the following expression for the nth moment of the RT density:

$$\overline{\tau_\infty^n}(\vec{R})=n!\sum_{j=0}^{\infty}\lambda_j^n\psi_j(\vec{R})\int_\omega d\vec{r}\,\psi_j(\vec{r}). \tag{A11}$$

Upon substitution of Eq. (A11) in Eq. (2.13a), one obtains the following representation for the Laplace transform of the RT density:

$$\hat{F}_\infty(k|\vec{R})=\sum_{j=0}^{\infty}\frac{1}{1+k\lambda_j}\psi_j(\vec{R})\int_\omega d\vec{r}\,\psi_j(\vec{r}). \tag{A12}$$

It is also easy to check that differentiation, as in Eq. (2.13b), reproduces Eq. (A11). This forms the Kac integral equation approach. We shall now show that for a three-dimensional sphere one can find the eigenvalues and eigenfunctions of Eq. (A9), which leads to the explicit relations already derived in the sequel.

Using Eq. (A2) to perform the integral over orientations, the Kac integral equation simplifies for the unit sphere to

$$\int_0^1\frac{\psi(\rho)}{\max(r,\rho)}\rho^2d\rho=\lambda\psi(r), \tag{A13}$$

where $r=|\vec{r}|$. Breaking the integral into two parts, for $0\leqslant\rho\leqslant r$ and $r\leqslant\rho\leqslant1$ [cf. Eq. (A6)], it is easy to verify that the eigenfunctions and eigenvalues are given by

$$\psi_j(r)=\frac{1}{\sqrt{2\pi}\,r}\sin[(j+1/2)\pi r], \tag{A14a}$$

$$\lambda_j=[(j+1/2)\pi]^{-2}. \tag{A14b}$$

The eigenfunctions are normalized so that $4\pi\int_0^1\psi_j(r)^2r^2dr=1$. Additionally, one has that

$$4\pi\int_0^1\psi_j(r)r^2dr=(-1)^j\sqrt{8\pi}\lambda_j. \tag{A15}$$

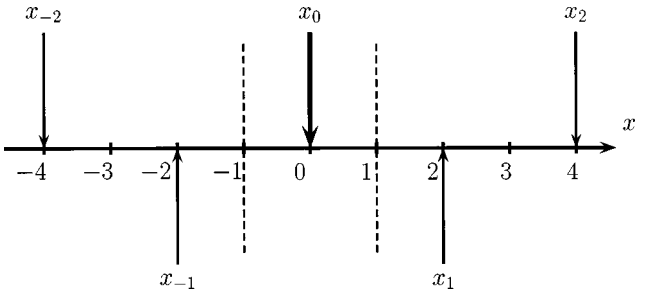

FIG. 3. The initial location of the particle, $x_0=0$, between absorbing points (dashed lines) and its images, $x_j=2j$, giving rise to Eq. (A2).

Inserting these results into Eq. (A11) gives the moments in their Fourier representation, Eq. (3.18), whereas use of Eq. (A12) gives the Laplace transformed density in its Fourier representation, Eq. (3.10).

APPENDIX B: LONG-TIME EXPANSION

To derive Eqs. (3.26) and (3.31), which provide a convenient long-time description for $F_\infty(\tau|R)$, we note that Eq. (3.30) may be rewritten as

$$F_\infty(\tau|R)=\frac{2}{R}\rho(1-R,\tau), \tag{B1}$$

where the probability density $\rho(x,\tau)$ is defined by

$$\rho(x,\tau)\equiv\sum_{j=-\infty}^{\infty}\frac{(-1)^j}{\sqrt{4\pi\tau}}\exp\left(-\frac{(x-x_j)^2}{4\tau}\right),\quad x_j\equiv2j. \tag{B2}$$

This $\rho(x,\tau)$ is just the solution for the one-dimensional problem of diffusion between two absorbing traps. As is well known, it can be written either in terms of (an infinite number of) images or an eigenfunction expansion (cf. Ref. [24]). The first representation converges rapidly for short times whereas the second converges rapidly for long times. The same relation holds between Eqs. (3.30) and (3.31).

In the present case, $\rho(x,\tau)$ obeys the equation

$$\frac{\partial\rho(x,\tau)}{\partial\tau}=\frac{\partial^2\rho(x,\tau)}{\partial x^2}, \tag{B3}$$

in the interval $-1\leqslant x\leqslant1$, with the initial condition $\rho(x,0)=\delta(x)$ and the boundary conditions $\rho(-1,\tau)=\rho(1,\tau)=0$. The solution in terms of images, which leads to Eq. (B2) above, is demonstrated schematically in Fig. 3.

The alternative solution is based on the observation that an eigenfunction of the operator $\partial^2/\partial x^2$ from Eq. (B3) is a periodic function in $[-1,1]$ which vanishes at the end points and is symmetric around the initial location, $x_0=0$. Thus the eigenfunctions are $\cos[\pi(j+1/2)x]$, which gives

$$\rho(x,\tau)=\sum_{j=0}^{\infty}\cos\left(\frac{\pi}{2}(2j+1)x\right)\exp\left(-\frac{\pi^2}{4}(2j+1)^2\tau\right). \tag{B4}$$

Using this solution at $x=1-R$ in Eq. (B1) we obtain the expression for $F_\infty(\tau|R)$ which, after simple manipulations, is reduced to Eq. (3.31). The latter reduces to Eq. (3.26) when $R=1$.

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