A note on confined diffusion

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Abstract.
The random motion of a Brownian particle confined in some finite domain is considered. Quite generally, the relevant statistical properties involve infinite series, whose coefficients are related to the eigenvalues of the diffusion operator. Unfortunately, the latter depend on space dimensionality and on the particular shape of the domain, and an analytical expression is in most circumstances not available. In this article, it is shown that the series may in some circumstances sum up exactly. Explicit calculations are performed for 2D diffusion restricted to a circular domain and 3D diffusion inside a sphere. In both cases, the short-time behaviour of the mean square displacement is obtained.

Keywords. Brownian motion. Colloids.
1. Introduction

Although the theory of Brownian motion has been one of the cornerstones of modern physics for more than one century [1], it still raises numerous fundamental questions [2]. Applications are found in various disciplines, especially in biophysics where technical progress allows nowadays for the detection of individual nanoparticles in living systems [3]. In many instances, the particles’ motion is strictly restricted to bounded domains. One can quote corralled motion of receptors on cell membrane [4, 5, 6], protein diffusion inside the cell nucleus [7], or transporter diffusion through nuclear pores [8, 9]. In a typical experiment, trajectories of tracer particles are recorded and analysed in terms of position correlations or mean square displacement. From those datas, information on the size of the diffusing objects or on their interactions with the surrounding medium can then be extracted [10].

In this article, we consider the motion of a Brownian particle confined in a domain $D$ of given size and shape. The statistical properties of the particle are described by the Green’s function $G(r, r', t)$, which represents the probability density of finding the particle at point $r$ and time $t$, together with the initial condition $G(r, r', 0) = \delta(r - r')$. The Green’s function satisfies the Fokker-Planck equation

$$\frac{\partial G}{\partial t} - D \nabla^2 G = \delta(r - r')\delta(t)$$

(1)

with $D$ the diffusion coefficient. Confinement is enforced through the reflecting boundary conditions on the frontier $\partial D$ of the domain [1]. It should be noticed that, because of the finite size of the system, translational invariance is broken and the Green’s function depends on $r$ and $r'$ separately. Once the propagator is known, all the statistical properties can, in principle, be evaluated. For instance, the mean square displacement (MSD) is obtained from

$$\langle \delta r^2(t) \rangle = \langle (r(t) - r(0))^2 \rangle$$

$$= \int d^d r \int d^d r' \ G(r, r', t) P_0(r') (r - r')^2$$

(2)

where $d$ is the dimension of the embedding space. The initial probability distribution is assumed to be uniform, $P_0(r') = V_d^{-1}$, with $V_d$ the volume of the domain.

Of particular interest is the short-time behaviour of the MSD. Let us define $\tau$ the relaxation time of the system. Simple dimensional analysis shows that $\tau$ scales as the square of the typical size of the domain divided by the diffusion coefficient. It appears intuitively clear that for $t \ll \tau$, the particle has not enough time to feel the influence of the boundary [11]. The expected behaviour for the MSD is then $\langle \delta r^2(t) \rangle \sim 2dDt$, but explicit derivation of this limit is however not always straightforward. Indeed, the solution of the diffusion equation is usually written as an infinite series, whose coefficients are related to the eigenvalues of the Laplacian. The latter actually depend on space dimensionality and on the particular shape of the domain. Unfortunately, an analytical expression for the eigenvalues is in most circumstances not available — with the notable exception of the problem in 1D. In this article, we focus on 2D diffusion in a circular
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domain and 3D diffusion inside a sphere. In both cases, the MSD is written as a sum of
reciprocal powers of zeros of derivatives of Bessel functions. The goal of this note is to
derive explicitly the short-time limit of the MSD. Though this point might sound rather
academic — since the result is known \textit{a priori} —, it certainly deserves some comments.
To the best of the author’s knowledge, this question has never been raised before. The
derivation outlined in this article is based on the expansion of entire functions as an
infinite product \cite{12}. This approach, originally developed by Euler and Rayleigh \cite{13},
has been extended recently by Muldoon and collaborators to derive convolution formulas
for Rayleigh functions \cite{14, 15}. Adapting this method to the relevant Bessel (or related)
functions allows us to recover the short-time limit of the MSD. The remaining of the
paper is organized as follows. We first recall in Section 2 some classical results concerning
1D diffusion. Then we present the calculation of the MSD on a disk in section 3 and
inside a sphere in section 4. Some concluding remarks are finally drawn in the last
section. In order to be complete, we give in the Appendix the corresponding Laplace
transforms of the MSD.

2. Diffusion on a line

To illustrate our point, we first consider 1D diffusion restricted to a segment of length
$L = 2a$. The Green’s function $G(x, x’, t)$ satisfies the diffusion equation \eqref{eq:diffusion}
together with the boundary conditions
\begin{equation}
\frac{\partial G}{\partial x}(0, x’, t) = \frac{\partial G}{\partial x}(L, x’, t) = 0.
\end{equation}
Defining the relaxation time \( \tau = a^2 / D \), the solution is written as a series \cite{16}
\begin{equation}
G(x, x’, t) = \frac{1}{L} + \frac{2}{L} \sum_{n=1}^{\infty} \exp \left[ - \left( \frac{n\pi}{2} \right)^2 \frac{t}{\tau} \right] \cos \left( \frac{n\pi x}{L} \right) \cos \left( \frac{n\pi x’}{L} \right).
\end{equation}
 Accordingly, the MSD $\langle \delta x^2(t) \rangle = \langle (x(t) - x(0))^2 \rangle$ reads
\begin{equation}
\langle \delta x^2(t) \rangle = \frac{L^2}{6} \left( 1 - \frac{96}{\pi^4} \sum_{p=0}^{\infty} \exp \left[ - \frac{\pi^2}{4} \frac{(2p + 1)^2}{(2p + 1)^4} \frac{t}{\tau} \right] \frac{1}{(2p + 1)^4} \right).
\end{equation}
As expected, it saturates to $\langle \delta x^2(t) \rangle = L^2 / 6$ in the long-time limit $t \gg \tau$. More
interesting is the behaviour of the MSD at short times. Indeed, writing the Taylor
expansion of the exponential up to first order, we get
\begin{equation}
\langle \delta x^2(t) \rangle = \frac{L^2}{6} - \frac{16L^2}{\pi^4} \sum_{p=0}^{\infty} \frac{1}{(2p + 1)^4} + \frac{16Dt}{\pi^2} \sum_{p=0}^{\infty} \frac{1}{(2p + 1)^4} + O \left( \frac{t^2}{\tau^2} \right).
\end{equation}
From the well-known results of the series \cite{12}
\begin{equation}
\sum_{p=0}^{\infty} \frac{1}{(2p + 1)^4} = \frac{\pi^4}{96}
\end{equation}

and
\begin{equation}
\sum_{p=0}^{\infty} \frac{1}{(2p + 1)^2} = \frac{\pi^2}{8}
\end{equation}
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we find that the MSD does not depend on the size L of the domain at short times, and recover in this limit the celebrated result
\[ \langle \delta x^2(t) \rangle = 2Dt \quad t \ll \tau. \]  
(6)

3. Confined diffusion in a circular domain

3.1. Green’s function in 2D

If the previous series are easily evaluated, the corresponding problem in two dimensions is more involved. In this section, we focus on the random motion of a tracer particle in a 2D circular domain of radius a. In this geometry, the Laplacian reads
\[ \nabla^2 = \frac{1}{\rho} \frac{\partial}{\partial \rho} \rho \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \varphi^2} \]  
(7)

where \( \rho = (\rho, \varphi) \) are the coordinates of the particle. The eigenfunctions of the radial part of \( \nabla^2 \) are the Bessel functions of the first kind \( J_n \), which are solutions of the following differential equation \[13\]
\[ x^2 J''_n(x) + xJ'_n(x) + (x^2 - n^2)J_n(x) = 0. \]  
(8)

The reflecting boundary conditions on the frontiers of the domain involve vanishing radial derivatives. It can be shown that for \( n \in \mathbb{N} \), \( J'_n(\alpha_{nm}) = 0 \), the zeros being arranged in ascending order of magnitude: \( 0 < \alpha_{n1} < \alpha_{n2} < \ldots \). The Green’s function of the problem is then given by the following expression \[16\]
\[
G(r, r', t) = \frac{1}{\pi a^2} + \frac{1}{\pi a^2} \sum_{n=-\infty}^{+\infty} \cos(n(\varphi - \varphi')) 
\times \sum_{m=1}^{\infty} \frac{\alpha_{nm}^2}{\alpha_{nm}^2 - n^2} \exp\left[-\frac{\alpha_{nm}^2 t}{\tau}\right] \frac{J_n(\alpha_{nm} \rho/a)}{J_n(\alpha_{nm}^2)} \]  
(9)

where we define the time-scale \( \tau = a^2/D \). From this solution, we obtain the MSD
\[
\langle \delta r^2(t) \rangle = a^2 \left(1 - 8 \sum_{m=1}^{\infty} \exp\left[-\frac{\alpha_{1m}^2 t}{\tau}\right] \frac{1}{\alpha_{1m}^2 (\alpha_{1m}^2 - 1)}\right). \]  
(10)

with \( \delta r(t) = r(t) - r(0) \). As expected, it saturates to \( \langle \delta r^2(t) \rangle = a^2 \) in the long-time limit \( t \gg \tau \). However, the short-time limit \( t \ll \tau \) is more difficult to obtain. Writing the first terms of the Taylor expansion, we get
\[
\langle \delta r^2(t) \rangle = a^2 - 8a^2 \sum_{m=1}^{\infty} \frac{1}{\alpha_{1m}^2 (\alpha_{1m}^2 - 1)} + 8Dt \sum_{m=1}^{\infty} \frac{1}{(\alpha_{1m}^2 - 1)} + O\left(\frac{t^2}{\tau^2}\right). \]

Obviously, the short-time behaviour should depend neither on the size nor on the particular shape of the domain. Rather, one expects to find \( \langle \delta r^2(t) \rangle \sim 4Dt \) for \( t \ll \tau \). We therefore have to get the numerical value of those sums in order to definitely check this point, and we now focus on generalized Rayleigh functions in order to elucidate this question.
3.2. Generalized Rayleigh functions

At first sight, the evaluation of the infinite series seems rather difficult to achieve. But as we shall see here, an explicit expression for the zeros $\alpha_{1k}$ is actually not required. We remind that the $\alpha_{1k}$’s are zeros of the Bessel function $J_1(x)$, the latter being given by

$$J_1(x) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!(n+1)!} \left( \frac{x}{2} \right)^{2n+1} = \frac{1}{2} \prod_{k=1}^{\infty} \left( 1 - \frac{x^2}{\alpha_{1k}^2} \right)$$  \hspace{1cm} (11)

The validity of the infinite product expansion follows from general properties of entire functions [12]. Let us then define the generalized Rayleigh function ‡

$$S_n = \sum_{k=1}^{\infty} (\alpha_{1k})^{-2n}$$  \hspace{1cm} (12)

with $n \geq 1$ an integer. Notice that the series is always well defined since $\alpha_{1k} \sim (k - \frac{1}{4}) \pi$ for large values of $k$ [17]. To evaluate $S_n$, we follow a method originally developed by Euler and Raleigh [13, 14, 15]. At a first step, we introduce a new function $f(x) = J_1'(\sqrt{x})$, with $x \geq 0$. The zeros of $f$ are $\xi_k = \alpha_{1k}^2$. From the representation of $J_1'$ as an infinite product (11), we write $f$ as

$$f(x) = \frac{1}{2} \prod_{k=1}^{\infty} \left( 1 - \frac{x}{\xi_k} \right).$$

Next, we may differentiate this expression logarithmically to obtain

$$\frac{f'(x)}{f(x)} = -\sum_{k=1}^{\infty} \frac{1/\xi_k}{1 - x/\xi_k} = -\sum_{k=1}^{\infty} \frac{1}{\xi_k} \sum_{n=0}^{\infty} \left( \frac{x}{\xi_k} \right)^n.$$

The last series is absolutely converging for $0 \leq x \leq 1$ (since $\alpha_{1k} > 1$ [17]). As a consequence, the order of summation can be interchanged. Also evaluating the left-hand side of the equality, we finally get

$$\sum_{n=1}^{\infty} x^n S_n = -\sqrt{x} \frac{J_1''(\sqrt{x})}{2} J_1'(\sqrt{x}).$$  \hspace{1cm} (13)

All the required quantities can be deduced from this result. First, we evaluate the series $\sum_{n=1}^{\infty} S_n$. This is done easily if we choose $x = 1$ in (13), and together with (8) we find

$$\sum_{n=1}^{\infty} S_n = \frac{1}{2}.$$  \hspace{1cm} (14)

Next, each series $S_n$ can be obtained by identification of the coefficient of $x^n$. Given the Taylor expansion (11) of the Bessel function $J_1$, we readily get

$$S_1 = \frac{3}{8}.$$  \hspace{1cm} (15)

Though the series with $n \geq 2$ can be evaluated following the same procedure, they will not be required for our purpose.

‡ Original Rayleigh functions are defined as the sum of reciprocal powers of zeros of Bessel functions. Here, we consider zeros of derivatives of Bessel functions.
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3.3. Statistical properties

Coming back to the original problem, we first need to calculate the series
\[ \sum_{m=1}^{\infty} \frac{1}{(\alpha_{1m}^2 - 1)} = \sum_{m=1}^{\infty} \frac{1}{\alpha_{1m}^2} \frac{1}{1 - \alpha_{1m}^{-2}} = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} (\alpha_{1m})^{-2n}. \]

Interchanging the order of summation, we obtain
\[ \sum_{m=1}^{\infty} \frac{1}{(\alpha_{1m}^2 - 1)} = \sum_{n=1}^{\infty} S_n = \frac{1}{2}. \]  \hspace{1cm} (16)

The other term is not more difficult to evaluate. Indeed, we have
\[ \sum_{m=1}^{\infty} \frac{1}{\alpha_{1m}^2 (\alpha_{1m}^2 - 1)} = \sum_{m=1}^{\infty} \frac{1}{(\alpha_{1m}^2 - 1)} - \sum_{m=1}^{\infty} \frac{1}{\alpha_{1m}^3} = \sum_{n=1}^{\infty} S_n - S_1 \]

so that we find
\[ \sum_{m=1}^{\infty} \frac{1}{\alpha_{1m}^2 (\alpha_{1m}^2 - 1)} = \frac{1}{8}. \]  \hspace{1cm} (17)

We indeed recover the right behaviour for the MSD at short times
\[ \langle \delta r^2(t) \rangle = a^2 - 8a^2 \times \frac{1}{8} + 8Dt \times \frac{1}{2} + O \left( \frac{t^2}{\tau^2} \right) \]
\[ = 4Dt \quad t \ll \tau \]  \hspace{1cm} (18)
as expected for 2D diffusion.

At this point, it should be noticed that the method cannot be extended to systematically get each order of the expansion of the MSD. Indeed, since the corresponding series do not converge, it is not possible to interchange the order of summation with the Taylor expansion. Actually, this remark already holds for the problem in 1D — see (5), and reflects the fact the MSD is a non-analytical function of time. Indeed, it can be checked from the large s expansion of the Laplace transform (A.2) of the MSD that the next to leading term is proportional to \( t^{3/2} \).

4. Diffusion confined inside a sphere

4.1. Green’s function in 3D and statistical properties

Similar questions arise for the diffusion of a particle confined in a sphere of radius a. In this geometry, the Laplacian reads
\[ \nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}. \]  \hspace{1cm} (19)

Eigenfunctions of the angular part of \( \nabla^2 \) are the spherical harmonics \( Y_{lm}(\theta, \phi) \), with eigenvalues \( -l(l+1) \). Eigenfunctions of the radial part are the spherical Bessel functions defined as \( j_l(x) = (\pi/2)^{1/2} x^{-1/2} J_{l+1/2}(x) \), with \( l \) a positive integer. They satisfy the following differential equation [13]
\[ x^2 j''_l(x) + 2x j'_l(x) + (x^2 - l(l-1)) j_l(x) = 0. \]  \hspace{1cm} (20)
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We also need to enforce reflecting boundary conditions on the surface of the sphere. To this aim, we define \( \beta_n \) the (non-zero) zeros of the derivatives of the spherical Bessel functions, \( j'_l(\beta_n) = 0 \). They are arranged in ascending order of magnitude: \( 0 < \beta_{11} < \beta_{12} < \ldots \). The normalization condition for the spherical Bessel functions is

\[
\int_0^a dr r^2 j_l \left( \frac{\rho}{a} \right)^2 = \frac{a^3}{2\beta_n^2} \left( \beta_n^2 - l(l+1) \right) j_l(\beta_n)^2
\]

so that the Green's function for diffusion confined inside a sphere reads

\[
G \left( r, r', t \right) = \frac{3}{4\pi a^3} + \frac{2}{a^3} \sum_{l=0}^{+\infty} \sum_{m=-l}^l Y_{lm}(\theta, \phi) Y_{lm}^*(\theta', \phi')
\]

\[
\times \sum_{n=1}^{\infty} \frac{\beta_n^2}{\beta_n^2 - l(l+1)} \exp \left[ -\frac{\beta_n^2 t}{\tau} \right] \frac{j_l \left( \frac{\rho}{a} \right) j_l \left( \frac{\rho'}{a} \right)}{j_l(\beta_n)^2}.
\]

Here, we used the same definition \( \tau = a^2/D \).

4.2. Statistical properties

From (22), we readily find \( \langle r^2(t) \rangle = 3a^2/5 \). The MSD is then

\[
\langle \delta r^2(t) \rangle = \frac{6a^2}{5} - 2 \langle r(t)r(0) \cos \gamma \rangle
\]

with \( \gamma \) the angle between the vectors \( r(t) \) and \( r(0) \). Rewriting \( \cos \gamma = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi - \phi') \) in terms of spherical harmonics

\[
\cos \gamma = \frac{4\pi}{3} \sum_{m=-1}^1 Y_{1m}^*(\theta, \phi) Y_{1m}(\theta', \phi')
\]

one can easily convince oneself that only the terms with \( l = 1 \) give a non-zero contribution to the mean value. We get after some algebra

\[
\langle \delta r^2(t) \rangle = \frac{6a^2}{5} - 12a^2 \sum_{n=1}^{\infty} \exp \left[ -\frac{\beta_n^2 t}{\tau} \right] \frac{1}{\beta_n^2 (\beta_n^2 - 2)}.
\]

As expected, the MSD saturates to \( \langle \delta r^2(t) \rangle \propto a^2 \) in the long-time limit \( t \gg \tau \), whereas for short times \( t \ll \tau \) we find

\[
\langle \delta r^2(t) \rangle = \frac{6a^2}{5} - 12a^2 \sum_{n=1}^{\infty} \frac{1}{\beta_n^2 (\beta_n^2 - 2)} + 12Dt \sum_{n=1}^{\infty} \frac{1}{\beta_n^2 - 2} + \mathcal{O} \left( \frac{t^2}{\tau^2} \right).
\]

The situation is similar to that in 2 dimensions, and we now detail the calculation of the infinite series.
4.3. Short-time behaviour

First, we rewrite the series that appear in the Taylor expansion of the MSD. After some elementary manipulations, we find

\[
\sum_{k=1}^{\infty} \frac{1}{\beta_{1k}^2 - 2} = \frac{1}{2} \sum_{k=1}^{\infty} \sum_{n=1}^{\infty} \left( \frac{\sqrt{2}}{\beta_{1k}} \right)^{2n} = \frac{1}{2} \sum_{n=1}^{\infty} \sigma_n
\]

where the series \( \sigma_n \), with \( n \) an integer \( \geq 1 \), is defined as

\[
\sigma_n = \sum_{k=1}^{\infty} \left( \frac{\sqrt{2}}{\beta_{1k}} \right)^{2n}.
\]

Note that \( \beta_{11} > \sqrt{2} \) so that all sums do converge. The other term is given by

\[
\sum_{k=1}^{\infty} \frac{1}{\beta_{1k}^2} \left( \frac{1}{\beta_{1k}^2 - 2} \right) = \frac{1}{2} \sum_{k=1}^{\infty} \frac{1}{\beta_{1k}^2 - 2} - \frac{1}{2} \sum_{k=1}^{\infty} \frac{1}{\beta_{1k}^2}
\]

\[
= \frac{1}{4} \left( \sum_{n=1}^{\infty} \sigma_n - \sigma_1 \right).
\]

The central point is to evaluate the series \( \sigma_n \). To this aim, it appears convinient to consider the function \( j'_1(\sqrt{2}x) \), whose zeros are given by \( \zeta_k = \beta_{1k}/2 \). We then write \( j'_1(\sqrt{2}x) \) as an infinite product

\[
\sum_{k=1}^{\infty} x^n \sigma_n = -\sqrt{x} \frac{j''_1(\sqrt{2}x)}{2 j'_1(\sqrt{2}x)}.
\]

From this result, we may draw the following conclusions:

- for \( x = 1 \), the numerical value of the right-hand side can be obtained from the differential equation (20) satisfied by the spherical Bessel function. Since \( 2j''_1(\sqrt{2}) + 2\sqrt{2}j'_1(\sqrt{2}) = 0 \), it is found

\[
\sum_{n=1}^{\infty} \sigma_n = 1.
\]

- the series \( \sigma_1 \) is obtained by identification of the linear term in (26). The Taylor expansion of the modified Bessel function being \( j_1(x) = \frac{x}{3} - \frac{x^3}{36} + O(x^5) \), we obtain

\[
\sigma_1 = \frac{3}{5}.
\]

Bringing everything together, we obtain the expected result for 3D diffusion, namely

\[
\langle \delta r^2(t) \rangle = \frac{6a^2}{5} - 12a^2 \times \frac{1}{4} \left( 1 - \frac{3}{5} \right) + 12Dt \times \frac{1}{2} + O \left( \frac{t^2}{\tau^2} \right)
\]

\[
= 6Dt \quad t \ll \tau.
\]
5. Conclusion

To summarize, we have derived explicitly the mean square displacement for confined diffusion in a disk or a sphere. Since the results involve zeros of derivatives of Bessel functions, the numerical values of the relevant series are not easily obtained. To bypass this difficulty, we used a powerful method based on the expansion of entire functions as an infinite product. This allowed us to explicitly check that $\langle \delta r^2(t) \rangle \sim 2dDt$ in the short-time limit. Extension to more general domain shapes or space dimensions is straightforward, provided that the eigenfunctions of the Laplacian are known. This approach can also be adapted for adsorbing or mixed boundary condition, and might as well be relevant for the study of polymer chains under confinement. Indeed, the partition function of a polymer satisfies a diffusion-like equation [18], where the time variable is replaced by the polymerization index $N$. In this case, the limit $t \ll \tau$ would correspond to $R_g = \sqrt{Nb^2/6} \ll a$, with $a$ the typical dimension of the cavity and $b$ the Kuhn length.

Finally, we have to mention that the actual problem becomes more involved in the (highly relevant) physical situation of a confined colloidal suspension. Indeed, hydrodynamic interactions with the bounding surface have to be accounted for if the particles are moving in a liquid, and the diffusion coefficient is not expected to be constant anymore. Instead, theoretical [19] and experimental [20, 21, 22] works have revealed that the mobility is in fact a function of position — or, more precisely, of the distance to the surface. In addition, the diffusion coefficient may also be time-dependent when the bounding surface is soft, like a liquid-liquid interface or a fluid membrane. In some situations, it may even be possible to observe anomalous diffusion, in which case the mean square displacement follows a power law $\langle \delta r^2(t) \rangle \sim t^\alpha$, with $\alpha \neq 1$, over a notable range of displacements and observation times [23, 24].

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Appendix A. Laplace transform of the MSD

In this Appendix, we give the expression of the Laplace transform of the MSD. Defining $\sigma_d(t) = \langle \delta r^2(t) \rangle$, where $d$ is the dimensionality of space, the Laplace transform $\tilde{\sigma}_d(s) = \int_0^\infty dt \exp[-st] \sigma_d(t)$ is evaluated by solving directly the diffusion equation in terms of the variable $s$ rather than $t$. Average values are then easily evaluated since no infinite series are involved. Notice however that $\tilde{\sigma}_d(s)$ can also be obtained by direct Laplace transform of the results (5), (10) and (24), though the method described in this article has to be extended in order to evaluate the corresponding series. The result is

$$\tilde{\sigma}_1(s) = \frac{2D}{s^2} \left[ 1 - \frac{1}{\sqrt{s\tau}} \tanh \left( \sqrt{s\tau} \right) \right]$$

(A.1)
for diffusion confined on a segment. For diffusion in a disk, one gets

$$\tilde{\sigma}_2(s) = \frac{4D}{s^2} \left[ 1 - \frac{1}{\sqrt{s\tau}} I_1(\sqrt{s\tau}) \right]$$

(A.2)

with $I_1$ the modified Bessel function. Finally, the Laplace transform of the MSD for diffusion confined inside a sphere is

$$\tilde{\sigma}_3(s) = \frac{6D}{s^2} \left[ 1 + \frac{\tanh(\sqrt{s\tau}) - \sqrt{s\tau}}{(s\tau + 2)\tanh(\sqrt{s\tau}) - 2\sqrt{s\tau}} \right].$$

(A.3)

Asymptotic limits follow in a straightforward way.

References

[1] Chandrasekhar S 1943 Rev. Mod. Phys. 15 1
[2] Hänggi P and Marchesoni F 2005 Chaos 15 026101
[3] Cognet L, Tardin C, Boyer D, Choquet D, Tamarat P and Lounis B 2003 Proc. Natl. Acad. Sci. USA 100 11350
[4] Saxton M J 1993 Biophys. J. 64 1766
[5] Daumas F, Destainville N, Millot C, Lopez A, Dean D and Salomé L 2003 Biophys. J. 84 356
[6] Murase K, Fujiwara T, Umemura Y, Susuki K, Iono R, Yamashita H, Saito M, Murakoshi H, Ritchie K and Kusumi A 2004 Biophys. J. 86 4075
[7] Kues T, Peters R and Kubitscheck U 2001 Biophys. J. 80 2954
[8] Salman H, Zbaida D, Rabin Y, Chatenay D and Elbaum M 2001 Proc. Natl. Acad. Sci. USA 98 7247
[9] Bickel T and Bruismma R 2002 Biophys. J. 83 3079
[10] Gambin Y, Lopez-Esparza R, Reffay M, Sierecky E, Gov N S, Genest M, Hodges R S and Urbach W 2006 Proc. Natl. Acad. Sci. USA 103 2098
[11] Kac M 1966 Am. Math. Month. 73 1
[12] Arfken G B and Weber H J 1995 Mathematical Methods for Physicists 4th Edition (San Diego: Academic Press)
[13] Watson G N 1995 A Treatise on the Theory of Bessel Functions 2nd Edition (Cambridge: Cambridge University Press)
[14] Muldoon M E and Raza A 1998 J. Phys. A: Math. Gen. 31 9327
[15] Gupta D P and Muldoon M E 2000 J. Phys. A: Math. Gen. 33 1363
[16] Carslaw H S and Jaeger J C 1959 Conduction of Heat in Solids 2nd Edition (Oxford: Oxford University Press)
[17] Abramowitz M and Stegun I A (eds) 1965 Handbook of Mathematical Functions (New York: Dover Publications)
[18] Doi M and Edwards S F 1986 The Theory of Polymer Dynamics (Oxford: Clarendon Press)
[19] Happel J and Brenner H 1991 Low Reynolds Number Hydrodynamics (Dordrecht: Kluwer)
[20] Lan K H, Ostrowsky N and Sornette D 1986 Phys. Rev. Lett. 57 17
[21] Faucheux L P and Libchaber A J 1994 Phys. Rev. E 49 5158
[22] Dufresne E, Squires T M, Brenner M P and Grier D G 2000 Phys. Rev. Lett. 85 3317
[23] Fradin C, Abu-Arish A, Granek R and Elbaum M 2003 Biophys. J. 84 2005
[24] Bickel T 2006 Brownian motion near a liquid-like membrane Preprint cond-mat/0601400