Diffusing diffusivity: Rotational diffusion in two and three dimensions

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We consider the problem of calculating the probability distribution function (pdf) of angular displacement for rotational diffusion in a crowded, rearranging medium. We use the diffusing diffusivity model and following our previous work on translational diffusion [R. Jain and K. L. Sebastian, *J. Phys. Chem. B* **120**, 3988 (2016)], we show that the problem can be reduced to that of calculating the survival probability of a particle undergoing Brownian motion, in the presence of a sink. We use the approach to calculate the pdf for the rotational motion in two and three dimensions. We also propose new dimensionless, time dependent parameters, $\alpha_{rot,2D}$ and $\alpha_{rot,3D}$, which can be used to analyze the experimental/simulation data to find the extent of deviation from the normal behavior, i.e., constant diffusivity, and obtain explicit analytical expressions for them, within our model. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4984085>]

I. INTRODUCTION

Diffusion in crowded systems such as cells is usually very heterogeneous,^{1,2} i.e., the value of diffusion coefficient, D , varies over space. Further, even at a specific location, it changes as a function of time, as the surroundings are always rearranging. Diffusion even when confined to the cell membrane has the same kind of characteristics—membranes though two dimensional are not only quite heterogeneous and crowded but also rearranging continuously with time.³ Thus in a typical single particle tracking experiment in a cell or a membrane, the diffusing particle experiences a constantly changing environment, resulting in a time varying diffusion coefficient. Experiments on the motion of particles inside biological cells or cell membranes have often shown that diffusion in such crowded environments is anomalous, i.e., the mean square displacement (MSD) of the particle does not scale linearly in time, $\langle x^2(t) \rangle \sim t$ (this is usually referred to as the Fickian motion), but scales as a different power-law in time, $\langle x^2(t) \rangle \sim t^\alpha$, with $\alpha \neq 1$. When $\alpha > 1$, the motion is called superdiffusive and was first observed by Bouchaud *et al.*^{4,5} for a tracer particle in polymer-like, breakable micelles. Other examples of superdiffusive motion include tracer diffusion in randomly moving barriers,⁶ diffusion in a two-dimensional (2D) complex plasma,⁷ and several activated processes⁸ where diffusion is assisted by an external force. For the more familiar cases of diffusion inside crowded environments, the motion is usually subdiffusive, with $\alpha < 1$. A lot of effort has been made both experimentally^{9–13} and theoretically^{14–17} to understand the nature of subdiffusive motion. More details on the topic anomalous transport in crowded media can be found in the review by Höfling and Franosch.¹⁸ On theoretical front, the two most commonly used models to explain the subdiffusive motion are the continuous time random walk (CTRW) and fractional Brownian motion (FBM).^{19–21} CTRW, based on a broad distribution of dwell times, can be easily distinguished from the FBM by testing non-ergodicity.²² In

an interesting study, Tabei *et al.*²³ demonstrated that the transport of insulin granules in biological cells can be mapped on to a subordinated random walk which combines both FBM and CTRW.

Apart from the observed subdiffusive motion in crowded media, in many recent experiments performed with single particles in crowded systems like colloidal suspensions,^{24,25} actin networks,²⁴ and supercooled liquids,²⁶ it has been found that the displacement of the particle under observation does not always have a Gaussian distribution. What is even more surprising is the fact that in spite of the non-Gaussianity, the MSD remains Fickian, i.e., the MSD is proportional to time, a feature usually associated with the normal Brownian motion. This Brownian yet anomalous motion of particles in complex systems seems to be a generic phenomenon and has been reported in many physicochemical and socio-economic processes. The phenomenon has been seen in the diffusion of hard spheres in colloidal suspensions,^{27–29} simulations of hard sphere fluids,³⁰ diffusive motion in supercooled liquids,³¹ tracer diffusion in crowded media of either larger spheres²⁹ or polymers,^{32,33} diffusion in systems close to the glass transition point,³⁴ price dynamics,³⁵ and financial returns.³⁶ Banks *et al.*³⁷ used variable length scale fluorescence correlation spectroscopy (VLS-FCS) to determine the mean square displacement of a diffusing protein molecule as a function of time. Further, the technique provides a way to determine whether the probability distribution function for displacement is Gaussian or not. Their studies showed that the diffusion of protein molecules in crowded dextran solutions is Brownian, yet anomalous. Yethiraj *et al.*²⁹ simulated the diffusion of a tracer colloidal particle immersed in a concentrated solution of larger spheres and found a non-Gaussian behavior at large distances. Xue *et al.*³⁸ studied the diffusion of nanoparticles suspended in polymer solutions. They found a time varied and size-dependent non-Gaussianity, which they ascribe to hopping diffusion.³⁹ Sung *et al.*⁴⁰ have suggested that the non-Gaussianity can be interpreted as a

result of the non-ergodic nature of the system. Because of the spatial heterogeneity, the particle often gets caught in a pocket with a specific value for D . As long as the particle is inside one of such pockets, the distribution of displacements is Gaussian but an ensemble average over many such particles leads to a non-Gaussian distribution.

Chubynsky and Slater,⁴¹ in their analysis of the “diffusing diffusivity” model, show that at short times, the spatial probability distribution is exponential if one considers the diffusion coefficient D to be exponentially distributed. For long times, they performed simulations to show that the distribution crosses over to being Gaussian. The model assumes that the rearrangement of the environment is on a time scale longer than that of the diffusion process, so that it is always possible to define a local diffusion coefficient and that even the variation of the diffusion coefficient due to the movement of the particle from one spatial region to another can be captured by a stochastic $D(t)$. In a recent paper,⁴² we gave a general class of analytically solvable models where we modelled D as a random function of time. With this model, we were able to find analytical solutions and explain all the limits observed in the experiments/simulations. Our approach is very much similar to the dynamic disorder model of Zwanzig^{43–45} and forms an interesting case of it where exact analytical solutions can be obtained. Other approaches to model diffusion of a particle in a rough landscape^{46,47} involve the presence of fluctuating random potential in the Langevin equation in addition to the usual noise term. For instance, in the overdamped limit of motion, the Langevin equation for these models may be written as $\zeta \dot{x}(t) = U'(x) + \eta(t)$, with $U(x)$ being a random potential, ζ is the friction coefficient, and $\eta(t)$ is the noise which is usually taken to be Gaussian white noise. With this approach, very interesting experiments and theoretical work have been done in the recent past.^{47,48} Intuitively, it would appear that the diffusion of a particle on a rough landscape is equivalent to a diffusion process with spatially varying diffusivity. However, no proof of this seems to exist in the literature, and it is likely that the two are not the same.

In the present paper, we extend our model of diffusing diffusivity to the problem of rotational diffusion in a crowded, rearranging system. Several single-molecule experiments have been performed in the recent past in this regard, viz., the orientational diffusion of dye molecules in polymer thin films,^{49,50} wobbling dynamics of dipoles in porous media,^{51,52} diffusion of nano-doublers in living cells,⁵³ etc. Mazza *et al.*⁵⁴ performed molecular dynamics simulations to probe the rotational and translational dynamics of water at low temperatures. In their study, they found that the heterogeneities in rotational and translational motions are strongly correlated which they relate to the same physical reason—defects in the hydrogen-bonded network of water. Sung *et al.*⁴⁰ have performed simulations for the diffusion of dumbbells in a 2-dimensional porous medium of stationary hard disks. They showed that at low volume fractions, the diffusion is ergodic as the dumbbell moves in a percolating network allowing it to explore many regions of varying diffusivities. This leads to a distribution of angular displacements which is Gaussian. However for a different volume fraction, the system is non-ergodic,

due to the absence of a percolating network. The dumbbells cannot escape from their respective neighbourhoods. Thus after averaging over all dumbbells (the ensemble average), the distribution becomes exponential even though each individual dumbbell is found to have a Gaussian distribution. The salient features of this kind of diffusion process have been summarised by Metzler, in a nice, brief overview⁵⁵ (see also Ref. 56).

In this paper, we extend our earlier model of diffusing diffusivity,⁴² to find an exact expression for the distribution of angular displacements at all times. Although the rotational and translational motions for a particle diffusing in a heterogeneous environment are usually correlated, as shown by Mazza *et al.*,⁵⁴ we focus in this paper only on the process of rotational diffusion. For translational motion, the details can be found in an earlier work.⁴² The MSD for angular displacement as function of time is found to be quite simple. For translational diffusion, a non-Gaussianity parameter has been defined and used to analyze the experimental and simulation data. We propose a similar “non-normal parameter” whose value would be zero, if the behavior of the probability distribution is similar to that for constant diffusivity, but is different from zero if the spread in diffusivity affects the probability distribution for rotational motion. Our results are of great interest, as there are experiments on rotational motion in crowded systems,^{49,50} and should be useful in the analysis of such experiments. Further it should be possible to verify them in detail using the experimental setup proposed by Matse *et al.*,^{57,58} who investigated the Brownian motion of a colloidal particle near a wall. They were able to observe a diffusing-diffusivity regime where non-Gaussian displacements coexist with a linear MSD.

The rest of the paper is organised in the following manner. Section II A introduces our notation and summarises the results for the normal rotational diffusion in 2D. It also serves the purpose of providing a ready reference to compare with the results of Sec. II B, where we present the results for diffusing diffusivity. Sections III A and III B summarise the results for three dimensions. Finally, in Sec. IV we summarize our conclusions.

II. ROTATIONAL DIFFUSION IN TWO DIMENSIONS (2D)

A. Normal diffusivity

We consider the rotational diffusion of a dipole (or a needle) confined to a plane, which needs only one angle coordinate to specify its orientation in the plane [see Fig. 1(a)]. The equation for its orientational diffusion is

$$\frac{\partial P(\phi, t)}{\partial t} = D \frac{\partial^2}{\partial \phi^2} P(\phi, t), \quad (1)$$

where D is the rotational diffusion coefficient with the dimension s^{-1} and $\phi \in (-\pi, \pi]$. At $t = 0$, we assume that the dipole is oriented along the $+ve$ x -axis for which $\phi = 0$. With this initial condition, the solution to the diffusion equation becomes

$$P(\phi, T) = \frac{1}{2\pi} \sum_{m=-\infty}^{\infty} e^{im\phi} e^{-m^2 DT}. \quad (2)$$

FIG. 1. Schematic of the rotational diffusion of a dipole vector (shown in red color) (a) in 2D and (b) in 3D. The initial orientation of the vector is represented by the dashed arrow.

This sum can be evaluated exactly to give $P(\phi, T) = \frac{1}{2\pi} \vartheta_3\left(\frac{\phi}{2}, e^{-DT}\right)$, where the theta function, $\vartheta_3(z, q)$, is defined by $\vartheta_3(z, q) = 1 + 2 \sum_{m=1}^{\infty} q^{m^2} \cos(2mz)$. Using the identity (see <http://functions.wolfram.com/EllipticFunctions/EllipticTheta3/16/01/>),

$$\vartheta_3(z, q) = \frac{\sqrt[4]{-1} \sqrt{\pi} e^{\frac{z^2}{\ln(q)}} \vartheta_3\left(\frac{i\pi z}{\ln(q)}, e^{\frac{\pi^2}{\ln(q)}}\right)}{\sqrt{-i \ln(q)}}, \quad (3)$$

the above can also be rewritten as

$$P(\phi, T) = \frac{1}{\sqrt{4\pi DT}} e^{-\frac{\phi^2}{4DT}} \vartheta_3\left(-\frac{i\pi\phi}{2DT}, e^{-\frac{\pi^2}{DT}}\right). \quad (4)$$

The mean square angular displacement (MSD) for the rotational diffusional motion is defined as

$$\langle |\hat{u}(T) - \hat{u}_0|^2 \rangle = 2(1 - \langle \cos \phi \rangle). \quad (5)$$

Here $\hat{u}(T)$ is the unit vector denoting the orientation of dipole moment vector at time T , whereas $\hat{u}_0$ is the unit vector pointing along the $+ve$ x -axis (initial conditions). Using Eq. (2) one gets

$$\langle |\hat{u}(T) - \hat{u}_0|^2 \rangle = 2(1 - e^{-DT}). \quad (6)$$

1. Small T behavior

For small values of T and ϕ , i.e., $DT \ll 1$ such that $e^{-\frac{\pi^2}{DT}} \ll 1$ and $|\phi| \ll \pi$, the theta function can be approximated as $\vartheta_3\left(-\frac{i\pi\phi}{2DT}, e^{-\frac{\pi^2}{DT}}\right) \sim 1 + 2e^{-\frac{\pi^2}{DT}} \cosh\left(\frac{\pi\phi}{DT}\right) \approx 1$. Using this in Eq. (4), $P(\phi, T)$ can be approximated in this limit as $P(\phi, T) \sim \frac{1}{\sqrt{4\pi DT}} e^{-\frac{\phi^2}{4DT}}$. This implies that the distribution function for small values of T is Gaussian (see Fig. 2).

At short times such that $DT \ll 1$, and therefore angular displacement also is small such that $\cos \phi \approx 1 - \phi^2/2$, we can simplify the expression for the MSD to give $\langle \phi^2 \rangle = 2DT$. This is equivalent to the translational diffusion in one dimension for which the MSD of the displacement x obeys $\langle x^2 \rangle \sim T$. The above expression for the MSD implies that at short times the random walker has not yet probed the curvature of the circle in 2D on which it moves.

FIG. 2. Log-linear plots of probability distribution function $P(\phi, T)$ for different values of DT .

2. Large T behavior

In the limit $T \rightarrow \infty$, the distribution becomes uniform, i.e., $\lim_{T \rightarrow \infty} P(\phi, T) = \frac{1}{2\pi}$. Figure 2 shows the log-linear plots of $P(\phi, T)$ versus ϕ for different values of the dimensionless variable DT . We notice that the distribution function resembles Gaussian for fairly large values of DT and becomes uniform only for very large values of DT .

As time lapses one discovers that diffusion is indeed happening on the periphery of a circle and not on a straight line. In the case of translational diffusion, the MSD keeps growing linearly in time but for rotational diffusion it is bound by a maximum value, i.e., $\langle |\hat{u}(T) - \hat{u}_0|^2 \rangle = 2$, for $DT \gg 1$. The large T limit also implies $\langle \hat{u}(T) \cdot \hat{u}(0) \rangle = 0$.

B. Diffusing diffusivity

The diffusion equation for the rotational Brownian motion, with a time dependent diffusion coefficient, $D(t)$, may be written as

$$\frac{\partial P(\phi, t)}{\partial t} = D(t) \frac{\partial^2}{\partial \phi^2} P(\phi, t). \quad (7)$$

With the initial condition that at $t = 0$, the dipole moment vector is oriented along the $+ve$ x -axis, the solution becomes

$$P(\phi, T) = \frac{1}{2\pi} \sum_{m=-\infty}^{\infty} e^{im\phi} e^{-m^2 \int_0^T dt D(t)}. \quad (8)$$

$D(t)$ undergoes stochastic time evolution with time. Averaging over all possible realisations of $D(t)$, we get

$$\langle P(\phi, T) \rangle_D = \frac{1}{2\pi} \sum_{m=-\infty}^{\infty} e^{im\phi} \left\langle e^{-m^2 \int_0^T dt D(t)} \right\rangle_D, \quad (9)$$

where $\langle \dots \rangle_D$ stands for averaging over all realisations of $D(t)$. As there is no chance of confusion, in the following, we shall use $P(\phi, T)$ itself to denote $\langle P(\phi, T) \rangle_D$. $D(t)$ evolves stochastically and calculating $\langle e^{-m^2 \int_0^T dt D(t)} \rangle_D$ is simply a problem of random walk with absorption. As $D(t)$ has to be positive at all times, we model it⁴² as the square of the distance from the origin of a fictitious isotropic harmonic oscillator undergoing Brownian motion in two dimensions. Thus we take

$$D(t) = x^2(t) + y^2(t), \quad (10)$$

where $\{x(t), y(t)\}$ are the position coordinates of the oscillator. It may be mentioned here that the model can be

easily solved in the case where the oscillator is n -dimensional (see Ref. 42 for details). Assuming the Brownian oscillator to have the frequency ω and a “diffusion coefficient” F , its probability distribution $\mathcal{G}(x, y, t)$ obeys the Smoluchowski equation⁵⁹

$$\frac{\partial \mathcal{G}(x, y, t)}{\partial t} = \left[F \left\{ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right\} + \frac{\partial}{\partial x} \omega x + \frac{\partial}{\partial y} \omega y \right] \mathcal{G}(x, y, t).$$

As D depends only on the radial distance of the oscillator from the origin, one can easily get the Fokker-Planck equation for diffusivity to be

$$\frac{\partial \pi(D, t)}{\partial t} = \frac{\partial}{\partial D} \left(4FD \frac{\partial}{\partial D} + 2\omega D \right) \pi(D, t). \quad (11)$$

This equation has a steady state solution given by $\pi_{eq}(D, t) = \frac{1}{D_0} e^{-D/D_0}$, with $D_0 = \frac{2F}{\omega}$.

We can now evaluate $\langle e^{-m^2 \int_0^T dt D(t)} \rangle_D$ following Refs. 42, 60, and 61 and get

$$\langle e^{-m^2 \int_0^T dt D(t)} \rangle_D = \int_0^\infty dD_i \int_0^\infty dD_f \pi_a(D_f, T|D_i, 0) \pi_{eq}(D_i), \quad (12)$$

where $\pi_a(D_f, T|D_i, 0)$ is the probability that a random walker starting at D_i at the time $t = 0$ would be found at D_f at the time T , given that its position D undergoes diffusion governed by Eq. (11). π_a obeys the reaction-diffusion equation

$$\frac{\partial \pi_a(D, t|D_i, 0)}{\partial t} = \left\{ \frac{\partial}{\partial D} \left(4FD \frac{\partial}{\partial D} + 2\omega D \right) - m^2 D \right\} \times \pi_a(D, t|D_i, 0). \quad (13)$$

Following Refs. 42 and 61, we can evaluate the propagator to get

$$P(\phi, T) = \frac{1}{2\pi} \sum_{m=-\infty}^{\infty} e^{im\phi} P_m(T), \quad (14)$$

with

$$P_m(T) = \frac{4\omega \sqrt{\omega^2 + 4Fm^2} e^{-T(\sqrt{\omega^2 + 4Fm^2} - \omega)}}{(\sqrt{\omega^2 + 4Fm^2} + \omega)^2 - (\sqrt{\omega^2 + 4Fm^2} - \omega)^2 e^{-2T\sqrt{\omega^2 + 4Fm^2}}}. \quad (15)$$

Introducing the dimensionless variables $\tilde{T} = \omega T$ and $\tilde{D}_0 = D_0/\omega = 2F/\omega^2$, one can rewrite P_m in terms of dimensionless quantities as $P_m = \tilde{P}_m(\tilde{T}, \tilde{D}_0)$ with

$$\tilde{P}_m(\tilde{T}, \tilde{D}_0) = \frac{4\sqrt{1 + 2\tilde{D}_0 m^2} e^{-\tilde{T}(\sqrt{1 + 2\tilde{D}_0 m^2} - 1)}}{(\sqrt{1 + 2\tilde{D}_0 m^2} + 1)^2 - (\sqrt{1 + 2\tilde{D}_0 m^2} - 1)^2 e^{-2\tilde{T}\sqrt{1 + 2\tilde{D}_0 m^2}}}. \quad (16)$$

From Eqs. (14) and (16), we can now evaluate any moment of the distribution. They are given by the following relation:

$$\langle e^{-in\phi} \rangle = \int_{-\pi}^{\pi} d\phi P(\phi, T) e^{-in\phi} = \tilde{P}_n(\tilde{T}, \tilde{D}_0). \quad (17)$$

Thus we have the exact expression for any moment of the probability distribution. The mean-square displacement (MSD) in this case becomes

$$\langle |\hat{u}(T) - \hat{u}_0|^2 \rangle = 2(1 - \tilde{P}_1(\tilde{T}, \tilde{D}_0)) = 2 \left(1 - \frac{4\sqrt{1 + 2\tilde{D}_0} e^{-\tilde{T}(\sqrt{1 + 2\tilde{D}_0} - 1)}}{(\sqrt{1 + 2\tilde{D}_0} + 1)^2 - (\sqrt{1 + 2\tilde{D}_0} - 1)^2 e^{-2\tilde{T}\sqrt{1 + 2\tilde{D}_0}}} \right). \quad (18)$$

1. Small T behavior

For small values of time such that $\tilde{T} \ll 1$, one obtains the MSD from Eq. (18) to be

$$\langle |\hat{u}(T) - \hat{u}_0|^2 \rangle \sim 2\tilde{D}_0 \tilde{T}. \quad (19)$$

Also, in the short time limit, $\tilde{P}_m(\tilde{T}, \tilde{D}_0)$ of Eq. (15) can be approximated as

$$\tilde{P}_m(\tilde{T}, \tilde{D}_0) \approx \frac{1}{1 + \tilde{D}_0 \tilde{T} m^2}.$$

Therefore in this limit, the probability density function is given by

$$P(\phi, T) \approx \frac{1}{2\pi} \sum_{m=-\infty}^{\infty} \frac{1}{1 + \tilde{D}_0 \tilde{T} m^2} e^{im\phi}. \quad (20)$$

This sum can be evaluated exactly (see Appendix A for details). Thus for short times, we have

$$P(\phi, T) \approx \frac{1}{2} \sqrt{\frac{1}{\tilde{D}_0 \tilde{T}}} \left(e^{-\frac{|\phi|}{\sqrt{\tilde{D}_0 \tilde{T}}}} + \cosh(\phi/\sqrt{\tilde{D}_0 \tilde{T}}) e^{-\pi/\sqrt{\tilde{D}_0 \tilde{T}}} \times \text{cosech}(\pi/\sqrt{\tilde{D}_0 \tilde{T}}) \right). \quad (21)$$

At short times and for small angular displacements, only the first term is significant and therefore we expect that the distribution to be exponential in this limit (see Fig. 3). This is in agreement with the arguments presented by Slater and Chubynsky,⁴¹ i.e., at short times, it is only the distribution of diffusivity that is important and not its time evolution. It may be noted that this short term limit is just a case of static disorder.⁴³

FIG. 3. Probability distribution function for different values of the dimensionless parameter, $\tilde{D}_0$: (a) 0.1, (b) 1, and (c) 10. For smaller $\tilde{D}_0$, which means a faster relaxation of the environment, the pdf resembles a Gaussian function. On the other hand, for larger values of $\tilde{D}_0$, the environment does not relax fast, and hence the distribution becomes exponential, as may be easily seen from a comparison of the figures for different values of $\tilde{D}_0$.

2. Large T behavior

In the limit $\tilde{T} \gg 1$, we have

$$\tilde{P}_m(\tilde{T}, \tilde{D}_0) \sim e^{-\tilde{D}_0 \tilde{T} m^2}.$$

Thus the probability distribution function in large $\tilde{T}$ limit becomes

$$P(\phi, T) \sim \frac{1}{2\pi} \sum_{m=-\infty}^{\infty} e^{-\tilde{D}_0 \tilde{T} m^2} e^{im\phi}. \quad (22)$$

This has the same form as the probability distribution function of normal diffusivity, given in Eq. (2). Therefore, for large values of $\tilde{T}$, the angular distribution function in the case of diffusing diffusivity becomes similar to the case of normal diffusivity, with the average diffusion coefficient $\tilde{D}_0$. In Fig. 3, we have plotted the logarithm of $P(\phi, T)$ versus ϕ for different sets of values of the dimensionless parameters $\tilde{T}$ and $\tilde{D}_0$. Physically, $\tilde{T}$ is the ratio of the observation time T to the relaxation time of the environment ω^{-1} . Likewise, $\tilde{D}_0$ is the ratio of relaxation versus diffusive time scales. From the plots of Fig. 3(b), we see that at short times the distribution is exponential as predicted by Eq. (21) which crosses over to the form predicted by Eq. (22) at longer times. We also notice from Fig. 3(c) that for the larger value of parameter $\tilde{D}_0$, which also implies that diffusion is faster than the environment relaxation, the exponential distribution prevails for longer observational times. However, for smaller values of $\tilde{D}_0$, the distribution starts resembling a Gaussian function even at short times, see Fig. 3(a). In the limit of large $\tilde{T}$, the MSD becomes

$$\langle |\hat{u}(T) - \hat{u}_0|^2 \rangle \sim 2 \left(1 - e^{-\tilde{D}_0 \tilde{T}} \right).$$

This has the same form as the MSD for normal diffusivity, Eq. (6). In the limit $\tilde{T} \rightarrow \infty$, the MSD is constant.

C. Non-normal parameter for rotational diffusion in 2D

For translational diffusion, a non-Gaussianity parameter has been defined (see, for example, the work of Chubynsky and Slater⁴¹ or Metzler *et al.*⁵⁶) and found very useful for analyzing the experimental data. For diffusion in one dimension, the parameter is defined by

$$\alpha_2 = \frac{\langle x^4 \rangle}{3\langle x^2 \rangle^2} - 1. \quad (23)$$

The parameter is zero if the probability distribution is Gaussian. We now define a similar parameter for rotational diffusion. The fourth moment for rotational diffusion may be defined by

$$\langle |\hat{u}(T) - \hat{u}_0|^4 \rangle = 2(3 + \langle \cos(2\phi) \rangle - 4\langle \cos \phi \rangle). \quad (24)$$

For the case of constant diffusivity, this is found to be

$$\langle |\hat{u}(T) - \hat{u}_0|^4 \rangle = 2 \left(3 + e^{-4DT} - 4e^{-DT} \right). \quad (25)$$

Hence, it is easy to see that the parameter $\alpha_{rot,2D}$ defined by

$$\alpha_{rot,2D} = \frac{1}{3} \frac{\langle |\hat{u}(T) - \hat{u}_0|^4 \rangle}{\left(\langle |\hat{u}(T) - \hat{u}_0|^2 \rangle \right)^2} - \frac{1}{24} \langle |\hat{u}(T) - \hat{u}_0|^2 \rangle \times \left(\langle |\hat{u}(T) - \hat{u}_0|^2 \rangle - 8 \right) - 1 \quad (26)$$

would have a value zero, if the diffusion occurs with a constant diffusion coefficient. Hence we propose that in the case of diffusing diffusivity, this parameter can be used to find whether the diffusion occurs with a constant diffusion coefficient or not. Also the magnitude of its deviation from zero would be an indicator of how large the spread of the diffusion coefficient is. Thus, this should be a useful parameter to analyze the experimental/simulation data. For our model of diffusing diffusivity, we find

$$\langle |\hat{u}(\tilde{T}) - \hat{u}_0|^4 \rangle = 2 \left(3 + \frac{4\sqrt{1+8\tilde{D}_0} e^{-\tilde{T}(\sqrt{1+8\tilde{D}_0}-1)}}{(\sqrt{1+8\tilde{D}_0}+1)^2 - (\sqrt{1+8\tilde{D}_0}-1)^2 e^{-2\tilde{T}\sqrt{1+8\tilde{D}_0}}} - \frac{16\sqrt{1+2\tilde{D}_0} e^{-\tilde{T}(\sqrt{1+2\tilde{D}_0}-1)}}{(\sqrt{1+2\tilde{D}_0}+1)^2 - (\sqrt{1+2\tilde{D}_0}-1)^2 e^{-2\tilde{T}\sqrt{1+2\tilde{D}_0}}} \right). \quad (27)$$

FIG. 4. Non-normal parameter as a function of $\tilde{T}$ for different values of parameter $\tilde{D}_0$. The line marked as normal corresponds to the case of constant diffusivity.

Hence using Eqs. (18) and (27), it is possible to calculate the value of the parameter $\alpha_{rot,2D}$ for the case of diffusing diffusivity. In Fig. 4 we give a plot of this quantity, as a function of the dimensionless variable $\tilde{T}$ for different values of $\tilde{D}_0$. The figure shows that $\alpha_{rot,2D}$ is non-zero, in the short time limit (small $\tilde{T}$). For a fixed $\tilde{D}_0$, it can be shown analytically that $\alpha_{rot,2D} \rightarrow 1$ as $\tilde{T} \rightarrow 0$ and that $\alpha_{rot,2D} \rightarrow 0$ as $\tilde{T} \rightarrow \infty$.

D. Discussion

$\tilde{D}_0$ is the dimensionless diffusion coefficient of the diffusivity. If it is small ($\tilde{D}_0 \ll 1$), the diffusivity changes slowly. As the value of $\tilde{D}_0$ increases, the environment changes more rapidly, and the probability distribution becomes “normal” faster. At short times such that $\tilde{T} \ll 1$, we have

$$\langle |\hat{u}(T) - \hat{u}_0|^2 \rangle \sim 2\tilde{D}_0\tilde{T},$$

thereby the diffusion is Fickian. As $T \rightarrow \infty$, the MSD is constant. Figure 5 shows the plots of MSD versus $\tilde{T}$ for various values of $\tilde{D}_0$.

The dimensionless parameter $\tilde{D}_0$ is the ratio of average diffusivity ($D_0 = 2F/\omega$) to ω , where ω^{-1} is the time of relaxation of the environment. Thus, a larger value of $\tilde{D}_0$ implies a fast diffusion of the particle, in comparison with the relaxation of the surroundings. This means that for larger values of $\tilde{D}_0$, the equilibrium uniform distribution will be attained sooner because of high average diffusivity, but due to the slower relaxation of surroundings the distribution function will be non-Gaussian at small time scales, i.e., $\tilde{T} \ll 1$. This is in agreement with the

FIG. 5. MSD as a function of dimensionless parameter $\tilde{T}$ with different values of $\tilde{D}_0$.

expression of Eq. (21), see also Fig. 3(c). On the other hand if $\tilde{D}_0$ is small, then the average diffusivity is small on the time scale of relaxation of the surroundings. This implies that the particle diffuses slowly and it takes a lot of time to reach the equilibrium uniform distribution but at the same time due to the faster relaxation of surroundings, the distribution function is closer to Gaussian, see the plots in Fig. 3(a). This is also evident from the plots of the MSD versus time for different values of $\tilde{D}_0$ (see Fig. 5). As the value of $\tilde{D}_0$ increases, from the bottom to top, the MSD approaches its limiting value of 2 sooner.

III. ROTATION IN THREE DIMENSIONS (3D)

A. Normal diffusivity

The diffusion equation for the rotational Brownian motion in three dimensions is

$$\frac{\partial P(\theta, \phi, t)}{\partial t} = -D\hat{L}^2 P(\theta, \phi, t), \quad (28)$$

where D is the rotational diffusion coefficient with dimensions s^{-1} , $\theta \in [0, \pi]$ is the azimuthal angle, and $\phi \in [0, 2\pi]$ is the polar angle [see Fig. 1(b)]. The operator $\hat{L}^2$ is defined as

$$\hat{L}^2 = - \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\}. \quad (29)$$

The formal solution of the diffusion equation is

$$P(\theta, \phi, T) = \langle \theta, \phi | e^{-DT\hat{L}^2} | \theta_0, \phi_0 \rangle.$$

Notice that we have used here the Dirac bracket notation. $|\theta_0, \phi_0\rangle$ represents the initial state, where (θ_0, ϕ_0) specify the initial direction of the dipole. With the introduction of a complete set of spherical harmonics $Y_{lm}(\theta, \phi)$, the solution becomes

$$P(\theta, \phi, T) = \sum_{l=0}^{\infty} \sum_{m=-l}^l e^{-l(l+1)DT} Y_{lm}^*(\theta_0, \phi_0) Y_{lm}(\theta, \phi). \quad (30)$$

Assuming that the dipole moment vector is oriented along the $+ve$ z -axis at $t=0$, the function $P(\theta, \phi, T)$ becomes independent of ϕ and therefore after integrating over ϕ , we get

$$P(\theta, T) = \sum_{n=0}^{\infty} \frac{2n+1}{2} P_n(\cos(\theta)) e^{-n(n+1)DT}, \quad (31)$$

where $P_n(\cos(\theta))$ is the Legendre polynomial of degree n . The problem of rotational diffusion can be mapped onto the quantum mechanical problem of the rigid rotor. For a path integral representation of the probability density $P(\theta, T)$, see the book by Zinn-Justin.⁶² The average value of any function $A(\theta)$ is now evaluated using the following formula:

$$\langle A(\theta) \rangle = \int_0^\pi d\theta \sin(\theta) A(\theta) P(\theta, T). \quad (32)$$

For instance, the MSD is defined as

$$\langle |\hat{u}(T) - \hat{u}_0|^2 \rangle = 2(1 - \langle \cos(\theta) \rangle). \quad (33)$$

Here $\hat{u}(T)$ is the unit vector denoting the orientation of the dipole moment vector at time T , where as $\hat{u}_0$ is the unit vector

pointing along the $+ve$ z -axis (initial conditions). The MSD using the formula in Eq. (32) now becomes

$$\langle |\hat{u}(T) - \hat{u}_0|^2 \rangle = 2(1 - e^{-2DT}). \quad (34)$$

At short times such that $DT \ll 1$, and therefore angular displacement is also small such that $\cos(\theta) \sim 1 - \theta^2/2$, we can simplify the expression for the MSD to give

$$\langle \theta^2 \rangle \sim 4DT. \quad (35)$$

This is equivalent to the translational diffusion in a $2D$ -plane for which MSD is $\langle r^2 \rangle \propto T$, where r is the displacement in two dimensions. The above expression for MSD implies that at short times, we have not yet probed the curvature of the sphere. However as time lapses, the MSD saturates as diffusion is occurring in a bounded region. In the limit $T \rightarrow \infty$, $\langle |\hat{u}(T) - \hat{u}_0|^2 \rangle = 2$. The large T limit also implies $\langle \hat{u}(T) \cdot \hat{u}_0 \rangle = 0$, i.e., in the large T limit, there is no correlation between the initial and final directions of the dipole moment vector.

Moreover at short times and for small values of θ , the probability density function $P(\theta, T)$ can be approximated as⁶²

$$P(\theta, T) \approx \frac{1}{4\pi DT} \left(\frac{\theta}{\sin(\theta)} \right)^{1/2} e^{-\frac{\theta^2}{4DT}}.$$

Further, approximating $\sin(\theta) \approx \theta$ for small θ values, we get

$$P(\theta, T) \approx \frac{1}{4\pi DT} e^{-\frac{\theta^2}{4DT}}. \quad (36)$$

In Fig. 6, we have shown the log-linear plots of $P(\theta, T)$ as a function of θ for different values of the dimensionless variable DT . It may be noticed that the distribution function resembles Gaussian for fairly large values of DT and becomes uniform only for rather large values of DT .

B. Diffusing diffusivity

For a time dependent diffusion coefficient $D(t)$, the diffusion equation for the rotational motion in 3D may be written as

$$\langle |\hat{u}(T) - \hat{u}_0|^2 \rangle = 2(1 - \langle \cos(\theta) \rangle) = 2(1 - \tilde{f}_1(\tilde{T}, \tilde{D}_0)) = 2 \left[1 - \frac{4\sqrt{1+4\tilde{D}_0} e^{-(\sqrt{1+4\tilde{D}_0}-1)\tilde{T}}}{(\sqrt{1+4\tilde{D}_0}+1)^2 - (\sqrt{1+4\tilde{D}_0}-1)^2 e^{-2\tilde{T}\sqrt{1+4\tilde{D}_0}}} \right]. \quad (42)$$

1. Small T behavior

At short times such that $\tilde{T} \ll 1$, we have

$$\langle |\hat{u}(T) - \hat{u}_0|^2 \rangle \sim 4\tilde{D}_0\tilde{T}.$$

Therefore, in the short time limit, the diffusion is Fickian as in the case of constant diffusivity. As $T \rightarrow \infty$, the MSD becomes constant as diffusion happens in a confined space.

Also, in the small $\tilde{T}$ limit, using Eqs. (39) and (40), $\tilde{f}_n(\tilde{T}, \tilde{D}_0)$ can be approximated as

$$\tilde{f}_n(\tilde{T}, \tilde{D}_0) \approx \frac{1}{1 + \tilde{D}_0\tilde{T}n(n+1)}.$$

FIG. 6. Probability distribution function for different values of DT .

$$\frac{\partial P(\theta, \phi, t)}{\partial t} = -D(t)\tilde{L}^2 P(\theta, \phi, t). \quad (37)$$

With our model of “diffusing diffusivity,”⁴² the propagator $P(\theta, t)$ (after integrating out ϕ variable) can be evaluated exactly to give

$$P(\theta, T) = \sum_{n=0}^{\infty} \frac{2n+1}{2} P_n(\cos(\theta)) \tilde{f}_n(\tilde{T}, \tilde{D}_0), \quad (38)$$

with

$$\tilde{f}_n(\tilde{T}, \tilde{D}_0) = \frac{4\alpha_n e^{-(\alpha_n-1)\tilde{T}}}{(\alpha_n+1)^2 - (\alpha_n-1)^2 e^{-2\alpha_n\tilde{T}}} \quad (39)$$

and

$$\alpha_n = \sqrt{1 + 2\tilde{D}_0 n(n+1)}. \quad (40)$$

From Eq. (38), we can now evaluate any moment of the distribution. They are given by the following relation:

$$\langle P_m(\cos(\theta)) \rangle = \int_0^\pi d\theta \sin(\theta) P_m(\cos(\theta)) P(\theta, T) = \tilde{f}_m(\tilde{T}, \tilde{D}_0). \quad (41)$$

Thus, we have the exact expression for any moment of the probability distribution. The MSD in this case becomes

Therefore, in this limit, the probability density function, $P(\theta, T)$, is given by

$$P(\theta, T) \approx \sum_{n=0}^{\infty} \frac{2n+1}{2} P_n(\cos(\theta)) \frac{1}{1 + \tilde{D}_0\tilde{T}n(n+1)}. \quad (43)$$

We notice that the fraction $\frac{1}{1 + \tilde{D}_0\tilde{T}n(n+1)}$ can be written as the following integral:

$$\frac{1}{1 + \tilde{D}_0\tilde{T}n(n+1)} = \int_0^\infty dD \frac{1}{D_0} e^{-D/D_0} e^{-n(n+1)DT},$$

FIG. 7. Probability distribution function for different values of the dimensionless parameter, $\tilde{D}_0$: (a) 0.1, (b) 1, and (c) 10. For smaller $\tilde{D}_0$, which means a faster relaxation of the environment, the pdf resembles a Gaussian function. On the other hand, for larger values of $\tilde{D}_0$, the distribution function attains its equilibrium value faster implying that diffusion is occurring at a faster rate.

where we have temporarily switched back to dimensioned variables. Using this, we get

$$P(\theta, T) \approx \int_0^\infty dD \frac{1}{D_0} e^{-D/D_0} \times \left[\sum_{n=0}^\infty \frac{2n+1}{2} P_n(\cos(\theta)) e^{-n(n+1)DT} \right]. \quad (44)$$

The expression inside the square brackets is exactly that of the probability density function for the constant diffusivity case, see Eq. (31). Therefore, we have

$$P(\theta, T) \approx \int_0^\infty dD \frac{1}{D_0} e^{-D/D_0} P_D(\theta, T), \quad (45)$$

where $P_D(\theta, T)$ is the probability density function for the constant diffusivity case. This relation again is in agreement with the arguments given by Slater and Chubynski.⁴¹ Substituting for $P_D(\theta, T)$ for short times and small θ values from Eq. (36) into Eq. (45) gives

$$P(\theta, T) \approx \frac{1}{2\pi D_0 T} K_0 \left(\frac{\theta}{\sqrt{D_0 T}} \right), \quad (46)$$

where $K_\nu(z)$ is the modified Bessel function of second kind of order ν .⁶³

For large values of z , the Bessel function, $K_\nu(z)$ has the following asymptotic expansion:⁶³

$$K_\nu(z) \sim \sqrt{\frac{\pi}{2z}} e^{-z} \left[1 + \frac{4\nu^2 - 1}{8z} + \mathcal{O}(z^{-2}) \right].$$

FIG. 8. Non-normal parameter as a function of $\tilde{T}$ for different values of parameter $\tilde{D}_0$.

Thus, in the limit of small T , the tail behavior of the function $P(\theta, T)$ is governed by

$$P(\theta, T) \sim \sqrt{\frac{1}{8\pi\theta(D_0 T)^{3/2}}} e^{-\frac{\theta}{\sqrt{D_0 T}}}.$$

2. Large T behavior

In the limit of large T (i.e., $\tilde{T} \gg 1$), $\tilde{f}_n(\tilde{T}, \tilde{D}_0)$ is given by

$$\tilde{f}_n(\tilde{T}, \tilde{D}_0) \approx e^{-n(n+1)\tilde{D}_0\tilde{T}}.$$

Therefore, in the limit of large T , $P(\theta, T)$ becomes

$$P(\theta, T) \approx \sum_{n=0}^\infty \frac{2n+1}{2} P_n(\cos(\theta)) e^{-n(n+1)D_0 T}, \quad (47)$$

which has the same form as the probability density function for the constant diffusivity case, see Eq. (31). Thus, in the long time limit, the problem of diffusion inside a heterogeneous, rearranging environment becomes similar to the problem of diffusion in a homogeneous environment with a constant value for diffusivity.

In Fig. 7, we have shown log-linear plots of probability density, $P(\theta, T)$, versus θ for different values of the dimensionless parameters $\tilde{T}$ and $\tilde{D}_0$. From the plots, we see that at short times the behavior of $P(\theta, T)$ is governed by the Bessel function of Eq. (46) which crosses over to the Gaussian form predicted by Eq. (47) at longer times. Also, the smaller the value of $\tilde{D}_0$ the faster becomes the cross over to Gaussian as the environment relaxes faster in comparison to the particle diffusion. Just the way the parameter $\alpha_{rot,2D}$ was defined, it is possible to define a parameter $\alpha_{rot,3D}$ for the three dimensional case. The details are given in Appendix B. We give a plot of $\alpha_{rot,3D}$ in Fig. 8.

IV. CONCLUSIONS

We have presented an analysis of the diffusing diffusivity model for the rotational Brownian motion. For a particular set of such models, it has been shown that calculating the probability distribution function for angular displacement is equivalent to the problem of calculating the survival probability of a particle undergoing Brownian motion, in the presence of a sink.

More specifically, we have considered a model of diffusivity in which it is modelled by Eq. (10). This model assumes that D is the square of the distance of a two-dimensional Brownian oscillator from the origin. With this approach, we have calculated the pdf for rotational motion in two and three dimensions.

In analogy to the non-Gaussianity parameter of translational motion, we have proposed two new dimensionless, time dependent non-normal parameters $\alpha_{rot,2D}$ and $\alpha_{rot,3D}$ for the rotational motion in 2D and 3D, respectively. We argue that these parameters can be used to analyze the extent of deviation from the normal diffusive behavior and hence should be useful for analysing the experimental/simulation data to find the extent of deviation from the normal behavior, i.e., constant diffusivity.

It may now be asked how generic our model is. We note that it is possible to find the exact analytical solution even if one assumes that the harmonic oscillator is n -dimensional. Analysis of this^{41,42} shows that the results are not very sensitive to the model, at least for translational diffusion. Further, one can easily argue that the diffusing diffusivity model for translational diffusion would lead to Fickian behaviors as well as Gaussian distributions in the long time limit, when the probability distribution for D has finite first and second moments.⁶⁴ On the other hand, if the first and second moments are not finite, different results can be expected. It was found in Ref. 64 that for a probability distribution for D having a power law tail of the form $D^{-1-\alpha}$, the probability distribution function for displacements becomes a Lévy stable distribution with stability index 2α . This leads to superdiffusion in the large T limit. Further, it is an interesting question, as to whether diffusing diffusivity models can lead to subdiffusion. This happens if one assumes models for which the diffusion coefficient obeys a time fractional diffusion equation. In fact, in crowded media, it seems quite likely that this would be the situation. These interesting possibilities are currently under investigation and our preliminary results suggest that the dynamics in this case is subdiffusive.

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APPENDIX A: EVALUATION OF SUM IN EQ. (20)

One can rewrite $\frac{1}{1+D_0Tm^2}$ in the form of the following integral:

$$\frac{1}{1+D_0Tm^2} = \frac{1}{2} \sqrt{\frac{1}{D_0T}} \int_{-\infty}^{\infty} dx e^{-\frac{|x|}{\sqrt{D_0T}}} e^{-imx}.$$

Thus from Eq. (20), $P(\phi, T)$ becomes

$$P(\phi, T) \approx \frac{1}{4\pi} \sqrt{\frac{1}{D_0T}} \int_{-\infty}^{\infty} dx e^{-\frac{|x|}{\sqrt{D_0T}}} \left(\sum_{m=-\infty}^{\infty} e^{im(\phi-x)} \right).$$

Using the identity,

$$\sum_{m=-\infty}^{\infty} e^{imy} = 2\pi \sum_{m=-\infty}^{\infty} \delta(y - 2m\pi),$$

we obtain

$$P(\phi, T) \approx \frac{1}{4\pi} \sqrt{\frac{1}{D_0T}} \int_{-\infty}^{\infty} dx e^{-\frac{|x|}{\sqrt{D_0T}}} \times \left(\sum_{m=-\infty}^{\infty} 2\pi \delta(\phi - x - 2m\pi) \right),$$

or

$$P(\phi, T) \approx \frac{1}{2} \sqrt{\frac{1}{D_0T}} \sum_{m=-\infty}^{\infty} e^{-\frac{|\phi-2m\pi|}{\sqrt{D_0T}}}.$$

But, for $\phi \in (-\pi, \pi]$,

$$|\phi - 2m\pi| = \begin{cases} |\phi|, & \text{if } m = 0 \\ -\phi \operatorname{sign}(m) + 2|m|\pi & \text{if } m \neq 0 \end{cases}.$$

Therefore,

$$\sum_{m=-\infty}^{\infty} e^{-\frac{|\phi-2m\pi|}{\sqrt{D_0T}}} = e^{-\frac{|\phi|}{\sqrt{D_0T}}} + \cosh(\phi/\sqrt{D_0T}) e^{-\pi/\sqrt{D_0T}} \times \operatorname{cosech}(\pi/\sqrt{D_0T}),$$

and hence

$$P(\phi, T) \approx \frac{1}{2} \sqrt{\frac{1}{D_0T}} \left(e^{-\frac{|\phi|}{\sqrt{D_0T}}} + \cosh(\phi/\sqrt{D_0T}) e^{-\pi/\sqrt{D_0T}} \times \operatorname{cosech}(\pi/\sqrt{D_0T}) \right). \quad (\text{A1})$$

APPENDIX B: NON-NORMAL PARAMETER FOR ROTATIONAL DIFFUSION IN 3D

The second and fourth order moments for rotational diffusion in 3D are defined as

$$m_2 = \langle |\hat{u}(T) - \hat{u}_0|^2 \rangle = 2(1 - \langle \cos \theta \rangle) = 2(1 - e^{-2DT}) \quad (\text{B1})$$

and

$$m_4 = \langle |\hat{u}(T) - \hat{u}_0|^4 \rangle = 4(1 + \langle \cos^2 \theta \rangle - 2\langle \cos \theta \rangle) = \frac{8}{3}(2 + e^{-6DT} - 3e^{-2DT}). \quad (\text{B2})$$

Here $\hat{u}(T)$ is the unit vector specifying the orientation of dipole at time T and $\hat{u}_0$ is the unit vector pointing along the initial orientation of the dipole at $t = 0$. We now define the following parameter, at all times, if we substitute expressions for m_2 and m_4 :

$$\alpha_{rot,3D} = \frac{1}{2} \frac{m_4}{m_2^2} + \frac{1}{6} m_2 - 1. \quad (\text{B3})$$

It can be easily verified that for the case of constant diffusivity, $\alpha_{rot,3D}$ is identically equal to zero, at all times. Now, for the case of diffusing diffusivity, using the equations of Sec. III B, we get

$$m_4 = \frac{16}{3} \left(1 + \frac{2\sqrt{1+12\tilde{D}_0} e^{-\tilde{T}(\sqrt{1+12\tilde{D}_0}-1)}}{(\sqrt{1+12\tilde{D}_0}+1)^2 - (\sqrt{1+12\tilde{D}_0}-1)^2 e^{-2\tilde{T}\sqrt{1+12\tilde{D}_0}}} - \frac{6\sqrt{1+4\tilde{D}_0} e^{-\tilde{T}(\sqrt{1+4\tilde{D}_0}-1)}}{(\sqrt{1+4\tilde{D}_0}+1)^2 - (\sqrt{1+4\tilde{D}_0}-1)^2 e^{-2\tilde{T}\sqrt{1+4\tilde{D}_0}}} \right). \quad (\text{B4})$$

The second moment, m_2 , is given by Eq. (42) of Sec. III B. It is easy to check that in the limit $\tilde{T} \rightarrow 0$, $\alpha_{rot,3D} \rightarrow 1$ and that when $\tilde{T} \rightarrow \infty$, $\alpha_{rot,3D} \rightarrow 0$.

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