Abstract

Diffusion processes, because of their applications to a wide range of phenomena, have been a subject of great scientific interest ever since Einstein formulated the celebrated theory of Brownian motion. Brownian motion is the most commonly known class of diffusion and is the dominant form of molecular transport in physical systems which are usually driven by thermal noise e.g. dissolution of sugar in water. It is also the simplest case of a random process where it is assumed that the time scale of motion of diffusing particle is much larger than that of the solvent molecules. This causes an extreme separation of time scales- one associated with the slower diffusing particle, and the other associated with the faster solvent molecules. This in turn leads to two fundamental laws of Brownian motion : (1) the mean square displacement (MSD) of particle is proportional to the time lapsed, i.e. $\langle x^2 \rangle \propto T$. It is usually referred to as Fickian motion and (2) the probability distribution function (pdf) of displacements is Gaussian with the width of distribution scaling as $\sqrt{T}$ (this is equivalent to say that the motion is Fickian). However, there are many other diffusion processes which can not be classified as Brownian motion and hence are termed as *anomalous diffusion*. A diffusion process can be termed as anomalous if any one or both the laws of Brownian motion are violated.

There are a lot of phenomena in which is diffusion is anomalous, i.e. where the pdf is not Gaussian but a stable distribution with a functional form $f(|x|/T^{\alpha/2})$ such that the width of distribution increases like $T^{\alpha/2}$ with $\alpha \neq 1$. The Brownian motion, on the other hand, would lead to a Gaussian distribution with $\alpha = 1$. In the past, it has been usually assumed that if $\alpha \neq 1$, i.e. if the diffusion is non-Fickian, then the distribution would also be non-Gaussian. Conversely, if $\alpha = 1$, then the distribution would be Gaussian. This was so well accepted that it was almost never tested until recently. In a series of experiments

from Granick's group [1, 2] where the environment undergoes structural rearrangement on a time scale less than that of observation of diffusion, non-Gaussian distributions have been realized. Even more interesting, coexisting with this non-Gaussian distribution was observed a MSD which was found to be vary linearly in time at all times irrespective of the actual form of the distribution. In these experiments, the pdf was found to be exponential at short times which then crossed over to being Gaussian at large enough time scales.

Chubynsky and Slater [3] have analyzed the "diffusing diffusivity" model, in which diffusion coefficient changes as a stochastic function of time, because of the rearrangement of environment. Assuming an exponential distribution of diffusivity at small time scales, these authors showed analytically that (1) the diffusion is Fickian and (2) the distribution of displacements, after averaging the Gaussian pdf over the exponential distribution of diffusivity, becomes non-Gaussian (exponential). The width of this non-Gaussian distribution increases as $\sqrt{T}$. At larger time scales, they performed simulations and the result was a cross over to Gaussian distribution. Following their work, we have proposed a class of "diffusing diffusivity" models which we have been able to solve analytically at all time scales, using the methods of path integrals [4]. In the thesis, we are interested in developing models of diffusing diffusivity that could be used to describe different kinds of anomalous diffusion processes. We show that our model of diffusing diffusivity is equivalent to another important class of physical processes, i.e. that of the Brownian motion with absorption, or the reaction-diffusion process. In reaction-diffusion models, the concentration of a chemical substance changes in space and time because of its reaction with another substance while the diffusion causes the spread in the concentrations of various substances. The connection of diffusing diffusivity model to the reaction-diffusion model is particularly useful as one can now have different models of diffusivity describing its diffusion while, interestingly the reaction term remains unchanged.

In our first model, diffusivity is modeled as a simple Brownian process. More precisely, we take $D(t) = \boldsymbol{\xi}^2(t)$ where $\boldsymbol{\xi}$ is the position vector of an n-dimensional harmonic oscillator executing Brownian motion. For the case $n = 2$, the equilibrium distribution of diffusivity is an exponential, thereby making this particular case an ideal choice to compare our results with the numerical results of Chubynsky and Slater [3]. We have shown that our results are in very good agreement with theirs [5]. Further, our model is quite generic and it is possible to find exact analytical solution with arbitrary value of n. The non-Gaussianity parameter, which is a measure of deviation from normality, has been evaluated exactly as a function of time and n. At short times, the value of parameter is non-zero, signifying non-Gaussian dynamics which eventually becomes zero in the large time limit, marking an onset of Gaussian dynamics. For larger values of n, the non-Gaussianity starts disappearing faster implying an earlier onset of Gaussian behavior.

The model has been applied to the problem of calculating survival probability of a free particle in crowded, rearranging and bounded regions. We have obtained exact results for this problem where we have shown that for larger compartments and faster relaxation of the surroundings, diffusion inside a crowded, rearranging medium is similar to the diffusion in a homogeneous medium with a constant diffusivity. We have also studied the model for rotational diffusion process. We have obtained simple analytical expressions for the probability distribution and the mean square angular displacement in arbitrary dimensions. As in the case of translation diffusion, a non-Gaussianity parameter quantifies the extent of deviation from Gaussian dynamics, we have defined in a similar fashion a non-normal parameter for rotational diffusion. This could be useful in analyzing the experimental data to find the extent of deviation from normal diffusion. In another study, we have used the model of diffusing diffusivity for the diffusion of a harmonic oscillator in crowded, rearranging environment. We have obtained two interesting results here namely (1) the expression for the MSD in case of diffusing diffusivity is of same kind as that for the case of constant diffusivity and (2) the probability distribution function remains non-Gaussian even in the limit of very large time unlike the previous cases where it eventually crosses over to become Gaussian.

In our model of diffusivity, and also in the model of Chubynsky and Slater [3], the distribution of diffusivity decays to zero exponentially fast, implying that the probability of having a large value of D is rather small. However, there are cases where the distribution of D is broad and therefore D can occasionally have a large value with a sizable probability. We have analyzed a model of diffusivity where it evolves as a Lévy flight process. More precisely, the distribution of diffusivity decays as power-law of the form $D^{-1-\alpha}$ with $0 < \alpha < 1$, in the limit of large time. The distribution of displacements with this model is found to be a stable distribution with a time dependent width. The width of the distribution increases as $\sqrt{T}$, as in the case of Fickian dynamics but at longer times it increases at a much faster rate as $T^{1/2\alpha}$. Thus, the dynamics is Fickian at short times and superdiffusive at long times.

After studying the models of diffusivity where it evolves as a Brownian process and as a Lévy flight process, respectively, we have also studied a model of diffusivity where it evolves as a subdiffusive process. For that we have modeled diffusivity as a continuous time random walk (CTRW) process such that it attains an exponential distribution in the equilibrium limit. This model is actually a generalization of our first model of diffusing diffusivity with a parameter $\alpha \in (0, 1]$. The problem of diffusing diffusivity, in this case, is shown to be equivalent to a class of models known as *reaction-subdiffusion systems*. We have analyzed two such models of reaction-subdiffusion. With both these models, we get all the results of our first model of diffusivity if $\alpha = 1$. Within the first model, the MSD is found to increase linearly in time at all the time scales and for all values of $\alpha \in (0, 1]$, thereby confirming a Fickian dynamics. Although the probability distribution function also becomes Gaussian in the limit of very large time for all values of α as is our first model of diffusing diffusivity yet the evolution of pdf from a non-Gaussian function to Gaussian is a very slow process. Smaller is the value of α, slower is the transition from non-Gaussian to Gaussian dynamics. The second model leads to subdiffusive dynamics in position space. The MSD here is shown to increase as T^α with a non-Gaussian pdf at all the time scales.