Abstract

Path integral approaches have been widely used for long in both quantum mechanics as well as statistical mechanics. In addition to being a tool for obtaining the probability distributions of interest (wave functions in the case of quantum mechanics), these methods are very instructive and offer great insights into the problem. In this thesis, path integrals are extensively employed to study some very interesting problems in both equilibrium and non-equilibrium statistical mechanics. In the non-equilibrium regime, we have studied, using a path integral approach, a very interesting class of anomalous diffusion, viz. the Lévy flights. In equilibrium statistical mechanics, we have evaluated the partition function for a class of molecules referred to as the hindered rotors which have a barrier for internal rotation. Also, we have evaluated the exact quantum statistical mechanical propagator for a harmonic potential with a time-dependent force constant, valid under certain conditions.

Diffusion processes have attracted a great amount of scientific attention because of their presence in a wide range of phenomena. Brownian motion is the most widely known class of diffusion which is usually driven by thermal noise. However, there are other classes of diffusion which cannot be classified as Brownian motion and therefore, fall under the category of *Anomalous diffusion*. As the name suggests, the properties of this class of diffusion are very different from those for usual Brownian motion. We are interested in a particular class of anomalous diffusion referred to as Lévy flights in which the step sizes taken by the particle during the random walk are obtained from what is known as a Lévy distribution. The diverging mean square displacement is a very typical feature for Lévy flights as opposed to a finite mean square displacement with a linear dependence on time in the case of Brownian motion. Lévy distributions are characterized by an index α where $0 < \alpha \leq 2$. When $\alpha = 2$, the distribution becomes a Gaussian and when $\alpha = 1$, it reduces

to a Cauchy/Lorentzian distribution.

In the overdamped limit of friction, the probability density or the propagator associated with Lévy flights can be described by a position space fractional Fokker-Planck equation (FFPE) [1–3]. Jespersen *et al.* [4] have solved the FFPE in the Fourier domain to obtain the propagator for free Lévy flight (absence of an external potential) and Lévy flights in linear and harmonic potentials. We use a path integral technique to study Lévy flights. Lévy distributions rarely have a compact analytical expression in the position space. However, their Fourier transformations are rather simple and are given by $e^{-D|p|^{\alpha}}$ where D determines the width of the distribution. Due to the absence of a simple analytical expression, attempts in the past to study Lévy flights using path integrals in the position space [5, 6] have not been very successful. In our approach, we have tried to make use of the elegant representation of the Lévy distribution in the Fourier space and therefore, we write the propagator in terms of a two-dimensional path integral - one over paths in the position space (x) and the other over paths in the Fourier space (p). We shall refer to this space as the 'phase space'. Such a representation is similar to the Hamiltonian path integral of quantum mechanics which was introduced by Garrod [7]. If we try to perform the path integral over Fourier variables first, then what remains is the usual position space path integral for Lévy flights which is rather difficult to solve. Instead, we perform the position space path integral first which results in expressions which are rather simple to handle. Using this approach, we have obtained the propagators for free Lévy flight and Lévy flights in linear and harmonic potentials in the overdamped limit [8]. The results obtained by this method are in complete agreement with those obtained by Jesepersen *et al.* [4]. In addition to these results, we were also able to obtain the exact propagator for Lévy flights in a harmonic potential with a time-dependent force constant which has not been reported in the literature. Another interesting problem that we have considered in the overdamped limit is to obtain the probability distribution for the area under the trajectory of a Lévy particle. The distributions, again, were obtained for free Lévy flight and for Lévy flights subjected to linear and harmonic potentials. In the harmonic potential, we have considered situations where the force constant is time-dependent as well as time-independent.

Like in the case of the overdamped limit, the probability distribution for Lévy flights in the underdamped limit of friction can also be described using a fractional Fokker-Planck equation, although in the full phase space. However, this has not yet been solved for any general value of α to obtain the complete propagator in terms of both position and velocity. Using our path integral approach, the exact full phase space propagators have been obtained for all values of α for free Lévy flights as well as in the presence of linear and harmonic potentials [8].

The results that we obtain are all exact when the potential is at the most harmonic. If the potential is higher than harmonic, like the cubic potential, we have used a semiclassical evaluation where, we extremize the action using an optimal path and further, account for fluctuations around this optimal path. Such potentials are very useful in describing the problem of escape of a particle over a barrier. The barrier crossing problem is very extensively studied for Brownian motion (Kramers problem) and the associated rate constant has been calculated in a variety of methods, including the path integral approach. We are interested in its Lévy analogue where we consider the escape of a particle driven by a Lévy noise over a barrier. On extremizing the action which depends both on phase space variables, we arrived at optimal paths in both the position space as well as the space of the conjugate variable, p. The paths form an infinite hierarchy of instanton paths, all of which have to be accounted for in order to obtain the correct rate constant. Care has to be taken while accounting for fluctuations around the optimal path since these fluctuations should be independent of the time-translational mode of the instanton paths. We arrived at an 'orthogonalization' scheme to perform the same. Our procedure is valid in the limit when the barrier height is large (or when the diffusion constant is very small), which would ensure that there is small but a steady flux of particles over the barrier even at very large times. Unlike the traditional Kramers rate expression, the rate constant for barrier crossing assisted by Lévy noise does not have an exponential dependence on the barrier height. The rate constant for wide range of α, other than for those very close to $\alpha = 2$, are proportional to D^{μ} where, $\mu \approx 1$ and D is the diffusion constant. These observations are consistent with the simulation results obtained by Chechkin *et al.* [9]. In addition, our approach when applied to Brownian motion, gives the correct dependence on D.

In equilibrium statistical mechanics we have considered two problems. In the first one, we have evaluated the imaginary time propagator for a harmonic oscillator with a time-dependent force constant ($\omega^2(t)$) exactly, when $\omega^2(t)$ is of the form $\lambda^2(t) - \dot{\lambda}(t)$ where $\lambda(t)$ is any arbitrary function of t. We have made use of Hamiltonian path integrals for this. The second problem that we considered was the evaluation of the partition function for hindered rotors. Hindered rotors are molecules which have a barrier for internal rotation. The molecule behaves like free rotor when the barrier is very small in comparison with the thermal energy, and when the barrier is very high compared to thermal energy, it behaves like a harmonic oscillator. Many methods have been developed in order to obtain the partition function for a hindered rotor. However, most of them are some what ad-hoc since they interpolate between free-rotor and the harmonic oscillator limits. We have obtained the approximate partition function by writing it as the trace of the density matrix and performing a harmonic approximation around each point of the potential [10]. The density matrix for a harmonic potential is in turn obtained from a path integral approach [11]. The results that we obtain using this method are very close to the exact results for the problem obtained numerically. Also, we have devised a proper method to take the indistinguishability of particles into account in internal rotation which becomes very crucial while calculating the partition function at low temperatures.