Random walk model for coordinate dependent diffusion in a force field

Rohan Maniar¹ and A. Bhattacharyay¹

¹Indian Institute of Science Education and Research, Pune, India

In this paper we develop a random walk model on lattice for coordinate dependent diffusion at constant temperature in contact with a heat bath. We employ here a coordinate dependent waiting time of the random walker to make the diffusivity coordinate dependent. The presence of a confining conservative force is modeled by appropriately breaking the isotropy of the jumps of the random walker to its nearest neighbors. We show that the equilibrium is characterized by the position distribution which is of modified Boltzmann form.

PACS numbers: 05.40.Jc, 05.10.Gg, 05.70.-a

INTRODUCTION

Coordinate dependent diffusivity of a Brownian particle (BP) when modeled by Langevin dynamics causes controversy because it involves multiplicative noise [1–3]. The source of controversy is in the stochastic integrals which result in a diffusion gradient driven spurious drift term in the corresponding Fokker-Plank equation. The controversy is mainly in physics literature where Stratonovich or Stratonovich-like conventions are used for stochastic integrations involving multiplicative noise [4–9]. These conventions produce spurious currents proportional to the diffusivity gradients which are then removed by adding counter terms in the Langevin dynamics. The removal of a part of the spurious probability current from the Fokker-Plank dynamics is done predominantly in the existing physics literature by demanding the Boltzmann distribution (BD) to ensure equilibrium in such systems [3]. It has been pointed out by one of the authors of this paper earlier that when removing the spurious part of the probability current one also tacitly ignores a part of legitimate diffusion current in order to have a Boltzmann distribution [10, 11]. Otherwise, the Boltzmann Distribution will not come out to be the equilibrium distribution of such a system if the diffusion current is kept as it should be for coordinate dependent diffusivity.

The motivation of the present paper is the numerical exploration of such a system of BP using a model which does not involve controversy related to the existence of multiplicative noise in the Langevin dynamics. We investigate here the equilibrium of a BP with coordinate dependent diffusivity which is confined over space. Employing Langevin dynamics to such a system is controversial due to the standard practice of adding or not adding additional terms to remove spurious currents. On the other hand molecular dynamics simulations of more realistic systems are much more computationally expensive. The question of employing Monte Carlo simulations does not exist in the presence of a possibility of having a modified Boltzmann distribution. In such a situation, a pure random walk model which has coordinate dependent hopping probabilities to account for the presence of a conservative confining force along with a waiting time gradient which will introduce coordinate dependent diffusivity could be an ideal simple way of numerical modeling. In the present paper we use this method of numerical investigation to show that the equilibrium distribution of a harmonically confined Brownian particle with coordinate dependent diffusivity is indeed a modified Boltzmann distribution. This method is simple but the outcome is startling and is fully consistent with analytic predictions of one of the present authors [10].

Using position dependent hopping probabilities of a Brownian walker on a lattice is not new [12–16]. This model has been extensively used in investigating heterogeneous diffusion processes when the coordinate dependent variation of hopping are in general drawn from some distribution to model a heterogeneous environment. In general, the bias in the jumping probability resulting in anisotropy can model the presence of a force on an over-damped particle and this method can be quite general [17]. This is exactly what is utilized in the present work to represent a confining force to a random walker in a one dimensional lattice for the sake of simplicity.

The other important elements which have been made use of are the waiting time of such a walker at a lattice cite to generate coordinate dependent diffusion at a constant temperature. By introducing a waiting time globally at each lattice point one can control the diffusivity of the walker globally. A local generalization of diffusivity then requires some coordinate dependence of this waiting time. The most important feature of this way of introducing diffusivity variation, as will be shown in this paper, is that it can be done over a constant temperature environment under a confinement. Once standardized, this very simplistic random walk model can actually capture Brownian motion over an inhomogeneous space when the inhomogeneity is not only due to the presence of a conservative force but also...
due to varied diffusivity over space.

In this paper we first establish the usefulness of this (above mentioned) methods of variation of diffusivity over space using a BP under harmonic confinement. Following which we embark on simulating coordinate dependent diffusive Brownian motion by employing a waiting time gradient over space. We obtain the equilibrium distribution of positions of such a walker to show that, besides having the Boltzmann factor, the distribution has an amplitude which is inversely proportional the coordinate dependent diffusivity. Then we demonstrate that the present model can also be generalized to take into account barrier overcoming processes.

It may be noted at this stage that the computational method employed in the paper for the particular problem at hand is extremely simple and inexpensive. However, this method has its advantage in particularly involving force fields of a system and not the free energy functional for the cases where the latter is not known or is not free of controversy. The problem to which this simple modeling is applied in the present paper is of this particular category. This modeling apparently although is employed here for an equilibrium process, can be generalized to non equilibrium cases when the hopping probabilities are not only functions of space but also of time. The method can also be generalized to continuous dynamics and in principle should work for a wide variety of forces with or without spatial confinement of the system.

RANDOM WALK MODEL OF LANGEVIN DYNAMICS IN HOMOGENEOUS SPACE

The Langevin dynamics of the form

\[ \dot{x} = F(x) + \Gamma \sqrt{2D\eta(t)} , \tag{1} \]

where \( x \) is the position of the BP in a force field \( F(x) = -\frac{\partial V(x)}{\partial x} \) and \( \Gamma \) is a damping constant, can be modeled by a random walker. In the above equation \( D \) is the diffusivity of the particle and \( \eta(t) \) is a Gaussian white noise of unit strength. As has been mentioned in the introduction the purpose of modeling this Langevin dynamics by random walks is to extend this model to a situation where the \( \Gamma \) and \( D \) are coordinate dependent. However, in the beginning we are interested in establishing our random walk model for uniform diffusivity in order to demonstrate consistency of different methods in tuning the diffusivity.

Consider the force free situation when Eq.(1) takes the shape \( \frac{d^2x}{dt^2} = \frac{\Gamma}{M} \) being represented by a random walker on a one dimensional lattice with jumping probability towards the nearest neighbour points being \( \frac{1}{2} \). In such a situation, one would get a pure diffusion with highest possible diffusivity on this lattice compared to the process when the particle has a non-zero probability \( p_s \) to stick to the lattice point. In the presence of a probability to stick to the lattice point being \( p_s \) and the jumping probabilities to the right and left being \( \frac{1}{2} \), the diffusivity of the particle will fall from this highest value. Fig.1 shows such a plot of a random walker’s diffusivity as a function of \( p_s \) where the diffusivity has been obtained by evaluating numerically \( D = \langle (x(t)-x(0))^2 \rangle \) for a long enough time \( t \) and \( \langle \cdot \rangle \) indicates an ensemble average over 10000 particles. Everywhere in what follows all the ensemble averages are over this set of 10000 particles. Corresponding to all the points in the graph (Fig.1) there is a constant \( p_s \) everywhere on the lattice characterizing a constant global diffusivity. The time is measured in unit steps in which the particle either jumps to the right or left nearest lattice points with probability \( \frac{1}{2} \) to maintain isotropy of the process or sticks to the point with a probability \( p_s \). As one can see the dependence is linear and on performing a linear fit we get the R square of the fit to be 0.999. Having known the dependence of the diffusivity on this waiting time probability \( p_s \), we can make \( D \) a function of space (coordinates) by making \( p_s \) a function of the coordinates.

![FIG. 1: The plot for Diffusivity as a function of stick probability.](image-url)
p_a = 1 - p_s - \epsilon F(x) \) where \( \epsilon \) is a small number. Note that, the \( \Gamma \) in the Langevin dynamics (Eq.(1)) is just a scale factor in units of which we are going to get the force term for a known diffusivity \( D \). The factor \( \epsilon \) is in general set to be a small number to determine how far up the potential \( V(x) \) the BP will rise under given conditions of the force. This will make the parameter \( \epsilon \) in the present model capture a global temperature of the system.

As a special case, consider a harmonic potential \( V(x) = \frac{kx^2}{2} \) where the drift velocity is \( \frac{\Gamma}{k} \). The probabilities to jump towards or against the force are now \( p_t = \frac{1-p_s}{2} + \frac{\epsilon F(x)}{k} \) and \( p_a = \frac{1-p_s}{2} - \frac{\epsilon F(x)}{k} \). For the sake of convenience we introduce a new term \( N_0 \) where \( \frac{1}{2N_0} = \frac{\epsilon}{k} \). By setting \( p_s = 0.2 \) and \( p_s = 0.6 \) in the presence of only nearest neighbour jumps, we evolve the walker and arrive at the Gaussian distributions of the position of the walker as shown in Fig.2(a) and (b). To verify the Gaussian nature of the figures mentioned we plot the log of number of particles at a position coordinate \( x \) vs \( x^2 \) and performed a linear fit. This was done for \( x \) between \(-60 \) and \( 60 \) and the R square for this fit was 0.9920.

We can perform a few immediate checks here. We find out the diffusivity of the systems corresponding to any \( p_s \) value. Having known that the mean square displacement (MSD) of the BP in the presence of the force will go as

< x^2(t) > = \frac{D\Gamma}{k} (1 - e^{-2s\Gamma}) = A(1 - e^{-R\Gamma}) \quad (2)

we get the universal relation \( \frac{DA}{R^2} = 2 \). Evidence for the same is presented in Table.1 where we show that the universal relation holding for different values of \( p_s \). Fig.3(a) shows the time variation of the MSD for \( p_s = 0.2, 0.4 \) and 0.6 where \( N_0 = 600 \) and Fig.3(b) shows the plot of MSD against time for \( p_s = 0.4 \) and \( N_0 = 200, 400, 600 \). Note the important feature shown by these two graphs being that the saturation value of the MSD being \( A = \frac{DA}{R^2} \) varies with \( N_0 \) and not with \( p_s \). Thus, the temperature of the system \( \frac{D\Gamma}{k} = \frac{k_B T}{N_0} \) in equilibrium where \( D\Gamma = k_B T \) with \( k_B \) being Boltzmann constant could be tuned by the \( N_0 \). The other important thing is that, the variation of the diffusivity by the change of the sticking probability does not affect the temperature of the system as is shown by Fig.3(a). This particular feature of the tuning of the diffusivity by \( p_s \) will allow us to introduce a coordinate dependent diffusivity by making \( p_s \) a function of space without changing the temperature.

### TABLE I: Verification of the universal relation \( \frac{DA}{R^2} = 2 \) for different values of \( p_s \)

| \( p_s \) | R  | A  | D  | \( \frac{DA}{R^2} \) |
|-------|----|----|----|---------------------|
| 0.0  | 0.00389 | 255.77 | 0.506 | 1.95 |
| 0.1  | 0.00365 | 249.18 | 0.447 | 2.05 |
| 0.2  | 0.00323 | 250.37 | 0.396 | 2.03 |
| 0.3  | 0.00277 | 251.42 | 0.354 | 1.97 |
| 0.4  | 0.00250 | 244.27 | 0.305 | 1.99 |
| 0.5  | 0.00197 | 251.66 | 0.249 | 1.99 |
| 0.6  | 0.00161 | 247.68 | 0.199 | 2.01 |
| 0.7  | 0.00120 | 249.01 | 0.150 | 1.99 |
| 0.8  | 0.00080 | 252.20 | 0.099 | 2.05 |

**RANDOM WALK MODEL OF LANGEVIN DYNAMICS WITH COORDINATE DEPENDENT DIFFUSIVITY**

Let us first employ a ramp in the diffusivity of the above mentioned model system by introducing a gradient of the sticking probability \( p_s \). This is done by varying the sticking probability as follows:

\[
p_s = \begin{cases} 
  a & \text{for } x \leq -25 \\
  \frac{(b-a)(x-25)}{50} + b & \text{for } -25 \leq x \leq 25 \\
  b & \text{for } 25 \leq x 
\end{cases}
\]

FIG. 2: Gaussian distribution for \( p_s = 0.2 \) (Fig.2(a)) and \( p_s = 0.6 \) (Fig.2(b))
(a) Time dependence of MSD for $p_s = 0.2, 0.4, 0.6$ where $N_0 = 600$

(b) Time dependence of MSD for $p_s = 0.4$ where $N_0 = 200, 400, 600$

FIG. 3: Time dependence of MSD for a BP in a harmonic potential for varying values of $p_s$ and $N_0$

where $a$ and $b$ are any two values of $p_s$. In Fig. 4(a) and (b) we show the modified Gaussian distribution of the stationary distributions of the system for $a = 0.4$, $b = 0.8$, $N_0 = 1000$ and $a = 0.2$, $b = 0.8$, $N_0 = 500$ respectively. The numerically obtained distributions are fitted to the distributions $P(x) = \frac{N}{D(x)} \exp \left(\frac{k x^2}{D(x)}\right)$ and we obtain the parameter $k_B T/k$ from the MSD of the system as is set by the fixed $N_0$ and the $D(x)$ is found out from its correspondence with the $p_s$ variation as shown in Fig. 1. To verify that the stationary distribution does indeed follow the modified BD we plot log of number of particles at $x$ multiplied with the value of the diffusivity at $x$ vs $x^2$ and perform a linear fit. The linear fits for the first and the second systems are shown in Fig. 4(c) and Fig. 4(d) respectively. The fit is done taking $x$ between $-44$ and $46$ and the R square values for these fits are 0.985 and 0.993 respectively. The excellent agreement of the numerical distribution with the theoretical one demonstrate the modified Boltzmann distribution of such a BP under confinement in equilibrium with a heat bath.

We generalize this method to the case of a double well potential to show that the present model can indeed be utilized for barrier overcoming processes. The double well potential is of the form $V(x) = -\alpha x^2 + \beta x^4$ using

FIG. 4: Modified BD for the case of coordinate dependent diffusivity in a harmonic potential
the same procedure as mentioned for the harmonic confinement. The simulation of the double well system \( N_0 = \frac{\alpha}{\beta} = 2000 \) with \( \alpha = 5.0 \) and \( \beta = 0.0125 \) are set. Fig.5(a) shows the stationary distribution for particles in the case of a double well potential with a coordinate dependent \( p_s \) ramp. The sticking probability was varied as

\[
p_s = \begin{cases} 
0.2 & \text{if } x \leq -100 \\
\frac{(0.6)(x-100)}{200} & -100 \leq x \leq 100 \\
0.8 & \text{if } x \geq 100 
\end{cases}
\]

Fig.5(b) is a plot of log of number of particles at \( x \) multiplied with the diffusivity at \( x \) vs \( x \). The curve is fit to a function of the form \( f(x) = A - cx^2 + dx^4 \). Here, the shift \( A = \ln N \) where \( N \) is the overall normalization constant. From the fit, the magnitude of the constants \( c \) and \( d \) are coming out to be \( c = 0.0051 \) and \( d = 1.272 \times 10^{-5} \). This shows that the ratio of \( \alpha \) to \( \beta \) is almost the same as that of \( c \) to \( d \) which it should be. This was done for \( x \) between -25 and 25 and the R square value of the fit was 0.996. For comparison, Fig.5(c) is a plot of log of number of particles at \( x \) vs \( x \) where the continuous curve is the same function \( f(x) = A - cx^2 + dx^4 \). The left right asymmetry clearly indicates the absence of the \( D(x) \) dependent amplitude of the distribution which is missing in this case.

Having seen the numerical results of the equilibrium distribution of a BP with coordinate dependent diffusivity and damping let us have a look at the theoretical derivation of the same for the sake of completeness. In the following we show the derivation of the equilibrium distribution of the BP following the method shown in [10, 11] which relies on Smoluchowski equation obtained by adopting Itô convention for multiplicative noise.

Consider the overdamped dynamics of the BP when its diffusivity and damping are functions of coordinate.

\[
\dot{x} = \frac{F(x)}{\Gamma(x)} + \sqrt{2D(x)} \eta(t).
\] (3)

Here, \( D(x) \) is a coordinate dependent diffusivity in 1D and \( \Gamma(x) \) is the coordinate dependent damping. The corresponding Smoluchowski equation in Itô convention will look like

\[
\frac{\partial P(x, t)}{\partial t} = \frac{\partial}{\partial x} \left[ -\frac{F(x)P(x, t)}{\Gamma(x)} + \frac{\partial D(x)P(x, t)}{\partial x} \right].
\] (4)

The \( P(x, t) \) in the above equation is the probability density of the BP. For equilibrium distribution of this probability density we have to consider it to be independent of time and the distribution will follow from the condition of detailed balance which requires the square bracketed terms on the right hand side of the above equation set to zero. The detailed balance will straight forwardly give the equilibrium distribution of the system to be

\[
P(x) = \frac{N}{D(x)} \exp \int_{-\infty}^{x} \frac{F(x')}{D(x')\Gamma(x')}dx',
\] (5)

where \( N \) is a normalization constant. This distribution can be written as

\[
P(x) = \frac{N}{D(x)} \exp \frac{-V(x)}{k_B T},
\] (6)

when the Stokes-Einstein relation \( D(x)\Gamma(x) = k_B T \) holds locally and \( F(x) = -dV(x)/dx \). In the present case
of the numerical modeling the Stokes-Einstein relation holds locally as we have already seen.

**DISCUSSION**

In this paper, we have introduced a numerical method to introduce coordinate dependent diffusivity of a BP in a constant temperature environment. This Brownian motion, by construction, is such that the Stokes-Einstein relation holds locally i.e. \( D(x)\Gamma(x) = k_B T \). The temperature of the system can be tuned by another parameter which determines how much up the potential barrier the BP is allowed to move. This simple model captures an ideal situation for the equilibrium of a BP with coordinate dependent diffusivity at a constant temperature with a heat-bath.

The result shows excellent agreement with the theoretical prediction that the equilibrium distribution of such a BP under confinement will be a modified Boltzmann distribution with a diffusivity dependent amplitude. This is a very important result which actually encodes in the equilibrium distribution the sources of both the inhomogeneity of space, namely, the conservative force and the coordinate dependent diffusivity. In the presence of the local validity of the Stokes-Einstein relation, the damping is slaved by the diffusivity and that is well captured by our model system.

The present computational model can also include barrier overcoming processes which we have shown by considering a double well potential. This is a very simple model on lattice which can even be employed to any form of conservative force field at a constant temperature with a coordinate dependent diffusivity. One can explore this method of random walk modelling for different biological processes where coordinate dependence of the diffusivity is needed at a constant temperature, for example, protein folding on a lattice.

* Electronic address: a.bhattacharyay@iiserpune.ac.in

[1] Sokolov I M 2010 *Chem. Phys.* **375** 359-363
[2] Tupper P F and Yang X 2012 *Proc. R. Soc. A* **468** 3864-3881
[3] Leibovich N and Barkai E 2019 *Phys. Rev. E* **99** 042138
[4] Lau A W C and Lubensky T C 2007 *Phys. Rev. E* **76** 011123
[5] Sancho J M, San Miguel M and Dürre D 1982 *J. Stat. Phys.* **28** 291-305
[6] Sancho J M 2011 *Phys. Rev. E* **84** 062102
[7] Schnitzer M J 1993 *Phys. Rev. E* **48** 2553-2568
[8] Farago O and Gronbech-Jensen N 2014 *Phys. Rev. E* **89** 013301
[9] Farago O and Gronbech-Jensen N 2014 *J Stat. Phys.* **156** 1093-1110
[10] Bhattacharyay A 2019 *Physica A* **515** 665-670
[11] Bhattacharyay A 2019 arXiv:1901.08358v4
[12] Gates D J and Westcott M 1982 *J. Phys. A: Math. Gen.* **15** L267
[13] Codling E A, Plank M J and Benhamou S 2008 *J. R. Soc. Interface* **5** 813
[14] Grebenkov D S and Tupikina L 2018 *Phys. Rev. E* **97** 012148
[15] Hou R, Cherstvy A G, Metzler R and Akimoto T 2018 *Phys. Chem. Chem. Phys.* **20** 20827
[16] Long S 2019 *Adv. Math. Phys.* 3479715
[17] Falco R and Evans M R 2017 *J. Stat. Mech.* 023204