Computer Simulation of Brownian motion of a particle in presence a harmonic potential

Project submitted towards partial fulfilment of the requirement for the Degree of Master of Science (Physics) at Jadavpur University

By

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ABSTRACT

In the following project work we have calculated the survival probability of Brownian particle in presence of an absorbing wall in case of free diffusion. Next we have calculated the survival probability of the Brownian particle in presence of an absorbing wall in a three phase system. We have also derived the Fokker Planck equation for a Brownian particle in presence of a harmonic potential and numerically solved the probability function of the particle in presence of a harmonic potential.

INTRODUCTION

Computer simulations of Brownian motion are currently being used to study a wide range of phenomena in colloidal and macromolecular systems. With the growth in computing power, simulations were pioneered by Fixman (1978b), Ermak & McCammon (1978), Pear & Weiner (1979) and Helfand, Wasserman & Weber(1980) to study the relaxation and rheology of polymer chains. Now, in addition, simulations are being used to study the hydrodynamic thickness of a layer of polymer absorbed on a wall (Parnas & Cohen 1991), dynamic light scattering from a polymer chain (Rey, Freire & Garcia de la Torre 1989), the rheology of colloidal dispersions (Heyes & Melrose 1993; Rigos & Wilemski 1992; Shenvood 1992) and site-specific biochemical reactions (Luty et al. 1993; Nambi, Wierzbicki & Allison 1992; Northrup& Erickson 1992).Diffusive Brownian motion describes the slow changes in configuration of complex colloidal and macromolecular systems. Systems of a few molecules change more rapidly and are more appropriately described by molecular dynamics simulations,which involve integrating Newton's equations of motion for each of the interacting molecules. For the slower diffusive changes of the configuration of larger systems,one can set the inertia to zero, which suppresses the rapid process of inertia-friction relaxation of momentum. In order to determine the correct description of the Brownian diffusion of some complex systems, we shall however find it necessary to consider the system before the mass is set to zero, because the limit of vanishing mass is a singular limit. In this case we shall use a Langevin description of the system, in which Newton's equations have an added random force representing the action of the thermal motions. A Lagrangian formulation of Newton's equations will sometimes be employed which will enable us to cast the Langevin equation in terms of generalized coordinates. For simple systems with only a few degrees of freedom, the diffusive motion is best studied numerically by solving the appropriate partial differential equation for the probability distribution function in the space of possible configurations, a partial differential equation similar to the advection-diffusion equation for temperature. For more complex systems with many degrees of freedom, numerical simulation of random walks of the diffusive Brownian motion through the different configurations can be more economical. The computational trade-off is between the rapidly increasing storage requirements of the partial differential equation over many dimensions against the slowly improving N-'/* statistical errors when taking averages over N simulated random walks. In some special circumstances, such as a steady system with conservative forces, the

probability distribution of configurations is known analytically. However in general, for example for transient phenomena and for systems with non-conservative external forces as occur in shearing flows, one must seek the probability distribution by numerical methods.

The numerical algorithm to simulate the diffusive random walks is straightforward in very simple systems. To any systematic motion driven by a steady force, one must add a random displacement at each time-step. The amplitude of these independent random displacements is chosen proportional to the square root of the size of the time-step, which ensures that the random walks have a variance which grows linearly in time independent of the size of the time-step. Quite small time-steps can therefore be necessary when there is a small spatial structure to be resolved. The basic algorithm had been included later , along with questions of numerical accuracy and stability, and the question of statistical accuracy in taking averages over time.When the Brownian system becomes large and complex, three problems can arise which require the basic algorithm to be modified. The purpose of this paper is to,collect and to illustrate these problems. The first problem, which was noted and resolved by Ermak & McCammon in 1978, occurs when the diffusivity changes with the configuration. Unless a correction is made to the basic algorithm, configurations of high diffusivity are erroneously depleted as a result of vigorous random walks away from such configurations, compared with more feeble random walks returning from the surrounding configurations with a smaller diffusivity. There are several ways to modify the basic algorithm, with perhaps the easiest being a half-step scheme proposed by Fixman (1978a).

1.1Brownian Motion

Brownian motion is the random motion of sufficiently small microscopic particles suspended in a fluid (a liquid or a gas) resulting from their collision with the fast moving molecules in the fluid If you've ever watched dust-motes dancing in a sunbeam then you've observed Brownian motion. It is the jerky, fluttering motion of particles in fluids such as air or water. While the effect was known as least since the ancient Greeks, it is named after the botanist Robert Brown, who in 1827 first described the motion in detail. He demonstrated that it was not caused by some living organism, but was never able to determine its cause. While there were suspicions that the motion was caused by the collision of atoms against the particles, it wasn't confirmed until Einstein's 1905 paper "Investigations on the theory of Brownian Movement." He obtained a relation

between the macroscopic diffusion constant D and the atomic properties of matter. The relation is

$$D = \frac{RT}{N_a 6\pi\eta a} = \frac{k_B T}{6\pi\eta a}$$

Where R is the gas constant, N_a = 6.023×10^{23}/mole is Avogadro's number, T is the temperature, η is the viscosity of the liquid and a is the radius of the Brownian particle. Also kB = R/NA is Boltzmann's constant.

The theory of Brownian motion is perhaps the simplest approximate way to treat the dynamics of non-equilibrium systems. The fundamental equation is called the Langevin equation; it contain both frictional forces and random forces. The fluctuation-dissipation theorem relates these forces to each other. The random motion of a small particle (about one micron in diameter) immersed in a fluid with the same density as the particle is called Brownian motion.

Although it's now common knowledge that things are made up of atoms, the idea was long seen as controversial. In the early 1800s John Dalton proposed that matter consists of indestructible spherical particles known as atoms, and that these atoms came in various types called elements. Dalton was mainly trying to address the fact that chemical reactions between different types of materials (elements) seemed to occur in particular ratios. The atomic model explained this process well, but required atoms to be so extraordinarily tiny that we had no hope of observing them. By the late 1800s Ludwig Boltzmann had expanded the idea into a kinetic theory of gases, in which he proposed that the properties of a gas, such as its temperature and pressure, were due to the the motion and interactions of atoms and molecules. This provided a theoretical way to connect heat (thermodynamics) with the Newtonian ideas of work and energy

1.1.1 Einstein's theory

Einstein's theory of Brownian motion is the macroscopic manifestation of the microscopic. The chaotic perpetual motion of a Brownian particle is the result of its collisions with the molecules of the surrounding fluid. The Brownian particle is much bigger and heavier than the colliding molecules of the fluid. The radius a of the Brownian particle is typically 10^{-9} m < a < 5×10^{-7} m . Therefore each collision has a negligible effect, but the superposition of many small interactions produces an observable effect. The molecular collisions of a Brownian particle occur in very rapid succession and their number is tremendous. Thus a Brownian particle (e.g., colloidal gold particles of radius 50 μ) will suffer about 10^{20} collisions per second if immersed in liquid under normal conditions containing a number of molecule N of the order of the Avogadro number. This frequency is so high that the small changes in the particle's path caused by each single impact are too fine to be discerned experimentally. However, in one hundredth of a second the average imbalance, $\sqrt{N}$, will be of order 10^9, enough to make a change in the velocity of Brownian particle. In other words, the agitated motion of Brownian particles much slower than that of the atoms is the result of random and rapid collisions due to density fluctuations in the fluid and thus it is a macroscopic manifestation of the microscopic structure of matter. Time scales There are in general three vastly different time scales $\tau_s \approx 10^{-20}$s $\ll \tau_\beta \approx 10^{-3} \rightarrow$10–7 10^{-7}s $\ll \tau_r$. Here τ_s is the short atomic scale, $\tau_\beta$is the Brownian timescale for the relaxation of the particle velocity and τ_r is the relaxation time for the Brownian particle. In dense colloidal suspensions τ_r can become very long of the order of minutes or hours.

Simulation of Brownian Motion

Computer simulations of Brownian walks can be made by adding at each time-step of δt a random displacement Ar_n ,to the systematic displacement

$$v^s(x)\delta t, :$$

$$x_{n+1} = x_n + v^s(x)\delta t \ + Ar_n$$

Here r_n is a random number chosen with zero mean and independently of the random numbers at previous time-steps, and *A* is an amplitude selected so that the variance of the random part of the walk $\langle (x - x_0 - v^s(t - t_0))^2 \rangle$ grows linearly in time as $2D(t - t_0)$.Note that it is not necessary for the random numbers to have a Gaussian distribution. Note also that some standard random number generators do not have the required independence between adjacent numbers. As the commonly available random numbers are uniformly distributed on the interval [-0.5, 0.5], we assume that they have a variance $\langle r_n^2 \rangle = \frac{1}{12}$. It follows immediately that the amplitude of the random displacements is then given by,

$$A = (24\ D\ \delta t)^{0.5}.$$

Figure 1 shows fifteen such simulated random walks *x(t),* starting at $t = 0$ from x = 0, with no systematic velocity $v^s(x) = 0$ and with unit diffusivity $D = 1$. Five of the random walks have a time-step $\delta t = 10^{-2}$, five have $\delta t = 10^{-3}$ and five $\delta t = 10^{-4}$,viewed on an $O(1)$ time-scale, the random behavior of the walks with the different time-steps is indistinguishable. Moreover the excursions grow in time like the solid curves $\pm(2Dt)^{\frac{1}{2}}$.

While the above forward time-stepping scheme is the simplest algorithm, higher order schemes offer no improvements in accuracy because the changing random number creates a discontinuous velocity and the higher-order schemes require that the velocity and several of its derivatives be continuous before producing greater accuracy.

Program:-

```
program random_motion
real::x,t,dt,xtheo,x2,x1,s
integer::i,j
call random_seed()
open(1,file='data0.001.dat',status='unknown')
open(2,file='data0.002.dat',status='unknown')
open(3,file='data0.003.dat',status='unknown')
open(4,file='data0.004.dat',status='unknown')
```

```
open(5,file='data0.005.dat',status='unknown')
do j=1,5
t=0;x=0;dt=0.001;xtheo=0;x2=0
do i=1,10000
    write(j,*)t,x,xtheo,x2
    call random_number(rf)
    rf=rf-0.5
    x1=x
    t=t+dt
    x=x+rf*sqrt(24*dt)
    s=x1-x
    x2=s*s
    xtheo=(2*dt)
    enddo
    enddo
end program
```

Graph:-

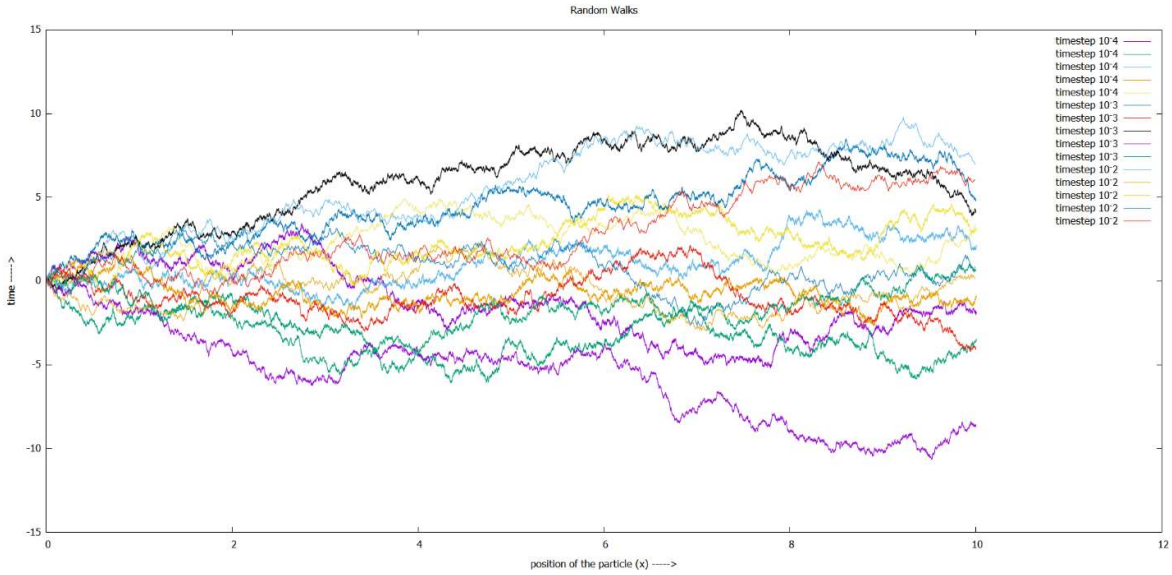


Fig. - Random walks. Fifteen simulated diffusion random walks *x(t),* starting at t = 0 from x = 0, with no systematic velocity $v^s = 0$ and with unit diffusivity D = 1. Five of the random walks have a time-step $\delta t = 10^{-4}$,five have $\delta t = 10^{-3}$ and five $\delta t = 10^{-2}$

Now we move on to define the Langevin equation, which defines the motion of a Brownian particle.

However before defining Langevin and Fokker Planck (which will be eventually derived from the Langevin equation and is a partial differential equation defining the motion of a Brownian particle)equation, we try and define a few essential terms used.

1.1.2 Markov Process

A random process whose future probabilities are determined by its most recent values is called a Markov process. A stochastic process $x(t)$ is called Markov if for every n and $t_1 < t_2 \ldots < t_n$, we have

$$P\left(x\left(t_n\right) \leq x_n \mid x\left(t_{n-1}\right), \ldots, x\left(t_1\right)\right) = P\left(x\left(t_n\right) \leq x_n \mid x\left(t_{n-1}\right)\right).$$

This is equivalent to

$$P\left(x\left(t_n\right) \leq x_n \mid x(t) \text{ for all } t \leq t_{n-1}\right) = P\left(x\left(t_n\right) \leq x_n \mid x\left(t_{n-1}\right)\right)$$

1.1.3 Stochastic process

In probability theory and related fields, a stochastic or random process is a mathematical object usually defined as a collection of random variables. Historically, the random variables were associated with or indexed by a set of numbers, usually viewed as points in time, giving the interpretation of a stochastic process representing numerical values of some system randomly changing over time, such as the growth of a bacterial population, an electrical current fluctuating due to thermal noise, or the movement of a gas molecule. Stochastic processes are widely used as mathematical models of systems and phenomena that appear to vary in a

random manner. The term random function is also used to refer to a stochastic or random process, because a stochastic process can also be interpreted as a random element in a function space.

1.2. Langevin equation

The Langevin equation is the Master Equation which is used to describe the time evolution of a brownian system that can be modelled as being in a probabilistic combination of states at any given time and the switching between states is determined by a transition rate matrix

If a small particle of mass m is immersed in a fluid, a friction force will act on the particle. The simplest expression for such a friction or damping force is given by Stoke's law,

$$F_c = -\alpha v \qquad (1.1)$$

Therefore the equation of motion for the particle in the absence of additional forces reads,

$$m\dot{v} + \alpha v = 0 \qquad (1.2)$$

or

$$\dot{v} + \gamma v = 0; \qquad \gamma = \frac{\alpha}{m} = \frac{1}{\tau} \qquad (1.3)$$

Thus an initial velocity $v(0)$ decreases to zero with the relaxation time $\tau = \frac{1}{\gamma}$ according to

$$v(t) = v(0)e^{-\frac{t}{\tau}} = v(0)e^{-\gamma t} \qquad (1.4)$$

The physics behind the friction is that the molecules of the fluid collide with the particle. The momentum of the particle is transferred to the molecules of the fluid and the velocity of the particle therefore decreases to zero. The differential equation (1.3) is a deterministic equation, i.e., the velocity $v(t)$ at time t is completely determined by its initial value according to (1.4).

For the sake of simplicity we shall treat the problem of Brownian motion in one dimension. We consider a particle of mass m whose center of mass co-ordinate at time t is given by x(t) and whose corresponding velocity is v = dx/dt.

This particle is immersed in a liquid at the absolute temperature T. it would be a complex task to describe in detail the interaction of center of mass coordinate x with all the many degrees of freedom other than x. These other degrees of freedom can be regarded as constituting a heat reservoir at some temperature T and their interaction with x can be lumped into some net fluctuating force $F_t(t)$ effective in determining the time dependence of x. In addition, the particle may also interact with some external systems, such as gravity or electromagnetic fields, through a force denoted by F(x,t) . The velocity v of the particle may be different from its mean value in equilibrium.

From newton's 2nd law of motion, the motion of the center of mass coordinate x is given by,

$$m\frac{dv}{dt} = F(x,t) + F_t(t) \qquad (1.5)$$

Here very little is known about the fluctuating force $F_t(t)$. Basically $F_t(t)$ must depend on the positions of very many atoms which are in constant motion. Thus $F_t(t)$ is some rapidly fluctuating function of the time t and varies in a highly irregular fashion.

Equation (1) holds for each member of the ensemble and since $F_t(t)$ is rapidly fluctuating function of time , so it follows from equation that v also fluctuates in time . The time dependence of v may also exhibit a more slowly varying trend. One can focus attention on the ensemble average $\bar{v}$ of the velocity, which is a much more slowly varying function of the time than v itself, where

$$v = \underline{v} + v' \qquad (1.6)$$

Where v' is rapidly fluctuating part of v and whose mean vanishes i.e.

$$< v' > = 0$$

The slowly variying part $\underline{v}$ is important because it is of primary significance in determining the behavior of the particle over long period of time. To check its time dependence we have to integrate equation (1) over some time interval τ which is small on a macroscopic scale, which gives the result

$$m[v(t+\tau) - v(t)] = F(x,t)\tau + \int_t^{t+\tau} F_t(t')\,dt' \qquad (1.7)$$

Where we have assumed that the external force F(t) is very slowly varying so that it changes by a negligible amount during the time τ . The last integral in (3) is very small since $F_t(t)$ changes sign many times in this time interval. So one might assume that any slowly varying part of v should be due to the external force F(x,t) and hence one can write ,

$$m\frac{d\underline{v}}{dt} = F(x,t) \qquad (1.8)$$

The interaction force $F_t(t)$ must actually be affected by the motion of the particle in such a way that $F_t(t)$ itself also contains a slowly varying part $\overline{F}$ tending to restore the particle to equilibrium. Hence one can write,

$$F_t = \underline{F} + F' \qquad (1.9)$$

Where F' is the rapidly fluctuating part of $F_t(t)$ whose average value vanishes. The slowly varying part $\overline{F}$ must be some function of $\overline{v}$ which is such that $\overline{F}(\overline{v}) = 0$ in equilibrium when $\overline{v} = 0$. If $\overline{v}$ is not too large , $\overline{F}(\overline{v})$ can be expanded in a power series in $\overline{v}$ whose first nonvanishing term must be linear in $\overline{v}$. Thus $\overline{F}$ must have the general form ,

$$\underline{F} = -\alpha\underline{v} \qquad (1.10)$$

Where α is some positive constant (called the ''Friction Constant") and where the minus sign indicates explicitly that the force $\overline{F}$ acts in such a direction that it tend to reduce $\overline{v}$ to zero as time increases.

In the general case the slowly varying part of equation (1) becomes then

$$m\frac{d\underline{v}}{dt} = F(x,t) + \underline{F} = F(x,t) - \alpha\underline{v} \qquad (1.11)$$

If one includes the rapidly fluctuating parts v' and F'(t) of equation (2) and (5), then the equation (1) can be rewritten as follows

$$m\frac{dv}{dt} = F(x,t) - \alpha v + F'(t) \qquad (1.12)$$

Where we have put $\alpha\overline{v} \approx \alpha v$ with negligible error since the rapidly fluctuating contribution αv' can be neglected compared to the predominant fluctuating term F'(t). The equation (8) is called the ''Langevin equation''. It differs from the original equation (1) by explicitly decomposing the force F(t) into a slowly varing part –αv and into a fluctuating part F'(t) which is purely random i.e. its mean value always vanishes irrespective of velocity or position of the particle.

In presence of an external force the equation can be written as,

$$m\dot{v} = -\alpha v + F_E(t) + F_t(t)$$

Where, $F_E(t)$ is the external force given by, $F_E(t) = -\frac{\partial V(x)}{\partial x}$

2. Calculation of mean square displacement

In absence of any external forces the equation (8) is given by,

$$m\frac{dv}{dt} = -\alpha v + F'(t) \qquad (2.1)$$

From "Stoke's law", the frictional force on a macroscopic spherical particle of radius a moving with a velocity v through a liquid of viscosity η is –αv where

$$\alpha = 6\pi\eta a \qquad (2.2)$$

Consider the situation of thermal equilibrium. Now multiplying both sides of (9) by x we can write,

$$mx\frac{d\dot{x}}{dt} = m[\frac{d}{dt}(x\dot{x}) - \dot{x}^2] = -\alpha x\dot{x} + xF'(t) \qquad (2.3)$$

Now taking ensemble average of both sides of above equation , we can write

$$m\langle\frac{d}{dt}(x\dot{x})\rangle - m\langle\dot{x}^2\rangle = -\alpha\langle x\dot{x}\rangle + \langle xF'(t)\rangle \qquad (2.4)$$

Again, the equipartition theorem yields $\frac{1}{2}m\langle\dot{x}^2\rangle = \frac{1}{2}k_BT$

As mean value of the fluctuating force F'(t) always vanishes irrespective of the value of the v or x. Hence $\langle xF'\rangle = \langle x\rangle\langle F'\rangle = 0$. So from equation (12) we can write,

$$m\langle\frac{d}{dt}(x\dot{x})\rangle = m\frac{d}{dt}(x\dot{x}) = k_BT - \alpha(x\dot{x}) \qquad (2.5)$$

On integration on may obtain,

$$(x\dot{x}) = Ce^{-\gamma t} + \frac{k_BT}{\alpha} \qquad (2.6)$$

Where C is the constant of integration. Here we have introduced the definition $\gamma = \frac{\alpha}{m}$ so that γ^{-1} denotes a characteristic time constant of the system.

Assuming that each particle in the ensemble starts out at t = 0 at the position x = 0, so that x measures the displacement from the initial position, the constant C in equation (13) must be such that

$$0 = C + \frac{k_BT}{\alpha}$$

or,
$$C = -\frac{k_BT}{\alpha}$$

So from equation (14) we get

$$(x\dot{x}) = \frac{1}{2}\frac{d}{dt}(x^2) = \frac{k_B T}{\alpha}(1 - e^{-\gamma t}) \qquad (2.7)$$

Again integrating the equation one can get

$$\langle x^2 \rangle = \frac{2k_B T}{\alpha}[t - \gamma^{-1}(1 - e^{-\gamma t})] \qquad (2.8)$$

Now, in the high friction limit ($t >> \gamma^{-1}$, $e^{-\gamma t} \rightarrow 0$) ,the above equation becomes

$$\langle x^2 \rangle = \frac{2k_B T}{\alpha} t \qquad (2.9)$$

The particle then behaves like a diffusing particle executing a random walk so that $\langle x^2 \rangle \propto t$.

Again, the diffusion equation leads us to the relation

$$\langle x^2 \rangle = 2Dt \qquad (2.10)$$

Comparing equations (17) and (18) we get the diffusion coefficient by

$$D = \frac{k_B T}{\alpha} = \frac{k_B T}{\gamma m} \qquad (2.10.1)$$

Consider an inertialess particle moving in one dimension at position x at time *t*. Assuming that friction is linear in the velocity, a steady force $f^s(x)$ will produce a steady or systematic velocity $v^s(x) = \frac{f^s}{\alpha}$, where α is the coefficient of friction. The diffusion coefficient of the Brownian motion is given by the Stokes-Einstein relation $D=\frac{kT}{\alpha}$, *where kT* is the Boltzmann temperature.

<u>Mean Square Displacement vs Time Plot:-</u>

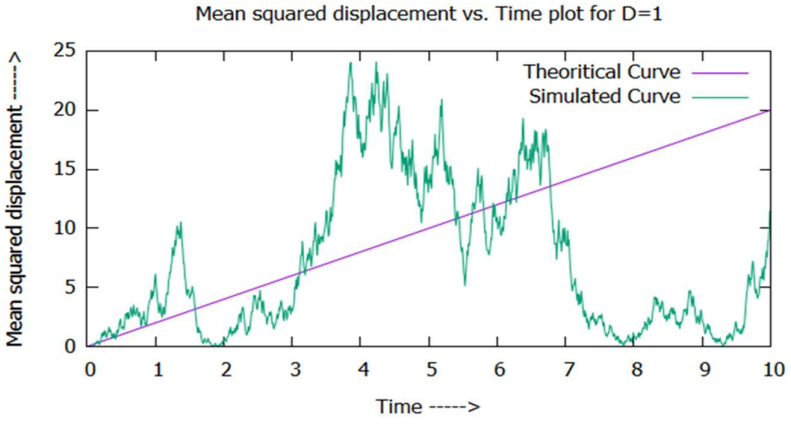


Fig-1 With time step dt=10^{-2}

Theory predicts that the squared displacement should increase in proportional to the time. The theoretical value of displacement squared is plotted with a violet line.

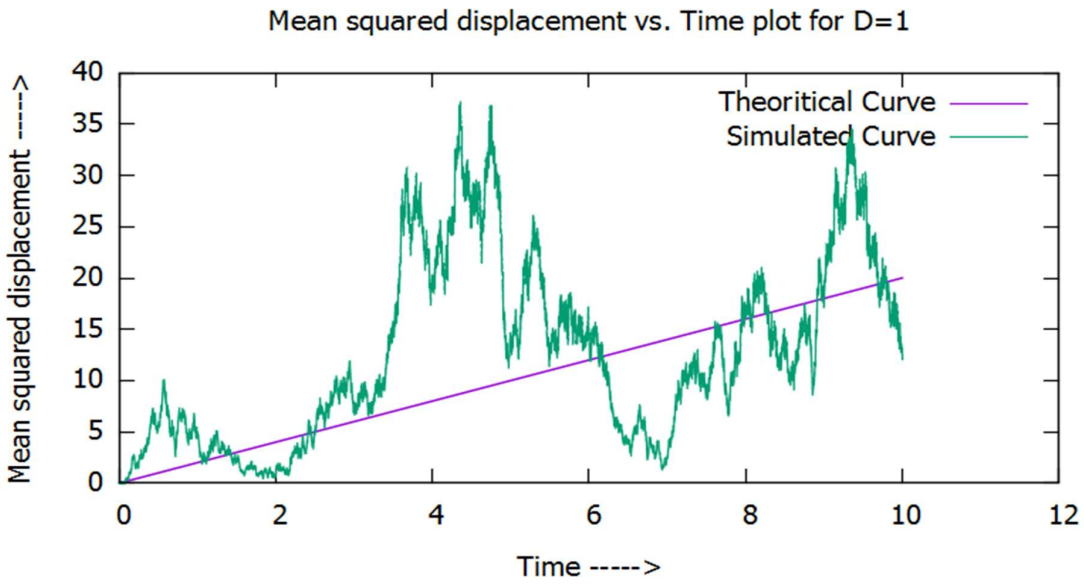


Fig 2 With time step dt=10^{-4}

So, here is an important thing to notice that if we lower the time steps the results concerning the theoretical and that from simulation matched in better accuracy.

3. Langevin to Fokker Planck: -

A Fokker Planck equation was first used by Fokker and Planck to describe the Brownian motion of particles.

If a Brownian particle of mass m is immersed in a fluid in absence of any additional forces but having damping forces then the equation of motion for the particle from equation (1.8) can be written as follows,

$$m\frac{dv}{dt} = -\alpha v(t) + F_t(t) \qquad (3.1)$$

Or,

$$\dot{v} + \gamma v = \Gamma(t) \qquad (3.2)$$

Here we have introduced the fluctuating force per unit mass

$$\Gamma(t) = F_t(t)/m \qquad (3.3)$$

Which is called Langevin force. Equation (3.2) is called a stochastic differential equation because it contains the stochastic force $\Gamma(t)$.

We assume that its average over the ensemble should be zero.

$$\langle \Gamma(t) \rangle = 0 \qquad (3.3a)$$

Because the equation of motion of the average velocity $<v(t)>$ should be given by (1.2). If we multiply two Langevin forces at different times we assume that the average value is zero for time differences $(t' - t)$ which are larger than the duration time τ_0 of a collision,

i.e.,

$$\langle \Gamma(t)\Gamma(t') \rangle = 0 \qquad for\ |t - t'| \geq \tau_0 \qquad (3.4)$$

This assumption seems to be reasonable, because the collisions of different molecules of the fluid with the small particle are approximately independent.

Usually, the duration time τ_0 of a collision is much smaller than the relaxation time $\tau = \frac{1}{\gamma}$ of the velocity of the small particle. We may therefore take the limit $\tau_0 \to 0$ as a reasonable approximation, giving

$$\langle \Gamma(t)\Gamma(t') \rangle = q\delta(t - t') \qquad (3.5)$$

The δ function appears because otherwise the average energy of the small particle cannot be finite as it should be according to the equipartition law (1.5). Where it is furthermore shown that the noise strength q of the Langevin force is then given by

$$q = \frac{2\gamma kT}{m} \qquad (3.6)$$

A noise force with the δ correlation (1.11) is called white noise, because the spectral distribution which is given by the Fourier transform of (1.11) is then

independent of the frequency ω. If the stochastic forces $\Gamma(t)$ are not δ correlated, i.e., if the spectral density depends on the frequency, one uses the term colored noise.

We now want to solve equation (3.2) for the initial condition that at time $t = 0$ the stochastic variable v has the sharp value V_0. For this initial condition the solution of (3.2) reads as

$$v(t) = v_0 + \int_0^t e^{-\gamma(t-t')}\Gamma(t')dt' \tag{3.7}$$

By using (3.2) we obtain for the correlation function of the velocity as

$$\langle v(t_1)v(t_2)\rangle = v_0^2 e^{-\gamma(t_1+t_2)} + \int_0^{t_1}\int_0^{t_2} e^{-\gamma(t_1+t_2-t_1'-t_2')} q\delta(t_1'-t_2')dt_1'dt_2' \tag{3.8}$$

To calculate the double integral, we integrate over t_2' first. The integration over t_1' then runs only from 0 to t_2 or t_1 whatever is less (Fig. 3.1). We therefore have the 2nd integral as

$$\int_0^{t_1}\int_0^{t_2} e^{-\gamma(t_1+t_2-t_1'-t_2')} q\delta(t_1'-t_2')dt_1'dt_2' = q\int_0^{\min(t_1,t_2)} e^{-\gamma(t_1+t_2-2t_1')}\,dt_1'$$
$$= \frac{q}{2\gamma}(e^{-\gamma|t_1-t_2|} - e^{-\gamma(t_1+t_2)})$$

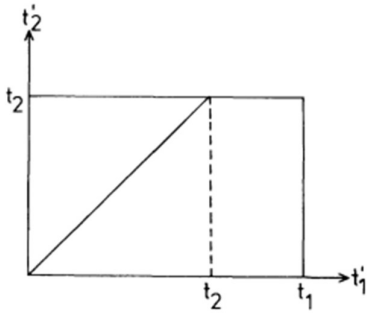


Fig. 3.1. Region of integration of the integral in (3.8) for $t_1 \geq t_2$. The integrand is different from zero only on the line $t'_1 = t'_2$

It is easily seen that (3.8) does not change by interchanging t_1 and t_2. Thus the final result for the velocity correlation function is given by

$$\langle v(t_1)v(t_2)\rangle = v_0^2 e^{-\gamma(t_1+t_2)} + \frac{q}{2\gamma}(e^{-\gamma|t_1-t_2|} - e^{-\gamma(t_1+t_2)}) \tag{3.9}$$

For large t_1 and t_2, i.e., $\gamma t_1 \gg 1$, $\gamma t_2 \gg 1$, the velocity correlation function is independent of the initial velocity v_0 and is only a function of the time difference $(t_1 - t_2)$,

i.e., $$\langle v(t_1)v(t_2)\rangle = \frac{q}{2\gamma} e^{-\gamma|t_1-t_2|} \qquad (3.10)$$

In the stationary state the average energy of the Brownian particle is therefore given by,

$$\langle E\rangle = \frac{1}{2} m\langle [v(t)]^2\rangle = \frac{1}{2} m \frac{q}{2\gamma} \qquad (3.11)$$

As mentioned earlier, the constant q is determined so that the average energy is given according to the equipartition law of classical statistical mechanics by

$$\langle E\rangle = \frac{1}{2} kT \qquad (3.12)$$

Hence we obtain for the constant q in (3.2)

$$q = \frac{2\gamma kT}{m}. \qquad (3.13)$$

3.1 One Dimensional Fokker planck equation

The general form of Fokker planck equation for one variable x has the following form

$$\frac{\partial P(x,t)}{\partial t} = \left[-\frac{\partial}{\partial x} D^{(1)}(x) + \frac{\partial^2}{\partial x^2} D^{(2)}(x)\right] P(x,t) \qquad (3.1.1)$$

In above equation $D^{(2)}(x) > 0$ is called the diffusion coefficient and $D^{(1)}(x)$ is the drift coefficient. The drift and diffusion coefficients may also depend on time. Above equation is seen to be a special Fokker-Planck equation where the drift coefficient is linear and the diffusion coefficient is constant. Equation (3.1.1) is an equation of motion for the distribution function *W(x, t).* Mathematically, it is a linear second-order partial differential equation of parabolic type. Roughly speaking, it is a diffusion equation with an additional first-order derivative with respect to *x.* In the mathematical literature, (3.1.1) is also called a forward Kolmogorov equation.

3.2 How Does a Fokker-Planck Equation Arise?

The complete solution of a macroscopic system would consist in solving all the microscopic equations of the system. Because we cannot generally do this we use instead a stochastic description, i.e., we describe the system by macroscopic variables which fluctuate in a stochastic way. The Fokker-Planck equation is just an equation of motion for the distribution function of fluctuating macroscopic variables. For a deterministic treatment we neglect the fluctuations of the macroscopic variables, i.e we neglect the diffusion term from the Fokker Planck equation,

$$\frac{\partial P(x,t|x',t')}{\partial t} = -\frac{\partial}{\partial x}\{D^{(1)}P(x,t|x',t')\} + \frac{\partial^2}{\partial x^2}\{D^{(2)}P(x,t|x',t')\} \quad (3.2.1)$$

Equation (3.1.2) is then equivalent to the differential equation

$$\frac{dx}{dt} = \dot{x} = D^{(1)}(x) \quad (3.2.2)$$

Table 1.1 gives a schematic representation of the following three stages of treating a system. A rigorous derivation of stochastic treatment should start with microscopic description. The deterministic treatment should then follow from the stochastic treatment by neglecting the fluctuations, as indicated by the big arrows. The drift and diffusion coefficients $D^{(1)}(x)$ and $D^{(2)}(x)$ especially should be derived rigorously from the microscopic equations. Such a rigorous derivation may be very complicated or even impossible. In this case, one may start with the deterministic equation and use heuristic arguments to obtain the stochastic description, as indicated by the small arrow in Table 1.1. In the heuristic

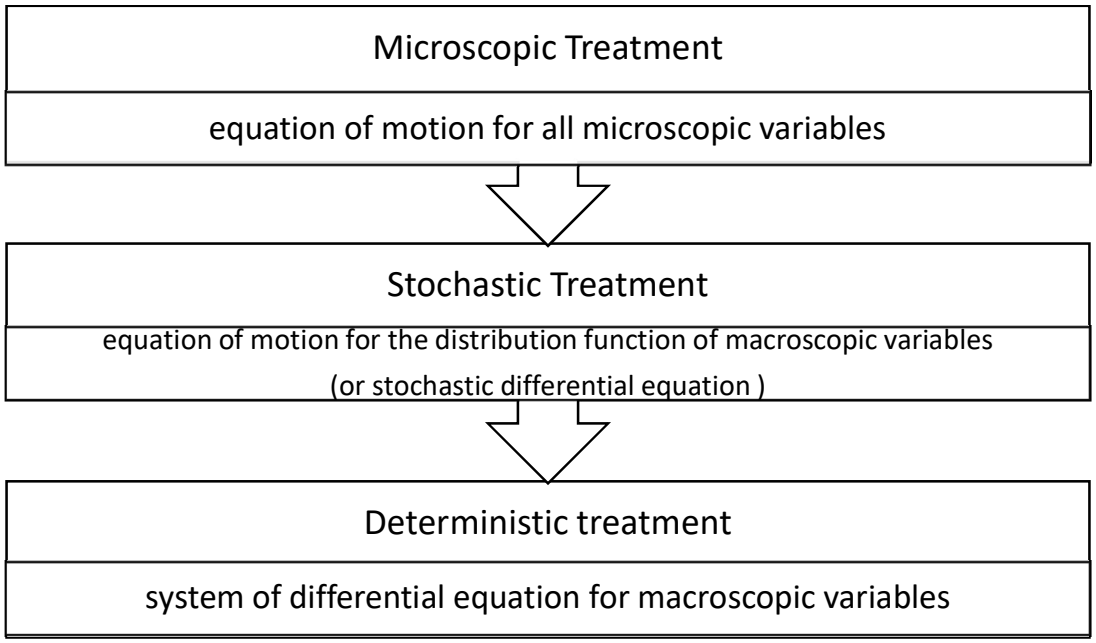


Table : Three stages of treating a system

treatment one usually adds some Langevin forces to the deterministic equation (3.2.2) and thus obtains a stochastic differential equation which is equivalent (for properly chosen Langevin forces) to a Fokker-Planck equation. The noise strength may then be determined by some other arguments, for example by use of the equipartition theorem. We thus obtain the Fokker-Planck equation (3.2.1) for Brownian motion of a particle.

The Fokker-Planck equation is of course not the only equation of motion for the distribution function. Other equations like the Boltzmann equation and master equation are discussed shortly below. The Fokker-Planck equation is one of the simplest equations for continuous macroscopic variables. It usually appears for variables describing a macroscopic but small subsystem, like the position and velocity for the Brownian motion of a small particle, a current in an electrical circuit, the electrical field in a laser. If the subsystem is larger the fluctuations may then usually be neglected and thus one has a deterministic equation. In those cases, however, where the deterministic equations are not stable, a stochastic description is then necessary even for large systems.

3.3 Fokker-Planck Equation

A solution to the one-dimensional Fokker–Planck equation, with both the drift and the diffusion term. In this case the initial condition is a Dirac delta function centred away from zero velocity. Over time the distribution widens due to random impulses.

In statistical mechanics, the Fokker–Planck equation is a partial differential equation that describes the time evolution of the probability density function of the velocity of a particle under the influence of drag forces and random forces, as in Brownian motion. The equation can be generalized to other observables as well. It is named after Adriaan Fokker and Max Planck, and is also known as the Kolmogorov forward equation, after Andrey Kolmogorov, who independently discovered the concept in 1931.[1] When applied to particle position distributions, it is better known as the Smoluchowski equation (after Marian Smoluchowski), and in this context it is equivalent to the convection–diffusion equation. The case with zero diffusion is known in statistical mechanics as the Liouville equation. Fokker-Planck equation is obtained from Master equation through Kramers–Moyal expansion.

The first consistent microscopic derivation of the Fokker–Planck equation in the single scheme of classical and quantum mechanics was performed by Nikolay Bogoliubov and Nikolay Krylov.

The Smoluchowski equation is the Fokker–Planck equation for the probability density function of the particle positions of Brownian particles

3.3 Purpose of the Fokker-Planck Equation

By solving the Fokker-Planck equation one obtains distribution functions from which any averages of macroscopic variables are obtained by integration. Since the application of the Fokker-Planck equation is not restricted to systems near thermal equilibrium, we may as well apply it to systems far from thermal equilibrium, for instance, the laser. The statistics of laser light may very well be

treated by a Fokker-Planck equation. An ion in a superionic conductor under the influence of an additional strong external field would also be a system far from thermal equilibrium, a simple model of which can be treated by a Fokker-Planck equation. The Fokker-Planck equation not only describes stationary properties, but also the dynamics of systems, if the appropriate time-dependent solution is used.

4.Kramers-moyal expansion :-

In stochastic processes, Kramers–Moyal expansion refers to a Taylor series expansion of the Master equation, named after Hans Kramers and José Enrique Moyal. This expansion transforms the integro differential Master equation to a partial differential equation.

The definition of the transition probability that the probability density $W(x, t+\tau)$ at time $t+\tau$ and the probability density $W(x,t)$ at time t are connected by ($\tau \geq 0$)

$$W(x, t+\tau) = \int P(x, t+\tau|x', t)W(x', t)dx' \ . \ (4.1)$$

To derive an expression for the differential $\frac{\partial W(x,t)}{\partial t}$, we must know the transition probability $P(x, t+\tau|x', t)$ for small τ. We first assume that we know all the moments ($n \geq 1$)

$$M_n(x', t, \tau) = \langle [x(t+\tau) - x(t)]^n \rangle|_{x(t)=x'} = \int (x - x')^n P(x, t+\tau|x', t)dx \quad (4.2)$$

where,

$$D^{(n)}(x, t) = \frac{1}{n!} lim_{\tau \to 0} \frac{1}{\tau} \langle [x(t+\tau) - x]^n \rangle|_{x(t)=x} \Big|_{x(t)=x'}$$

means that at time t the random variable has the sharp value x'. We now derive a general expansion of the transition probability in following way, *starting* from the identity

$$P(x,t+\tau|x',t) = \left[1+\sum_{n=1}^{\infty}\frac{1}{n!}\left(-\frac{\partial}{\partial x}\right)^n M_n(x,t,\tau)\right]\delta(x-x') \quad (4.3)$$

And using the formal Taylor series expansion of the δ function in the form

$$\begin{aligned}\delta(y-x) &= \delta(x'-x+y-x') \\ &= \sum_{n=0}^{\infty}\frac{(y-x')^n}{n!}\left(\frac{\partial}{\partial x'}\right)^n \delta(x'-x) \\ &= \sum_{n=0}^{\infty}\frac{(y-x')^n}{n!}\left(-\frac{\partial}{\partial x}\right)^n \delta(x'-x) \qquad (4.4)\end{aligned}$$

And $$\delta(x-x')f(x') = \delta(x-x')f(x) \qquad (4.5a)$$

we get,

$$\begin{aligned}P(x,t+\tau|x',t) &= \sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{\partial}{\partial x}\right)^n \int (y-x')^n P(x,t+\tau|x',t)dy\,\delta(x'-x) \\ &= \left[1+\sum_{n=1}^{\infty}\frac{1}{n!}\left(-\frac{\partial}{\partial x}\right)^n M_n(x',t,\tau)\right]\delta(x'-x) \\ &= \left[1+\sum_{n=1}^{\infty}\frac{1}{n!}\left(-\frac{\partial}{\partial x}\right)^n M_n(x,t,\tau)\right]\delta(x'-x) \qquad (4.5)\end{aligned}$$

In deriving the second line of (4.5) we use (4.2) and for the last line $\delta(x-x') = \delta(x'-x)$ and (4.5a).

Inserting (4.5) into (4.1) leads to,

$$\begin{aligned}W(x,t+\tau) - W(x,t) &= \frac{\partial W(x,t)}{\partial t}\tau + O(\tau^2) \\ &= \sum_{n=1}^{\infty}\frac{1}{n!}\left(-\frac{\partial}{\partial x}\right)^n \int W(x',t)\,M_n(x,t,\tau)\,\delta(x'-x)dx' \\ &= \sum_{n=1}^{\infty}\frac{1}{n!}\left(-\frac{\partial}{\partial x}\right)^n W'(x,t)M_n(x,t,\tau) \qquad (4.6)\end{aligned}$$

we now assume that the moments M_n can be expanded into a Taylor series with respect to τ ($n \geq 1$)

$$\frac{M_n(x,t,\tau)}{n!} = D^{(n)}(x,t)\tau + O(\tau^2) \qquad (4.7)$$

The term with τ^0 must vanish, because for $\tau = 0$ the transition probability P has the initial value

$$P(x,t|x',t) = \delta(x-x') \qquad (4.8)$$

which leads to vanishing moments (4.2). By taking into account only the linear terms in τ we thus have

$$\frac{\partial W(x,t)}{\partial t} == \sum_{n=1}^{\infty}\left(-\frac{\partial}{\partial x}\right)^n D^{(n)}(x,t)W(x,t) = L_{KM}W(x,t) \qquad (4.9)$$

where the differential symbol acts on $D^{(n)}(x,t)$ and *W(x,* t). The Kramers-Moyal operator L_{KM} is defined by

$$L_{KM}\ (x,\ t) = \sum_{n=1}^{\infty}\left(-\frac{\partial}{\partial x}\right)^n D^{(n)}(x,t) \qquad (4.10)$$

Equation (4.9) is the Kramers-Moyal expansion. For non-Markovian processes, the conditional probability in (4.1) depends on the values of the stochastic variable *x(t')* at all earlier times *t' <t*. Hence also the moments (4.2) and their expansion coefficients $D^{(n)}$ which occur in (4.9) depend on these earlier times for non-Markovian processes. For Markov processes, $D^{(n)}$ do not depend on the values of *x(t')* at these earlier times. With respect to time *t,* (4.9) is then a differential equation of first order and the distribution function *W(x, t)* is uniquely determined by integration of (4.9) starting with the initial distribution *W(x, to) (t> to)* and for appropriate boundary conditions. Therefore we assume that the process described by the probability density *W(x,* t) is a Markov process.

The transition probability *P(x,tIx',t')* is the distribution *W(x,t)* for the special initial condition *W(x,*t') = δ(x-x'). Thus the transition probability must also obey (4.9),

i.e.,

$$\frac{\partial P(x,t|x_0,t_0)}{\partial t} = \sum_{n=1}^{\infty}\left(-\frac{\partial}{\partial x}\right)^n D^{(n)}(x,t)P(x,t|x_0,t_0) = L_{KM}P(x,t|x_0,t_0) \qquad (4.11)$$

Where the initial condition of *P* is given by (4.8) with *t* replaced by t_0.

4.1 Fokker Planck Equation in one dimension

If the Kramers-Moyal expansion (4.9) stops after the second term we get the Fokker-Planck equation given by,

$$\frac{\partial P(x,t|x',t')}{\partial t} = L_{FP}P(x,t|x',t') \qquad (4.12)$$

Where,

$$L_{FP}=-\frac{\partial}{\partial x}D^{(1)}+\frac{\partial^2}{\partial x^2}D^{(2)}$$

Thus the Fokker Planck equation in one dimension is,

$$\frac{\partial P(x,t|x',t\prime)}{\partial t}=-\frac{\partial}{\partial x}\{D^{(1)}P(x,t|x',t')\}+\frac{\partial^2}{\partial x^2}\{D^{(2)}P(x,t|x',t')\} \qquad (4.13)$$

5. Fokker planck for free diffusion

From "Stoke's law", the frictional force on a macroscopic spherical particle of radius a moving with a velocity v through a liquid of viscosity η is –αv where

$$\alpha = 6\pi\eta a \qquad (5.1)$$

Considering the physical process of Brownian motion of a particle in absence of any external forces then the equation (1.11) becomes,

$$m\frac{dv}{dt} = -\alpha v + F'(t) \qquad (5.2)$$

And $\frac{dx}{dt} = v$

For high viscous limit $\frac{dv}{dt} = 0$, so from equation (5.2) we can write

$$\frac{dx}{dt} = \frac{1}{\alpha}F'(t) = \frac{1}{\gamma m}F'(t) = \frac{1}{\gamma}\Gamma(t) \qquad (5.3)$$

Where $\Gamma(\mathrm{t}) = \frac{1}{m}F'(t)$ and $\langle\Gamma(\mathrm{t})\rangle = 0$ and $\langle\Gamma(t)\Gamma(t')\rangle = q\delta(t-t')$

Comparing with equation (A.1) (refer to appendix) with equation (5.3) we have

$$h(x,t) = 0$$

$$g(x,t) = \frac{1}{\gamma}$$

- Which is a constant so that $g'(x,t) = 0$

Thus the equation (4.13) transforms as

$$\frac{\partial P(x,t|x_0,t_0)}{\partial t} = D\frac{\partial^2}{\partial x^2}P(x,t|x_0,t_0) \qquad (5.4)$$

As , $\frac{q}{2}g^2 = \frac{2\gamma kT}{2*m} * \frac{1}{\gamma^2} = \frac{kT}{\gamma m} = D$

The equation (5.4) is known as free diffusion equation.

5.1 Solution of the free diffusion equation:

Let us consider the particle at x_0 so one can get the boundary condition for the solution is $P(x, t = 0) = \delta(x - x_0)$ and another boundary condition states that the probability must vanish at $x \longrightarrow \infty$ i.e.

$P(x \longrightarrow \infty, t) \longrightarrow 0.$

Introducing the space Fourier transform of P(x,t) and its inverse,

$$\tilde{P}(k,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} P(x,t) e^{-ikx}\, dx$$

And

$$P(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{P}(k,t) e^{ikx}\, dk$$

The diffusion equation transforms into the simple form

$$\frac{\partial \tilde{P}}{\partial t} = -k^2 D \tilde{P} \qquad (5.4a)$$

On integration we have

$$\tilde{P}(k,t) = \tilde{P}(k,t=0) e^{-k^2 Dt} \qquad (5.5)$$

From the boundary condition,

$$\tilde{P}(k,t=0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} P(x,t=0) e^{-ikx}\, dx$$

$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \delta(x - x_0) e^{-ikx}\, dx \; = \frac{1}{\sqrt{2\pi}} e^{-ikx_0}$$

So

$$,\tilde{P}(k,t) = \frac{1}{\sqrt{2\pi}} e^{-ik\ _0}\ e^{-k^2 Dt}$$

Taking the inverse transform of the solution in k-space, we finally have

$$P(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{P}(k,t) e^{ikx}\, dk$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-ikx_0}\, e^{-k^2Dt} e^{ikx}\, dk$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-(k^2Dt - i\ (x-x_0))}\, dk$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-[(k\sqrt{Dt})^2 - \frac{2ik(x-x_0)\sqrt{Dt}}{2\sqrt{Dt}} + (\frac{i(x-x_0)}{2\sqrt{Dt}})^2] + (\frac{i(x-x_0)}{2\sqrt{Dt}})^2}\, dk$$

$$= \frac{1}{2\pi} e^{-(\frac{(x-x_0)}{2\sqrt{Dt}})^2} \int_{-\infty}^{\infty} e^{-[k\sqrt{Dt} - \frac{i(x-x_0)}{2\sqrt{Dt}}]^2}\, dk$$

$$= \frac{1}{4\pi Dt} e^{-\frac{(x-x_0)^2}{4D}}$$

Now let's introduce an absorbing wall at x=0. An absorbing wall at x = 0 means that the particles are removed from the interval (−∞, 0) as soon as they first hit x = 0. This can occur for example when a chemical reaction at the wall causes molecule to be absorbed or changed to a different chemical species. Another more mathematical reason of using absorbing BC is when one is interested in looking at the first passage time of a process as we will see later. The appropriate BC for an absorbing wall at x = 0 is

P (x=0,t) = 0 ∀t (5.6)

i.e. there is a zero probability of finding particles at the wall, since they are immediately absorbed.

To satisfy the BC at x = 0 the idea consists in introducing a sink, or negative image at position $-x_0$ and extending the problem to the entire space. This gives

$$P(x,t) = \frac{1}{\sqrt{4\pi Dt}}[e^{-\frac{(x-x_0)^2}{4D}} - e^{-\frac{(x+x_0)^2}{4D}}] \qquad x \geq 0 \qquad (5.7)$$

In this case the x ≥ 0 tail of the first term which describes free diffusion is not cancelled by the second term, but rather the second term describes a further particle loss. Because of particle removal by the wall at x = 0, the total number of particles is not conserved. It is interesting to compute the number of particles at time t by using the fundamental solution

$$S(t) = \int_0^{\infty} P(x,t)\, dx$$

- Which is also known as survival probability.

So,

$$S(t) = \int_0^{\infty} P(x,t)\,dx$$

$$= \frac{1}{\sqrt{4\pi Dt}} \int_0^{\infty} [e^{-\frac{(x-x_0)^2}{4Dt}} - e^{-\frac{(x+x_0)^2}{4D}}]\,dx$$

$$= \frac{1}{\sqrt{4\pi Dt}} [\int_0^{\infty} e^{-\frac{(x-x_0)^2}{4Dt}}\,dx - \int_0^{\infty} e^{-\frac{(x+x_0)^2}{4Dt}}\,dx]$$

$$= \frac{1}{\sqrt{4\pi Dt}} [\int_0^{x_0} e^{-\frac{(x-x_0)^2}{4Dt}}\,dx + \int_{x_0}^{\infty} e^{-\frac{(x-x_0)^2}{4Dt}}\,dx$$

$$- \int_0^{x_0} e^{-\frac{(x+x_0)^2}{4Dt}}\,dx - \int_{x_0}^{\infty} e^{-\frac{(x+x_0)^2}{4D}}\,dx]$$

Let,

$(x - x_0) = z$ and $(x + x_0) = z'$

$$S(t) = \frac{1}{\sqrt{4\pi Dt}} [\int_{-x_0}^{0} e^{-\frac{z^2}{4Dt}}\,dz + \int_0^{\infty} e^{-\frac{z^2}{4D}}\,dz - \int_{x_0}^{0} e^{-\frac{z'^2}{4Dt}}\,dz' - \int_0^{\infty} e^{-\frac{z'^2}{4D}}\,dz']$$

$$S(t) = \frac{1}{\sqrt{4\pi Dt}} [\int_{-x_0}^{0} e^{-\frac{z^2}{4Dt}}\,dz - \int_{x_0}^{0} e^{-\frac{z'^2}{4D}}\,dz']$$

$$S(t) = 2 * \frac{1}{\sqrt{4\pi Dt}} \int_0^{x_0} e^{-\frac{z^2}{4D}}\,dz$$

Let,

$$\text{p} = \frac{z}{\sqrt{2Dt}}$$

So,

$$S(t) = 2 * \frac{1}{\sqrt{4\pi Dt}} * \sqrt{4Dt} \int_0^{x_{0/\sqrt{4D}}} e^{-p^2}\,dp$$

$$= \frac{2}{\sqrt{\pi}} \int_0^{x_{\frac{0}{\sqrt{4Dt}}}} e^{-p^2}\,dp$$

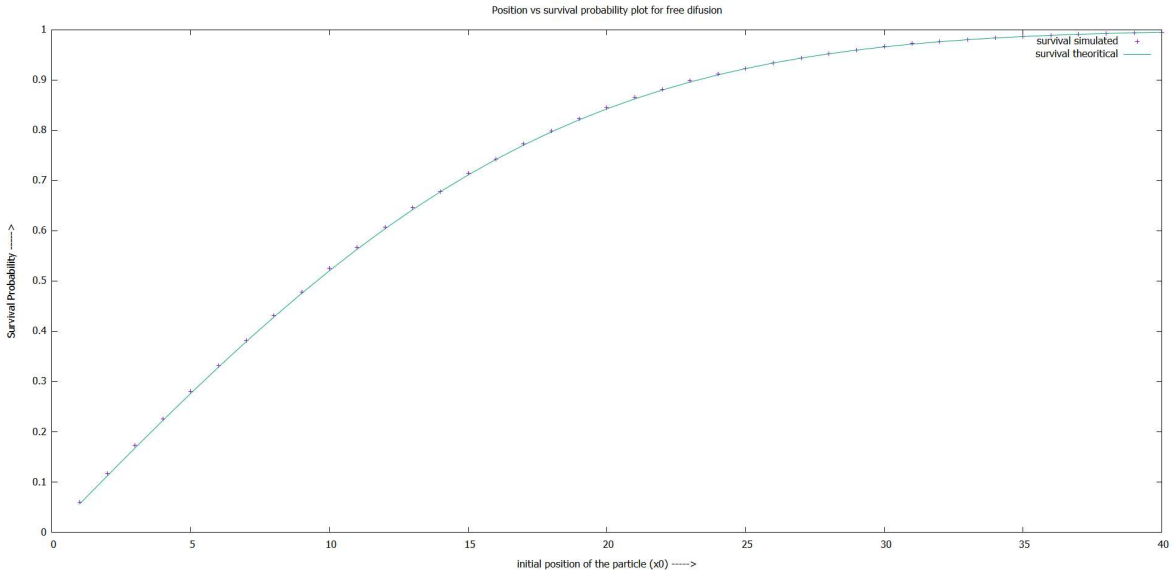
$$S(t) = erf(x_{0/\sqrt{4Dt}}) \qquad (5.8)$$

Where the error function is defined as

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, dt$$

We plotted the above survival probability (5.8) for different initial values of particle position.

Plot for survival probability in the free diffusion equation



NOTE:- The survival probability asymptotically saturates to 1. This implies that if the particle is released at very large x, it will still be absorbed at some point of time.

Program:-

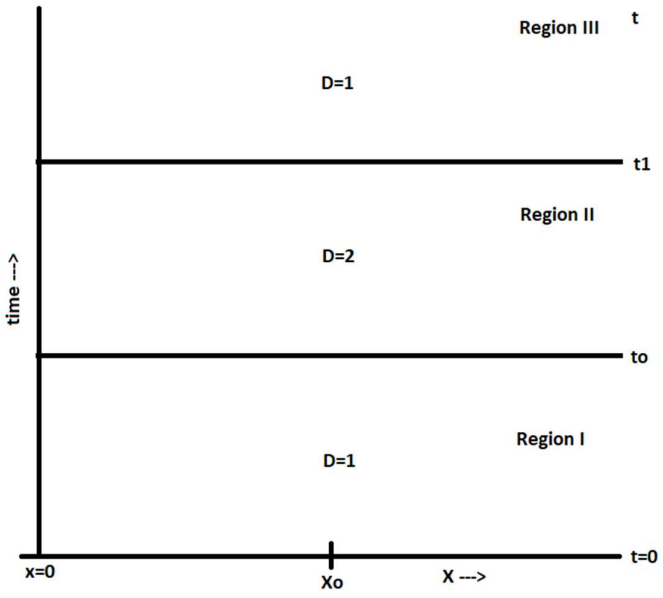
```
!program for brownian motion project
Program brownstep1_single_stage
Integer:: i,j,m,n,countsucc,k
Real:: a,dt,D,epsa,r,fptsum,survival_prob,c,fpt!fptdef1,fptdef2
real,parameter::pi=3.14159
Real,Dimension(0:10002) :: fx
```

```
dt=0.01
m=100000
n=10000
D=1.0
epsa=0.0001
open(1,file='1phase_survival1.txt',status='unknown')
write(1,*)'initial_Position   ','survival_simu   ','survival_theo'
Do k=100,4000,100
x0=k*0.01
fx(0)=x0
countsucc=0
Call random_seed()
Do i=0,m
Do j=0,n
Call random_number(r)
r=(r-0.5)
fx(j+1)=fx(j)+r*sqrt(24.0*D*dt)
If(fx(j+1)<epsa) then
countsucc=countsucc+1
exit
End if
End do
End do
a=m-countsucc
survival_prob=a/m
c=erf(x0/20)
e=(x0/(pi*100*20))*exp(-(x0*x0)/400)
```

```
write(1,*)x0,survival_prob,c
end do
close(1)
End program brownstep1_single_stage
```

5.2 Motion Of A Brownian Particle In a Three Phase System In Presence Of An Absorbing Wall

Now we are extending this one phase simple free diffusion case of a Brownian particle to the three phase free diffusion problem as shown in figure and we are interested in determining the survival probability in this case.



In absence of any external forces the physical process of Brownian motion of a particle can be represented by the Fokker planck equation as given by equation (5.4). But having three different regions with different diffusivity constants (D_1, D_2, D_3) there present three Fokker planck equation with three different probabilities.

The corresponding Fokker planck equation are,

1. $\frac{\partial P_1}{\partial t} = D_1 \frac{\partial^2 P_1}{\partial x^2}$ (5.9)
2. $\frac{\partial P_2}{\partial t} = D_2 \frac{\partial^2 P_2}{\partial x^2}$ (5.10)
3. $\frac{\partial P_3}{\partial t} = D_3 \frac{\partial^2 P_3}{\partial x^2}$ (5.11)

Let us consider the particle at x_0 so one can get the boundary condition for the solution is $P_1(x, t = 0) = \delta(x - x_0)$ and another boundary condition states

that the probability must vanish at $x \longrightarrow \infty$ i.e. P($x \longrightarrow \infty, t$) $\longrightarrow 0$. And let's introduce an absorbing wall at x=0. The appropriate BC for an absorbing wall at x = 0 is P(x=0,t) = 0 ∀t i.e. there is a zero probability of finding particles at the wall, since they are immediately absorbed.

So the boundary conditions that arises are given by,

For Region 1:
$$P_1(x=0,t)=0$$
$$P_1(x\to\infty,t)=0 \qquad (5.12)$$
$$P_1(x,t=0)=\delta(x-x_0)$$

For Region 2:
$$P_2(x=0,t)=0$$
$$P_2(x\to\infty,t)=0 \qquad (5.13)$$
$$P_2(x,t=t_0)=P_1(x,t=t_0)$$

For Region 3:
$$P_3(x=0,t)=0$$
$$P_3(x\to\infty,t)=0 \qquad (5.14)$$
$$P_3(x,t=t_1)=P_3(x,t=t_1)$$

As the boundary condition and corresponding Fokker planck equation of region I are similar to the problem of free diffusion in one phase, the solution will be same as equation (5.7) , where D being replaced by D_1. Thus the general solution of region I is given by,

$$P_1(x,t)=\frac{1}{\sqrt{4\pi D_1 t}}\left[e^{\frac{-(x-x_0)^2}{4D_1 t}}-e^{\frac{-(x+x_0)^2}{4D_1 t}}\right] \qquad (5.15)$$

For the second region,

The diffusion equation is,

$$\frac{\partial P_2}{\partial t}=D_2\frac{\partial^2 P_2}{\partial x^2}$$

As the above Fokker planck equation is the same in form of one phase free diffusion case, after fourier decomposition one can write similar to equation (5.4a),

$$\frac{\partial \widetilde{P_2}(k,t)}{\partial t}=-k^2 D_2 \widetilde{P_2}(k,t)$$

On integration we get,

$$\widetilde{P_2}(k,t)=\widetilde{P_2}(k,t=t_0)e^{-k^2 D(t-t_0)} \qquad (5.16)$$

From the boundary condition,

$$P_2(x,t_0) = P_1(x,t_0) = \frac{1}{\sqrt{4\pi D_1 t_0}}\left[e^{\frac{-(x-x_0)^2}{4D_1t_0}} - e^{\frac{-(x+x_0)^2}{4D_1t_0}}\right]$$

Thus, after Fourier decomposition $P_2(x,t)\ at\ t = t_0$ can be written as,

$$\widetilde{P_2}(k,t=t_0) = \frac{1}{\sqrt{2\pi}}\int P_2(x,t_0)e^{ikx}\,dx$$

$$= \frac{1}{\sqrt{2\pi}}\int \frac{1}{\sqrt{4\pi D_1 t_0}}\left\{e^{\frac{-(x-x_0)^2}{4D_1t_0}} - e^{\frac{-(x+x_0)^2}{4D_1t_0}}\right\}e^{ikx}\,dx$$

$$= \frac{1}{\sqrt{8\pi^2 D_1 t_0}}\int \left\{e^{-\left[\frac{(x+x_0)^2}{4D_1t_0} - ikx\right]} - e^{-\left[\frac{(x+x_0)^2}{4D_1t_0} - ikx\right]}\right\}dx$$

$$= \frac{1}{\sqrt{8\pi^2 D_1 t_0}}\int e^{-\left[\left\{\frac{(x-x_0)^2}{4D_1t_0} - \frac{2(x-x_0)}{2\sqrt{D_1t_0}}\cdot ik\sqrt{D_1t_0} + \left(ik\sqrt{D_1t_0}\right)^2\right\} + \left(ik\sqrt{D_1t_0}\right)^2 + ikx_0\right]}dx \quad -$$

$$\frac{1}{\sqrt{8\pi^2 D_1 t_0}}\int_{-\infty}^{\infty} e^{-\left[\left\{\frac{(x+x_0)^2}{4D_1t_0} - \frac{2(x+x_0)}{2\sqrt{D_1t_0}}\cdot ik\sqrt{D_1t_0} + (ik\sqrt{D_1t_0})^2\right\} + (ik\sqrt{D_1t_0})^2 - ikx_0\right]}dx$$

$$= \frac{1}{\sqrt{8\pi^2 D_1 t_0}}e^{-k^2D_1t_0 + ikx_0}\int e^{-\left[\frac{(x-x_0)}{2\sqrt{D_1t_0}} - ik\sqrt{D_1t_0}\right]^2}dx -$$

$$\frac{1}{\sqrt{8\pi^2 D_1 t_0}}e^{-k^2D_1t_0 - ikx_0}\int e^{-\left[\frac{(x+x_0)}{2\sqrt{D_1t_0}} - ik\sqrt{D_1t_0}\right]^2}dx$$

Now, let,

$$\frac{x-x_0}{2\sqrt{D_1t_0}} - ik\sqrt{D_1t_0} = z$$

Thus,

$$dx = 2\sqrt{D_1t_0}\,dz$$

$$\widetilde{P_2}(k,t=t_0) = \frac{1}{\sqrt{8\pi^2 D_1 t}}e^{-k^2D_1t_0 + ikx_0}2\sqrt{D_1t_0}\int_{-\infty}^{\infty} e^{-z^2}\,dz$$

$$-\frac{1}{\sqrt{8\pi^2 D_1 t}}e^{-k^2D_1t_0 - ikx_0}2\sqrt{D_1t_0}\int_{-\infty}^{\infty} e^{-z^2}\,dz$$

$$= \frac{1}{\sqrt{2\pi}}\left[e^{-k^2D_1t_0 + ikx_0} - e^{-k^2D_1t_0 - ikx_0}\right] \qquad (5.17)$$

Now, from equation (5.16)

$$\tilde{P}_2(k,t) = \tilde{P}_2(k,t_0)e^{-k^2D_2(t-t_0)}$$

$$= \frac{1}{\sqrt{2\pi}}[e^{-k^2 D_1 t_0 + ikx_0} e^{-k^2 D_2 (t-t_0)} - e^{-k^2 D_1 t_0 - ikx_0} e^{-k^2 D_2 (t-t_0)}]$$

Applying inverse Fourier transformation, we get,

$$P_2(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{P}_2(k,t) e^{-ik} \; dk$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} [e^{-k^2 D_1 t_0 + ikx_0 - k^2 D_2 (t-t_0)} - e^{-k^2 D_1 t_0 - ikx_0 - k^2 D_2 (t-t_0)}] e^{-ikx} \, dk$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} [e^{-k^2 \{(D_1 - D_2)t_0 + D_2 t\} - ik(x - x_0)} - e^{-k^2 \{(D_1 - D_2)t_0 + D_2 t\} - ik(x + x_0)}] \, dk$$

$$= \frac{1}{2\pi} \int e^{-[\{(k\sqrt{\{(D_1 - D_2)t_0 + D_2 t\}})^2 + \frac{2k\sqrt{\{(D_1 - D_2)t_0 + D_2 t\}}\, i(x - x_0)}{2\sqrt{\{(D_1 - D_2)t_0 + D_2 t\}}} + (\frac{i(x - x_0)}{2\sqrt{\{(D_1 - D_2)t_0 + D_2 t\}}})^2\} + (\frac{i(x - x_0)}{2\sqrt{\{(D_1 - D_2)t_0 + D_2 t\}}})^2]} \, dk$$

$$- \frac{1}{2\pi} \int e^{-[\{(k\sqrt{\{(D_1 - D_2)t_0 + D_2 t\}})^2 + \frac{2k\sqrt{\{(D_1 - D_2)t_0 + D_2 t\}}\, i(x + x_0)}{2\sqrt{\{(D_1 - D_2)t_0 + D_2 t\}}} + (\frac{i(x + x_0)}{2\sqrt{\{(D_1 - D_2)t_0 + D_2 t\}}})^2\} + (\frac{i(x + x_0)}{2\sqrt{\{(D_1 - D_2)t_0 + D_2 t\}}})^2]} \, dk$$

$$= \frac{1}{2\pi} e^{-\frac{(x - x_0)^2}{4\{(D_1 - D_2)t_0 + D_2 t\}}} \int e^{-\{(k\sqrt{\{(D_1 - D_2)t_0 + D_2 t\}}) + \frac{i(x - x_0)}{2\sqrt{\{(D_1 - D_2)t_0 + D_2 t\}}}\}^2} \, dk$$

$$- \frac{1}{2\pi} e^{-\frac{(x + x_0)^2}{4\{(D_1 - D_2)t_0 + D_2 t\}}} \int e^{-\{(k\sqrt{\{(D_1 - D_2)t_0 + D_2 t\}}) + \frac{i(x + x_0)}{2\sqrt{\{(D_1 - D_2)t_0 + D_2 t\}}}\}^2} \, dk$$

$$= \frac{1}{\sqrt{4\pi(D_1 - D_2)t_0 + D_2 t}} [exp[-\frac{(x - x_0)^2}{4\{(D_1 - D_2)t_0 + D_2 t\}}] - exp[-\frac{(x + x_0)^2}{4\{(D_1 - D_2)t_0 + D_2 t\}}]]$$

For the third region ,

The diffusion equation for region 3 is given by,

$$\frac{\partial P_3}{\partial t} = D_3 \frac{\partial^2 P_3}{\partial x^2}$$

As the above Fokker planck equation is the same in form of one phase free diffusion case, after fourier decomposition one can write similar to equation (x.x),

$$\frac{\partial \widetilde{P_3}(k,t)}{\partial t} = -k^2 D_3 \widetilde{P_3}(k,t) \qquad (5.18)$$

On integration we get,

$$\widetilde{P_3}(k,t) = \widetilde{P_3}(k, t = t_1) e^{-k^2 D_3 (t - t_1)} \qquad (5.19)$$

Here the imposing boundary condition is

$$P_3(x,t_1) = P_2(x,t_1) = \frac{1}{\sqrt{4\pi(D_1-D_2)t_0+D_2t_1}}\left[exp\left[\frac{-(x-x_0)^2}{4\{(D_1-D_2)t_0+D_2t_1\}}\right] - exp\left[\frac{-(x+x_0)^2}{4\{(D_1-D_2)t_0+D_2t_1\}]}\right]\right.$$

Hence from the boundary condition of $P_3(x,t)$ at $t = t_1$ can be written as,

$$\widetilde{P_3}(k,t=t_1) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} P_3(x,t_1)e^{ikx}\,dx$$

$$= \frac{1}{\sqrt{8\pi^2\{(D_1-D_2)t_0+D_2t_1\}}}\int_{-\infty}^{\infty}\left[exp\left[\frac{-(x-x_0)^2}{4\{(D_1-D_2)t_0+D_2t_1\}} + ikx\right] - exp\left[\frac{-(x+x_0)^2}{4\{(D_1-D_2)t_0+D_2t_1\}]} + ikx\right]\right]dx$$

Let,

$$4\{(D_1-D_2)t_0 + D_2t_1\} = A$$

Then,

$$\widetilde{P_3}(k,t=t_1) = \frac{1}{\pi\sqrt{2A}}\int_{-\infty}^{\infty}\left[exp\left[\frac{-(x-x_0)^2}{A} + ikx\right] - exp\left[\frac{-(x+x_0)^2}{A} + ikx\right]\right]dx$$

$$= \frac{1}{\pi\sqrt{2A}}\int_{-\infty}^{\infty} e^{-\left[\left(\frac{(x-x_0)}{\sqrt{A}}\right)^2 - 2\frac{(x-x_0)ik\sqrt{A}}{2\sqrt{A}} + \left(\frac{ik\sqrt{A}}{2}\right)^2\right] + \left(\frac{ik\sqrt{A}}{2}\right)^2 + ikx_0}\,dx$$

$$- \int_{-\infty}^{\infty} e^{-\left[\left(\frac{(x+x_0)}{\sqrt{A}}\right)^2 - 2\frac{(x+x_0)ik\sqrt{A}}{2\sqrt{A}} + \left(\frac{ik\sqrt{A}}{2}\right)^2\right] + \left(\frac{ik\sqrt{A}}{2}\right)^2 - ikx_0}\,dx$$

$$= \frac{1}{\pi\sqrt{2A}}e^{ikx_0 - \frac{k^2A}{4}}\int e^{-\left(\frac{(x-x_0)}{\sqrt{A}} - \frac{ik\sqrt{A}}{2}\right)^2} - \frac{1}{\pi\sqrt{2A}}e^{-ikx_0 - \frac{k^2A}{4}}\int e^{-\left(\frac{(x+x_0)}{\sqrt{A}} - \frac{ik\sqrt{A}}{2}\right)^2}$$

$$= \frac{1}{\sqrt{2\pi}}\left[e^{ikx_0 - \frac{k^2A}{4}} - e^{-ikx_0 - \frac{k^2A}{4}}\right]$$

$$= \frac{1}{\sqrt{2\pi}}\left[e^{ikx_0 - k^2\{(D_1-D_2)t_0+D_2t_1\}} - e^{-ikx_0 - k^2\{(D_1-D_2)t_0+D_2t_1\}}\right]$$

Now, from equation (5.19),

$$\widetilde{P_3}(k,t) = \widetilde{P_3}(k,t=t_1)e^{-k^2D_3(t-t_1)}$$

$$= \frac{1}{\sqrt{2\pi}}\left[e^{ikx_0 - k^2\{(D_1-D_2)t_0+D_2t_1\}} - e^{-ikx_0 - k^2\{(D_1-D_2)t_0+D_2t_1\}}\right]e^{-k^2D_3(t-t_1)} \qquad (5.20)$$

Again, by Inverse Fourier Transform,

$$P_3(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{P}_3(k,t)\, e^{-ikx}\, dk$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} [e^{ikx_0 - k^2\{(D_1-D_2)t_0 + D_2 t_1\}} - e^{-ikx_0 - k^2\{(D_1-D_2)t_0 + D_2 t_1\}}] e^{-k^2 D_3 (t-t_1)}\, e^{-ikx} dk$$

$$= \frac{1}{2\pi} \int_{\infty}^{\infty} [e^{-k^2[\{(D_1-D_2)t_0 + D_2 t_1\} + D_3(t-t_1)] - ik(x-x_0)} - e^{-k^2[\{(D_1-D_2)t_0 + D_2 t_1\} + D_3(t-t_1)] - ik(x+x_0)}]\, dk$$

Now let,

$$A_1 = \{(D_1 - D_2)t_0 + D_2 t_1\} + D_3(t - t_1)$$

So,

$$P_3(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} [e^{-k^2 A_1 - ik(x-x_0)} - e^{-k^2 A_1 - ik(x+x_0)}]\, dk$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-\left(\left(k\sqrt{A_1}\right)^2 + \frac{2ik(x-x_0)\sqrt{A_1}}{2\sqrt{A_1}} + \left(\frac{i(x-x_0)}{2\sqrt{A_1}}\right)^2\right) + \left(\frac{i(x-x_0)}{2\sqrt{A_1}}\right)^2} dk$$

$$- \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-((k\sqrt{A_1})^2 + \frac{2ik(x+x_0)\sqrt{A_1}}{2\sqrt{A_1}} + (\frac{i(x+x_0)}{2\sqrt{A_1}})^2) + (\frac{i(x+x_0)}{2\sqrt{A_1}})^2} dk$$

$$= \frac{1}{2\pi} e^{-\left(\frac{x-x_0}{2\sqrt{A_1}}\right)^2} \int_{-\infty}^{\infty} e^{-\left(k\sqrt{A_1} + \frac{i(x-x_0)}{2\sqrt{A_1}}\right)^2} dk$$

$$- \frac{1}{2\pi} e^{-\left(\frac{x+x_0}{2\sqrt{A_1}}\right)^2} \int_{-\infty}^{\infty} e^{-\left(k\sqrt{A_1} + \frac{i(x+x_0)}{2\sqrt{A_1}}\right)^2} dk$$

$$= \frac{1}{\sqrt{4\pi\{(D_1-D_2)t_0 + (D_2-D_3)t_1 + D_3 t\}}} [e^{-\frac{(x-x_0)^2}{4\{(D_1-D_2)t_0 + (D_2-D_3)t_1 + D_3 t\}}} - e^{-\frac{(x+x_0)^2}{4\{(D_1-D_2)t_0 + (D_2-D_3)t_1 + D_3 t\}}}] \quad (5.21)$$

So, finally, the probabilities in the three different phases for a three phase Brownian system,

Is given by,

$$P_1(x,t) = \frac{1}{\sqrt{4\pi D_1 t}} [e^{\frac{-(x-x_0)^2}{4D_1 t}} - e^{\frac{-(x+x_0)^2}{4D_1 t}}]$$

$$P_2(x,t) = \frac{1}{\sqrt{4\pi(D_1 - D_2)t_0 + D_2 t}} [exp[-\frac{(x-x_0)^2}{4\{(D_1 - D_2)t_0 + D_2 t\}}] - exp[-\frac{(x+x_0)^2}{4\{(D_1 - D_2)t_0 + D_2 t\}}]$$

$$P_3(x,t)=\frac{1}{\sqrt{4\pi\{(D_1-D_2)t_0+(D_2-D_3)t_1+D_3t\}}}\left[e^{-\frac{(x-x_0)^2}{4\{(D_1-D_2)t_0+(D_2-D_3)t_1+D_3t\}}}-e^{-\frac{(x+x_0)^2}{4\{(D_1-D_2)t_0+(D_2-D_3)t_1+D_3t\}}}\right]$$

Survival probability for phase 1 is similar to that of the free diffusion survival probability in one phase with the substitution D=D_1, since the boundary conditions for phase 1 is similar to the diffusion and hence the probability obtained is also equal to the probability obtained in the diffusion equation with the substitution D=D_1, which is given by,

$$S_1(t) = erf(x_{0/\sqrt{4D_1t}})$$

Calculation of Survival Probability of the Brownian particle for region2

The survival probability $S_2(t)$ in region 2 is given by,

$$S_2(t) = \int_0^\infty P_2(x,t)\,dx$$

$$= \frac{1}{\sqrt{4\pi\{(D_1-D_2)t_0+(D_2)t_1\}}}\int_0^\infty\left[e^{-\frac{(x-x_0)^2}{4\{(D_1-D_2)t_0+(D_2)t_1\}}}-e^{-\frac{(x+x_0)^2}{4\{(D_1-D_2)t_0+(D_2)t_1\}}}\right]dx$$

Let,

$$4\{(D_1-D_2)t_0+D_2t_1\}=B$$

Therefore,

$$S_2(t)=\frac{1}{\sqrt{B}}\left[\int_0^\infty e^{-\frac{(x-x_0)^2}{B}}\,dx-\int_0^\infty e^{-\frac{(x+x_0)^2}{B}}\,dx\right]$$

$$=\frac{1}{\sqrt{B}}\left[\int_0^{x_0} e^{-\frac{(x-x_0)^2}{B}}\,dx+\int_{x_0}^\infty e^{-\frac{(x-x_0)^2}{B}}\,dx-\int_0^{x_0} e^{-\frac{(x+x_0)^2}{B}}\,dx\ -\int_{x_0}^\infty e^{-\frac{(x+x_0)^2}{B}}\,dx\right]$$

Let,

$$(x-x_0)=z \text{ and } (x+x_0)=z'$$

Hence the equation becomes,

$$S_2(t)=\frac{1}{\sqrt{B}}\left[\int_{-x_0}^0 e^{-\frac{z^2}{B}}\,dz+\int_0^\infty e^{-\frac{z^2}{B}}\,dz-\int_{x_0}^0 e^{-\frac{z'^2}{B}}\,dz'\ -\int_0^\infty e^{-\frac{z'^2}{B}}\,dz'\right]$$

$$S_2(t) = \frac{1}{\sqrt{B}}\left[\int_{-x_0}^{0} e^{-\frac{z^2}{B}}\, dz - \int_{x_0}^{0} e^{-\frac{z'^2}{B}}\, dz'\right]$$

Or,

$$S_2(t) = 2 * \frac{1}{\sqrt{B}} \int_{0}^{x_0} e^{-\frac{z^2}{B}}\, dz$$

Let,

$$p = \frac{z}{\sqrt{B}}$$

Thus we get,

$$S_2(t) = 2 * \frac{1}{\sqrt{B\pi}} * \sqrt{B} \int_{0}^{x_{0/\sqrt{B}}} e^{-p^2}\, dp$$

$$= \frac{2}{\sqrt{\pi}} \int_{0}^{\frac{x_0}{\sqrt{4\{(D_1 - D_2)t_0 + (D_2)t_1\}}}} e^{-p^2} \mathrm{dp}$$

$$= erf\left(x_{0/\sqrt{4\{(D_1 - D_2)t_0 + (D_2)t_1\}}}\right)$$

Thus the survival probability for phase 2 is given by,

$$S_2(t) = erf\left(x_{0/\sqrt{4\{(D_1 - D_2)t_0 + (D_2)t_1\}}}\right)$$

<u>Calculation of Survival Probability of the Brownian particle for region3</u>

The survival probability in region 3, $S_3(t)$

$$S_3(t) = \int_{0}^{\infty} P_3(x,t)\, dx$$

$$= \frac{1}{\sqrt{4\pi\{(D_1 - D_2)t_0 + (D_2 - D_3)t_1 + D_3 t\}}} \int_{0}^{\infty} \left[e^{-\frac{(x - x_0)^2}{4\{(D_1 - D_2)t_0 + (D_2 - D_3)t_1 + D_3 t\}}} - e^{-\frac{(x + x_0)^2}{4\{(D_1 - D_2)t_0 + (D_2 - D_3)t_1 + D_3 t\}}}\right] dx$$

Let,

$$4\{(D_1 - D_2)t_0 + (D_2 - D_3)t_1 + D_3 t\} = A$$

$$= \frac{1}{\sqrt{A}}\left[\int_{0}^{\infty} e^{-\frac{(x - x_0)^2}{A}}\, dx - \int_{0}^{\infty} e^{-\frac{(x + x_0)^2}{A}}\, dx\right]$$

$$= \frac{1}{\sqrt{A}}\left[\int_{0}^{x_0} e^{-\frac{(x - x_0)^2}{A}}\, dx + \int_{x_0}^{\infty} e^{-\frac{(x - x_0)^2}{A}}\, dx - \int_{0}^{x_0} e^{-\frac{(x + x_0)^2}{A}}\, dx - \int_{x_0}^{\infty} e^{-\frac{(x + x_0)^2}{A}}\, dx\right]$$

Let,

$$(x - x_0) = z \text{ and } (x + x_0) = z'$$

Then, the Survival Probability is given by,

$$S_3(t) = \frac{1}{\sqrt{A}}[\int_{-x_0}^{0} e^{-\frac{z^2}{A}}\,dz + \int_{0}^{\infty} e^{-\frac{z^2}{A}}\,dz - \int_{x_0}^{0} e^{-\frac{z'^2}{A}}\,dz' \qquad - \int_{0}^{\infty} e^{-\frac{z'^2}{A}}\,dz']$$

Or,

$$S_3(t) = \frac{1}{\sqrt{A}}[\int_{-x_0}^{0} e^{-\frac{z^2}{A}}\,dz - \int_{x_0}^{0} e^{-\frac{z'^2}{A}}\,dz']$$

Or,

$$S_3(t) = 2 * \frac{1}{\sqrt{A}}\int_{0}^{x_0} e^{-\frac{z^2}{A}}\,dz$$

Let,

$$p=\frac{z}{\sqrt{A}}$$

Then,

$$S_3(t) = 2 * \frac{1}{\sqrt{A\pi}} * \sqrt{A}\int_{0}^{x_{0/\sqrt{A}}} e^{-p^2}\,dp$$

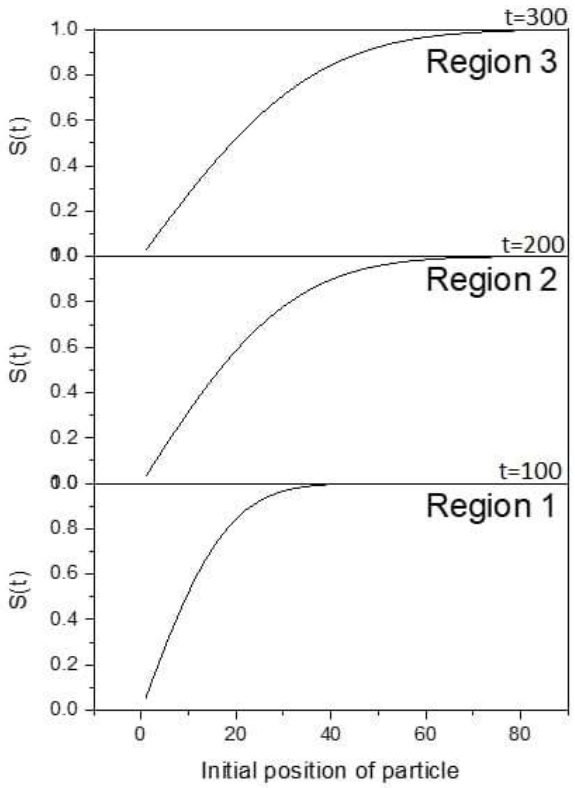
$$= \frac{2}{\sqrt{\pi}}\int_{0}^{x_{\frac{0}{\sqrt{4\{(D_1-D_2)t_0+(D_2-D_3)t_1+D_3t\}}}}} e^{-p^2}\,dp$$

$$= erf(x_{0/\sqrt{4\{(D_1-D_2)t_0+(D_2-D_3)t_1+D_3t\}}})$$

Therefore, the survival probability for region 3 is given by.

$$S_3(t) = erf(x_{0/\sqrt{4\{(D_1-D_2)t_0+(D_2-D_3)t_1+D_3t\}}})$$

Survival Probability Plot For Motion Of A Brownian Particle In a Three Phase System In Presence Of An Absorbing Wall



The Plot shows the survival probability of the particle in three different regions. We have plotted the results concerning calculated and analytical survival probabilities for the three regions [having survival probabilities $S_1(t), S_2(t), S_3(t)$] as in free diffusion case with t_0=100 for region1, t_1=200 for region 2, t=300 for region 3.The required simulation is same for the one phase free diffusion case with the diffusivity part replaced by the modified diffusivity part . We take the constants as

$$D_1 = 1, D_2 = 2, D_3 = 3$$

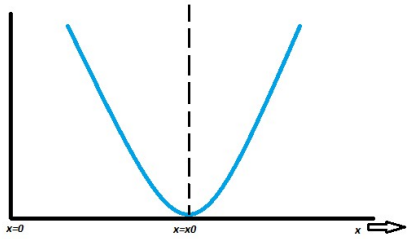
6.DERIVATION OF FOKKER PLANCK EQUATION FROM LANGEVIN EQUATION IN PRESENCE OF A HARMONIC POTENTIAL

The Langevin equation of a particle in presence of a harmonic potential,

V(x)=$\frac{1}{2}k(x-x_0)^2$

Is given by,

$$\dot{v} = -\gamma v + \Gamma(t) - \frac{k(x-x_0)}{m}$$



$$\dot{v} = 0$$

$$\dot{x} = \frac{\Gamma(t)}{\gamma} - \frac{k(x-x_0)}{\gamma m}$$

From Kramers-Moyal expansion(4)

We have,

$$D^n(x,t) = \frac{1}{n!}\lim_{\tau\to 0}\frac{1}{\tau}\langle[x(t+\tau)-x(t)]^n\rangle$$

Therefore,

$$D^1(x,t) = \lim_{\tau\to 0}\frac{1}{\tau}\langle[x(t+\tau)-x(t)]\rangle$$

$$D^2(x,t) = \frac{1}{2!}\lim_{\tau\to 0}\frac{1}{\tau}\langle[x(t+\tau)-x(t)]^2\rangle$$

Now the general form of a Langevin equation is given by,

$\dot{x} = h(x,t)+g(x,t)\,\Gamma(t)$

Comparing the equations,

We have, h(x,t)= - $\frac{k(x-x_0)}{m}$

g(x,t)= $\frac{1}{\gamma}$

In integral form, the above equation(1) can be written as,

$x(t+\tau) - x(t) = -\frac{k}{m}\int_t^{t+\tau}(x-x_0)\,dt' + \int_t^{t+\tau}\frac{\Gamma(t')}{\gamma}dt'$

Therefore,

$\langle[x(t+\tau) - x(t)]\rangle = -\frac{k}{m}(x-x_0)\tau$

[since, $\langle\Gamma(t)\rangle = 0, the\ second\ term\ goes\ to\ zero$]

[Comparing with Appendix 1, we get the same result]

Therefore,

$D^1(x,t) = -\frac{k}{m}(x-x_0)$

Now,

$[x(t+\tau) - x(t)]^2 = [-\frac{k}{m}\int_t^{t+\tau}(x-x_0)\,dt' + \int_t^{t+\tau}\frac{\Gamma(t')}{\gamma}dt'] [-\frac{k}{m}\int_t^{t+\tau}(x-x_0)\,dt' + \int_t^{t+\tau}\frac{\Gamma(t')}{\gamma}dt']$

$\langle[x(t+\tau) - x(t)]^2\rangle = \left[-\frac{k(x-x_0)}{m}\tau\right]^2 + \frac{1}{\gamma^2}\iint\langle\Gamma(t')\Gamma(t'')\rangle\,dt'\,dt''$

Now,

$$\langle\Gamma(t')\Gamma(t'')\rangle = q\delta(t'-t'')$$

Therefore,

$\langle[x(t+\tau) - x(t)]^2\rangle = \left[-\frac{k(x-x_0)}{m}\tau\right]^2 + \frac{1}{\gamma^2}\iint q\delta(t'-t'')\,dt'\,dt''$

$$= \left[-\frac{k(x-x_0)}{m}\tau\right]^2 + \frac{q}{\gamma^2}$$

Where, q=$\frac{2k_BT\gamma}{m}$, where , k_B *is Boltzman constant*

Therefore,

$D^2(x,t) = \frac{q}{2\gamma^2}$

[the first term goes to zero in the limit $\tau \to 0$ since it has a τ^2 term]

Finally the Fokker Planck equation for a Brownian particle in presence of a harmonic potential is given by,

$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(\frac{k}{\gamma m}(x - x_0)\right)P(x,t) + D\frac{\partial^2 P(x,t)}{\partial x^2}$

Where, D=$\frac{k_BT}{\gamma m}$

We solve the above equation numerically,

With the following boundary conditions,

$$P(x = 0, t = t_0) = 0$$

$$\frac{\partial j_x}{\partial x} = 0, at\ x = x_0$$

Where,

$$j_x = \frac{\partial}{\partial x}\left(\frac{k}{\gamma m}(x-= t_0) + D\frac{\partial}{\partial x}\right)P(x,t)$$

$$P(x \to \infty, t = t_0) = 0$$

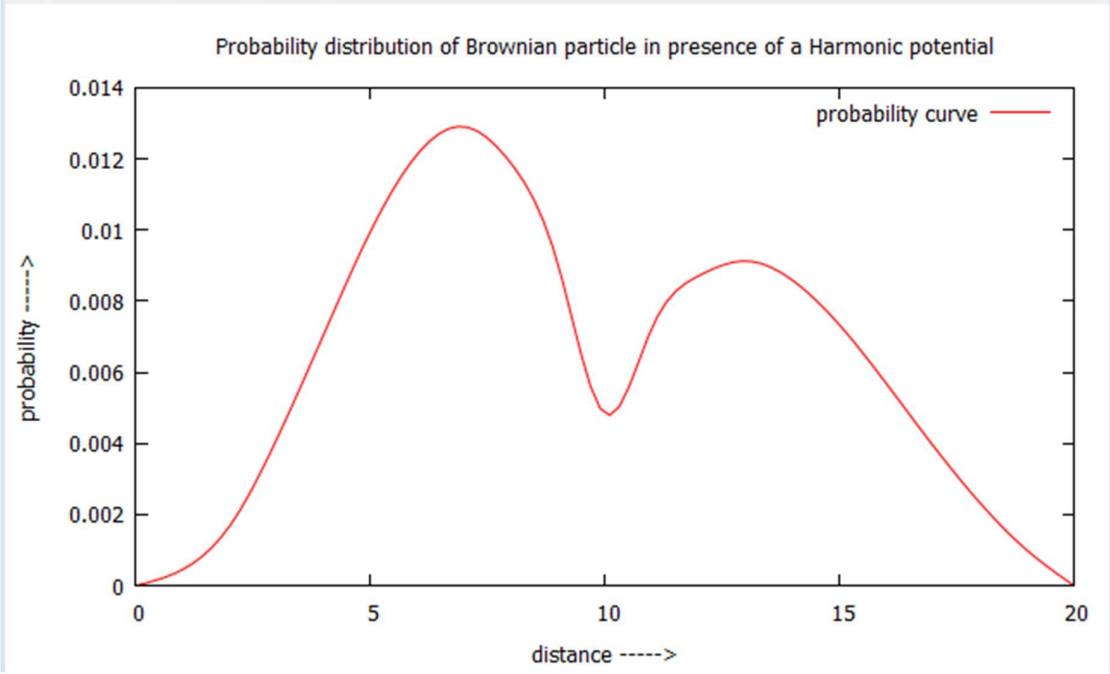
And, $P_1(x,t)$

Thus in the given problem we have an absorbing boundary at x=0 and the particle starts from x=$= x_0$ at t=$= t_0$.

Solving this pair of equation analytically, it is not straight forward because one of them is confined in a finite domain while the other one is valid in a semi infinite domain. Therefore the problem of matching at the point x=x0 becomes sensitive to time scales. Hence we try to solve the Fokker Planck equation derived above numerically by computer simulation . In simulation of the following program, we have considered the initial condition,

$$P(x,\tau)=\frac{1}{\sqrt{4\pi Dt}}\left[e^{-\frac{(x-x_0)^2}{4Dt}}-e^{-\frac{(x+x_0)^2}{4Dt}}\right]$$

i.e we have considered that the particle was initially diffusing freely as in the free diffusion case without the presence of any potential till time t=τ. After time τ, a potential $V(x)=\frac{1}{2}(x-x_0)^2$ i.e a harmonic potential is placed at x= x_0. Thus the particle diffuses in presence of a potential from time τ upto time t. The diffusion constant D has been taken as D=1 and the drift constant D1 has been taken as D1=0.1. The Brownian particle starts its random motion after time τ from position x_1 = 8.



The program has been run for t=5 and x=20

Simulation of the given problem

```
PROGRAM Diffusion_with_FTCS_Scheme

integer::n,i,j,x=10,t=5

real::P1(200,200),dt,dx,D,c,c1,D1,P2(200,200),T3,T4,c0,alpha,beta

open(1,file='FTCS1.dat',status='unknown')

do i=1,t

P1(1,i)=0.0

P2(x,i)=0.0

enddo

write(1,*)1,P1(1,t)

!define required parameters

dt=0.1;dx=0.5;D=1;D1=0.1;

 c=D*dt/(dx*dx)

c0=D1*dt

 c1=c0/dx

!let boundary situated at x0=5 and particle starts at x1=4

 x0=5;x1=4

 !defining initial steady initial value upto boundary x0

 do j=1,t

 do i=2,x0

 T3=(1.0/sqrt(4.0*3.14159*D*10.0))*(exp(-((i-x1)**2.0)/4.0*D*10.0)-exp(-
((i+x1)**2.0)/4.0*D*10.0))

 P1(i,j)=T3

 !write(1,*)i,P1(i,t)

 enddo

 enddo
```

```
 !particle initially starts at x=x1

 P1(x1,1)=1.0

  !process starts and we get final probability after time t

 do j=1,t

 do i=2,x0

 P1(i,j+1)=((1+c0)*P1(i,j))+(c*(P1(i+1,j)-2.0*P1(i,j)+P1(i-1,j)))+(c1*(P1(i+1,j)-P1(i,j))*(i-
x0))

  if(j==t)then

  write(1,*)i,P1(i,t)

  endif

 enddo

 enddo

 !applying boundary condition at boundary

do j=1,t

    P2(x0,j)=P1(x0,j)

end do

!again defining initial steady initial value from boundary x0 upto end

 do j=1,t

 do i=x0+1,x-1

 T3=(1.0/sqrt(4.0*3.14159*D*10.0))*(exp(-((i-x1)**2.0)/4.0*D*10.0)-exp(-
((i+x1)**2.0)/4.0*D*10.0))

 P2(i,j)=T3

 !write(1,*)i,P2(i,t)

 enddo

 enddo

 !process starts and we get final probability after time t

 do j=1,t
```

```
 do i=x0+1,x-1

 P2(i,j+1)=((1+c0)*P2(i,j))+(c*(P2(i+1,j)-2.0*P2(i,j)+P2(i-1,j)))+(c1*(P2(i+1,j)-P2(i,j))*(i-
x0))

if(j==t)then

write(1,*)i,P2(i,t)

endif

enddo

enddo

write(1,*)x,P2(x,t)

 END PROGRAM
```

Appendix – I

Kramers-Moyal Expansion Coefficients

For one stochastic variable x, the general Langevin equation has the form

$$\dot{x} = h(x,t) + g(x,t)\Gamma(t) \qquad \text{(A.1)}$$

Usually a formal general solution of the above stochastic differential equation cannot be given. As shown before, we can set up a Fokker-Planck equation by which the probability density of the stochastic variable can be calculated. In this Fokker-Planck equation the following Kramers-Moyal expansion coefficients enter:

$$D^{(n)}(x,t) = \frac{1}{n!}\lim_{\tau\to 0}\frac{1}{\tau}\langle[x(t+\tau)-x]^n\rangle|_{x(t)=x} \qquad \text{(A.2)}$$

In equation (A.2) $x(t+\tau)$ ($\tau > 0$) is a solution of (A.1) which at time *t* has the sharp value at x(t) = *x*. To derive these Kramers-Moyal expansion coefficients, we first write the differential equation (A.1) in the form of an integral equation

$$x(t+\tau) - x = \int_t^{t+\tau}[h(x(t'),t') + g(x(t'),t')\Gamma(t')]dt' \qquad \text{(A.3)}$$

and assume that h and *g* can be expanded according to (*$\frac{\partial}{\partial x}$* performed on h and *g* is denoted by a prime, i.e., $\frac{\partial\,(h(x(t'),t')}{\partial x(t')}\Big|_{x(t')=x} = \frac{\partial\, h(x,t')}{\partial x} = h'(x,t')$ and similar for *g)*

$$h(x(t'),t') = h(x,t') + h'(x,t')(x(t')-x) + \ldots.$$
$$g(x(t'),t') = g(x,t') + g'(x,t')(x(t')-x) + \ldots. \qquad \text{(A.4)}$$

Inserting (A.4) in (A.3) leads to

$$x(t+\tau) - x = \int_t^{t+\tau} h(x,t')dt' + \int_t^{t+\tau} h'(x,t')(x(t')-x)dt' \ldots.$$
$$+ \int_t^{t+\tau} g(x,t')\Gamma(t')dt' + \int_t^{t+\tau} g'(x,t')(x(t')-x)\Gamma(t')dt' \ldots. \qquad \text{(A.5)}$$

for $x(t')-x$ in the integrand we iterate (A.5), producing

$$x(t+\tau) - x = \int_t^{t+\tau} h(x,t')dt' + \int_t^{t+\tau} h'(x,t')\int_t^{t'} h(x,t'')dt''\,dt' +$$
$$\int_t^{t+\tau} h'(x,t')\int_t^{t'} g(x,t'')\Gamma(t'')dt''\,dt' + \ldots + \int_t^{t+\tau} g(x,t')\Gamma(t')dt' +$$
$$\int_t^{t+\tau} g'(x,t')\int_t^{t'} h(x,t'')\,\Gamma(t')dt''d\int_t^{t+\tau} g'(x,t')\int_t^{t'} g(x,t'')\Gamma(t'')\,\Gamma(t')dt''dt' \ldots. \qquad \text{(A.6)}$$

By repeated iterations only Langevin forces and the known functions *g(x, t)* and *h(x, t)* and their derivatives appear on the right-hand side of (A.6). If we now take the average of (A.6) we have using

$$\langle \Gamma(t) \rangle = 0 \text{ and } \langle \Gamma(t)\Gamma(t') \rangle = q\delta(t-t') \qquad \text{(A.7)}$$

$$\langle x(t+\tau) - x \rangle = \int_t^{t+\tau} h(x,t')dt' + \int_t^{t+\tau} h'(x,t') \int_t^{t'} h(x,t'')dt''\, dt' + ..$$
$$\int_t^{t+\tau} g'(x,t') \int_t^{t'} g(x,t'')q\delta(t''-t')\, dt''dt' \ldots . \text{(A.8)}$$

If we take for the δ function, for instance, the function $\delta_x(t)$ symmetric around the origin, and finally take $\varepsilon \to 0$, we have

$$\int_t^{t'} g(x,t'')q\delta(t''-t')\, dt'' = q\, g(x,t')$$

and therefore get,

$$\langle x(t+\tau) - x \rangle = \int_t^{t+\tau} h(x,t')dt' + \int_t^{t+\tau} h'(x,t') \int_t^{t'} h(x,t'')dt''\, dt' + ..$$
$$+q \int_t^{t+\tau} g'(x,t')g(x,t')dt' \ldots . \qquad \text{(A.9)}$$

In the limit $\tau \to 0$ we thus arrive at

$$D^{(1)}(x,t) = h(x,t) + g'(x,t)g(x,t)$$

The other integrals not written down in (A.9) do not contribute in the limit $\tau \to 0$.This is seen as follows: each Langevin force on the right-hand side of (A.6) is accompanied by an integral. The lowest terms are written down in (A.6). Higher terms vanish for the limit in (A.2). For instance, integrals of the form

$$\langle \int_t^{t+\tau} \ldots \Gamma(t_1) \int_t^{t_1} \ldots \Gamma(t_2) \int_t^{t_2} \ldots \Gamma(t_3) \int_t^{t_3} \ldots \Gamma(t_4)\, dt_1 dt_2 dt_3 dt_4 \rangle$$

Can only give a contribution proportional to τ^2 which vanishes for the limit in (A.2). Integrals not containing the Langevin force are proportional to τ^n, where *n* is the number of integrals. For the limit in (A.2) thus only terms with only one such integral will survive. Using these arguments we obtain for the second coefficient

$$D^{(2)}(x,t) = \frac{1}{2}\lim_{\tau\to 0}\frac{1}{\tau}\int_t^{t+\tau} g'(x,t') \int_t^{t'} g(x,t'')q\delta(t''-t')\, dt''dt'$$

$$= \frac{q}{2} g^2(x,t) \qquad \text{(A.10)}$$

By using these arguments for the higher coefficients $D^{(n)}$ we conclude that they all vanish for $n \geq 3$. The final result is

$$D^{(1)}(x,t) = h(x,t) + g'(x,t)g(x,t)$$

$$D^{(2)}(x,t) = \frac{q}{2} g^2(x,t)$$

$$D^{(n)}(x,t) = 0 \qquad \text{for } n \geq 3. \qquad \text{(A.11)}$$

In addition to the deterministic drift $h(x,t)$, $D^{(1)}$ contains a term which is called
the spurious drift or the noise-induced drift

$$D^{(1)}{}_{noise-ind} = g'(x,t)g(x,t) \qquad \text{(A.12)}$$

It stems from the fact that during a change of $\Gamma(t)$ also x(t) changes and therefore <g(x(t),t)$\Gamma(t)$> is no longer zero.

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