Implementation of Langevin Model for different potentials

By

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Certificate of Examination

This is to certify that the dissertation titled "**Implementation of Langevin Model for different potentials**" submitted by **Lakshita** (Reg.No. MP18006) for the partial fulfilment of MSc programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

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Dated: April 30, 2021

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Dipanjan Chakraborty at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

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In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Dipanjan Chakraborty

(Supervisor)

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Abstract

Equilibrium Statistical Mechanics is the study of the large systems on which statistical methods and probability theories are applied. It is concerned with the properties of the matter at the thermal equilibrium, i.e. there is no net flow of heat between the system and surroundings. It aims to derive not only the general laws of thermodynamics but also the thermodynamic functions of a given system. The real system in statistical mechanics is considered to be in various possible states, collection of which is termed as *ensemble*.
However, the systems are subjected to time-dependent phenomenons which are not in the state of thermal equilibrium. Hence, the study of Non-Equilibrium Statistical Mechanics is important to analyze the behaviour of such systems with time as a parameter. The fluctuations also play an important role in these systems. But there is a difficulty in dealing with such systems as we don't have any postulates for non-equilibrium states.
A powerful approach to such non-equilibrium states and the fluctuations is stochastic differential equations which accurately model the large number of physical situations. The Langevin model is a mathematical model used to understand the dynamics of the molecular systems by writing the equations of motion for the particle in a fluid medium. In this thesis, the Langevin model is used to study the behaviour of particle in a fluid medium under different potentials. The time correlation functions and mean squared values of velocity and positions are plotted as a function time to observe how the particle is behaving at shorter and longer time scales. It is also observed whether the behaviour of the particle at longer time limits matches with that at thermal equilibrium.

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Chapter 1

Non-Equilibrium Statistical Mechanics

1.1 Introduction

Equilibrium Statistical Mechanics (ESM) helps us understand the behaviour of average values of the system at the thermal equilibrium. It also enables us to deal with the fluctuations of physical quantities about their mean values only at the thermal equilibrium. We can say that ESM only deals with systems at thermal equilibrium. It does not deal with the time-dependent phenomena. All the ensembles considered in ESM - microcanonical, canonical and the grand canonical concerns to the systems in thermal equilibrium.

However, in real life we usually deal with the open systems (which exchange both energy and matter with the surroundings) which are not in thermal equilibrium with other systems with which they interact. The time variation of these systems must be dealt with. So, we go beyond ESM to non-equilibrium statistical mechanics in which time is taken as a variable parameter. But there is a serious difficulty in dealing with these systems. As the ESM resides on the postulate that all the accessible microstates of an isolated system in thermal equilibrium are equally probable. But there is no such postulate in NESM. We do know that if a system is slightly disturbed away from the thermal equilibrium, it will return back to the state of equilibrium. But we do not have the complete understanding of

all the possible non-equilibrium states, those far away from the equilibrium. Biological systems, for instance typically operate under the far from equilibrium conditions.

Fluctuations are an important part of the natural processes. They make the processes undetermined and statistical in nature. In the systems with a large number of degree of freedom, one would expect randomness and irregularity in the systems. One such simplest process is the Brownian motion which corresponds to the irregular motion of the large particles suspended in the fluid. These large particles will experience collisions with the fluid particles, which produce no effect on an average, giving rise to random walks. Early investigations of this phenomena were made on pollen grains, dust particles or various other objects of colloidal size. Later it was made clear that this theory can be applied to many other phenomena. In particular, the theory of Brownian motion has been extended to situations where 'Brownian particle' is not a real particle but some collective property of a macroscopic system. To study these collective properties, we use *stochastic* approach based on the **Langevin equation**. This is a model in which random force or noise part is introduced in the equation of motion of the particles with prescribed statistical properties[2].

1.2 Probability Density Function

Probability Density function, $P_a(x)dx$ is defined as the probability of the event a to happen lies between x and x + dx. This density function is normalisable,

$$\int_{-\infty}^{\infty} P_a(x)dx = 1. \tag{1.1}$$

Similarly, Joint PDF $P_{a,b}(x,y)dxdy$, is defined as the probability of the event a to occur lies in the interval x and x+dx and the probability of the event b to occur lies in the

interval y and y+dy.

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, P_{a,b}(x,y) = 1 \tag{1.2}$$

If the two variables x and y are *independent* of each other then, the Joint PDF can be reduced to the $P_{a,b}(x,y) = P_a(x)P_b(y)$.

Now we will define the probability density function for the particles in a fluid at the thermal equilibrium. Consider a container of volume V filled with the ideal gas i.e. there are no interactions between the particles. The gas is in equilibrium with its surroundings. The probability density function (PDF) for a given particle at the equilibrium is defined as the $\rho_{eq}(\vec{r},\vec{v})$. Since the particle is free to move inside the container and probability distribution of v is given by the *Maxwellian* distribution of velocities,

$$\rho_{eq}(\vec{r},\vec{v}) = \frac{1}{V}\sqrt{\frac{m}{2\pi k_B T}}\; e^{\frac{-mv^2}{2k_B T}} \tag{1.3}$$

If we ask of what happens to the particle inside the container as a function of time given the initial conditions (r_0, v_0, t_0); then we talk of Conditional PDF which is denoted as $\rho(\vec{r},\vec{v},t|\vec{r_0},\vec{v_0},t_0)$.

We know that as $(t - t_0) \to \infty$, system will tend towards thermal equilibrium, so it will follow the equation (1.3). Also as $(t - t_0) \to 0$, the PDF is written as,

$$\rho(\vec{r},\vec{v},t|\vec{r_0},\vec{v_0},t_0) = \delta^3(\vec{r} - \vec{r_0})\delta^3(\vec{v} - \vec{v_0}) \tag{1.4}$$

Now we know the extreme conditions for this Conditional PDF, but we don't know how the particle will behave in between. For that we will introduce the Langevin model and write the equations of motion for this particle.

Chapter 2

Langevin Model

2.1 Brownian Motion and Langevin Equation

In this model, we write an appropriate equation of motion for the system, in which its interaction with other degrees of freedom is modeled in terms of stochastic or random force with suitable statistical properties.

Consider a particle of mass m having initial velocity v_0 at some instant t_0 immersed in the fluid medium. It is in thermal equilibrium with the molecules of the fluid. The latter causes some fluctuations in the velocity of the particle via some small collisions with the particle which is a random process. At large times, we expect the average velocity of the particle to be zero, no matter what v_0 was. At any time t, we can write the Newton's equation of motion of the particle as,

$$m\dot{v}(t) = F(t) \tag{2.1}$$

where F(t) is the total force on the particle. Let there be an external force as well so,

$$F(t) = F_{int}(t) + F_{ext}(t), \tag{2.2}$$

where $F_{ext}(t)$ is the applied external force and $F_{int}(t)$ is the internal force arising from the bombardment of the molecules of the fluid. The $F_{int}(t)$ is a *random force*, as it arises due to random collisions of the particle with the fluid molecules.

The internal force is divided into a systematic part and a fluctuating part. Both these forces come from the interaction of the particle with its environment.

$$F_{int}(t) = \eta(t) + F_{sys}(t) \tag{2.3}$$

Here, $\eta(t)$ is truly a random force (fluctuations) whose average is zero and is independent of the state of motion of the particle. $F_{sys}(t)$ is a deterministic force that depends on the state of motion of particle, it generally prevents very large velocity fluctuations from building up. If the speed of the particle is very large at some instant of time, it will experience more collisions with the fluid molecules which will slows down its speed. We generally assume the $F_{sys}(t)$ to be frictional force proportional to the instantaneous velocity of the particle, directed *opposite* to it.

$$F_{sys}(t) = -m\gamma v(t), \tag{2.4}$$

where γ is the **viscous drag coefficient**. From Stoke's law, we know that the drag force on the sphere of mass m, radius a flowing in a viscous medium with viscosity ν is given as: $m\gamma = 6\pi\nu a$ So, the equation of motion we get for the particle is,

$$m\dot{v}(t) = -m\gamma v(t) + \eta(t) + F_{ext}(t), \tag{2.5}$$

with initial condition v(0) = v_0. This is the famous **Langevin equation** for the Brownian particle. It is a linear stochastic differential equation for the velocity of the particle of mass m with v as the driven variable and η is the noise that induces randomness in the velocity.

The solution of this equation is,

$$v(t) = v_0 e^{-\gamma t} + \frac{1}{m}\int_{t_0}^{t} dt_1 e^{-\gamma(t-t_1)}[\eta(t_1) + F_{ext}(t_1)], \tag{2.6}$$

Now we will talk about the random (fluctuations) force, $\eta(t)$. This force is supposed to come from the impacts of the Brownian particle with the molecules of the surrounding medium. The force during an impact is supposed to vary with extreme rapidity over the time of observation. So, we will summarize the force by giving its first and second moments as time averages over the infinitesimal time interval.

Since, mean value of the random force is zero at all times, i.e.

$$\overline{\eta(t)} = 0 \text{ for all t.} \tag{2.7}$$

Note:

1. $\overline{(.....)}$ is the conditional average over all the possible realizations of random force $\eta(t)$.
2. $< (.....) >$ is the total average over all the possible values of the initial conditions as well. We can do this by integrating the function with the probability distribution function i.e.
$$< v(t) >= \int_{-\infty}^{\infty} \rho_{eq}(v_0)\, \overline{v(t)} dv_0$$

So, we can write,

$$\overline{v(t)} = v_0\, e^{-\gamma t} + \frac{1}{m}\int_{0}^{t} dt_1\, e^{-\gamma(t-t_1)}\, F_{ext}(t_1), \tag{2.8}$$

because F_{ext} is imposed from the outside on the system and is unaffected by any averaging. In absence of any external force acting on the system, above equation will be

reduced to,

$$\overline{v(t)} = v_0\, e^{-\gamma t} \tag{2.9}$$

Therefore,

$$\lim_{t\to+\infty} \overline{v(t)} = 0 \tag{2.10}$$

This shows that the state of thermal equilibrium is maintained with the friction in the system: the dissipative mechanism helps the fluctuations to damp out with time and restore the system to equilibrium.

The mean squared velocity in the absence of applied force is written as:

$$\overline{v^2(t)} = v_0^2 e^{-2\gamma t} + \frac{1}{m^2}\int_0^t dt_2 \int_0^t dt_1 e^{-\gamma(t-t_1)-\gamma(t-t_2)}\, \overline{\eta(t_1)\eta(t_2)} \tag{2.11}$$

The cross terms vanishes as $\overline{\eta(t)} = 0$. The simplest assumption we make is that $\eta(t)$ is a random force or a **white noise** i.e., it is *delta-correlated, stationary, Gaussian and Markov process* (random process in which future of the process is independent of the past, given the present). So, $\eta(t)$ has no memory at all; its autocorrelation function can be written into product of averages,

$$\overline{\eta(t_1)\eta(t_2)} = (\overline{\eta(t_1)})\,(\overline{\eta(t_2)}) = 0 \text{ for all } t_1 \neq t_2. \tag{2.12}$$

Therefore, the random force is not related at two different times and is independent of each other, no matter how close t_1 and t_2 are. Since the random force is stationary; it means that it is a function of the magnitude of the time difference only i.e. $|t_1 - t_2|$. Hence the autocorrelation function must be of the form,

$$\overline{\eta(t_1)\eta(t_2)} = 2B\,\delta(t_1 - t_2), \tag{2.13}$$

B is the measure of the strength of the white noise.

So, we define the random force (fluctuating force or white noise) as:

$$< \eta(t) >= 0 \tag{2.14}$$

$$< \eta(t_1)\eta(t_2) >= 2B\,\delta(t - t') \tag{2.15}$$

The delta function in time indicates that there is no correlation between impacts at different instants of time t and t$'$. Also, the fluctuating force has the **Gaussian distribution** determined by these moments.

Putting the values in the equation 2.15, we get the mean squared velocity as:

$$\overline{v^2(t)} = v_0^2\, e^{-2\gamma t} + \frac{B}{m^2\gamma}\,(1 - e^{-2\gamma t}). \tag{2.16}$$

As $t \to \infty$,

$$\overline{v^2(t)} = \frac{B}{m^2\gamma} \tag{2.17}$$

From Equilibrium Statistical Mechanics, we know that the mean squared velocity is proportional to the absolute temperature T at the thermal equilibrium;

$$< v^2(t) >_{eq} = \frac{k_B T}{m} \tag{2.18}$$

Hence, both the equations 2.17 and 2.18 should be equal, so,

$$B = m\gamma k_B T. \tag{2.19}$$

This is a very important result in NESM. This is the **Fluctuation Dissipation Theorem**. It relates the strength of random noise B with the magnitude of friction coefficient γ. If an object is moving through a fluid, it experiences a drag. Drag dissipates kinetic energy, turning it into heat. The corresponding fluctuation due to heat is Brownian motion. An

object in a fluid does not sit still, but rather moves around with a small and rapidly-changing velocity as molecules in the fluid bump into it. Brownian motion converts heat energy into kinetic energy, the reverse of drag.

2.2 Correlation Functions

Equilibrium statistical mechanics is based on the idea of ensembles. Thermodynamic properties of the system can be found by calculating the partition function, Z of the ensemble. Similarly, in Non-equilibrium Statistical Mechanics various properties of the systems can be found by a pair of correlation functions. A fundamental difference between the two is that there is only one equilibrium state while there are many non-equilibrium states. We cannot write various partition functions for different states, hence we deal with time correlation functions which play the same role as partition functions.

2.2.1 Time Average vs. Ensemble average

Noise is a stochastic process consisting of a randomly varying function of time and space. We cannot talk of the single event at a certain time or position, we can only discuss the average quantities over a certain time interval or averaged quantity of many identical systems at a given time. The former is called as the *time* average and the latter as *ensemble* average. Let us consider N systems which produce the noisy waveforms $x^i(t)$,

Correlation function describes how the observable x at time t is related to its value at t′. It is also referred to as the *autocorrelation* function to distinguish it from the correlation functions of x with other observables. It is written as $C_{xx}(t,t')$.

$$C_{xx}(t,t') = < x^i(t)x^i(t') > = \lim_{\tau\to\infty} \frac{1}{\tau} \int_0^\tau dt'\, x(t')\, x(t+t') \tag{2.20}$$

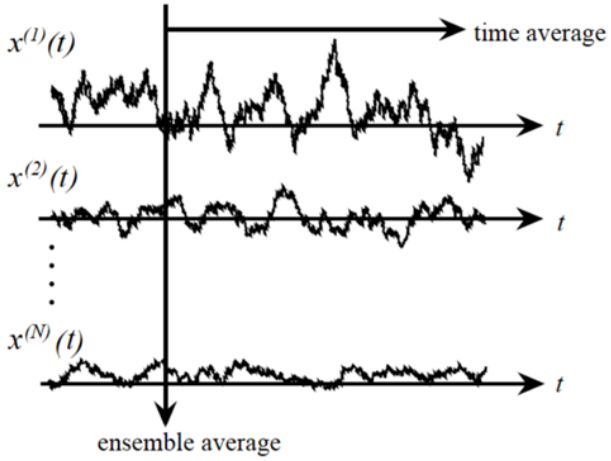


Figure 2.2.1: Ensemble average vs. Time average

This is the Time correlation function.

Similarly, Ensemble averaged correlation function is written as,

$$\begin{aligned} C_{xx}(t,t') &= \lim_{N\to\infty} \frac{1}{N} \sum_{i=1}^{N} x^i(t) x^i(t') \\ &= \int_{-\infty}^{\infty} x_1(t) x_2(t') p(x_1, x_2, t, t') dx_1 dx_2 \end{aligned} \tag{2.21}$$

Here, $x_1 = x(t)$, $x_2 = x(t')$ and $p(x_1, x_2, t, t')dx_1 dx_2$ is the probability density function such that x is found in the range between x_1 and $x_1 + dx_1$ at time t and also in the range between x_2 and $x_2 + dx_2$ at time t′.

If the system under investigation is *ergodic*, a long time average is equivalent to an equilibrium ensemble average. It is often said that time averaging and ensemble averaging are identical for statistically stationary systems. A stationary random process is defined as the one whose statistical properties do not change with time. In particular, the autocorrelation function of a stationary random process is a function only of the difference of the two time arguments involved, and not of the two arguments separately [7].

Chapter 3

Computational Results

3.1 Particle in Gaussian white noise

My first task was to solve the Langevin equation considering only the white noise term on the particle in the fluid medium. We are supposing the internal force due to molecular collisions to be zero. So, the equation of motion for this system is:

$$\dot{v}(t) = \eta(t) \tag{3.1}$$

The white noise is defined in the same way as in equations 2.14 and 2.15. Solving the above equation, we get:

$$v(t) = v_0 + \int \eta(t)dt \tag{3.2}$$

where v_0 is the initial velocity of the particle. If we calculate the average velocity of the particle, it will be equal to:

$$\overline{v(t)} = v_0, \tag{3.3}$$

since the average of white noise is zero. The total average of the velocity (over all the possible initial v_0 values) will be,

$$< v(t) > = \int_{-\infty}^{\infty} v_0 \, e^{-\frac{mv_0^2}{2k_BT}} \, dv_0$$
$$= 0.$$

The time correlation function of the velocity of the particle is equal to:

$$\overline{v(t)v(t')} = v_0^2 + \int_0^t dt_1 \int_0^{t'} dt_2 \, \overline{\eta(t_1)\eta(t_2)}$$

$$= v_0^2 + 2Bt(or\ t'). \tag{3.4}$$

Similarly, the total average of mean squared velocity will be,

$$< v^2(t) > = \int_{-\infty}^{\infty} (v_0^2 + 2Bt) \, e^{-\frac{mv_0^2}{2k_BT}} \, dv_0$$
$$= \frac{k_BT}{m} + 2Bt.$$

The mean squared displacement of the velocity of the particle is also same as time correlation function.

$$\overline{v^2(t)} = v_0^2 + 2Bt.$$

The figure 3.1.1 clearly shows the random movement of the particle around its mean position. Since the particle is not allowed to leave the volume, so it will not move in a particular direction, henceforth its mean velocity will be zero.

The figure 3.1.2 shows the computational results of this system. In this plot, I considered the initial velocity of the particle (v_0) to be zero. The three coloured lines represents the different values of B, the strength of white noise. For the blue line, the slope is 1, so the equation is: $< v(t)v(t') >= t$ as I took the 2B value to be equal to 1. We can verify

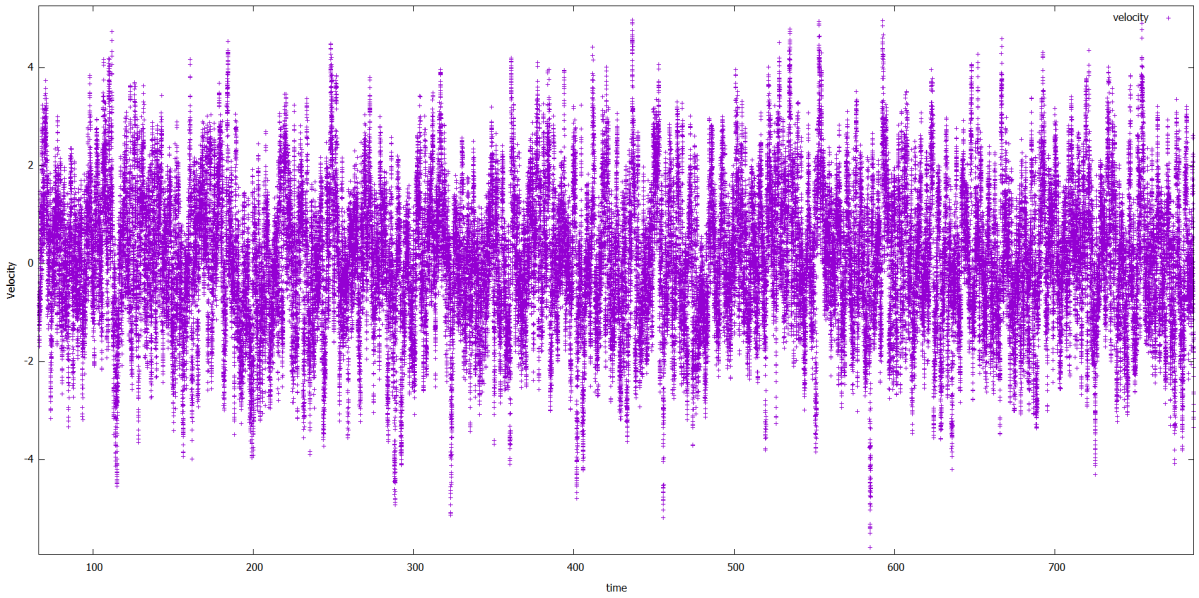


Figure 3.1.1: Velocity vs. time

that the analytical results are matching with the computational ones.

So, we can conclude from these expressions that,

- This is not a stationary system as its properties depend on time.
- The initial velocity of the particle persists for all time as its conditional average velocity.
- The mean squared displacement of the velocity of the particle is proportional to the time.
- As $\frac{1}{2}m < v^2(t) >= \frac{1}{2}k_B T$ (for 1D), this implies that the temperature of the system will also keep in increasing with time. For $t \to \infty$, the temperature will also be ∞, hence violating the results at the thermal equilibrium.

  Hence, the dissipative term plays an important role in maintaining the thermal equilibrium of the system.

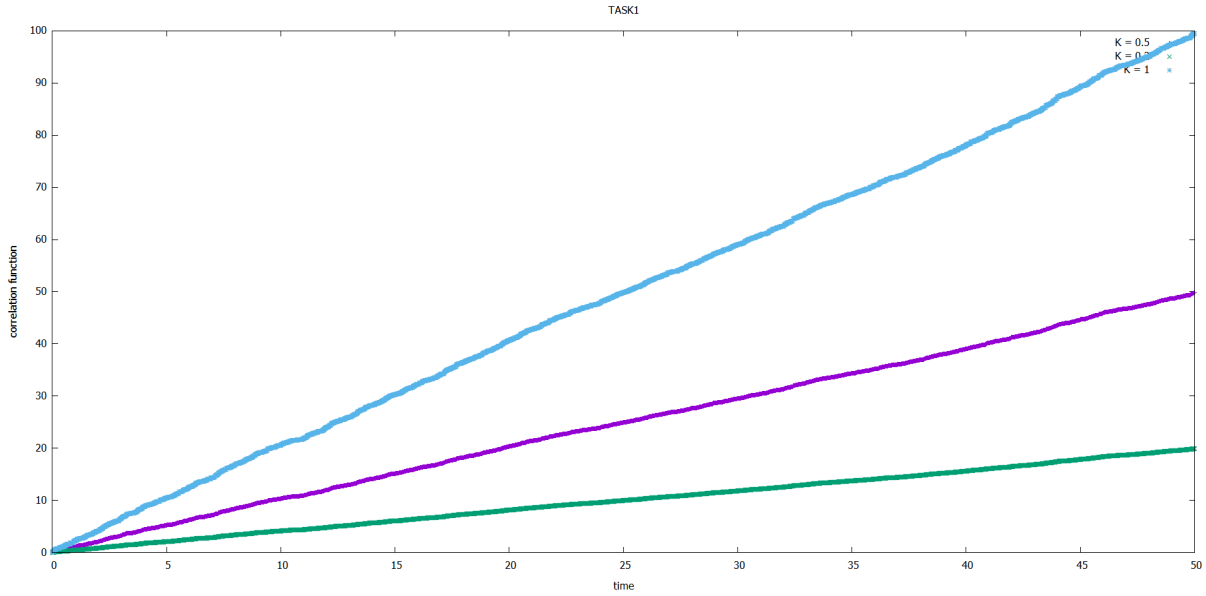


Figure 3.1.2: Time correlation function vs. time

3.2 Addition of drag force term

Now the dissipative term is also included in the Langevin equation:

$$\dot{v}(t) = -\gamma v(t) + \frac{1}{m}\eta(t) \tag{3.5}$$

So,

$$v(t) = v_0 e^{-\gamma t} + \frac{1}{m}\int_0^t dt_1 e^{-\gamma(t-t_1)}\eta(t_1),$$

If we calculate the average velocity of the particle, it will be equal to:

$$\overline{v(t)} = v_0 e^{-\gamma t}. \tag{3.6}$$

Similarly, the time correlation function of the velocity of the particle will be written as:

$$\overline{v(t)v(t')} = v_0^2 e^{-\gamma(t+t')} + \frac{1}{m^2}\int_0^t dt_2 \int_0^{t'} dt_1 e^{-\gamma(t-t_1)-\gamma(t'-t_2)}\,\overline{\eta(t_1)\eta(t_2)}$$

Putting the value of second moment of $\eta(t)$, we get the velocity correlation function as:

$$\overline{v(t)v(t')} = \frac{B}{m^2\gamma}e^{-\gamma|t-t'|} + (v_0^2 - \frac{B}{m^2\gamma})e^{-\gamma(t+t')} \tag{3.7}$$

Similarly, the mean squared velocity will be equal to:

$$\overline{v^2(t)} = \frac{B}{m^2\gamma} + (v_0^2 - \frac{B}{m^2\gamma})e^{-2\gamma t} \tag{3.8}$$

The total average mean squared velocity is,

$$\begin{aligned} < v^2(t) > &= \int_{-\infty}^{\infty} \rho(v_0)\, \overline{v^2(t)}\, dv_0 \\ &= \frac{B}{m^2\gamma} + (\frac{k_B T}{m} - \frac{B}{m^2\gamma})e^{-2\gamma t} \\ &= \frac{k_B T}{m}. \end{aligned}$$

since the total average should be independent of time and we also know from the Fluctuation - Dissipation relation that $B = m\gamma k_B T$.

So, we can conclude that:

- The average velocity of the particle is simply that of a damped particle in the absence of white noise. It is equal to zero for very longer times.
- The mean squared velocity will be a constant $(= \frac{B}{m^2\gamma})$ at the thermal equilibrium (at longer times).
- The auto correlation function of the velocity of the particle is proportional to the difference of t and t$'$ noticing that the second term will be zero at the thermal equilibrium. Therefore, it is a *stationary* system.
- The velocity correlation is an exponentially correlated function at the thermal equilibrium.

- From the expression of velocity autocorrelation 3.7, we can notice that the γ^{-1} has the units of time. This is known as the **velocity correlation time**, the time scale over which the system returns to the thermal equilibrium when disturbed out of that state by a small perturbation.

3.3 Solving the Langevin equation for position of particle

Now we will solve the Langevin equation for the position of the particle as a function of time, x(t). The equations of motion are,

$$\begin{aligned} \dot{x}(t) &= v(t); \\ m\dot{v}(t) &= -m\gamma v(t) + \eta(t). \end{aligned} \tag{3.9}$$

We already solved the second equation for v(t) in the section 3.2. Now we will solve the for x(t).

$$x(t) = x_0 + \int_0^t v(t')\, dt'$$

The average displacement of the particle is,

$$\begin{aligned} \overline{x(t)} &= x_0 + \int_0^t v_0 e^{-\gamma t'} dt' \\ &= x_0 + \frac{v_0}{\gamma}(1 - e^{-\gamma t}). \end{aligned} \tag{3.10}$$

The average position of the particle is same as its initial position, coincides with that of the particle which does not experience any force though the average of noise is zero. For

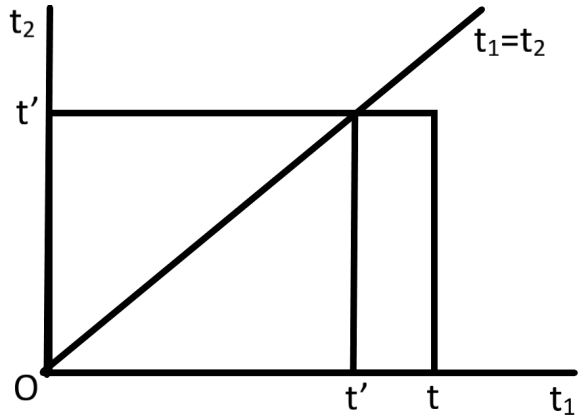


Figure 3.3.1: The region of integration over t_1 and t_2 for the case of $(t > t')$. The $t_1 = t_2$ line divides the square into two equal parts. Hence area under the square can be written as twice the area of one triangle, where t_2 will be integrated from 0 to t_1 and t_1 will run from 0 to t'. Similarly, in the rectangle region, integration of t_1 will run from t' to t and of t_2 will run from 0 to t'.

the calculation of variance in position, we have the expression as,

$$\begin{aligned}
\overline{x(t)x(t')} &= x_0^2 + \int_0^t dt_1 \int_0^{t'} dt_2\, \overline{v(t)v(t')} \\
&= x_0^2 + \frac{B}{m^2\gamma} \int_0^t dt_1 \int_0^{t'} dt_2\, e^{-|t_1-t_2|} \\
&= x_0^2 + \frac{B}{m^2\gamma}(2\int_0^{t'} dt_1 \int_0^{t_1} dt_2\, e^{-(t_1-t_2)} + \int_{t'}^t dt_1 \int_0^{t'} dt_2\, e^{-(t_1-t_2)}) \\
&= x_0^2 + \frac{B}{m^2\gamma^3}(2\gamma t' + e^{-\gamma t'} + e^{-\gamma t} - e^{-\gamma(t-t')} - 1) \\
&= x_0^2 + \frac{k_B T}{m\gamma^2}(2\gamma t' + e^{-\gamma t'} + e^{-\gamma t} - e^{-\gamma(t-t')} - 1) \qquad (t > t')
\end{aligned}$$

We can observe that the correlation is a function of both t and t′, hence the position of the particle is not a stationary random process in contrast to the velocity of the particle. The mean squared displacement of the particle is,

$$\overline{x^2(t)} = x_0^2 + \frac{2k_B T}{m\gamma^2}(\gamma t - 1 + e^{-\gamma t}). \tag{3.11}$$

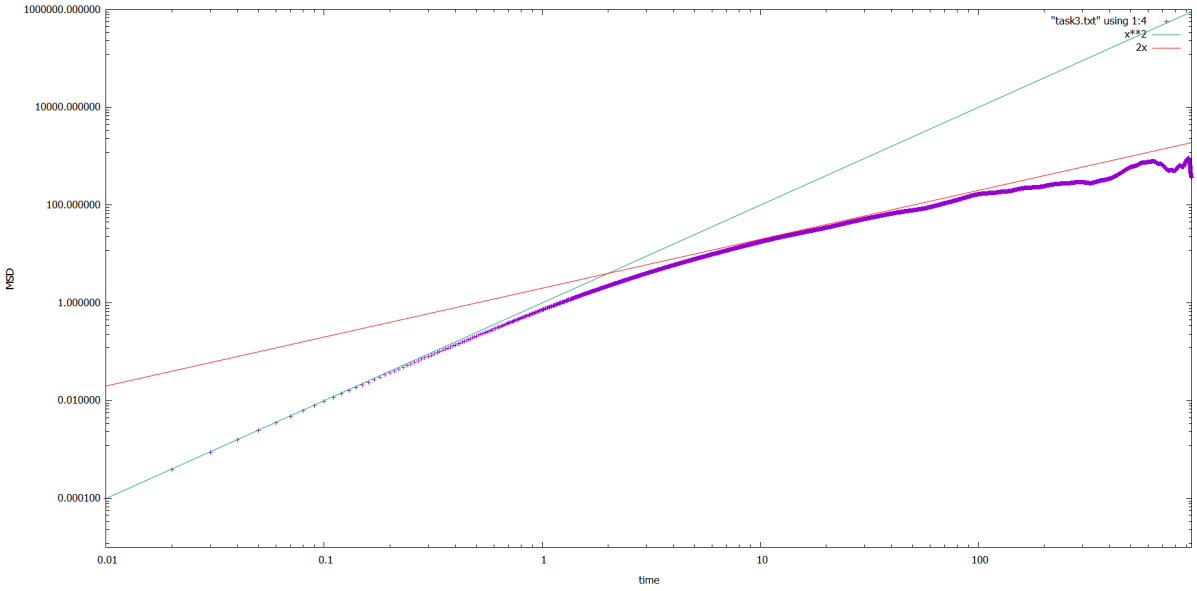


Figure 3.3.2: The mean squared displacement with time is shown. The purple line corresponds to the original data curve. We can see that the green line(which corresponds to $f(x) = x^2$ fit curve) coincides with the purple line at smaller time scales i.e. shows the ballistic behaviour of the particle while the red line (which corresponds to the curve $f(x) = 2x$) coincides with the data curve at larger time scales which shows the diffusive behaviour of the particle.

For the limit $\gamma t \to 0$, the above expression is reduced to,

$$\overline{x^2(t)} = \frac{k_B T}{m} t^2.$$

The particle is following the **ballistic** motion for smaller time scales. Similarly, in the limit $\gamma t >> 1$, the mean squared displacement is,

$$\overline{x^2(t)} = \frac{2k_B T}{m\gamma} t. \tag{3.12}$$

Hence, the root mean square of the distance increases as $\sqrt{t}$ with time. This is the characteristic behaviour of the diffusion. So, the diffusion constant, D is equal to

$$\overline{x^2(t)} = 2Dt \quad \text{for 1-D.}$$

So,

$$D = \frac{k_B T}{m\gamma}. \tag{3.13}$$

We can notice that D is inversely proportional to the γ or viscosity of the medium. So, the amount the particle gets kicked increases with decrease in the viscosity of the medium. This is the famous Einstein relation. This relation can be used to determine the value of Boltzmann constant(k_B) experimentally.

3.4 Brownian Oscillator

In the above section, we solved the Langevin equation for overdamped limits. Now we will repeat our analysis retaining the inertial term i.e.,

$$\begin{aligned} \dot{x}(t) &= v(t); \\ m\dot{v}(t) &= -m\gamma v(t) - m\omega_0^2 x(t) + \eta(t). \end{aligned} \tag{3.14}$$

An external potential of $V(x) = \frac{1}{2}kx^2$ is applied to the system. The tagged particle is harmonically bound in the fluid medium. Hence it will undergo an influence of restoring force $-m\omega_0^2 x$, where ω_0 is the frequency with which particle is oscillating in the medium.

Solving the equation, we get the shifted frequency as:

$$\omega_s^2 = \omega_0^2 - \frac{1}{4}\gamma^2 \tag{3.15}$$

Depending on the values of ω_0 and γ, we will be having three cases: underdamped ($\omega_0 > \frac{1}{2}\gamma$), critically damped ($\omega_0 = \frac{1}{2}\gamma$) and overdamped ($\omega_0 < \frac{1}{2}\gamma$). Performing the algebra of the equations using the Green's function with the given initial conditions

(x_0, v_0), we get the solution as,

$$\begin{aligned}\overline{x(t)} &= \frac{e^{\frac{-\gamma t}{2}}}{\omega_s}[(\omega_s \cos\omega_s t + \frac{\gamma}{2}\sin\omega_s t)x_0 + (\sin\omega_s t)v_0] \\ \overline{v(t)} &= \frac{e^{\frac{-\gamma t}{2}}}{\omega_s}[-(\omega_0^2 \sin\omega_s t)x_0 + (\omega_s \cos\omega_s t - \frac{\gamma}{2}\sin\omega_s t)v_0]\end{aligned} \tag{3.16}$$

Both $\overline{x(t)}$ and $\overline{v(t)}$ are tending to zero as $t \to \infty$ irrespective of the initial condition values (x_0, v_0). Likewise, we can calculate the values for mean square displacement and velocity at longer time scales:

$$\begin{aligned}< x^2(t) > &= \frac{k_B T}{m\omega_0^2} \\ < v^2(t) > &= \frac{k_B T}{m}\end{aligned} \tag{3.17}$$

Both the expressions matches with what we expect at the equilibrium conditions. We can also observe that the particle is not showing diffusive behaviour at long time limits i.e. not proportional to t as in the case when no external force was applied. We can also verify it physically. Since the particle is confined to move in a parabolic bowl shape potential, it can never reach infinity as a restoring force $-m\omega_0^2 x$ will always push the particle back to its mean position. This force is strong enough to overcome the fluctuating effects of the white noise which always diverges the particle at $t \to \infty$ limit.

Also, in this case of Brownian oscillator, both displacement and velocity are the stationary processes which was not the case when no external field was applied.

3.5 Particle in overdamped limits

Now consider the *overdamped* limits i.e. inertial term is put to zero. Also there is an external potential of $V(x) = \frac{1}{2}kx^2$ applied to the system. So there will be an extra trapping force $(-kx)$ experienced by the particle. So, now the equation of motion is changed to,

$$\begin{aligned} -\gamma\dot{x}(t) - kx + \eta(t) = 0. \\ \dot{x}(t) + \frac{k}{\gamma}x(t) = \frac{1}{\gamma}\eta(t) \end{aligned} \tag{3.18}$$

where k is the trapping constant. Let x_0 be the initial position of the particle. Solving the equation, we get the solution as,

$$x(t) = x_0\, e^{-\frac{k}{\gamma}t} + \int_0^t dt'\, e^{-\frac{k}{\gamma}(t-t')}\, \eta(t') \tag{3.19}$$

Average displacement of the particle will be,

$$\overline{x(t)} = x_0 e^{-\frac{k}{\gamma}t}. \tag{3.20}$$

The time correlation function of the position of the particle will be:

$$\overline{x(t)x(t')} = x_0^2 e^{-\frac{k}{\gamma}(t+t')} + \frac{1}{\gamma^2}\int_0^t dt_2 \int_0^{t'} dt_1 e^{-\frac{k}{\gamma}(t-t_1)-\frac{k}{\gamma}(t'-t_2)}\, \overline{\eta(t_1)\eta(t_2)}$$

Putting the value of second moment of $\eta(t)$, we get the result:

$$\overline{x(t)x(t')} = \frac{B}{\gamma k}e^{-\frac{k}{\gamma}|t-t'|} + (x_0^2 - \frac{B}{\gamma k})e^{-\frac{k}{\gamma}(t+t')} \tag{3.21}$$

The mean squared displacement of the particle will be:

$$\overline{x^2(t)} = \frac{B}{\gamma k} + (x_0^2 - \frac{B}{\gamma k})e^{-2\frac{k}{\gamma}t} \tag{3.22}$$

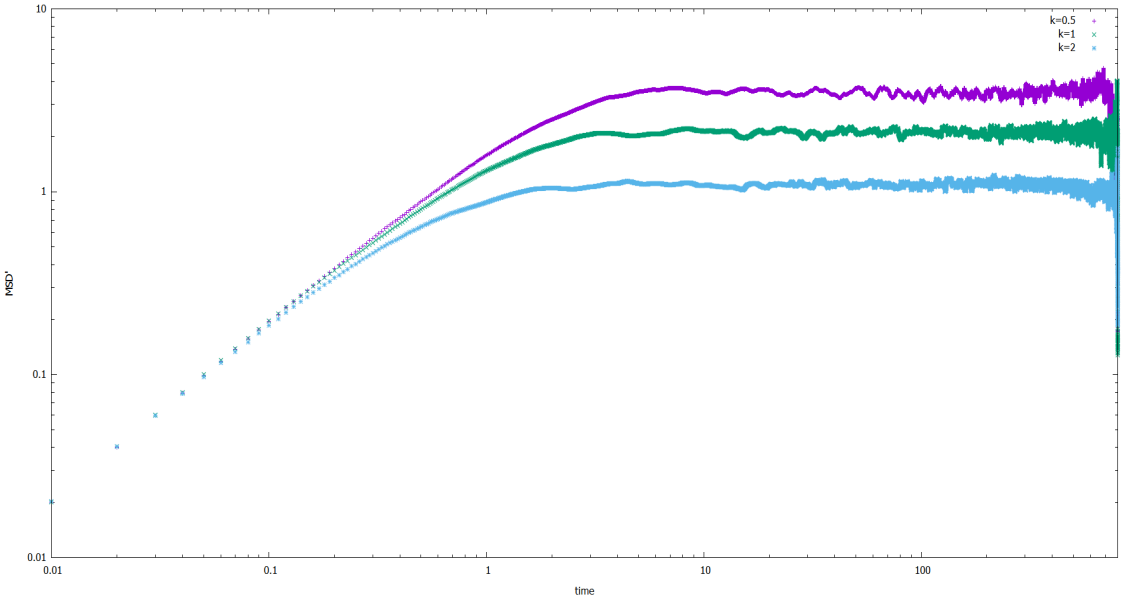
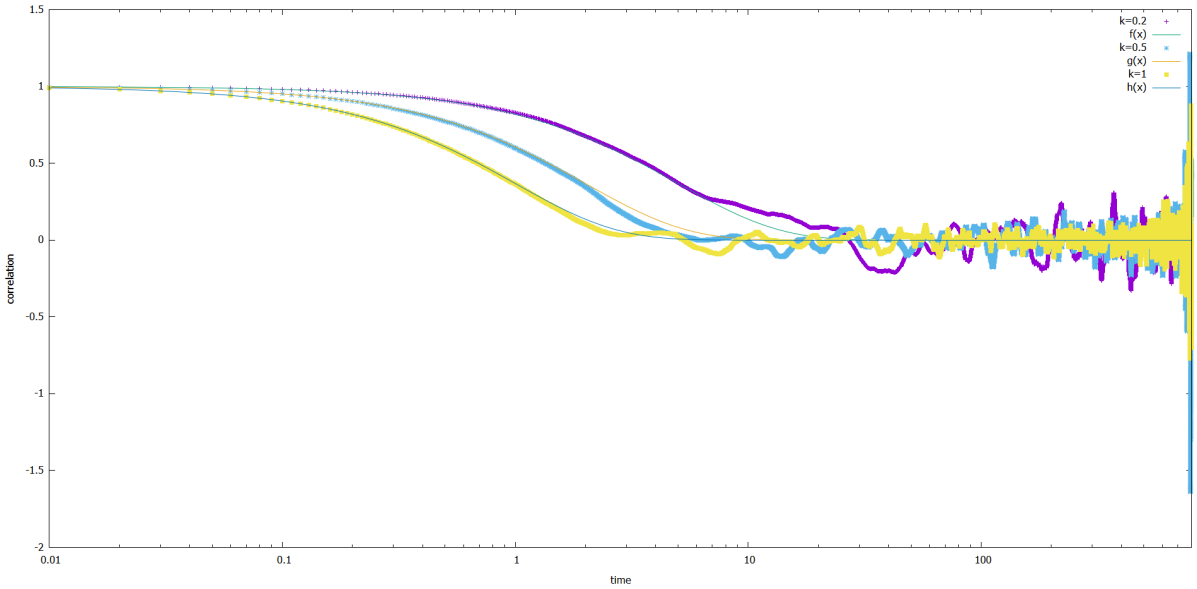


Figure 3.5.1: The mean squared displacement is plotted with the time in the overdamped limits. The quantities are plotted on the log-log scale. There is an approx. linear relation initially and then the value saturates to a constant value $(= \frac{k_B T}{m})$ for larger times.

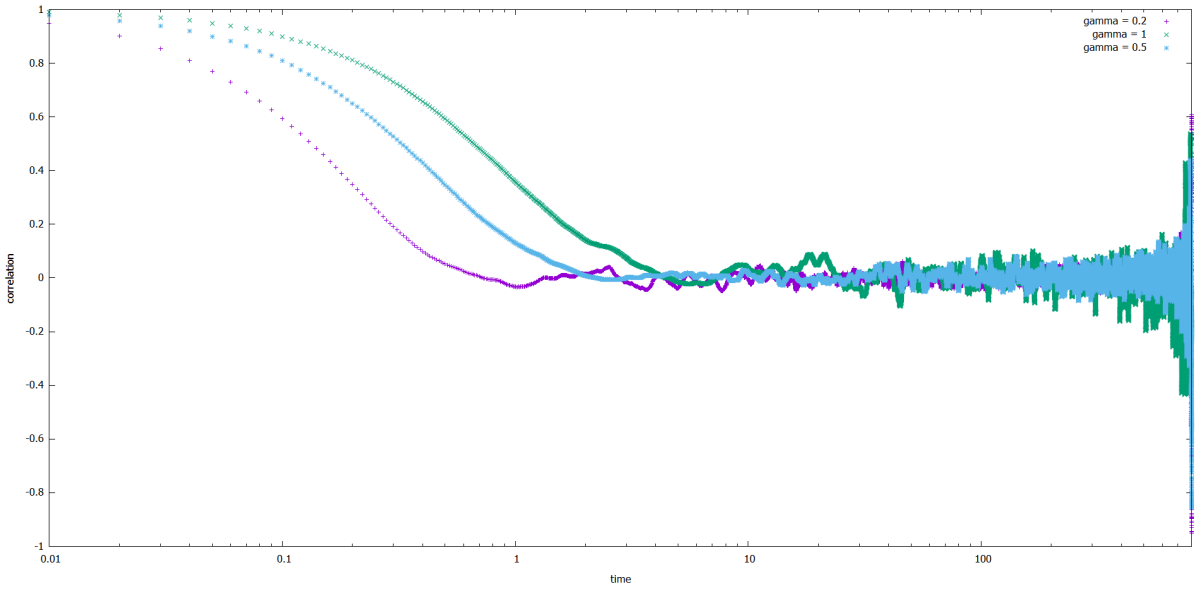
So, we can conclude that,

- The average displacement of the particle is zero i.e. it performs the random motion around its mean position.
- The autocorrelation function depends on the trapping constant(k) and the viscous drag coefficient(γ) as $e^{-\frac{k}{\gamma}|t-t'|}$. For a large value of trapping constant, the correlation value is decaying rapidly than for a smaller value of k.
- Similarly, the correlation between displacement values at different times stays for some longer time with the increase in the γ value. Both these conclusions are also verified by the computational results.
- It is a stationary process since the statistical properties do not depend upon time.
- The mean squared displacement value increases with the time initially and then attains a constant value at larger times.

Figure 3.5.2: The normalized autocorrelation function of the position of the particle vs. time. The time is plotted on the log scale. It is clear from the graph that correlation between velocities decays exponentially.



(a) The graph indicates the behaviour of autocorrelation function with the variations in k (trapping constant) value. From the graph, it is clear that with the increase in k value, the autocorrelation value is decaying faster. f(x), g(x), h(x) drawn in the plots are the fitting curves corresponding to each k value.



(b) The graph represents the behaviour of autocorrelation function with the variations in viscous drag coefficient γ value. The correlation function is decaying slower with the increase in gamma value.

3.6 Particles in Repulsive Potential

By far we consider one-particle system, i.e. there is only one particle in the fluid medium. There are no interactions between the tagged particle and the fluid molecules. Earlier we study the behaviour of the tagged particle in different types of systematic (deterministic) potentials: when dissipation term was added to the equation of motion, when the particle act as Brownian oscillator in the fluid medium and more. In all these cases, we neglected the interactions between the molecules.

Now we will consider a system of 512 particles in the fluid medium, interacting with each other. Particles are placed on the FCC lattice which means we already know the initial position of each particle in the system. In this case, the interaction between the particles is taken as repulsive; of the type $V = \frac{a}{r^{12}}$, where a is constant and r is the separation distance between the particles. Closer the particles, more will be the repulsive force between them. We can verify this from the formula too, closer the particles lesser will be the separation distance r and hence more will be the interaction potential or vice versa.

This potential is sufficient enough to hold the system together in the simulation, or we have to apply a potential which will act as a container for the particles, preventing them from drifting apart. Since the particles are confined in the 2D lattice, there will be some conditions on the particle's movement inside the lattice:

- *Periodic boundary conditions*: Consider this 2D lattice is reproduced throughout the space to form an infinite lattice. The properties of each reproduced box is same as the original one. As a molecule moves in the original box, we consider that its periodic images in the neighboring boxes will also move in the same way. If a particle move out of the box from any side, its image from the opposite side will enter the box so that particle number is conserved in the middle box. Hence, the

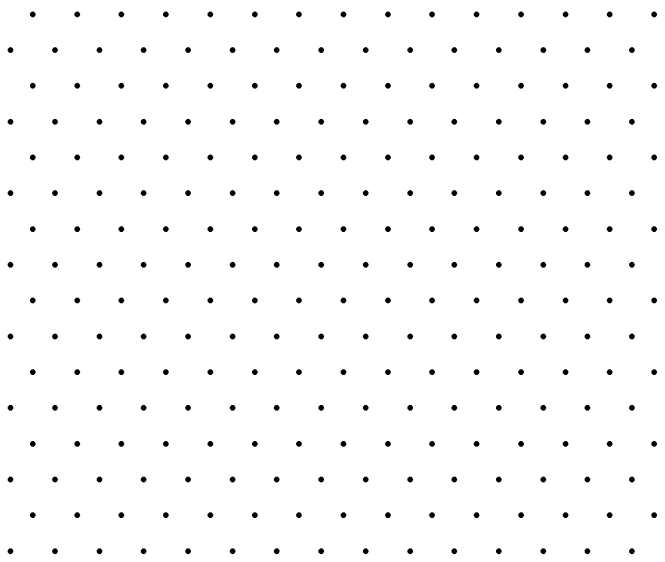


Figure 3.6.1: Particles are placed on the lattice sites in the FCC 2D lattice. Here the lattice constant is taken as one.

periodic boundary conditions are defined as,

$$\begin{aligned} r(x+L,y) &= r(x,y) \\ r(x,y+L) &= r(x,y) \end{aligned} \tag{3.23}$$

where r(x,y) is the position coordinate of the particle and L is the length of the lattice.

So, if any particle position lies outside the original box length, we will apply the conditions as:

$$\begin{aligned} if\ r_x(x,y) > L;\ r_x(x,y) &= r_x(x,y) - L \\ if\ r_x(x,y) < L;\ r_x(x,y) &= r_x(x,y) + L \end{aligned} \tag{3.24}$$

where $r_x(x,y)$ is the value of x coordinate of the particle. Similar conditions are for the y coordinate of the particle.

- *Potential Truncation*: Now we will calculate the forces on each particle in the system using the periodic boundary conditions. The force on each particle will be added pairwise. For N molecules there will be N-1 terms of the force. It is difficult to calculate the force due to each molecule if the value of N is very large. Also, the molecules closer will contribute more to the force than which are very far away. Therefore, we will restrict the terms using an approximation. The molecule will interact with only those molecules which are within a spherical cut-off radius (r_c) keeping the molecule at the centre. Hence, the contribution from the terms to the force which lie outside the cut off radius will be zero. This spherical cut off concept is taken as a small perturbation applied to the system and to ensure this, the cut off radius should be large. Usually the value of cut off radius is taken as $\frac{1}{2}L$ [1].

Appendix A

Box Muller Transformation

This transform is a random sampling method for generating pairs of normally distributed random numbers given a source of uniformly distributed random numbers [6]. If x_1 and x_2 are ***uniformly*** distributed between 0 and 1, then z_1 and z_2 as defined below have ***normal*** distribution with mean as 0 and variance as 1.

$$\begin{aligned} z_1 &= R\cos\theta = \sqrt{-2\ln x_1}\cos 2\pi x_2 \\ z_2 &= R\sin\theta = \sqrt{-2\ln x_1}\sin 2\pi x_2 \end{aligned} \tag{A.1}$$

Here, R^2 and θ are the random variables in the corresponding polar coordinates:

$$\begin{aligned} R^2 &= -2\ln x_1 \\ \theta &= 2\pi x_2 \end{aligned} \tag{A.2}$$

This transformation method is used while writing the code to obtain the value of $\eta(t)$ in the equation of motion in the code,

$$\eta(t) = \sqrt{\frac{2B}{dt}} * \text{Gaussian Random no.} \tag{A.3}$$

where $\eta(t)$ is the white noise part, B is the strength of white noise and dt is the step size of the integration.

Appendix B

Computation Codes

- **Notations:**

```
h = step size, k = trapping constant, K = Strength of
white noise, n = normalization constant,
g = dissipation constant, m = mass of particle,
L = lattice constant, sigma = repulsive coefficient.
msd = mean squared displacement,
corr = correlation function,
N = total no. of particles, r = position of particle,
v = velocity of particle, t = time, x,y,z,w = initial
coordinates, $r_c$ = cut off radius, F = total force
```

- **Brownian Oscillator:**

```
#include<iostream>
#include<cstdlib>
#include<iomanip>
#include<cmath>
#include<ctime>
#include<fstream>
```

```
using namespace std;

//Gaussian random generator
double sampleNormal() {
    double u = ((double) rand() / (RAND_MAX))*2-1 ;
    double v = ((double) rand() / (RAND_MAX))*2-1 ;
    double r = u * u + v * v;
    if (r == 0 || r > 1) return sampleNormal();
    double c = sqrt(-2 * log(r) / r);
    return u * c;
}

int main ()
{ float x[100], t[100], h, K, corr[100, k,
msd[100], v[100], n, g, m;
int i,j;
cout<< "enter the value of h: ";
cin >>h;
cout <<endl;
cout <<"enter the v(0): ";
cin >>v[0];
cout <<endl;
cout <<"enter the t(0): ";
cin >>t[0];
cout <<endl;
cout <<"enter the x(0): ";
cin >>x[0];
```

```
cout <<endl;
cout<<"enter the value of K, mass and gamma : " ;
cin >>K >>m >>g;
cout<<endl;

srand((unsigned) time(NULL));
ofstream file;

//to save the data in a file

file.open("task3.txt");
srand((unsigned) time(NULL));
for(i=0;i<95000;i++)
{
x[i+1] = x[i] + h*v[i];
v[i+1] = v[i] + h*((-g*v[i] - omega^2x[i]
+   sqrt((2*K)/h)*sampleNormal())/m);
t[i+1] = t[i] + h;
 }
float sum =0;
 float sum1 = 0;
 float count =0;
 for(i=0;i<95000;i++)
 { sum = sum +x[i];
 sum1 = sum1 + v[i];
count++; }
 float d=sum/count;
```

```
 float s = sum1/count;
 cout<<"the mean value of x and v: "
 <<d <<"\t"<<s <<endl;

//Normalization factor
float sum2= 0;
float count1=0;
for(i=0;i<95000;i++)
{
 sum2 = sum2 + x[i]*x[i];
 count1++; }
  n = sum2/count1;
  cout<<"the normalization factor is: " ;
  cout<<n <<endl;

  //Correlation function
for(j=0;j<95000;j++)
{
float sum3 =0;
float count2 =0;
for(i=0;i<(95000-j);i++)
{
sum3 = sum3 + x[i]*x[i+j];
count2++; }
 corr[j] = sum3/(n*count2);
}
```

```
//Mean square displacement
for(j=0;j<95000;j++)
{float sum4=0;
float count3 = 0;
for(i=0;i<(95000-j);i++)
{
 sum4 = sum4 + pow((x[i+j] - x[i]),2);
count3++;}

 msd[j] = sum4/count3;
}

//Printing values in the file
for(i=0;i<95000;i++)
{
file << t[i] <<"\t" <<v[i] <<"\t" <<x[i]
<<"\t" <<msd[i] <<"\t" <<corr[i] <<endl;}
file.close();
return 0;
}
```

- **For particles in Repulsive potential:**

```
#include<iostream>
#include<cstdlib>
#include<iomanip>
#include<cmath>
#include<ctime>
```

```
#include<fstream>
using namespace std;

//Gaussian random generator
double sampleNormal() {
    double u = ((double) rand() / (RAND_MAX))*2-1 ;
    double v = ((double) rand() / (RAND_MAX))*2-1 ;
    double r = u * u + v * v;
    if (r == 0 || r > 1) return sampleNormal();
    double c = sqrt(-2 * log(r) / r);
    return u * c;
}

int main ()
{
float x[250], y[250], z[250], w[250], t[250], r=0,
r1, h, K, corr[250], k, msd[250], v[250][250], n,
g, m, sigma, r_c, L, r_x[250][250], r_y[250][250],F;
int i, j, p=0, q;
int N, row, col;
cout <<"Enter the Number of rows: ";
cin>>row;
cout<<endl;
cout <<"Enter the Number of columns: ";
cin>>col;
cout<<endl;
cout<<"Enter the value of lattice constant: ";
```

```
cin>>L;
cout<<endl;

//Total number of particles
cout<<"Total number of particles: " ;
N = row*col + (row-1)*(col-1);
cout <<N <<endl;
cout<< "enter the value of h: ";
cin >>h;
cout <<endl;
cout <<"enter the t(0): ";
cin >>t[0];
cout <<endl;
cout <<"enter the value of cut off radius: ";
cin >>r_c;
cout <<endl;
cout<<"enter the value of K, mass,
sigma and gamma : " ;
cin >>K >>m >>sigma >>g;
cout<<endl;

//initial velocity of particles
for(j=0;j<N;j++)
 { v[0][j] = 0;
 }

//initial coordinates of atoms
```

```
x[0] = 0;
y[0] = 0;
z[0] = L/2;
w[0] = L/2;

//face centered cubic lattice
 cout <<" x          y:" <<endl;
for(j=0;j<col;j++)
{ y[j+1] = y[j] + L;
w[j+1] = w[j] + L;
 for(i=0;i<(row - row/2) ;i++)
{
  x[i+1] = x[i] + L;
  z[i+1] = z[i] + L;
  r_x[0][p] = x[i];
  r_x[0][p+1] = z[i];
  r_y[0][p] = y[j];
  r_y[0][p+1] = w[j];
p=p+2;}}

//printing the coordinates
for(i=0;i<N;i++)
{ cout <<r_x[0][i] <<"\t" <<r_y[0][i]<<endl;
}

ofstream file;
file.open("task4.txt");
```

```
srand((unsigned) time(NULL));

for(q=0;q<100;q++)
{ F=0;
for(i=0;i<(N-1);i++)
{
//periodic boundary condition
 for(j=i+1;j<N;j++)
{ float dx = r_x[q][i] - r_x[q][j];

float dy = r_y[q][i] - r_y[q][j];
if(dx>(L/2))
{ dx = dx-L;
}
else if(dx<(-L/2))
{ dx= dx+L;
}
else {dx = dx;
}
if(dy>(L/2))
{ dy = dy-L;
}
else if(dy<(-L/2))
{ dy= dy+L;
}
else { dy=dy;
}
```

```
 r1 = sqrt( dx*dx + dy*dy);

 //cut off radius approximation
 if(r1<=r_c)
 {
 F = F + 12*pow(sigma,12)/pow(r1,13);}
  }

r_x[q+1][i] = r_x[q][i] + h*v[q][i];
r_y[q+1][i] = r_y[q][i] + h*v[q][i];
v[q+1][i] = v[q][i] + h*(( F -g*v[q][i]
+ sqrt((2*K)/h)*sampleNormal())/m);
t[q+1] = t[q] + h;
 }}

//Mean square displacement
for(j=0;j<100;j++)
{ float dx1= 0, dy1=0;
float count3 =0, sum4 =0;
for(i=0;i<N;i++)
{
  dx1= dx1+ pow(r_x[j+1][i] - r_x[j][i],2);
  dy1= dy1+ pow(r_y[j+1][i] - r_y[j][i],2);
count3++;}
 sum4 = sqrt(dx1+dy1);
 msd[j] = sum4/count3;
}
```

```
//Printing values in the file
for(i=0;i<100;i++)
{
 file <<t[i] <<"\t" <<msd[i] ;
 file <<endl;}
file.close();
return 0;
}
```

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