1-Dimensional Harmonic Chain

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CONTENTS

1. DEFINING THE PROBLEM

Consider a one dimensional chain of N particles of mass M each, which interact with each other by harmonic potential with nearest neighbour approximation and the order of the particles remains the same always. This situation can be pictured as N particles each connected to its nearest neighbours with springs of the same spring constant k as shown in Figure 1.1.

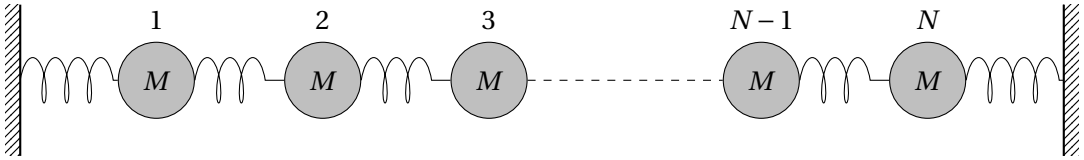


Figure 1.1: Chain of coupled oscillators each of mass m and connected by springs of spring constant k

The potential energy stored in each spring can be written as half of the spring constant times the square of its extension (compression is nothing but an extension with a negative sign). Thus, the total Hamiltonian of the system can be written as the following.

$$H = \sum_{l=1}^{N} \left\{ \frac{p_l^2}{2M} + \frac{1}{2}\cdot\frac{k}{2}[(x_l - x_{l-1})^2 + (x_{l+1} - x_l)^2] \right\} + \frac{1}{2}\cdot\frac{k}{2}\left(x_1^2 + x_n^2\right) \tag{1.1}$$

where x_l, p_l are the displacement of the lth particle from its equilibrium position and its momentum respectively. The boundary conditions here are taken to be $x_0 = x_{N+1} = 0$ and the walls on either sides are assumed to be particles of infinite masses. This total Hamiltonian of the system can be written in matrix form as

$$H = \frac{\langle p|p\rangle}{2M} + \frac{k}{2}\langle x|\Omega|x\rangle, \tag{1.2}$$

if $|p\rangle$, $|x\rangle$ and Ω are defined as

$$|p\rangle \equiv \begin{pmatrix} p_1 \\ p_2 \\ \vdots \\ p_N \end{pmatrix}, \qquad |x\rangle \equiv \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_N \end{pmatrix} \qquad \text{and} \qquad \Omega \equiv \begin{pmatrix} 2 & -1 & & & & \\ -1 & 2 & -1 & & & \\ & -1 & 2 & \ddots & & \\ & & \ddots & \ddots & -2 & \\ & & & -1 & 2 & -1 \\ & & & & -1 & 2 \end{pmatrix}_{N\times N}. \tag{1.3}$$

The derivation of the form (1.2) from (1.1) and the origin of the tridiagonal matrix Ω is presented in Appendix A. Matrices are denoted by uppercase alphabets while row and column vectors are denoted by Dirac's bra-kets in equation (1.2).

2. Analytical Solution

I will present a simple analytical solution of the system. I write the Hamiltonian (1.2), in terms of displacements and velocities as

$$H = \frac{1}{2} M \langle \dot{x}|\dot{x}\rangle + \frac{1}{2} M\omega_0^2 \langle x|\Omega|x\rangle. \tag{2.1}$$

where $\omega_0^2 = k/M$. One can find N eigenvalues and their corresponding eigenvectors of the matrix Ω to have the forms

$$\left(\frac{\omega_n}{\omega_0}\right)^2 = 4\sin^2\left(\frac{n\pi}{2(N+1)}\right) \tag{2.2}$$

and

$$|n\rangle = \frac{1}{\sqrt{\frac{N+1}{2}}} \begin{pmatrix} \sin\left(1\cdot\frac{n\pi}{N+1}\right) \\ \sin\left(2\cdot\frac{n\pi}{N+1}\right) \\ \vdots \\ \sin\left(N\cdot\frac{n\pi}{N+1}\right) \end{pmatrix} \tag{2.3}$$

respectively, where n can take integer values $1, 2, \cdots, N$ (The calculation is given in Appendix B). It can be verified that the obtained set of eigenvectors are orthonormal (See Appendix C for the proof). Thus, the diagonal transformation matrix

$$U \equiv \frac{1}{\sqrt{\frac{N+1}{2}}} \begin{pmatrix} \sin\left(1\cdot\frac{1\pi}{N+1}\right) & \sin\left(1\cdot\frac{2\pi}{N+1}\right) & \cdots & \sin\left(1\cdot\frac{N\pi}{N+1}\right) \\ \sin\left(2\cdot\frac{1\pi}{N+1}\right) & \sin\left(2\cdot\frac{2\pi}{N+1}\right) & \cdots & \sin\left(2\cdot\frac{N\pi}{N+1}\right) \\ \vdots & \vdots & \ddots & \vdots \\ \sin\left(N\cdot\frac{1\pi}{N+1}\right) & \sin\left(N\cdot\frac{2\pi}{N+1}\right) & \cdots & \sin\left(N\cdot\frac{N\pi}{N+1}\right) \end{pmatrix} \tag{2.4}$$

is orthogonal i.e., $U^T U = I$. The Hamiltonian (2.1) can be tranformed into the following form.

$$H = \frac{1}{2} M \left(\langle \dot{\tilde{x}} | \dot{\tilde{x}} \rangle + \langle \tilde{x} | W^2 | \tilde{x} \rangle \right). \tag{2.5}$$

where W is the diagonal matrix,

$$W \equiv \text{diag}(\omega_1, \omega_2, \ldots, \omega_N). \tag{2.6}$$

with ω_n's defined in equation (2.2).
From (2.5), the Hamilton's equations of motion can be written as

$$|\ddot{\tilde{x}}\rangle = -W^2 |\tilde{x}\rangle. \tag{2.7}$$

Solving these harmonic differential equations and putting in the initial conditions gives the following solution of the system.

$$|\tilde{x}(t)\rangle = \cos(Wt)|\tilde{x}(0)\rangle + \frac{\sin(Wt)}{W}|\dot{\tilde{x}}(0)\rangle \tag{2.8}$$

$$|\dot{\tilde{x}}(t)\rangle = -W\sin(Wt)|\tilde{x}(0)\rangle + \cos(Wt)|\dot{\tilde{x}}(0)\rangle \tag{2.9}$$

Solution (2.8-2.9) can be easily transformed back into the original coordinates to give

$$|x(t)\rangle = \left[U \cos(Wt)\, U^T |x(0)\rangle + U \sin(Wt)\, W^{-1} U^T |\dot{x}(0)\rangle \right] \tag{2.10}$$

and

$$|\dot{x}(t)\rangle = -\left[U \sin(Wt)\, W\, U^T |x(0)\rangle - U \cos(Wt)\, U^T |\dot{x}(0)\rangle \right]. \tag{2.11}$$

3. Integrated Heat Current

To obtain an expression for the integrated heat current to find the heat transported in a given time interval, one first has to arrive at a sound definition of differential heat current. Looking back at the total Hamiltonian of the system (1.1) one can write down the energy of each particle in the chain in the following form.

$$\epsilon_1 = \frac{p_1^2}{2M} + \frac{k}{2}\frac{1}{2}\left[2x_1^2 + (x_2 - x_1)^2\right] \tag{3.1}$$

$$\epsilon_l = \frac{p_l^2}{2M} + \frac{k}{2}\frac{1}{2}\left[(x_l - x_{l-1})^2 + (x_{l+1} - x_l)^2\right] \qquad \forall\ l \in \mathbb{Z} \cap (1, N) \tag{3.2}$$

$$\epsilon_N = \frac{p_1^2}{2M} + \frac{k}{2}\frac{1}{2}\left[(x_N - x_{N-1})^2 + 2x_N^2\right] \tag{3.3}$$

Upon taking time derivative of (3.2) and some simplifications using the equations of motion of the system, one obtains

$$\dot{e}_l = -\dot{\mathcal{J}}_{l+1,l} + \dot{\mathcal{J}}_{l,l-1} \quad , \tag{3.4}$$

where

$$\dot{\mathcal{J}}_{l+1,l} = -\frac{1}{2}k\left(\dot{x}_{l+1} + \dot{x}_l\right)\left(x_{l+1} - x_l\right). \tag{3.5}$$

Here $\dot{\mathcal{J}}_{l+1,l}$ can be identified as the instantaneous heat current through the bond connecting lth and $(l+1)$th particle. Here I define the integrated heat current Q(t) to be the total heat transported through a bond in a given interval of time t given by

$$\mathrm{Q}(t) = \int_0^t \dot{\mathcal{J}}_{l+1,l}(t')\ dt' \tag{3.6}$$

For evaluating this integral, one needs the current as a function of time. By doing certain manipulations, One can transform $\dot{\mathcal{J}}_{l+1,l}(\{|x\rangle, |\dot{x}\rangle\})$ in its current form into a function of $|\tilde{x}\rangle, |\dot{\tilde{x}}\rangle$

$$\dot{\mathcal{J}}_{l+1,l} = -\frac{k}{2}\left(\langle l+1| + \langle l|\right)|\dot{\tilde{x}}(t)\rangle\left(\langle l+1| - \langle l|\right)|\tilde{x}(t)\rangle \tag{3.7}$$

where $|l\rangle$ and $|l+1\rangle$ are lth and $(l+1)$th eigenvectors respectively. After substituting the solutions of the system $\{|\tilde{x}(t)\rangle,\ |\dot{\tilde{x}}(t)\rangle\}$ into (3.7) and calculating one can obtain the following time-integrable form of $\dot{\mathcal{J}}_{l+1,l}$.

$$\begin{aligned}\dot{\mathcal{J}}_{l+1,l} = -\frac{2k}{N+1}\sum_{m,n=1}^{N}\Bigg\{ &\sin\left(\frac{(2l+1)m\pi}{2(N+1)}\right)\cos\left(\frac{m\pi}{2(N+1)}\right)\cos\left(\frac{(2l+1)n\pi}{2(N+1)}\right)\sin\left(\frac{n\pi}{2(N+1)}\right)\\ &\Bigg[\ \sin\big((\omega_m+\omega_n)t\big)\left(\frac{\dot{\tilde{x}}_m(0)\dot{\tilde{x}}_n(0)}{\omega_n} - \omega_m\tilde{x}_m(0)\tilde{x}_n(0)\right)\\ &-\sin\big((\omega_m-\omega_n)t\big)\left(\frac{\dot{\tilde{x}}_m(0)\dot{\tilde{x}}_n(0)}{\omega_n} + \omega_m\tilde{x}_m(0)\tilde{x}_n(0)\right)\\ &+\cos\big((\omega_m-\omega_n)t\big)\left(\dot{\tilde{x}}_m(0)\tilde{x}_n(0) - \frac{\omega_m}{\omega_n}\tilde{x}_m(0)\dot{\tilde{x}}_n(0)\right)\\ &+\cos\big((\omega_m+\omega_n)t\big)\left(\dot{\tilde{x}}_m(0)\tilde{x}_n(0) + \frac{\omega_m}{\omega_n}\tilde{x}_m(0)\dot{\tilde{x}}_n(0)\right)\Bigg]\Bigg\}\end{aligned} \tag{3.8}$$

Putting this back into (3.6) and integrating one can obtain the expression for integrated heat current through a particular bond as

$$
\begin{aligned}
Q(t) \;=\; \frac{2k}{N+1}\sum_{m,n=1}^{N}\Bigg\{ & \sin\!\left(\frac{(2l+1)m\pi}{2(N+1)}\right)\cos\!\left(\frac{m\pi}{2(N+1)}\right)\cos\!\left(\frac{(2l+1)n\pi}{2(N+1)}\right)\sin\!\left(\frac{n\pi}{2(N+1)}\right) \\
& \Bigg[\;\left(\frac{\dot{\tilde{x}}_m(0)\dot{\tilde{x}}_n(0)}{\omega_n} \;-\; \omega_m\tilde{x}_m(0)\tilde{x}_n(0)\right)\left(\frac{\cos\big((\omega_m+\omega_n)t\big)-1}{\omega_m+\omega_n}\right) \\
& -\left(\frac{\dot{\tilde{x}}_m(0)\dot{\tilde{x}}_n(0)}{\omega_n} \;+\; \omega_m\tilde{x}_m(0)\tilde{x}_n(0)\right)\left(\frac{\cos\big((\omega_m-\omega_n)t\big)-1}{\omega_m-\omega_n}\right) \\
& -\left(\dot{\tilde{x}}_m(0)\tilde{x}_n(0) \;-\; \frac{\omega_m}{\omega_n}\tilde{x}_m(0)\dot{\tilde{x}}_n(0)\right)\left(\frac{\sin\big((\omega_m-\omega_n)t\big)}{\omega_m-\omega_n}\right) \\
& -\left(\dot{\tilde{x}}_m(0)\tilde{x}_n(0) \;+\; \frac{\omega_m}{\omega_n}\tilde{x}_m(0)\dot{\tilde{x}}_n(0)\right)\left(\frac{\sin\big((\omega_m+\omega_n)t\big)}{\omega_m+\omega_n}\right) \quad \Bigg]\Bigg\}.
\end{aligned}
\tag{3.9}
$$

In the above summation, for the terms for which $(m = n)$, it can be seen that *parts* of the term give 0/0 forms. In such cases one should be careful and replace those parts by their limiting values instead, which can be easily calculated as tending to 0. This is the expression of Integrated heat current as a function of time.

Now that I have a workable expression(though tedious to calculate by hand, a computer can do the job) to calculate Q(t) I wish to analyse the distribution of Q(t) and how it evolves with time as well as system size.

4. Equilibrium Distribution of Q

As the workable expression for Q(t) has been derived now, I wish to find the distribution of Q(t), for certain time interval t corresponding to the distribution of initial displacement and velocity vectors according to the given initial temperature T. If the system is at thermodynamic temperature T at time $t = 0$. Then, the distribution of initial states of the system is given by Boltzmann statistics as follows.

$$
P(\epsilon) = \frac{1}{Z}\exp\left(-\frac{\epsilon}{k_B T}\right) \tag{4.1}
$$

where
$P(\epsilon)$ = probability of the system being in the energy state ϵ,
k_B = Boltzmann's constant,
T = thermodynamic temperature of the system and
Z = Normalising constant also called as partition function of the system.

As we already know the Hamiltonian of the system is given by equation (1.2).

$$
H \;=\; \frac{\langle p|p\rangle}{2M} \;+\; \frac{k}{2}\,\langle x|\Omega|x\rangle
$$

Upon transforming this into the eigen-basis of Ω by using the diagonal transformation matrix of Ω i.e., U, one gets the following form for the Hamiltonian as shown in Appendix A.

$$
H \;=\; \frac{1}{2}\,M\,\langle\dot{\tilde{x}}|\dot{\tilde{x}}\rangle + \frac{1}{2}\,M\,\langle\tilde{x}|W^2|\tilde{x}\rangle \tag{4.2}
$$

$$
H \;=\; \frac{1}{2}M\sum_{i=1}^{N}\left\{\,\dot{\tilde{x}}_i^2 + \omega_i^2\,\tilde{x}_i^2\,\right\} \tag{4.3}
$$

By substituting this in the Boltzmann distribution 4.1, one gets

$$P(|\tilde{x}\rangle, |\dot{\tilde{x}}\rangle) = \frac{1}{Z} \exp\left(-\frac{1}{2} \frac{M}{k_B T} \sum_{i=1}^{N} \{ \dot{\tilde{x}}_i^2 + \omega_i^2 \tilde{x}_i^2 \} \right) \tag{4.4}$$

$$\implies \quad P(|\tilde{x}\rangle, |\dot{\tilde{x}}\rangle) = \frac{1}{Z} \prod_{i=1}^{N} \left(\left[\exp\left(\frac{-M\dot{\tilde{x}}_i^2}{2k_B T} \right) \right] \cdot \left[\exp\left(\frac{-M\omega_i^2 \tilde{x}_i^2}{2k_B T} \right) \right] \right). \tag{4.5}$$

Thus, in this basis, the distribution can be easily split into univariable Gaussian distributions each pertaining to an independent coordinate. Thus one can sample this distribution for the initial conditions by just sampling $2N$ gaussians separately. and joining them to form a single sample of initial conditions. This greatly reduces the complications of trying to sample from a multi-variable distribution with correlated variables. For simplicity, let us define

$$\tilde{y}_i = \omega_i \tilde{x}_i. \tag{4.6}$$

Then, equation (4.5) can be rewritten as

$$P(|\tilde{x}\rangle, |\dot{\tilde{x}}\rangle) = \frac{1}{Z} \prod_{i=1}^{N} \left(\left[\exp\left(\frac{-M\dot{\tilde{x}}_i^2}{2k_B T} \right) \right] \cdot \left[\exp\left(\frac{-M\tilde{y}_i^2}{2k_B T} \right) \right] \right) \tag{4.7}$$

From the above distribution it can be seen now that all the gaussians that the multivariate distribution is a composite of, have the same standard deviation. The normalisation constants for each of those distributions can be obtained to be the square root of 2π times the square of the standard deviation. From the distribution function (4.7) it is easily seen that the value of the standard deviation is $(\sqrt{k_B T/m})$. Thus, the value of the partition function which is also the normalisation constant for the full distribution can be shown to have the value

$$Z = \left(\frac{M}{2\pi k_B T} \right)^N \tag{4.8}$$

Thus, the distribution (4.7) can be rewritten in the following final form ready for sampling.

$$P(|\tilde{x}\rangle, |\dot{\tilde{x}}\rangle) = \prod_{i=1}^{N} \left(\frac{M}{2\pi k_B T} \left[\exp\left(\frac{-M\dot{\tilde{x}}_i^2}{2k_B T} \right) \right] \cdot \left[\exp\left(\frac{-M\tilde{y}_i^2}{2k_B T} \right) \right] \right) \tag{4.9}$$

I used Box-Müller sampling to sample a pair of values corresponding to $\dot{\tilde{x}}$ and $\tilde{y}$ from each of the bivariate gausssian

$$\left(\frac{M}{2\pi k_B T} \left[\exp\left(\frac{-M\dot{\tilde{x}}_i^2}{2k_B T} \right) \right] \cdot \left[\exp\left(\frac{-M\tilde{y}_i^2}{2k_B T} \right) \right] \right) \tag{4.10}$$

and sewn N of them together as the initial condition vectors $|\tilde{x}\rangle$ and $|\dot{\tilde{x}}\rangle$. Then these vectors can be transfromed back into the initial displacement and velocity vectors of the system using the inverse transform U^T. But for this problem it can be seen that Q(t) has simpler form as a function of $\{|\tilde{x}\rangle, |\dot{\tilde{x}}\rangle\}$ as compared to that of $\{|x\rangle, |\dot{x}\rangle\}$. Once, the distribution (4.9) is sampled for sufficient amount of samples for the initial conditions of

the system then those will be used to obtain the corresponding distribution of Q(t), for some particular value of time t.

The Box-Müller algorithm (Appendix D) for sampling an bivariate gaussian of two independent random variables, can sample two values from two independent gaussians at the same time. The algorithm proceeds as follows.

1. Sample two real numbers u_1 and u_2 respectively from $U_1(0,1)$ and $U_2(0,1)$ which are uniform distributions over the interval $(0,1)$.
2. Find the values of x and y that are each a sample from a gaussian by transforming u_1 and u_2 using the following transformation equations.

$$\begin{aligned} x &= \sqrt{-2\,\sigma^2 \ln(u_1)}\,\cos(2\pi u_2) \\ y &= \sqrt{-2\,\sigma^2 \ln(u_1)}\,\sin(2\pi u_2) \end{aligned} \tag{4.11}$$

For the particular case of this bivariate gaussian distribution (4.10), the transformation takes the form

$$\begin{aligned} \dot{\tilde{x}}_i &= \sqrt{-\frac{2k_BT}{m}\ln(u_1)}\,\cos(2\pi u_2) \\ \tilde{x}_i &= \frac{1}{\omega_i}\sqrt{-\frac{2k_BT}{m}\ln(u_1)}\,\sin(2\pi u_2) \end{aligned} \tag{4.12}$$

Thus, if we run the Box-Müller algorithm for N times we can combine them as N components of the two vectors $|\tilde{x}\rangle$ and $|\dot{\tilde{x}}\rangle$. By repeating this process several times we can sample the Boltzmann distribution corresponding to a particular temperature to obtain a set of $|\tilde{x}\rangle$'s and $|\dot{\tilde{x}}\rangle$'s for the next step of the analysis.

I have taken the units of all the physical quantities involved as the follwing in the problem.

1. MASS: 10^{-26} kg (~order of the mass of a carbon atom)
2. DISPLACEMENT: Å (Angstrom unit) (~order of the interatomic distances in graphite)
3. TIME: 10^{-13} seconds (~order of the periods of typical molecular vibrations)
4. TEMPERATURE: K (kelvin) (Thermodynamic temperature scale)

For the analysis, I have taken the size of the system to be 100 particles. Using the sampling procedure described above, I have sampled 1 million initial conditions from the Boltzmann distribution at temperature 375 K and I obtained the distribution of Q(t) various elapsed times and found that the distribution is a Gaussian in each case.(Figure 4.1 shows one such example.)

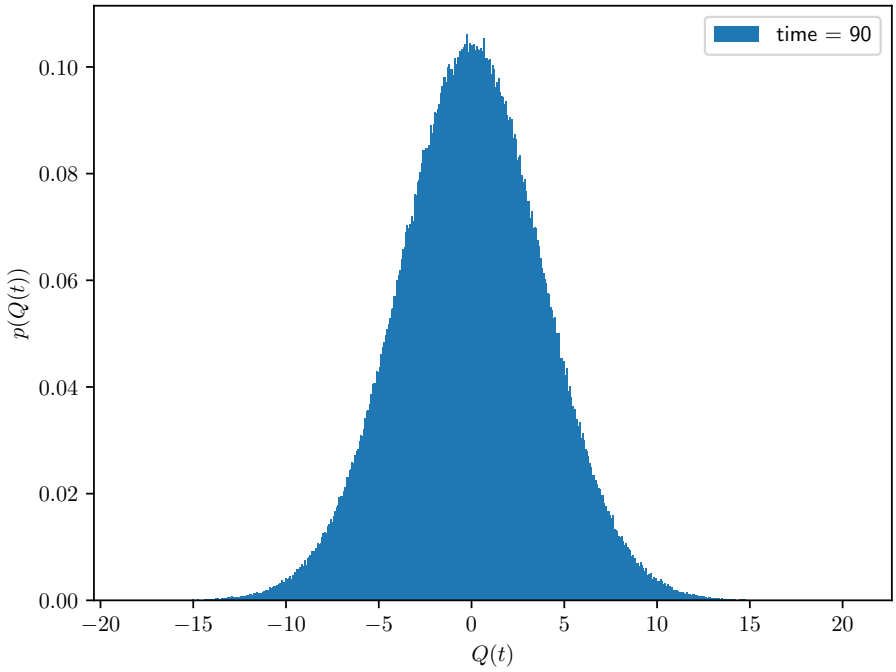


Figure 4.1: Distribution of Q(90.0) through the central bond of a 100 particle system for a set of initial conditions sampled from the Boltzmann distribution for the temperature 375K.

I also found that the distribution gradually widens(mathematically, the standard deviation of the distribution increases) with time though the distribution still is a Gaussian as shown in Figure 4.1.

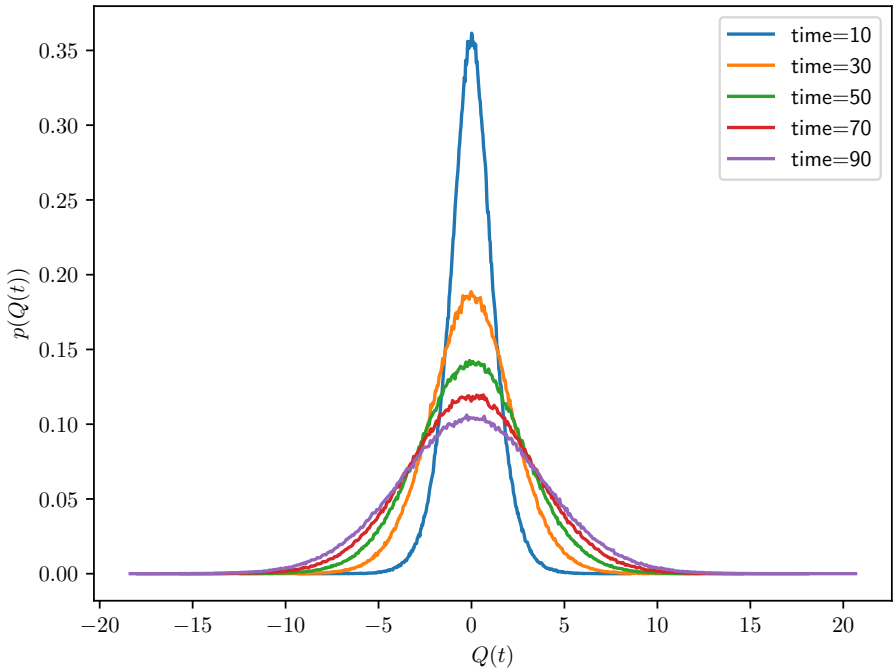


Figure 4.2: This plot shows the evolution of the distribution of Q(t) through the central bond with time, for N=100 particles, and initial equilibrium temperature of the system T=375K

As I have already presented in the above figure, the parameters of the distribution, particularly the standard deviation changes with time. I wish to find out an expression that quantifies this change. From the figure it can be seen that the mean of the distributions stays at 0 as one expects, because there is no gradient in the system to drive a finite current. It can be easily shown analytically as well that

$$\langle Q(t)\rangle = 0 \tag{4.13}$$

for all values of t. One can analytically calculate the mean and the variance of the distribution as a function of time. In this case, to simplify the problem I will only consider the net current Q(t) through the *central bond*. As $\langle Q(t)\rangle = 0$, the variance(the square of standard deviation) will only comprise of one term.

$$\langle Q^2(t)\rangle - \langle Q(t)\rangle^2 = \langle Q^2(t)\rangle \tag{4.14}$$

One can find this quantity analytically as mentioned already. After due calculation $\langle Q^2\rangle$ takes the following form.

$$\langle Q^2(t)\rangle = \left(\frac{2\omega_0 k_B T}{N+1}\right)^2 \sum_{\substack{m \text{ odd} \\ n \text{ even}}} \left\{\cos^2\left(\frac{m\pi}{2(N+1)}\right)\left(\frac{1-\cos\left((\omega_m+\omega_n)t\right)}{(\omega_m+\omega_n)^2} + \frac{1-\cos\left((\omega_m-\omega_n)t\right)}{(\omega_m-\omega_n)^2}\right)\right\} \tag{4.15}$$

$$1 \leq m, n \leq N$$

This calculation is performed after imposing two conditions:1. The system size N should be even and 2.The current is calculated for the central bond. The neat expression gives us a way to calculate $\langle Q^2(t)\rangle$ directly. I checked the validity of this analytical expression against the value of $\langle Q^2\rangle$ obtained by calculating the standard deviation from the distributions of $Q(t)$ obtained using the method stated in the start of this section. and found great quantitative agreement. From here I wish to investigate how this behaves as we increase the system size. Figure 4.3 shows the plot of this quantity($\langle Q^2(t)\rangle$) as a function of time for different sizes of the system.

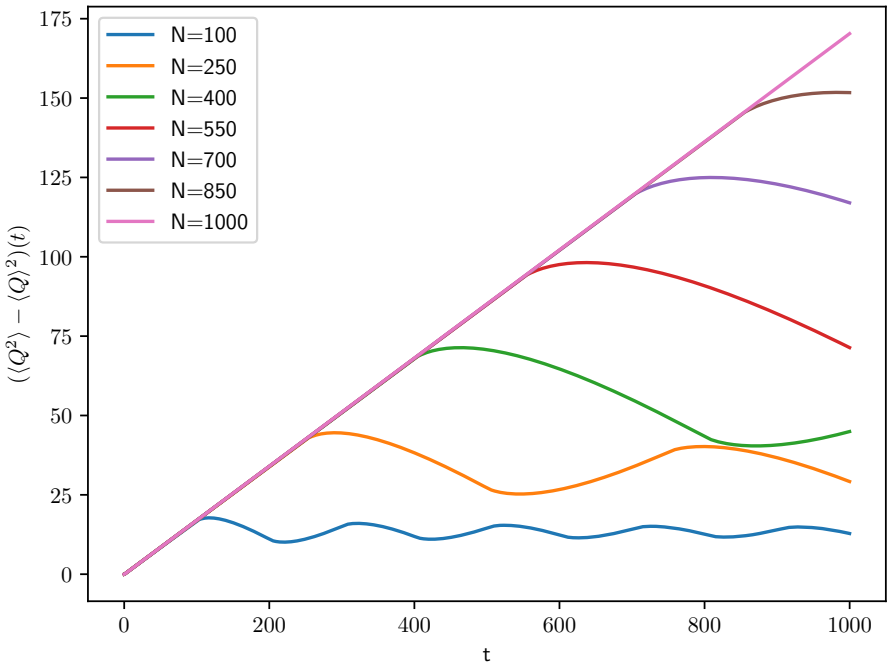


Figure 4.3: Plots of variance of Q(t) as a function of time corresponding to different system sizes.

From Figure 4.3 it can be inferred that the variance changes linearly with time for some initial period. It can also be observed that the linear portion of the curve is longer for larger system sizes and the extent of the linear portion is roughly increasing proportional to the system size. Extrapolating this behaviour one can make a wise guess that for a very large system ($N \to \infty$) the variance of the distribution increases linearly forever. It can also be seen in the figure that the slope of the straight line approaches a limit for large N. I wish to verify it by calculating the limiting form of (4.15). One can easily verify that upon taking the limit ($N \to \infty$) of (4.15), it can be converted into the following integral.

$$\langle Q^2 \rangle_{N\to\infty} = \int_0^{\pi/2} \int_0^{\pi/2} \cos^2 x \left(\frac{1-\cos\left(2\omega_0(\sin x+\sin y)\,t\right)}{4\omega_0^2(\sin x+\sin y)^2} + \frac{1-\cos\left(2\omega_0(\sin x-\sin y)\,t\right)}{4\omega_0^2(\sin x-\sin y)^2} \right) dy\, dx \quad (4.16)$$

The above integral seems impervious at first glance. And I do not expect it to yield a perfect straight line if solved analytically. In my efforts to integrate, I differentiated the integral twice with respect to time and simplified it to obtain the much simpler form

$$\frac{d^2}{dt^2}\langle Q^2 \rangle_{N\to\infty} = \left(\frac{2\omega_0 k_B T}{\pi}\right)^2 \int_0^{\pi/2} \cos^2 x \;\cos\left(2\omega_0 t \sin x\right) dx \int_0^{\pi/2} \cos\left(2\omega_0 t \sin y\, t\right) dy. \quad (4.17)$$

Using the Poisson's integral and the integral form of the Bessel function of the first kind [1], this integral can be solved to get $(d^2/dt^2)\langle Q^2 \rangle$ as the following function of time.

$$\frac{d^2}{dt^2}\langle Q^2 \rangle_{N\to\infty} = \frac{\omega_0\,(k_B T)^2\, \mathrm{J}_0(2\omega_0 t)\, \mathrm{J}_1(2\omega_0 t)}{t} \quad (4.18)$$

where J_0 and J_1 are the Bessel functions of the first kind of the zeroth and the first order, respectively. The above equation can be integrated using an identity of Bessel functions to obtain the following expression for the first time derivative of $\langle Q^2 \rangle$.

$$\frac{d}{dt}\langle Q^2 \rangle_{N\to\infty} = \omega_0\,(k_B T)^2 \left[2\omega_0 t \left(\mathrm{J}_0^2(2\omega_0 t) + \mathrm{J}_1^2(2\omega_0 t) \right) - \mathrm{J}_0(2\omega_0 t)\mathrm{J}_1(2\omega_0 t) \right] \quad (4.19)$$

The above equation(4.19) is nothing but the instantaneous slope of the function $\langle Q^2 \rangle$ as a function of time.

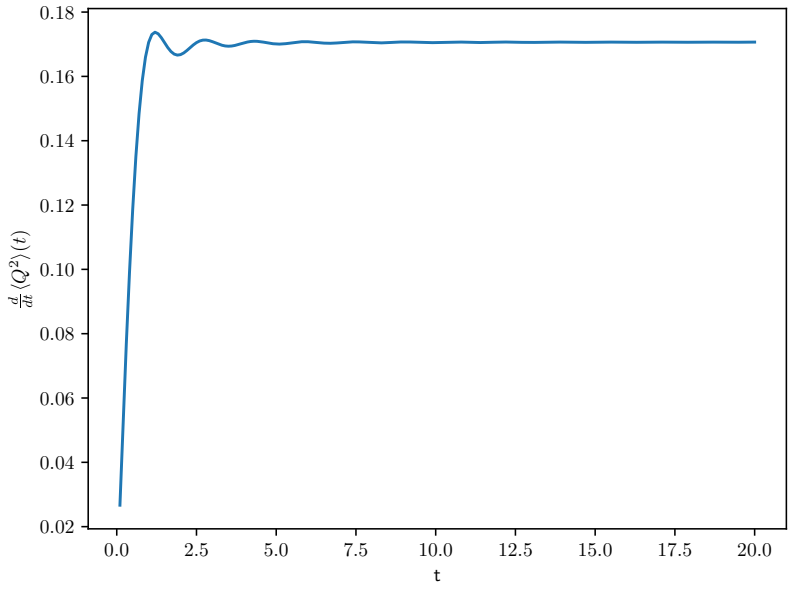


Figure 4.4: Plot of $(d/dt)\langle Q^2 \rangle$ as a function of time.

It can be seen from the figure 4.4, the function(which is the slope of $\langle Q^2 \rangle$) fluctuates for initially, settles down to a limiting value for large t. Thus, the asymptotic behaviour of the function(4.19) can be approximated by its limiting value at infinity. Using the indefinite integral calculated above and a definite integral formula involving Bessel functions [1], it can be concluded that the limit has the value

$$\lim_{t\to\infty} \frac{d}{dt}\langle Q^2 \rangle_{N\to\infty} = \frac{2\omega_0 \, (k_B T)^2}{\pi}. \tag{4.20}$$

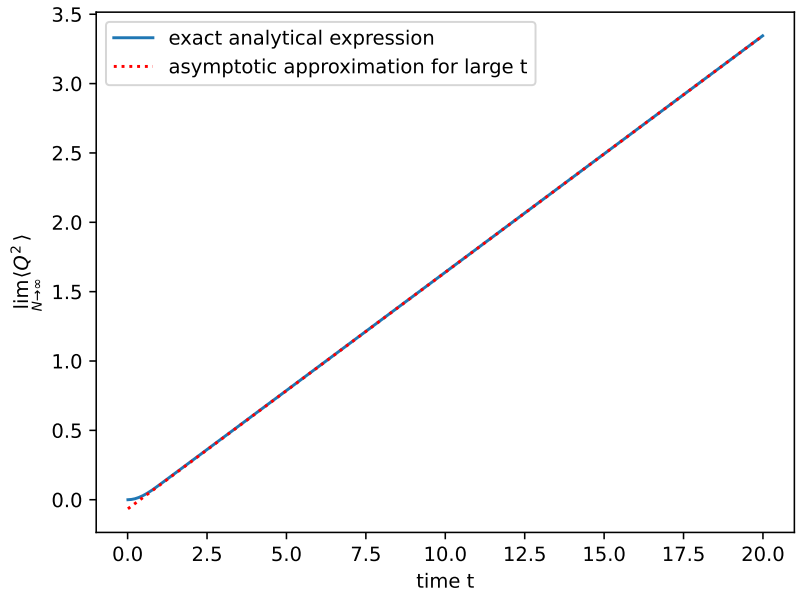
I integrated the first two terms of (4.19) using an indefinite integral of Bessel functions and the last term using another definite integral of Bessel functions and I simplified the result using the recurrence relations of Bessel functions from [1] to obtain

$$\langle Q^2 \rangle_{N\to\infty} = \omega_0 (k_B T)^2 \left\{ t \left[2\omega_0 t \left(J_0^2(2\omega_0 t) + J_1^2(2\omega_0 t) \right) - J_0(2\omega_0 t) J_1(2\omega_0 t) \right] + \frac{J_0^2(2\omega_0 t) - 1}{4\omega_0} \right\} \tag{4.21}$$

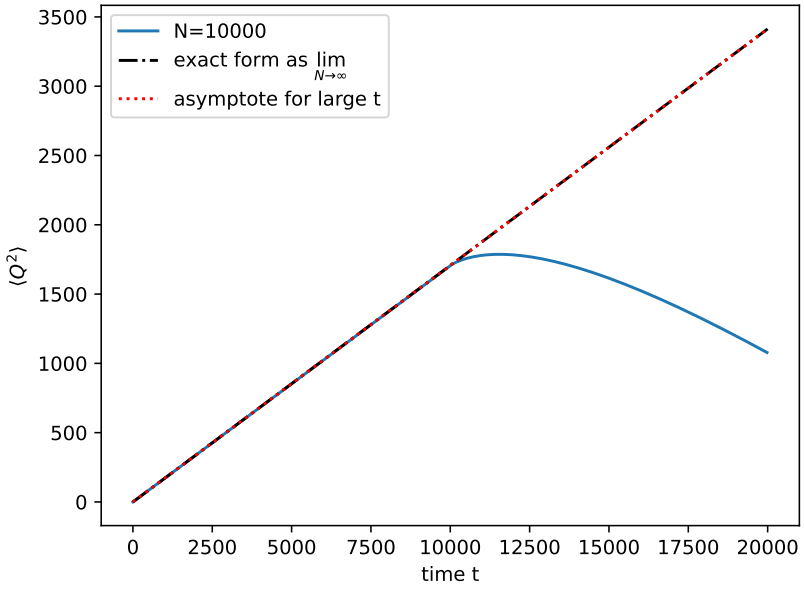
The quantity inside the square brackets in the above expression (4.21) is exactly the same as the one inside the square brackets in the expression (4.19). Thus, to calculate the asymptotic approximation of this function for large time period, I replace the quantity inside the square brackets with its limit given in (4.20) and I take the ($t \to \infty$) limit of the remaining term. Doing so I obtain the asymptotic expansion of $\langle Q^2 \rangle_{N\to\infty}$ for large t as the following linear curve.

$$\langle Q^2 \rangle_{N\to\infty} \simeq \frac{2\omega_0 (k_B T)^2}{\pi} \cdot t - \frac{(k_B T)^2}{4} \tag{4.22}$$

In the plot shown in Figure 4.5a, I compare the exact expression (4.21) with its asymptotic approximation (4.22). In Figure 4.5, I compare them both for large values of t with the plot for the case $N = 10000$.



(a)



(b)

Figure 4.5: Plots of $\langle Q^2\rangle$ calculated from different expressions:(a)comparing exact expression against asymptotic approximation of limiting value of $\langle Q^2\rangle$ as $N\to\infty$ for large t, (b)comparing the plots of exact expression and asymptotic approximation for large t of the limit of $\langle Q^2\rangle$ as $N\to\infty$ against that of $\langle Q^2\rangle$ for the case of $N = 10000$

For large t, it can be seen that the asymptotic straight line approximation is in excellent agreement with the exact expression and with the straight line portion of the plot for a large finite N case. It can also be observe from this plot 4.5 that the limiting form continues to follow the straight line path indefinitely as predicted.

A. Appendix: Writing the system Hamiltonian in matrix form

In section 1, Hamiltonian equation 1.1 is said to be mathematically equivalent to equation 1.2. This section deals with the proof of the same. Let us start from equation 1.1 i.e.,

$$H = \sum_{l=1}^{N} \left\{ \frac{p_l^2}{2m} + \frac{1}{2} \cdot \frac{k}{2} [(x_l - x_{l-1})^2 + (x_{l+1} - x_l)^2] \right\} + \frac{1}{2} \cdot \frac{k}{2} \left(x_1^2 + x_N^2\right) \tag{A.1}$$

I will expand this into individual summations and will proceed as follows.

$$H = \sum_{l=1}^{N} \left\{ \frac{p_l^2}{2m} + \frac{1}{2} \cdot \frac{k}{2} [2x_l^2 + x_{l-1}^2 + x_{l+1}^2 - 2x_l x_{l-1} - 2x_l x_{l+1}] \right\} + \frac{1}{2} \cdot \frac{k}{2} \left(x_1^2 + x_N^2\right) \tag{A.2}$$

Now, let us take the potential part (say V) of the Hamiltonian alone and expand it for the convenience of calculation.

$$\begin{aligned}
V &= \frac{1}{2} \cdot \frac{k}{2} \left[\left(2\sum_{l=1}^{N} x_l^2\right) + \left(\sum_{l=1}^{N} x_{l+1}^2\right) + \left(\sum_{l=1}^{N} x_{l-1}^2\right) - \left(2\sum_{l=1}^{N} x_l\, x_{l+1}\right) - \left(2\sum_{l=1}^{N} x_l\, x_{l-1}\right) + \left(x_1^2 + x_N^2\right) \right] \\
&= \frac{1}{2} \cdot \frac{k}{2} \left[\left(2\sum_{l=1}^{N} x_l^2\right) + \left(\sum_{l-1=1}^{N} x_{(l-1)+1}^2\right) + \left(\sum_{l+1=1}^{N} x_{(l+1)-1}^2\right) - \left(2\sum_{l=1}^{N} x_l\, x_{l+1}\right) - \left(2\sum_{l=1}^{N} x_l\, x_{l-1}\right) + \left(x_1^2 + x_N^2\right) \right] \\
&= \frac{1}{2} \cdot \frac{k}{2} \left[\left(2\sum_{l=1}^{N} x_l^2\right) + \left(\sum_{l=2}^{N+1} x_l^2\right) + \left(\sum_{l=0}^{N-1} x_l^2\right) - \left(2\sum_{l=1}^{N} x_l x_{l+1}\right) - \left(2\sum_{l=1}^{N} x_l x_{l-1}\right) + \left(x_1^2 + x_N^2\right) \right] \\
&= \frac{1}{2} \cdot \frac{k}{2} \left[\left(2\sum_{l=1}^{N} x_l^2\right) + \left(\sum_{l=2}^{N} x_l^2\right) + \left(\sum_{l=1}^{N-1} x_l^2\right) - \left(2\sum_{l=1}^{N} x_l x_{l+1}\right) - \left(2\sum_{l=1}^{N} x_l x_{l-1}\right) + \left(x_1^2 + x_N^2\right) \right]
\end{aligned} \tag{A.3}$$

In the last step $(N+1)$th term in the second summation and 0th term in the third term have been omitted as they evaluate to zero at all times. Now let write each summation as a matrix product in the above equation. I will refer to the sums as (A), (B), (C), (D), (E) and (F) respectively in the same order they appear in the equation. It can be easily verified that they can be written in matrix form as shown below where all the empty places in all the matrices are actually occupied by 0.

$$
\begin{aligned}
&\text{(A)}: && 2\sum_{l=1}^{N} x_l^2 = \begin{pmatrix} x_1 & x_2 & x_3 & \cdots & x_N \end{pmatrix} \begin{pmatrix} 2 & & & & \\ & 2 & & & \\ & & \ddots & & \\ & & & 2 & \\ & & & & 2 \end{pmatrix}_{N\times N} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ \vdots \\ x_N \end{pmatrix} \\
&\text{(B)}: && \sum_{l=2}^{N} x_{l+1}^2 = \begin{pmatrix} x_1 & x_2 & x_3 & \cdots & x_N \end{pmatrix} \begin{pmatrix} 0 & & & & \\ & 1 & & & \\ & & 1 & & \\ & & & \ddots & \\ & & & & 1 \end{pmatrix}_{N\times N} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ \vdots \\ x_N \end{pmatrix} \\
&\text{(C)}: && \sum_{l=1}^{N-1} x_{l-1}^2 = \begin{pmatrix} x_1 & x_2 & x_3 & \cdots & x_N \end{pmatrix} \begin{pmatrix} 1 & & & & \\ & \ddots & & & \\ & & 1 & & \\ & & & 1 & \\ & & & & 0 \end{pmatrix}_{N\times N} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ \vdots \\ x_N \end{pmatrix} \\
&\text{(D)}: && 2\sum_{l=1}^{N} x_l\, x_{l+1} = \begin{pmatrix} x_1 & x_2 & x_3 & \cdots & x_N \end{pmatrix} \begin{pmatrix} 0 & 2 & & & \\ & 0 & 2 & & \\ & & 0 & \ddots & \\ & & & 0 & 2 \\ & & & & 0 \end{pmatrix}_{N\times N} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ \vdots \\ x_N \end{pmatrix} \\
&\text{(E)}: && 2\sum_{l=1}^{N} x_l\, x_{l-1} = \begin{pmatrix} x_1 & x_2 & x_3 & \cdots & x_N \end{pmatrix} \begin{pmatrix} 0 & & & & \\ 2 & 0 & & & \\ & 2 & 0 & & \\ & & \ddots & 0 & \\ & & & 2 & 0 \end{pmatrix}_{N\times N} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ \vdots \\ x_N \end{pmatrix} \\
&\text{(F)}: && \left(x_1^2 + x_N^2\right) = \begin{pmatrix} ox_1 & x_2 & x_3 & \cdots & x_N \end{pmatrix} \begin{pmatrix} 1 & & & & \\ & 0 & & & \\ & & \ddots & & \\ & & & 0 & \\ & & & & 1 \end{pmatrix}_{N\times N} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ \vdots \\ x_N \end{pmatrix}
\end{aligned}
$$

Now we substitute (A), (B), (C), (D), (E) and (F) in equation A.3. It can be seen that each term has $|x\rangle$ on the left and $\langle x|$ on the right. Thus, I will just add (or subtract as per equation A.3) all the matrices in the middle of each term and obtain a single term containing only matrices for the potential. If one takes Λ to be that sum, then Λ can be shown to have the following value.

$$
\Lambda = 2\begin{pmatrix} 2 & -1 & & & & \\ -1 & 2 & -1 & & & \\ & -1 & 2 & \ddots & & \\ & & \ddots & \ddots & -1 & \\ & & & -1 & 2 & -1 \\ & & & & -1 & 2 \end{pmatrix}_{N\times N} \tag{A.4}
$$

Here I define Ω to be half of Λ.

$$\Omega \equiv \frac{1}{2}\Lambda = \begin{pmatrix} 2 & -1 & & & & \\ -1 & 2 & -1 & & & \\ & -1 & 2 & \ddots & & \\ & & \ddots & \ddots & -1 & \\ & & & -1 & 2 & -1 \\ & & & & -1 & 2 \end{pmatrix}_{N\times N} \tag{A.5}$$

With this, I can write the potential term V as

$$V = \frac{k}{2}\langle x|\Omega|x\rangle \tag{A.6}$$

where $|x\rangle$ is defined as

$$|x\rangle \equiv \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_N \end{pmatrix}. \tag{A.7}$$

It can be easily verified that the kinetic term (say T) in equation A.2 can be written as

$$T = \frac{1}{2m}\langle p|p\rangle, \tag{A.8}$$

if $|p\rangle$ is defined as

$$|p\rangle = \begin{pmatrix} p_1 \\ p_2 \\ \vdots \\ p_N \end{pmatrix}. \tag{A.9}$$

Thence, the total Hamiltonian of the system can be written as

$$H = \frac{\langle p|p\rangle}{2m} + \frac{k}{2}\langle x|\Omega|x\rangle. \tag{A.10}$$

This is the matrix form of the system Hamiltonian presented in section 1. As it can be seen, the potential term is a quadratic form and we can transform the whole equation into the eigen-basis of Ω. The diagonal transformation matrix of Ω is U as was obtained in section 2.

$$U \equiv \frac{1}{\sqrt{\frac{N+1}{2}}} \begin{pmatrix} \sin\left(1\cdot\frac{1\pi}{N+1}\right) & \sin\left(1\cdot\frac{2\pi}{N+1}\right) & \cdots & \sin\left(1\cdot\frac{N\pi}{N+1}\right) \\ \sin\left(2\cdot\frac{1\pi}{N+1}\right) & \sin\left(2\cdot\frac{2\pi}{N+1}\right) & \cdots & \sin\left(2\cdot\frac{N\pi}{N+1}\right) \\ \vdots & \vdots & \ddots & \vdots \\ \sin\left(N\cdot\frac{1\pi}{N+1}\right) & \sin\left(N\cdot\frac{2\pi}{N+1}\right) & \cdots & \sin\left(N\cdot\frac{N\pi}{N+1}\right) \end{pmatrix}, \tag{A.11}$$

Besides that, it was also proven in appendix C that

$$U = U^{\mathrm{T}} = U^{-1}. \tag{A.12}$$

Let us define the transform

$$U^{\mathrm{T}}|x\rangle \;=\; |\tilde{x}\rangle. \tag{A.13}$$

With these one can manipulate equation A.10 as follows.

$$H \;=\; \frac{\langle p|(UU^{\mathrm{T}})|p\rangle}{2m} \;+\; \frac{k}{2}\langle x|(UU^{\mathrm{T}})\Omega(UU^{\mathrm{T}})|x\rangle \tag{A.14}$$

$$H \;=\; \frac{(\langle p|U)(U^{\mathrm{T}}|p\rangle)}{2m} \;+\; \frac{k}{2}((\langle x|U)(U^{\mathrm{T}}\Omega U)(U^{\mathrm{T}}|x\rangle) \tag{A.15}$$

Thus, I can write the Hamiltonian in the eigen-basis of Ω as

$$H \;=\; \frac{\langle \tilde{p}|\tilde{p}\rangle}{2m} \;+\; \frac{k}{2\omega_0^2}\langle \tilde{x}|W^2|\tilde{x}\rangle \tag{A.16}$$

where W is the diagonal matrix consisting of all the (square roots of) eigenvalues of Ω whose values were calculated explicitly in section 2.

$$W \;=\; \begin{pmatrix} \omega_1 & & & \\ & \omega_2 & & \\ & & \ddots & \\ & & & \omega_N \end{pmatrix} \;=\; 2\,\omega_0 \begin{pmatrix} \sin\left(\frac{1\cdot\pi}{2(N+1)}\right) & & & \\ & \sin\left(\frac{2\cdot\pi}{2(N+1)}\right) & & \\ & & \ddots & \\ & & & \sin\left(\frac{1\cdot\pi}{2(N+1)}\right) \end{pmatrix} \tag{A.17}$$

It can be seen that equation A.16, can be written as a sum of quadratics of $|x\rangle$ and $|p\rangle$ with no mixed terms involved. Here, I rewrite A.16 again as follows using equation (**??**).

$$H \;=\; \frac{1}{2}\,m\,\langle \dot{\tilde{x}}|\dot{\tilde{x}}\rangle + \frac{1}{2}\,m\,\langle \tilde{x}|W^2|\tilde{x}\rangle \tag{A.18}$$

Equation (A.18) is the equation I will be using in its summation form as given below, while calculating and sampling the Boltzmann distribution for initial displacement and velocity vectors.

$$H \;=\; \frac{1}{2}m\sum_{i=1}^{N}\left\{\,\dot{\tilde{x}}_i^2 + \omega_i^2\,\tilde{x}_i^2\,\right\} \tag{A.19}$$

B. Appendix: Eigenvalues and Eigenvectors of Ω

The eigenvalue equation for Ω (1.3) can be written as

$$\Omega\,|y\rangle \;=\; \left(\frac{\omega_q}{\omega_0}\right)^2 |y\rangle, \tag{B.1}$$

where q is the index of the eigenvalue. As Ω is an $N \times N$ matrix, it is expected to have N eigenvalues and their corresponding eigenvectors. From the form of Ω, it can be said that the components of all the eigenvectors must satisfy

$$-\left(\frac{\omega_q}{\omega_0}\right)^2 y_l = (y_{l-1} - 2y_l + y_{l+1}). \tag{B.2}$$

I propose the ansatz

$$q_l = B_q \sin(ql) \tag{B.3}$$

for the lth component of the qth eigenvector $|q\rangle$. It can be easily verified that, the functions of the type $|q\rangle e^{i\omega_q t}$ (physically, eigen-modes vibrating with their eigen-frequencies) do satisfy and thus, are the solutions of the Hamilton's equations of motion for the system

$$|\ddot{x}\rangle \;=\; -\omega_0^2\,\Omega\,|x\rangle. \tag{B.4}$$

Hence, they must satisfy the system boundary conditions $x_0 = x_{N+1} = 0$. Putting these boundary conditions on the eigenvectors $q_0 = q_{N+1} = 0$ into the ansatz (B.3), the allowed values of q are found.

$$q \;=\; \frac{n\pi}{N+1} \qquad\qquad \text{for} \qquad n = 1, 2, ..., N. \tag{B.5}$$

By substituting the ansatz (B.3) in equation (B.2) and simplifying, one can get

$$\left(\frac{\omega_q}{\omega_0}\right)^2 \;=\; 4\,\sin^2\left(\frac{q}{2}\right). \tag{B.6}$$

Substituting the allowed values of q (B.5) in equation B.6, one gets the eigenvalues of Ω as

$$\left(\frac{\omega_n}{\omega_0}\right)^2 \;=\; 4\,\sin^2\left(\frac{n\pi}{2(N+1)}\right). \tag{B.7}$$

Substituting the same (B.5) in the ansatz (B.3) one can show that the normalised eigenvectors of Ω have the form

$$|n\rangle = \frac{1}{\sqrt{\frac{N+1}{2}}} \begin{pmatrix} \sin\left(1 \cdot \frac{n\pi}{N+1}\right) \\ \sin\left(2 \cdot \frac{n\pi}{N+1}\right) \\ \vdots \\ \sin\left(N \cdot \frac{n\pi}{N+1}\right) \end{pmatrix}. \tag{B.8}$$

The normalisation constant is calculated in Appendix C.

C. Appendix: Orthonormality of eigenvectors of Ω.

I will continue the proof with the following notation developed in section 2.

$$|n\rangle = \begin{pmatrix} \sin\left(1\cdot\frac{n\pi}{N+1}\right) \\ \sin\left(2\cdot\frac{n\pi}{N+1}\right) \\ \vdots \\ \sin\left(N\cdot\frac{n\pi}{N+1}\right) \end{pmatrix} \tag{C.1}$$

is the nth eigenvector. I will try to prove the orthogonality of different eigenvectors i.e., $\langle m|n\rangle = 0$ for all $m \neq n$. The proof proceeds like this:
Let $m \neq n$ for integral indices of the eigenvectors m and n. As already seen in section 2, m and n can only take values from 1 to N. Then,

$$\langle m|n\rangle = \begin{pmatrix} \sin\left(1\cdot\frac{m\pi}{N+1}\right) & \sin\left(2\cdot\frac{m\pi}{N+1}\right) & \cdots & \sin\left(N\cdot\frac{m\pi}{N+1}\right) \end{pmatrix} \begin{pmatrix} \sin\left(1\cdot\frac{n\pi}{N+1}\right) \\ \sin\left(2\cdot\frac{n\pi}{N+1}\right) \\ \vdots \\ \sin\left(N\cdot\frac{n\pi}{N+1}\right) \end{pmatrix}. \tag{C.2}$$

This can be written as

$$\langle m|n\rangle = \sum_{l=0}^{N+1} \left[\sin\left(l\cdot\frac{m\pi}{N+1}\right)\sin\left(l\cdot\frac{n\pi}{N+1}\right)\right] \tag{C.3}$$

It is worthwhile to mention that the $l = 0$ and $l = N+1$ are added to the actual summation as they both evaluate to 0 and have no effect on the value. This step will prove to be useful in evaluating the summation in subsequent steps. I will add or remove these terms from the summation as per our convenience in the following steps as well. The above expression can be written as follows.

$$\langle m|n\rangle = \frac{1}{2}\sum_{l=0}^{N+1} \left[\cos\left(l\cdot\frac{(m-n)\pi}{N+1}\right) - \cos\left(l\cdot\frac{(m+n)\pi}{N+1}\right)\right] \tag{C.4}$$

At this juncture, I will have to separate the proof into two different cases: 1. (m-n) is even and 2. (m-n) is odd. Let us take each of the cases separately.

case 1: even $(m-n)$

For this case we will omit $l = N+1$ term from the summation. After that, equation C.4 can be simplified in the following way.

$$\langle m|n\rangle = \frac{1}{2}\sum_{l=0}^{N} \left[\cos\left(l\cdot\frac{(m-n)\pi}{N+1}\right) - \cos\left(l\cdot\frac{(m+n)\pi}{N+1}\right)\right] \tag{C.5}$$

$$= \frac{1}{4}\sum_{l=0}^{N} \left(e^{\frac{i(m-n)\pi l}{N+1}} + e^{-\frac{i(m-n)\pi l}{N+1}} - e^{\frac{i(m+n)\pi l}{N+1}} - e^{-\frac{i(m+n)\pi l}{N+1}}\right) \tag{C.6}$$

$$= \frac{1}{4}\left[\sum_{l=0}^{N} e^{\frac{i(m-n)\pi l}{N+1}} + \sum_{l=0}^{N} e^{-\frac{i(m-n)\pi l}{N+1}} - \sum_{l=0}^{N} e^{\frac{i(m+n)\pi l}{N+1}} - \sum_{l=0}^{N} e^{-\frac{i(m+n)\pi l}{N+1}}\right] \tag{C.7}$$

Each of the terms on the right hand side of the equation can be recognised as geometric series and can be simplified into the following form.

$$\langle m|n\rangle = \left(\frac{1-e^{i(m-n)\pi}}{1-e^{\frac{i(m-n)\pi}{N+1}}} + \frac{1-e^{-i(m-n)\pi}}{1-e^{-\frac{i(m-n)\pi}{N+1}}} - \frac{1-e^{i(m+n)\pi}}{1-e^{\frac{i(m+n)\pi}{N+1}}} - \frac{1-e^{-i(m-n)\pi}}{1-e^{-\frac{i(m-n)\pi}{N+1}}}\right) \tag{C.8}$$

As $(m-n)$ is even, it can be easily seen that the numerators of each of the terms on the right hand side evaluate to 0. Thus,

$$\langle m|n\rangle = 0 \tag{C.9}$$

when $m \neq n$ and $(m-n)$ is even.

case 2: odd $(m-n)$

Let us go back to equation C.4. This can be modified as keeping the limits same and proceeding the same way as it was done before.

$$\langle m|n\rangle = \frac{1}{2}\sum_{l=0}^{N+1}\left[\cos\left(l\cdot\frac{(m-n)\pi}{N+1}\right) - \cos\left(l\cdot\frac{(m+n)\pi}{N+1}\right)\right] \tag{C.10}$$

$$= \frac{1}{4}\sum_{l=0}^{N+1}\left(e^{\frac{i(m-n)\pi l}{N+1}} + e^{-\frac{i(m-n)\pi l}{N+1}} - e^{\frac{i(m+n)\pi l}{N+1}} - e^{-\frac{i(m+n)\pi l}{N+1}}\right) \tag{C.11}$$

$$= \frac{1}{4}\left(\sum_{l=0}^{N+1} e^{\frac{i(m-n)\pi l}{N+1}} + \sum_{l=0}^{N+1} e^{-\frac{i(m-n)\pi l}{N+1}} - \sum_{l=0}^{N+1} e^{\frac{i(m+n)\pi l}{N+1}} - \sum_{l=0}^{N+1} e^{-\frac{i(m+n)\pi l}{N+1}}\right) \tag{C.12}$$

$$\begin{aligned} = \frac{1}{4}\Bigg(&\sum_{l=0}^{N} e^{\frac{i(m-n)\pi l}{N+1}} + e^{i(m-n)\pi} + 1 + \sum_{l=1}^{N+1} e^{-\frac{i(m-n)\pi l}{N+1}} \\ &- \sum_{l=0}^{N} e^{\frac{i(m+n)\pi l}{N+1}} - e^{i(m+n)\pi} - 1 - \sum_{l=1}^{N+1} e^{-\frac{i(m+n)\pi l}{N+1}}\Bigg) \end{aligned} \tag{C.13}$$

In the last step $l = N+1$ terms are taken out of the first and third summations while $l = 0$ terms are taken out of the second and fourth summations. Now, as in this case $(m-n)$ is odd,

$$e^{\pm i(m\pm n)\pi} = -1. \tag{C.14}$$

Using this and recognising like before, that each of the summations here is a geometric series, one can rewrite equation C.13 as the following.

$$\begin{aligned} \langle m|n\rangle = \Bigg[&\left(\frac{1-e^{i(m-n)\pi}}{1-e^{\frac{i(m-n)\pi}{N+1}}}\right) + e^{-\frac{i(m-n)pi}{N+1}}\left(\frac{1-e^{-i(m-n)\pi}}{1-e^{-\frac{i(m-n)\pi}{N+1}}}\right) \\ &- \left(\frac{1-e^{i(m+n)\pi}}{1-e^{\frac{i(m+n)\pi}{N+1}}}\right) - e^{-\frac{i(m+n)pi}{N+1}}\left(\frac{1-e^{-i(m-n)\pi}}{1-e^{-\frac{i(m-n)\pi}{N+1}}}\right)\Bigg] \end{aligned} \tag{C.15}$$

Again using the relation C.14, and some manipulations to the second and fourth terms one gets

$$\langle m|n\rangle = \left[\left(\frac{2}{1-e^{\frac{i(m-n)\pi}{N+1}}}\right) - \left(\frac{2}{1-e^{\frac{i(m-n)\pi}{N+1}}}\right) - \left(\frac{2}{1-e^{\frac{i(m+n)\pi}{N+1}}}\right) + \left(\frac{2}{1-e^{\frac{i(m+n)\pi}{N+1}}}\right) \right]. \tag{C.16}$$

In the above expression it can be seen that the first two terms and the next two terms cancel out giving out 0. Thus, in the second case as well,

$$\langle m|n\rangle = 0 \tag{C.17}$$

for odd $(m-n)$.

With this, the proof is completed for the assertion that all the eigenvectors in the given problem are orthogonal to each other. Another claim made in section 2 is that all the eigenvectors have the same norm. I will go on to prove this in the rest of this section.

To find out the norm of an eigenvector $|n\rangle$,

$$\langle n|n\rangle = \begin{pmatrix}\sin\left(\frac{n\pi}{N+1}\cdot 1\right) & \sin\left(\frac{n\pi}{N+1}\cdot 2\right) & \cdots & \sin\left(\frac{n\pi}{N+1}\cdot N\right)\end{pmatrix} \begin{pmatrix}\sin\left(\frac{n\pi}{N+1}\cdot 1\right)\\ \sin\left(\frac{n\pi}{N+1}\cdot 2\right)\\ \vdots \\ \sin\left(\frac{n\pi}{N+1}\cdot N\right)\end{pmatrix} \tag{C.18}$$

I will rewrite this in the following form.

$$\langle n|n\rangle = \sum_{l=0}^{N} \sin^2\left(\frac{n\pi}{N+1}\cdot l\right) \tag{C.19}$$

It is to be noted that $l=0$ term is added so that it will make it easier to evaluate the summation and it doesn't change the value of the summation. We proceed with the simplification as follows using the the expressions for geometric series.

$$\langle n|n\rangle = \frac{1}{2}\sum_{l=0}^{N}\left(1-\cos\left(\frac{2n\pi}{N+1}\cdot l\right)\right) \tag{C.20}$$

$$= \frac{N+1}{2} - \frac{1}{4}\sum_{l=0}^{N}\left(e^{\frac{2in\pi l}{N+1}} + e^{-\frac{2in\pi l}{N+1}}\right) \tag{C.21}$$

$$= \frac{N+1}{2} - \frac{1}{4}\left[\sum_{l=0}^{N} e^{\frac{2in\pi l}{N+1}} + \sum_{l=0}^{N} e^{-\frac{2in\pi l}{N+1}}\right] \tag{C.22}$$

$$= \frac{N+1}{2} - \frac{1}{4}\left[\left(\frac{1-e^{2in\pi}}{1-e^{\frac{2in\pi}{N+1}}}\right) + \left(\frac{1-e^{-2in\pi}}{1-e^{-\frac{2in\pi}{N+1}}}\right)\right] \tag{C.23}$$

It is known that for any integer n,

$$e^{\pm 2in\pi} = 1. \tag{C.24}$$

Using this, one can see that the square brackets in equation C.23 evaluate to zero. Thus I can finally rewrite the norm in (C.20) as the following.

$$\langle n|n\rangle \;=\; \frac{N+1}{2} \tag{C.25}$$

Looking at equation C.25, it an be easily understood that the norm of the eigenvector of the form (C.1) doesn't depend on the index of the eigenvector and only depends on the size of the system i.e., number of particles in the harmonic chain. Thus, the norm of every eigenvector is one and the same.

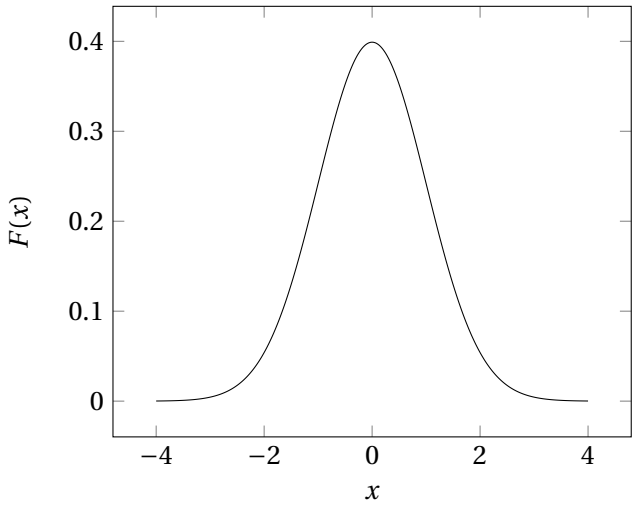
D. Appendix: Sampling Algorithms

This section briefly elaborates on some specific sampling algorithms that are used in the work for sampling probability distributions. Algorithms and the theory behind how and why they work will be explained.

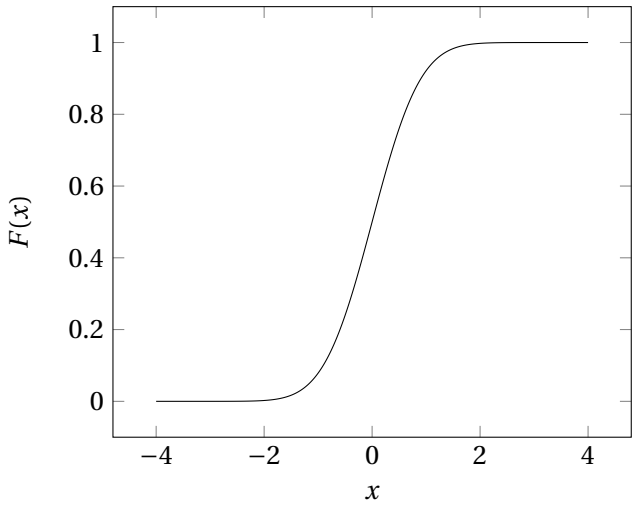
D.1. Inversion Sampling

Given a normalised PDF i.e., probability density function $f(x)$ of a random variable x, the inversion sampling algorithm can be written down as the following sequential steps.

1. Find the CDF i.e., cumulative density function $F(x)$ of the given PDF $f(x)$.
2. Invert the CDF $F(x)$ to find $F^{-1}(p)$.
3. Sample the required number of samples from $U(0,1)$ i.e., uniform distribution defined over (0,1),
4. Calculate $F^{-1}(x)$ for each sample. The set of values so calculated will be the samples from the distribution $f(x)$.



(a) Probability density function



(b) Cumulative density function

Figure D.1: The normal distribution

Now I will walk the reader through the details of why this seemingly random procedure does sample from the target distribution. Let $f(x)$ be the target distribution that we want to sample from, i.e., the probability density function for the random variable x is $f(x)$. Then the CDF for the given PDF

$$f : \mathbb{R} \to \mathbb{R}$$

is calculated as follows.

$$F(x) = \int_{-\infty}^{x} f(x')dx'. \tag{D.1}$$

Conversely, it also means that

$$\frac{dF}{dx} = f(x). \tag{D.2}$$

Any normalised PDF is a positive valued function throughout its domain. Thus, CDF, which is its integral is a strictly increasing function throughout the domain. For example, let us consider normal distribution. The PDF and CDF are shown in Figure D.1 and as expected F(x), the CDF is a strictly increasing function and thus also an invertible function. According to what had been defined so far,

$$f : \mathbb{R} \to \mathbb{R}, \tag{D.3}$$
$$F : \mathbb{R} \to (0,1) \qquad \text{and} \tag{D.4}$$
$$F^{-1} : (0,1) \to \mathbb{R}. \tag{D.5}$$

Now, going back to the algorithm one first samples a uniform distribution on $(0,1)$ and then inputs the samples into the function F^{-1}. Thus, in the domain of F^{-1} equal number of samples are sampled from equal intervals of length. Thus, the number of samples in an interval are directly proportional to its length. One can take a step further and use the fraction of samples an interval contains as the units for F(x) while plotting as shown in Figure D.1(b). Mathematically,

$$\begin{pmatrix}\text{Number of samples}\\ \text{in an interval in}\\ \text{the domain of } F^{-1}(x)\end{pmatrix} \propto \begin{pmatrix}\text{length of that}\\ \text{interval}\end{pmatrix}. \tag{D.6}$$

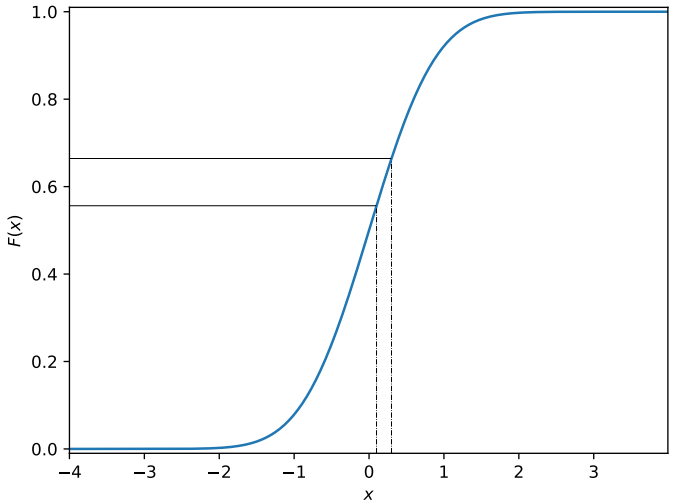


Figure D.2: CDF of a gaussian distribution showing how an interval on the y-axis transforms itself as another interval on the x-axis through the function $F^{-1}(x)$ or vice-versa

When the plot in Figure D.2 is examined carefully, it is observed that when a small interval on the y-axis(representing the domain of F^{-1}) is considered and its boundary points (say a and b) are input into the function F^{-1}, then the outputs ($F^{-1}(a)$ and $F^{-1}(b)$) would define a new interval with them as boundaries. And all the values inside and only inside the interval on the y-axis upon being input into F^{-1} would fall in the interval bounded by $F^{-1}(a)$ and $F^{-1}(b)$ on the x-axis. The approximate slope of the function around a point in the plot D.2 as shown in the figure can be calculated as rise(length of the interval taken around the point on the y-axis, say Δy) over run(length of the corresponding interval on the x-axis, say Δx). For sufficiently small interval we also know that the slope can be approximated by the derivative of $F(x)$ at that point. Thus,

$$\frac{\Delta y}{\Delta x} \simeq \frac{dF(x)}{dx} \tag{D.7}$$

As per equation D.6, it is known that Δy is proportional to the number of samples inside that length of the domain. Thus, one can write

$$\frac{\left(\begin{array}{c}\text{Number of samples}\\ \text{in an interval in}\\ \text{the domain of } F^{-1}(x)\end{array}\right)}{\Delta x(x)} \quad \propto \quad \frac{dF}{dx} \tag{D.8}$$

As per equation D.6, it is known that for a sufficiently small Δx. Thus, I can replace the RHS with the target PDF using equation (D.2). And it can be seen that the LHS is nothing but the density of samples around a point on the x axis. For sufficiently small intervals Δx and Δy the relation becomes more and more accurate and thus I will write,

$$\text{Density of samples} \quad \propto \quad f(x). \tag{D.9}$$

Thus, when one samples using the Inversion sampling algorithm they will in fact draw samples from the target distribution.

D.2. Box-Muller transform for sampling Gaussian distributions

The Box-Müller algorithm samples two values from two independent gaussians at a time and it is highly efficient as compared to the traditional inversion sampling when used for gaussian distribution. The method relies on the properties of a bivariate gaussian distribution and its polar form. The algorithm is as follows which was already outlined in 4.

1. Sample two real numbers u_1 and u_2 respectively from $U_1(0,1)$ and $U_2(0,1)$ which are uniform distributions over the interval $(0,1)$.

2. Find the values of x and y that are each a sample from a gaussian by transforming u_1 and u_2 using the following transformation equations.

$$\begin{aligned} x &= \sqrt{-2\,\sigma^2 \ln(u_1)}\,\cos(2\pi u_2) \\ y &= \sqrt{-2\,\sigma^2 \ln(u_1)}\,\sin(2\pi u_2) \end{aligned} \tag{D.10}$$

Now, let us take a brief look at how this comes about. First, instead of sampling one gaussian, Box-Müller, samples an ordered pair from a normalised bivariate distribution of two uncorrelated variables (say x and y)

$$f(x,y) = \frac{1}{2\pi\sigma^2}\,\exp\left(\frac{x^2+y^2}{2\sigma^2}\right). \tag{D.11}$$

This distribution can be transformed into its polar form

$$f(r,\theta) = \frac{1}{2\pi\sigma^2} \exp\left(\frac{r^2}{2\sigma^2}\right) \tag{D.12}$$

This can be split into two separate individual distributions of the variables r and θ, respectively.

$$f(r,\theta) = \left(\frac{1}{2\pi}\right) \cdot \left(\frac{1}{\sigma^2} \exp\left(\frac{r^2}{2\sigma^2}\right)\right) \tag{D.13}$$

Then these individual distributions are sampled for the values of r and θ which are then converted back to x and y using the following transformation.

$$\begin{aligned} x &= r\cos\theta \\ y &= r\sin\theta \end{aligned} \tag{D.14}$$

The individual distributions for r and θ are sampled using good old inversion sampling algorithm. The CDFs are found for each of the distributions and the samples from uniform distributions are input into them and the obtained values are transformed using (D.14). This whole procedure upon simplification will lead to the Box-Müller transform given in the equations (D.10).

REFERENCES

[1] *NIST Digital Library of Mathematical Functions*. https://dlmf.nist.gov/, Release 1.2.1 of 2024-06-15. F. W. J. Olver, A. B. Olde Daalhuis, D. W. Lozier, B. I. Schneider, R. F. Boisvert, C. W. Clark, B. R. Miller, B. V. Saunders, H. S. Cohl, and M. A. McClain, eds.