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Assignment

Problem Set 1: Brownian Motion

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by

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ABSTRACT

The aim of this report is to study the motion properties of a 1-D Brownian particle in thermal equilibrium, by modifying the system parameters to exclude or include a potential that acts on the particle itself. A set of repeated experiments is conducted in order to draw conclusions on the statistical properties that the particle shows, to obtain insights that can describe the particle motion in time and space depending on the parameters.

1 INTRODUCTION

In this report, we study the behaviour of a 1-dimensional Brownian particle in a thermal bath, conducting different experiments with different initial assumptions and studying the behaviour of the particle in space x and time t. Throughout the experiments, the constant settings of the problem are:

(1) $(t_0, x_0) = (0, 0)$ is the starting point of each Brownian particle;
(2) $k_B = 1$ is the Boltzmann constant value;
(3) $m = 1$ is the mass of each particle.

All the experiments are repeated for a number of $p = 1000$ different particles, that thus refers to the sample size.

For the 1-D case, and assuming fully-overdamped dynamics, the following Langevin equation describes the motion of the particle as

$$\frac{dx}{dt} = \frac{\tau}{m}\left(f(x) + \xi(t)\right) \tag{1}$$

where τ is the damping factor, $f(x)$ is a deterministic force depending on the position of the particle x and $\xi(t)$ is a random force that adds noise to the path of the particle. The main assumption on this random force is $\langle \xi(t) \rangle = 0$, i.e. the stationary average of the force is zero. Notice that this equation of motion implies that the particle has no inertia. Thus, the particle has initial equilibrium velocity

$$v_0 = \sqrt{\frac{k_B T}{m}} \tag{2}$$

In this case, the exact solution for the particle trajectory is

$$\begin{aligned} x(t) &= \frac{\tau}{m}\int_0^t \left(f(x(t')) + \xi(t')\right) dt' \\ &= \frac{\tau}{m}\int_0^t f(x(t'))dt' + \frac{\tau}{m}\int_0^t \xi(t')dt' \end{aligned} \tag{3}$$

which can be numerically integrated step by step using the Forward Euler method as

$$x[i+1] = x[i] + \Delta t \frac{\tau}{m} f(x[i]) + \sqrt{\frac{2k_B T\tau}{m}}\sqrt{\Delta t}\,\chi[i] \tag{4}$$

where $\chi \sim N(0,1)$ gives the realization of the random force $\xi(i)$ for each simulation step i.

2 FIRST EXPERIMENT

For the first experiment, the goal is to simulate the behaviour of a Brownian particle not subject to any external force. In this case, the equation of motion becomes

$$\frac{dx}{dt} = \frac{\tau}{m}\xi(t) \tag{5}$$

where thus the random noise term is the driver of the path of the particle. Given the solution for $\dot{x}$ from Equation (3), we have that

$$x(t) = \frac{\tau}{m}\int_0^t \xi(t')dt' \tag{6}$$

which can be integrated using Equation (4) setting $f(x) = 0\ \forall x$. The objective is to verify that the mean squared displacement[1] (MSD) of the particle $\langle x^2(t) \rangle$ behaves as a linear function of t described by

$$\langle x^2(t) \rangle = 2Dt \tag{7}$$

where $D = \tau v_0^2 = \frac{\tau k_B T}{m}$ is the diffusion coefficient in thermal equilibrium. Figure 1 shows a sample of 100 of the 1000 simulated paths for the particle. As the plot shows, each particle diffuses around the mean displacement $\langle x(t) \rangle \simeq 0\ \forall t$, as expected from the theory.

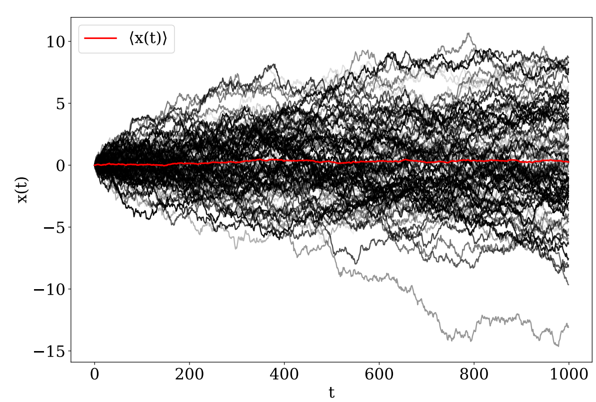


Figure 1: ***Sample path simulation for the particle. In red the average displacement (over 1000 particles) is displayed.***

To investigate the scaling of the mean square displacement, we simulate the path of $p = 1000$ particles for a number of timesteps $N = 1000$. The integration parameters are set as $\Delta t = 0.01$, so that $t_{max} = N\Delta t = 10$, the system temperature $T = 1$ and $\tau = 1$. Given these parameters, the theoretical value for the diffusion

[1] Note that this expression of the MSD is implied by the initial position value $x_0 = 0$.

coefficient results in $D = 1$. After simulating all the paths, the MSD is empirically measured as

$$\widehat{\langle x^2(i) \rangle} = \frac{1}{p}\sum_{i=1}^{p} x^2(i) \qquad , \ i = 1, ..., N \tag{8}$$

Then, on all the measurements of x, a line is fitted through a 1-degree polynomial fit, in order to obtain a function s.t.

$$\langle x^2(t) \rangle = \hat{\alpha} + \hat{\beta} t \tag{9}$$

If the theory holds, we should observe that $\hat{\alpha} = 0$ and $\hat{\beta} = 2D = 2\frac{\tau k_B T}{m} = 2$.

Results are shown in Figure 2. The plot exibits the linear behaviour of the MSD over time, with minimal deviations. The measured $\hat{\alpha} = 0.09$ is sufficiently[2] close to the expected value of $\hat{\alpha} = 0$, while the measured MSD relation with time results $\hat{\beta} = 1.984248$, which is sufficiently close to the theoretical value $\hat{\beta} = 2$. From these measurements, we can conclude that the estimated diffusion coefficient $\hat{D} = \hat{\beta}/2 = 0.992124$ is sufficiently close to its theoretical value $D = 1$.

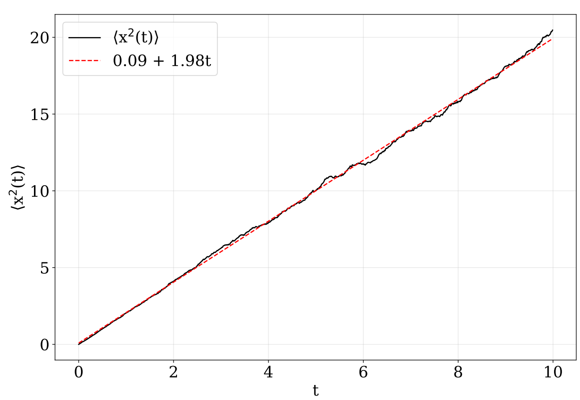


Figure 2: ***Estimated MSD (black line) and fitted polynomial regression (red line).***

We then experiment with different temperatures $T \in [10^1, 10^4]$ and plot the relation of D and T. Results are shown in Figure 3. As the plot indicates, the diffusion coefficient scales linearly with temperature, as the theoretical expression for D states.

3 SECOND EXPERIMENT

For the second experiment, we now let the particle be influenced by the following potential:

$$V(x) = \frac{1}{2}kx^2 - Ax^4 \tag{10}$$

that exhibits potential barriers at

$$\begin{gathered} \Delta = V(\pm x_b) \qquad s.t. \\ \frac{d}{dx}V(x) = kx - 4Ax^3 = 0 \\ x(k - 4Ax^2) = 0 \iff x_b = \pm\sqrt{\frac{k}{4A}} \end{gathered} \tag{11}$$

having ruled out the possibility of $x = 0$, which corresponds to the potential equilibrium well. The defined potential corresponds to the following force being applied to the particle

$$f_{V;A}(x) = -\frac{d}{dx}V(x) = -kx + 4Ax^3 \tag{12}$$

and, by setting $A = 0$ the resulting force is $f_{V;0}(x) = -kx$. This corresponds to a parabolic potential which has no barriers that can be escaped, thus resulting in the particle being confined to a certain movement determined by the energy of the system. The goal of this experiment is then to characterize this movement in the long term, deriving a limiting distribution $p(x; T)$ and controlling for the system energy given by T to observe the the behaviour of the distribution for different energy levels.

For this goal, we use Equation (4) where $f(x) = f_{V;0}(x)$ to simulate the path of $p = 1000$ particles. In this case, the estimation parameters are set as $N = 1000$, $\tau = 1$ and $k = 1$. However, in this case, additional considerations with regard to the integration step Δt must be taken into account. In particular, given the specified potential field, the particle behaves in such field with a motion that can be approximated by an harmonic oscillator in its deterministic part. It is known that, in such system, the angular velocity of the particle is

$$\omega = \sqrt{\frac{k}{m}} \tag{13}$$

which corresponds to an harmonic oscillation timescale of

$$t_{osc} = \frac{2\pi}{\omega} = 2\pi\sqrt{\frac{m}{k}} \tag{14}$$

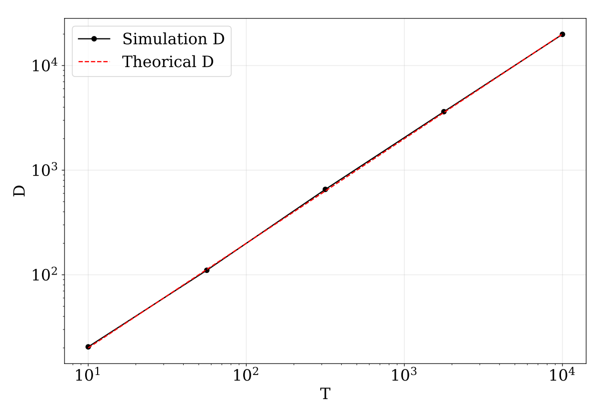


Figure 3: ***Estimated (black line) and theoretical (red line) relation of D as a function of T.***

[2] An investigation of the standard errors should be included here to ensure the statistical validity of these conclusions.

Thus, to ensure that the simulation correctly takes into account the deterministic movement given by the force $f_{V;0}$, it is necessary that $\Delta t < t_{osc}$ so that overshoot of the particle is avoided. Also, a second requirement is given by Equation (4), noticing that if the random component is greater than the deterministic one, the particle may behave mostly random, underestimating the effect of the force given by the potential. Thus, we need that

$$\Delta t \frac{\tau}{m} k|x_i| > \sqrt{\frac{2k_B T\tau}{m}} \sqrt{\Delta t} \tag{15}$$

where $|x_i|$ refers to the typical position of the particle which, in our setting, can be approximated by equating the effects of the potential energy and the thermal energy obtaining

$$\frac{1}{2}kx^2 = k_B T \Rightarrow |x| = \sqrt{\frac{2k_B T}{k}} \tag{16}$$

Thus, rearranging the terms, we obtain

$$\begin{aligned} \Delta t &> \left(\frac{2k_B T\tau}{km|x_i|}\right)^{2/3} = \\ &= \left(\frac{2k_B T\tau}{km\sqrt{\frac{2k_B T}{k}}}\right)^{2/3} = \\ &= \left(\frac{\sqrt{2}\tau}{m}\right)^{2/3} \left(\frac{k_B T}{k}\right)^{1/3} =: t_f \end{aligned} \tag{17}$$

These two conditions together imply that the integration timestep is bounded by

$$t_f < \Delta t < t_{osc} \tag{18}$$

To make this relation dimensionless, we then divide each member by t_{osc} obtaining[3]

$$\frac{t_f}{t_{osc}} < \Delta t' < 1 \tag{19}$$

Given our setting, the value of the oscillation timescale is $t_{osc} = 2\pi$ and $t_f = 2^{1/3}$, thus the rescaled lower bound value is

$$\frac{t_f}{t_{osc}} = \frac{2^{1/3}}{2\pi} \simeq 0.2 \tag{20}$$

and, consequently, the value $\Delta t = 0.5$ is set.

Results for the limiting distribution estimation are show in Figure 4. From the plot, it can be clearly seen that the displacement of the distribution widens with the temperature, and that the distribution shape is close to a Gaussian distribution. Indeed, we can show that the limiting distribution *is* a Gaussian distribution by analyzing the position of a particle x given the energy of the system E using the Boltzmann distribution

$$\mathbb{P}(x) = \frac{e^{-\beta E(x)}}{Z} \tag{21}$$

[3]From here onwards, the integration step Δt refers to the dimensionless step $\Delta t'$ as defined here.

where Z is the scaling factor. Then, knowing that the energy of the system is given by $E(x) = V(x) + K(x)$ and that the kinetic energy in the system is $K(x) = 0\ \forall x$, we can write

$$\mathbb{P}(x) = \frac{e^{-\beta \frac{1}{2} kx^2}}{Z} \tag{22}$$

From here, knowing that $-\beta\frac{1}{2}k = -\frac{1}{4Dt}$, we can conclude that $\beta = \frac{1}{2kDt}$ and $Z = \sqrt{4\pi Dt}$.

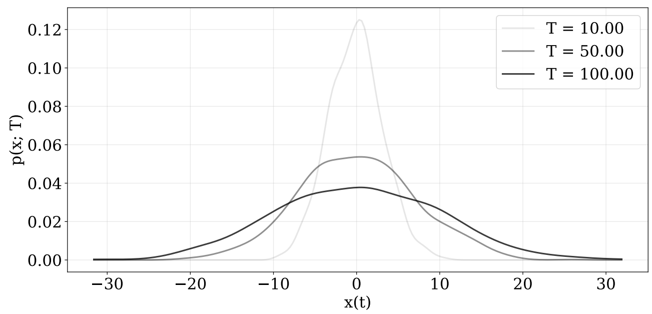


Figure 4: *Limiting distributions of the simulated paths for three different temperatures. The distribution is based on the position of each particle at the last iteration step.*

4 THIRD EXPERIMENT

For the third experiment, we consider the same potential defined in Equation (10) with the value $A = 1$ such that, in this case, the potential shows two symmetric barriers at

$$x_b = \pm\sqrt{\frac{k}{4}} \tag{23}$$

The goal of the experiment is to measure the escape times of the particles by measuring the first time the particles cross the barriers, thus escaping the potential well and diverging towards[4] $x \longrightarrow \infty$. Then, the escaping times distributions $p(\tau_1; T)$ are shown for different values of $k = [1, 4]$ and different temperatures[5]. The simulation parameters are set as $p = 1000$, $N = 1000$, $\Delta t = 0.5$, $\tau = 1$.

The resulting distributions are shown in Figure 5. The plots show that the resulting distributions are more centered over lower values of τ_1 with an increasing value of T and a decreasing value of k. Indeed, the average escaping time is lower for systems that have an higher energy, which affects the particles ability of reaching the potential barriers, while being lower also due to the position of the barrier itself, which approaches zero as $k \longrightarrow 0$. Both these factors increase the probability of having a low escaping time.

[4]To allow for computations, a cap is set at $|x| = 10^6$

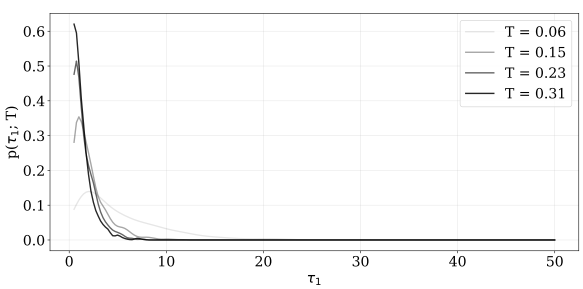
[5]In my case, using temperatures such that $T << \Delta$ showed that no particles would escape the barriers with computationally acceptable simulation steps. Thus, the decision was made to make the temperatures range in $T \in [\Delta_{min}, 5\Delta_{min}]$ where Δ_{min} is the potential height for the lowest value of k, i.e. $k = 1$.

With these results, we can further investigate the relationship between the average escaping time $\langle \tau_1 \rangle$ and the two parameters T and Δ, and the resulting computations are show in Figure 6 and Figure 7. For the dependence on T, it appears that the average escaping time follows a power-law distribution described by

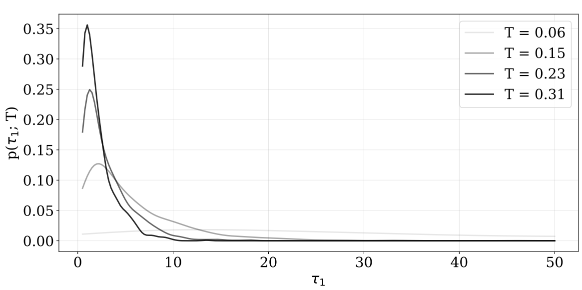
$$p(x) \propto x^{-\alpha} \tag{24}$$

with parameter $\alpha_\Delta > 1$, this parameter depending on the value of Δ which, ultimately, depends on k. In particular, increasing the barrier height Δ leads to higher values of $\langle \tau_1 \rangle$ both with an upward shift in the curve and an increasing power law parameter α, that increases the steepness of the curve. Also, with the increase of Δ, the beheaviour of the average waiting time seems to lose the property of the power law, acting more logarithmically. The power law behaviour of $\langle \tau_1 \rangle$ can be explained by the fact that very long escaping times are always possible when considering a system of infinite size, even if they have very low probability.

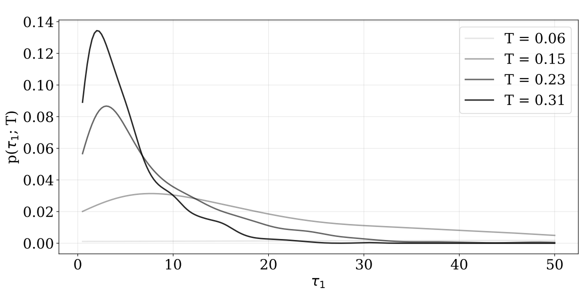
On the other hand, the relationship of $\langle \tau_1 \rangle$ with Δ exhibits the opposite behaviour. Indeed, the average waiting times increase with the value of the potential barrier height, behaving as a polynomial of power $0 < n < 1$. Again, the increase in temperature decreases the steepness of the curve other than shifting the curve downwards, leading to smaller $\langle \tau_1 \rangle$ values.



(a)



(b)



(c)

Figure 5: ***Escaping times distributions $p(\tau_1; T)$ for different values of $k = 1$ (fig. 5a), $k = 2$ (fig. 5b) and $k = 4$ (fig. 5c).***

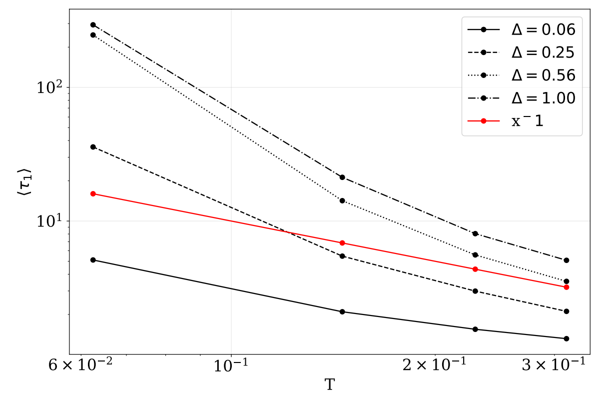


Figure 6: ***Estimated relationship between $\langle \tau_1 \rangle$ and T for different values of the barrier Δ.***

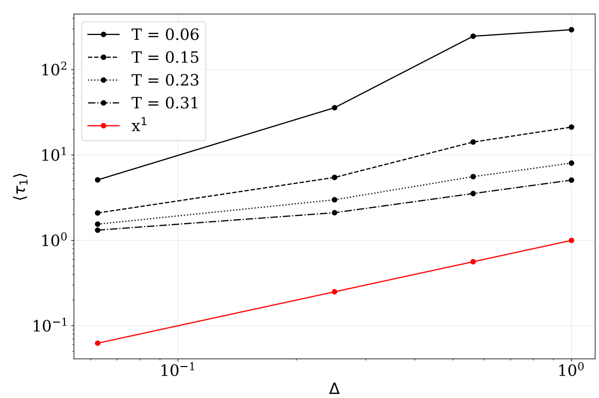


Figure 7: ***Estimated relationship between $\langle \tau_1 \rangle$ and Δ for different values of the temperature Δ.***