Self induced temperature gradients in Brownian dynamics

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Abstract

Contents

Chapter 1

Introduction

1.1 Brownian motion

Brownian motion is the motion that occurs when looking at microscopic particles that are suspended in a fluid, this motion is highly random and is due to molecules in the fluid colliding with the particle trillions of times per second. In principle if one knew the momenta and positions of all particles in a system, then one could use Newtonian mechanics to fully predict the future state of the system. However, for systems of interest in this project, we will be looking at systems with particle number on the order of Avagadro's number ($6.0221409 \cdot 10^{23}$). With systems of this size, a Newtonian description is completely impractical, so instead we will use a statistical approach, in this view the motion of a single Brownian particle suspended in a fluid at a given temperature (which we will call the bath) is random. Brownian motion was first observed by Robert Brown in 1827 [1], in these observations, Brown saw that microscopic particles (for example pollen grains) were in constant motion. He noticed that this motion was still present in inorganic material including granite and ground up Sphinx bones.

> To mention all the mineral substances in which I have found these molecules, would be tedious; and I shall confine myself in this summary to an enumeration of a few of the most remarkable. These were both of aqueous and igneous origin, as travertine, stalactites, lava, obsidian, pumice, volcanic ashes, and meteorites from various localities. Of metals I may mention manganese, nickel, plumhago, bismuth, antimony, and arsenic. In a word, in every mineral which I could reduce to a powder, sufficiently fine to be temporarily suspended in water, I found these molecules more or less copiously; and in some cases, more particularly in siliceous crystals, the whole body

submitted to examination appeared to be composed of them.
–**Robert Brown on what we now call Brownian particles**

Over half a century later, Einstein showed that Brownian motion was due to constant bombardment by water molecules in the surrounding environment [2], Einsteins theory of Brownian motion was then experimentally verified by Perrin [3]. The trajectory of a single Brownian particle can either be described stochastically or an ensemble of Brownian particles can be described by a probability distribution. Later work by Smoluchowski has allowed us to determine the evolution of the probability distribution of a Brownian particle mathematically using the Smoluchowksi equation which we will discuss in section 1.4. We will think of a Brownian particle moving in titled periodic potential of the form $V(x)$, as shown schematically in figure 1.1. In this figure we have a particle with a certain known probability density, the particle is agitated by thermal vibrations in a random diffusive manner, however there is also a forcing on the particles that we describe using the potential.

1.2   Brownian motors

Brownian motors are devices that can use stored energy to create directed motion on a microscopic scale. As well as being able to crank a rotor in the in the fashion of a traditional motor, they are also able to pump ions against a gradient and translocate molecules. Brownian motors have been implemented in the laboratory, for example Ref [4] created a stochastic heat engine by placing a single colloidal particle in a time dependent optical trap. Likewise, Ref [5] placed a colloidal particle in an optical tweezer and drove the particle with explosive vaporization of the surrounding liquid, thus demonstrating a thermal mechanism for Brownian motors. Brownian motors also include devices that can transport molecules over a long distance, for example Ref [6] placed DNA molecules in a time dependent potential to transport the molecules. A very important class of Brownian motors are those where the energy is supplied by a chemical reaction. None of the above experiments fit this criteria, however these types of motors are ubiquitous in biology [7, 8]. Recently, thanks to improvements in imaging techniques, researchers have been able to make highly detailed images of these motors and their working components [9].

The name Brownian motors is not a misnomer, a Brownian motor can be modeled as a Brownian particle diffusing over its free energy landscape [10], in the case of Brownian motion it is natural to think of the particle moving in a spatial coordinate x, however in the case of Brownian motors the interpretation of the coordinate x is more abstract. Often we will think of x as a reaction coordinate for a chemical reaction, or in the case
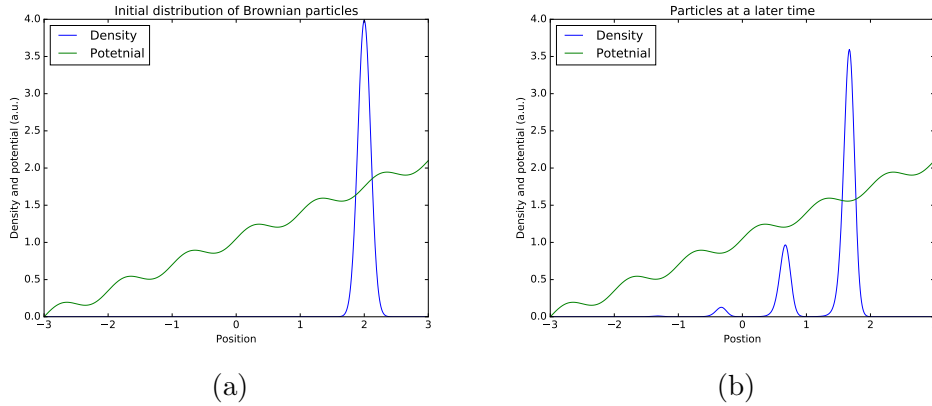
Figure 1.1: Schematic showing the probability density of particles diffusing in a one dimensional tilted periodic potential at a fixed temperature. We see that the particles tend to drift down the potential as they diffuse, this drift will be called the current J which we will quantify in section 1.4.

of a rotary motor, it could be the angle of the motor. Different types of Brownian motors have been explored in the literature, including the Feynman ratchet [11], the Landauer blowtorch [12], thermal ratchets [5], time dependent potentials [4, 6] and tilted periodic potentials [8, 13].

1.3 Classes of Brownian motors

Here we will discuss different classes of Brownian motors and their relationship to this project.

1.3.1 Feynman ratchet and pawl

The Feynman ratchet was initially discussed in the Feynman lectures [11] and was at first thought to be able to achieve greater than Carnot efficiency, however closer analysis showed that this was not possible [14]. The system works as follows, we have two boxes that are thermally insulated from one another that are connected by an axle that can rotate. In one box there is a ratchet and pawl connected to the axle that makes it easy for the axle to turn one way (say clockwise), but hard to turn the other way (anti-clockwise). In the other box the axle is connected to paddles that are being buffeted by a gas (which we call the bath). The motion of the paddles are random since they are dictated by Brownian motion, so the purpose of the ratchet and pawl is to rectify the Brownian motion of these paddles. One may think that this could be used to do work (for example by using the axle to lift a weight), however this is not true. The problem is that the ratchet and pawl themselves will also be subject to random motion so they will

sometimes allow the axle to turn anti-clockwise. To model the Feynman ratchet, we will need two degrees of freedom [15], this is beyond the scope of this project because we will only simulate systems with one degree of freedom.

1.3.2 Landauer blowtorch

The Landauer blowtorch scheme involves a temperature that varies in space [12]. As noted earlier, in order for the particles in Figure 1.1 to get out of potential wells, they will need to acquire thermal energy from the environment. Landauer's idea was to assist these particles by heating the environment at the hills that the particles need to climb. From this Landauer notes that [12] "The relative occupation of competing states of local stability is not determined solely by the characteristics of the locally favored states, but depends on the noise along the whole path connecting the competing states." This means that when we are modeling our system, we need to take non-constant temperatures into account.

1.3.3 Time dependent potentials

Both [4] [6] are examples of experiments where a time dependent potential was used to do work on molecules. In [6] DNA molecules are placed in a time dependent ratchet potential. When the electric field is on it creates a saw tooth shaped potential as shown in Figure 1.2, when the electric field is on, the molecules will go to the bottom of the wells and get stuck there. When the electric field is turned off however, the molecules will diffuse freely so that when the potential is turned back on at a later time, a large number of the molecules will then get trapped in the well to the left of where they were originally. Thus there is a net drift to the left.

1.3.4 Tilted periodic potentials

The tilted periodic potential (Figure 1.1) is of particular interest for this project because it can be used to model biological motors [8, 13]. One way to model Brownian motors of this class is to think of a reaction coordinate x that describes the conformation of a molecule in a chemical reaction. An example of this is the reaction ATP $\rightleftharpoons$ ADP + P, where ATP is adenosine tri-phosphate, ADP is adenosine di-phosphate and P is a lone phosphate molecule. This reaction coordinate is then coupled to a mechanical coordinate y so that each time that a reaction takes place, the motor will move in some way. Since this is a chemical reaction, the free energy will be decreased as time moves forwards. So a system that has a potential that is periodic in x is not sufficient to describe this situation, we will need
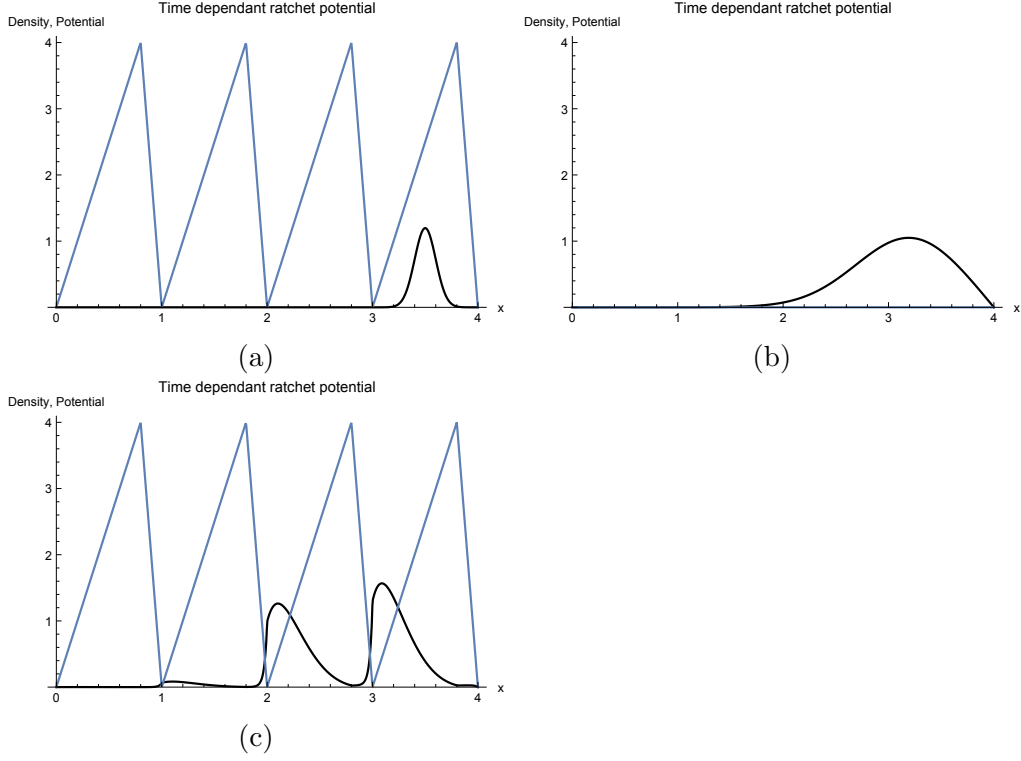
Figure 1.2: Schematic of particles diffusing in a time dependent potential, the blue line represents the potential and the black line represents the particle probability density. In (a) the particles are stuck in the first potential well, a certain time later the electric field is turned off and the particles diffuse freely as shown in part (b). When the potential is turned back on again (c), a large number of the particles will get stuck in the well to the left of the first one thus creating a net current to the left.

to "tilt" the potential by adding a forcing f. The value of f will depend on the ΔG of the reaction (i.e. how far out of equilibrium the reaction is). It is shown in [8] that this can be modeled by the two dimensional Smoluchowski equation. In this project we will only be modeling the one dimensional Somluchowski equation, so we will have to consider the case where x and y are tightly coupled. An example of tight coupling is the kinesin motor [13] that is used in cells to transport molecules. The kinesin motor is strongly bound to a track that it "walks" along, on each step the motor will hydrolyze an ATP molecule using the reaction shown above. This reaction liberates about $12k_BT$ Joules of energy that the motor uses to move forward. Kinesin motors are able to take many steps forward while taking few steps backwards all while falling off their track very infrequently [16].

1.4 The Smoluchowski equation interacting with the environment

As we will see, the diffusion is increased by increasing the temperature, while the derivative of the potential describes the external force on the particle. In some cases such as the Landauer blowtorch, the environment has a non uniform temperature held fixed by an external heat source [12]. With this in mind, we interpret Figure 1.1 as follows: Brownian particles are subject to a given potential and are agitated by thermal noise, these agitations can give the particles the energy to move over barriers created by the potential. As one could imagine, these thermal interactions draw energy from the environment causing the temperature of the environment to change. Normally two simplifying assumptions are made at this point [10], (i) that the thermal fluctuations created by the motor are very small compared to the thermal energy of the surrounding environment which is assumed to be effectively infinite, (ii) that when these temperature fluctuations occur, they diffuse away so rapidly that they do not need to be accounted for. In this project, we will question the second assumption in the case of Brownian motors. Assumption (ii) has also been questioned previously by Streater in the context of Brownian motion [17, 18]. In these articles, Streater investigates Brownian motion from a microscopic view and then comes up with a mathematical model to describe Brownian particles that are thermally coupled to the environment, he then goes on to prove that the model is thermostatistically consistent in the sense that energy is conserved and that entropy increases. We will explore a similar set of equations in the context of Brownian motors and we will try to determine the length scales at which the thermal interaction is important.

This project will be focused on understanding the behavior of the coupled partial differential equations given by:

$$J(x,t) = -\gamma^{-1} \frac{\partial}{\partial x} \left(\frac{\partial V(x,t)}{\partial x} P(x,t) + k_B \frac{\partial}{\partial x} [T(x,t)P(x,t)] \right) \quad (1.1)$$

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial J}{\partial x} \quad (1.2)$$

$$\frac{\partial T(x,t)}{\partial t} = -\kappa q(x,t) + D \frac{\partial^2 T(x,t)}{\partial x^2} \quad (1.3)$$

Where

- $P(x,t)$ is the probability density as a function of reaction coordinate x and time t

- $J(x,t)$ is called the current

- γ is the friction coefficient

- $V(x, t)$ is the potential for the motor

- k_B is the Boltzmann constant

- $q(x, t) = \partial_x V(x, t) J(x, t)$ is the heat from the motor

- κ is the thermal conductivity

- D is the thermal diffusivity

Equation (1.2) is called the Smoluschowski equation [19] and equation 1.3 is the heat equation. These equations make our intuitive notions more precise, we see that the first term on the right hand side of the Smoluchowski equation (equation 1.2) is a drift term that is forced by our potential and that the second term contains a diffusion term that is scaled by our temperature. In fact, Figure 1.1 was made by solving equation (1.2) numerically. Likewise, equation (1.3) also appeals to how our intuition of how the motor should effect its environment. The first term represents the heat flux being produced by the motor [15], while the second term represents the diffusion of temperature into the environment.

1.5 System thermodynamics

The potential energy of the particle is $U_P = \int V(x)P(x)dx$ and the thermal energy of the environment is $c_p \int T(x)dx$, where c_p is the specific heat capacity of the environment, with this we have.

$$E(t) = \int V(x)P(x, t)dx + c_p \int T(x, t)dx \tag{1.4}$$

By using the Smoluchowski equation and the heat equation, we can differentiate with respect to time to get:

$$\frac{dE}{dt} = \int V(x)\frac{\partial P}{\partial t}dx + c_p \int \frac{\partial T}{\partial t}dx \tag{1.5}$$

$$= -\int V(x)\frac{\partial J}{\partial x} + c_p \int -\kappa J(x)\frac{\partial V}{\partial x} + D\frac{\partial^2 T}{\partial x^2}dx \tag{1.6}$$

$$= [V(x)J(x)]_{-\infty}^{\infty} + \int \frac{\partial V}{\partial x}J(x)dx - \kappa c_p \int \frac{\partial V}{\partial x}J(x)dx + D\left[\frac{\partial T}{\partial x}\right]_{-\infty}^{\infty} \tag{1.7}$$

If there are no particles are flowing through the boundaries and if there is no heat flowing through the boundaries, then there is no exchange of

energy with the external environment. If we let $\kappa = \frac{1}{c_p}$, then the middle terms cancel and the first law is obeyed by the system.

As for the entropy, we have [18]

$$S(t) = -\int P(x,t)\log(P(x,t))dx + c_p \int \log(T(x,t))dx \qquad (1.8)$$

Differentiating with respect to time, we get

$$\frac{dS}{dt} = \int \frac{\partial J}{\partial x} + \frac{\partial J}{\partial x}\log P \ dx + c \int \frac{1}{T}\left(-\kappa J\partial_x V + c\beta\frac{\partial^2 T}{\partial x^2}\right)dx \qquad (1.9)$$

$$= [J\log P]_{\partial\Omega} - \int_{\partial\Omega} \frac{J}{P}\frac{\partial P}{\partial x}dx + [\frac{\partial J}{\partial x}]_{\partial\Omega} - \int_{\partial\Omega} \frac{J}{T}\frac{\partial V}{\partial x} + c\beta\int_{\partial\Omega}\frac{1}{T}\frac{\partial^2 T}{\partial x^2}dx \qquad (1.10)$$

We will denote the boundary terms with $B(t) = [J\log P]_{\partial\Omega} + [\frac{\partial J}{\partial x}]_{\partial\Omega}$, now the change in entropy becomes:

$$\frac{dS}{dt} = -\int_{\partial_\Omega}\frac{J}{P}\frac{\partial P}{\partial x} + \frac{J}{T}\frac{\partial V}{\partial x}dx + c\beta\int_{\partial_\Omega}\frac{1}{T}\frac{\partial^2 T}{\partial x^2}dx + B(t) \quad (1.11)$$

$$= \int_{\partial_\Omega}\frac{J^2}{TP} - \frac{J}{T}\frac{\partial T}{\partial x}dx + c\beta\int_{\partial_\Omega}\frac{1}{T}\frac{\partial^2 T}{\partial x^2}dx + B(t) \qquad (1.12)$$

where in the second equality we used the fact that $J = P\frac{\partial V}{\partial x} + \frac{\partial}{\partial x}(TP)$.

1.6 Bistable potentials and Kramers Rate

A bistable potential is one that has two stable minima and an intermediate unstable maximum, these potentials occur in a wide range of applications including digital logic [20], protein folding [21] and chemical reactions [22]. In the context of Brownian motion, understanding the nature of bistable potentials can help one to build a master equation describing more complicated potentials comprised of multiple deep wells [23, 24]. Consider the potential shown in Figure 1.3, if we begin in a state where we are certain that the particle is in the upper well, then as time passes, we should expect the probability distribution to move from point a over the barrier at b and into the well at point c. We will consider the regime where $E_B^+ = V(x_b) - V(x_a) \gg k_B T$, in this regime the rate at which the particles flow from a to c is given by the Eyring-Kramers law [25, 26], for our dimensionless equations, this has the form,

$$\kappa_+ = \frac{\sqrt{-V''(x_b)V''(x_a)}}{2\pi}\exp\left(\frac{-E_B^+}{T}\right) \qquad (1.13)$$
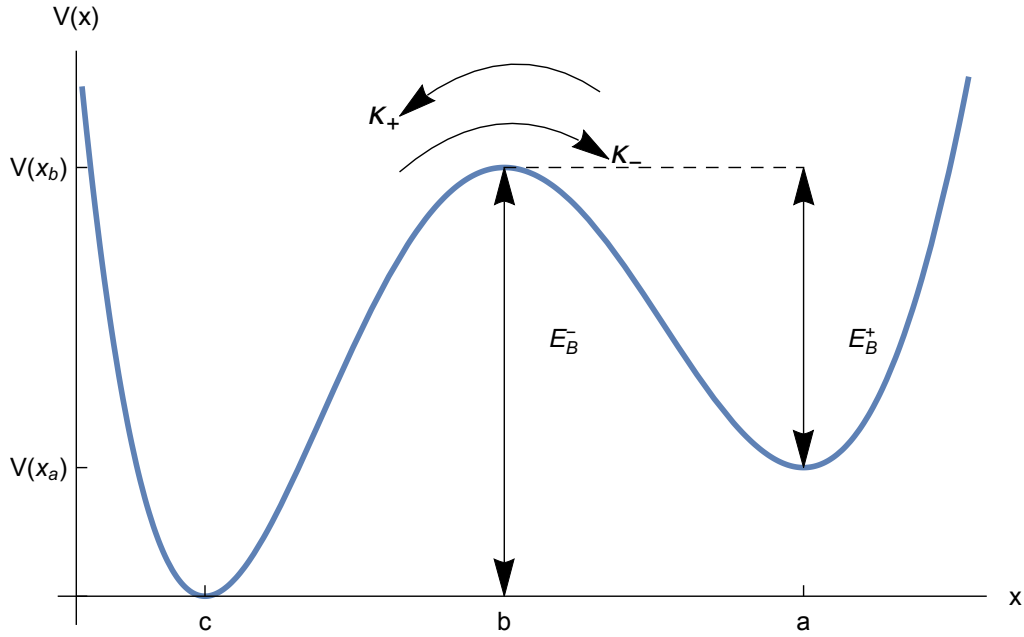
Figure 1.3: Bistable potential: In this plot we show the potential where we explore the Kramers rate, the potential has local minima at a and c and a maximum at b. If we begin with a probability distribution in the upper well, then the distribution will decay into the ground state of the upper well and then begin to decay into the lower well. The rate of flow from the upper well to the lower one will be denoted by κ_+ and the rate of flow from the lower well into the upper one will be denoted by κ_-.

Likewise, there will be a current flowing from c to a, we will denote this by κ_-, once we have calculated both of these rates, the population in the upper well will be given by:

$$\frac{dP_+}{dt} = \kappa_- P_-(t) - \kappa_+ P_+(t) \tag{1.14}$$

So, if we are certain that the particle is in the upper well to begin with, then we expect that the probability of a particle being in the upper well to satisfy

$$P_+(t) = \exp\left((\kappa_+ - \kappa_-)t\right). \tag{1.15}$$

We can also achieve this result numerically by starting the system off in the upper well and simulating forward while calculating the probability that the particle is in the upper well at each step. We then fit an exponential to this data and the fitted rate will be our numerically estimated Kramers rate.

Chapter 2

Methods

In order to see how these equations behave with time, we have to resort to numerical methods (see section 2.2). However we note that for a given potential there will be a stationary solution that we will refer to as the "steady state", given periodic boundary conditions, we will derive an analytical form for this steady state.

2.1   Steady state solution

In the steady state, we have:

$$\frac{\partial P(x,t)}{\partial t} \;=\; 0 \;=\; \frac{\partial J}{\partial x} \tag{2.1}$$

$$\frac{\partial T(x,t)}{\partial t} \;=\; 0 \;=\; -\kappa q(x,t) + \frac{\partial}{\partial x}\left(D\frac{\partial T(x,t)}{\partial x}\right) \tag{2.2}$$

Suppose that we have the following boundary conditions:

$$P(x=0) = P(x=L) \tag{2.3}$$

$$J(x=0) = J(x=L) \tag{2.4}$$

$$\left.\frac{\partial T}{\partial x}\right|_{x=0} = 0 = \left.\frac{\partial T}{\partial x}\right|_{x=L} \tag{2.5}$$

where L is the length scale of the system. Physically, these conditions say that the nett current flowing out of the boundaries is zero and that no heat escapes from the system, thus the energy of the sytem is conserved. Section 5.2 of [27] gives the steady state current as:

$$J_s = \left[\frac{2k_B T(L)}{\psi(L)} - \frac{2k_B T(0)}{\psi(0)}\right] P_s(0) \left[\int_0^L dx'/\psi(x')\right]^{-1} \tag{2.6}$$

with $\psi(x) \equiv \exp[-\int_0^x dx' \frac{\partial_x V(x')}{2k_B T(x')}]$. Meanwhile, the density is:

$$P_s(x) = P_s(0) \left[\frac{\int_0^x \frac{dx'}{\psi(x')} \frac{T(L)}{\psi(L)} + \int_x^L \frac{dx'}{\psi(x')} \frac{T(0)}{\psi(0)}}{\frac{T(x)}{\psi(x)} \int_0^L \frac{dx'}{\psi(x')}} \right] \tag{2.7}$$

In this case, J_s is a constant and $P_s(0)$ is also a constant. Assuming that we know these constants it is now possible to find the steady state temperature. We have:

$$\frac{\partial T}{\partial t} = 0 = -\kappa J_s \partial_x V + D \frac{\partial^2 T}{\partial x^2} \tag{2.8}$$

In one dimension, 2.8 can be written as an ordinary differential equation of the form

$$T''(x) = \frac{\kappa J_s}{D} V'(x) \tag{2.9}$$

We can solve this equation by integrating both sides twice to give:

$$T(x) = \frac{\kappa J_s}{D} \int_0^x V(x')dx' + \xi x + d \tag{2.10}$$

for unkown constants ξ and d. By applying the boundary condition 2.5, we find that

$$T'(0) = 0 = \frac{\kappa J_s}{D} V(0) + \xi \tag{2.11}$$

$$T'(L) = 0 = \frac{\kappa J_s}{D} V(L) + \xi \tag{2.12}$$

This implies that either $J_s = 0$ or $V(0) = V(L)$, meaning that the coupled system does not admit a steady state solution for a tilted potential. Later, we will see that it is possible to have a steady state in higher dimensions where the flow of heat from the environment can dissipate the heat produced by the Brownian particle. By recalling that $E = \int_0^L P(x')V(x')dx' + c \int_0^L T(x')dx'$ we are able to find an expression for d. First, we will integrate the temperature from 0 to L

$$\int_0^L T(x')dx' = \frac{\kappa J_s}{D} \int_0^L dx' \int_0^{x'} V(x'')dx'' + \xi \frac{L^2}{2} + dL \tag{2.13}$$

Therefore,

$$d = \frac{1}{L} \left(cE - c \int_0^L P(x')V(x')dx' - \frac{\kappa J_s}{D} \int_0^L dx' \int_0^{x'} V(x'')dx'' + \xi \frac{L^2}{2} \right) \tag{2.14}$$

It would seem that one should be able to calculate the steady state current and density directly from the equations shown above. However, we

notice that the constants J_s and $P_s(0)$ have to satisfy equations (2.6), (2.7) and (2.10) while also satisfying the normalization condition $\int_0^L P(x)dx = 1$. To do this we define an objective function given by

$$obj(J_s, P_s(0)) = \left(J_s - \left[\frac{2k_B T(L)}{\psi(L)} - \frac{2k_B T(0)}{\psi(0)} \right] P_s(0) \left[\int_0^L dx'/\psi(x') \right]^{-1} \right)^2$$
(2.15)

And we minimize this objective function with respect to J_s and $P_s(0)$ under the constraint $\int_0^L P(x)dx = 1$. Another way to do this is to guess a steady state density and temperature and use finite differencing to simulate forward in time until the transients die out.

2.2 Numerical simulation

2.2.1 Dimensionalizing the equations

Here we will non-dimensionalize the equations, to do this, introduce $\bar{x} = \frac{x}{L}$, then the Smoluchowski equation becomes

$$\frac{\partial P}{\partial t} = \gamma^{-1} \frac{1}{L^2} \frac{\partial}{\partial \bar{x}} \left(P \frac{\partial V}{\partial \bar{x}} + k_B \frac{\partial}{\partial \bar{x}}(TP) \right)$$
(2.16)

Now let E_0 be the potential energy difference along one period, i.e. $E_0 = \max(v_0(x)) - \min(v_0(x))$. Now we will introduce the dimensionless potential and the dimensionless temperature as $\hat{V}(x) = \frac{V(x)}{E_0}$ and $\hat{T}(x) = \frac{k_B T(x)}{E_0}$ respectively. Now the Smoluchowski equation becomes

$$\frac{\partial P}{\partial t} = \frac{E_0}{\gamma L^2} \frac{\partial}{\partial \bar{x}} \left(P \frac{\partial \hat{V}}{\partial \bar{x}} + \frac{\partial}{\partial \bar{x}}(\hat{T}P) \right)$$
(2.17)

Let $\tau = \frac{E_0}{\gamma L^2}$ and $\hat{P} = LP$, with this we have:

$$\frac{\partial \hat{P}}{\partial \tau} = \frac{\partial}{\partial \bar{x}} \left(\hat{P} \frac{\partial \hat{V}}{\partial \bar{x}} + \frac{\partial}{\partial \bar{x}}(\hat{T}\hat{P}) \right)$$
(2.18)

Now we define $\hat{J} = \frac{\gamma L^2}{E_0} J$, applying these definitions to the equation for the temperature evolution, we find that:

$$\frac{E_0^2}{\gamma k_B L^2} \frac{\partial \hat{T}}{\partial \tau} = -\kappa \frac{E_0}{\gamma L^2} \hat{J}(\bar{x}) \frac{E_0}{L} \frac{\partial \hat{V}}{\partial \bar{x}} + \frac{D E_0}{k_B L^2} \frac{\partial^2 \hat{T}}{\partial \bar{x}^2}$$
(2.19)

Now let $\alpha = \frac{\kappa k_B}{L}$ and $\beta = \frac{D\gamma}{E_0}$, then we have

$$\frac{\partial \hat{T}}{\partial \tau} = -\alpha \hat{J}(\bar{x}) \frac{\partial \hat{V}}{\partial \bar{x}} + \beta \frac{\partial^2 \hat{T}}{\partial \bar{x}^2}$$
(2.20)

14

As for the energy of the system, the dimensioned version is:

$$E(t) = \int P(x)V(x)dx + \frac{1}{\kappa}\int T(x)dx \qquad (2.21)$$

Let $\hat{E}(t) = \frac{E(t)}{E_0}$, we have:

$$\hat{E}(t) = \int \hat{P}\hat{V}d\bar{x} + \frac{L}{k_B\kappa}\int \hat{T}d\bar{x} \qquad (2.22)$$

$$= \int \hat{P}\hat{V}d\bar{x} + \frac{1}{\alpha}\int \hat{T}d\bar{x} \qquad (2.23)$$

So our system depends on the parameters α and β as well as the shape of the potential. Physically, α represents how much the motor will interact with the environment thermally and β represents how quickly the temperature diffuses.

2.2.2   Finite differences

The one dimensional equation can be solved on a discrete grid by using the finite differences method, the main idea behind this strategy is to approximate derivatives with equations of the form:

$$\frac{df}{dx} \approx \frac{f(x-h) - f(x+h)}{2h} \qquad (2.24)$$

for some small h. In our simulations, we will use the Crank Nicolson scheme to solve the equations. From now on, we will use the notation that $F(j\Delta x, n\Delta t) = F_j^n$, the key equation for the Crank Nicolson scheme is:

$$\frac{P_j^{n+1} - P_j^n}{\Delta t} = \frac{1}{2}(F_j^{n+1} + F_j^n) \qquad (2.25)$$

where F represents the right hand side of the equation that we are doing finite differences on. By applying finite differences to the dimensionless Smoluchowski equation (eq 2.18), we find that:

$$F_j^i = \frac{P_{j+1}^i \partial V_{j+1}^i - P_{j-1}^i \partial V_{j-1}^i}{2\Delta x} + \frac{P_{j+1}^i T_{j+1}^i - 2P_j^i T_j^i + P_{j-1}^i T_{j-1}^i}{\Delta x^2} \qquad (2.26)$$

We make the following definitions:

$$a_j^{n+1} = -\frac{\partial_x V_{j-1}^{n+1}}{2\Delta x} + \frac{T_{j-1}^{n+1}}{\Delta x^2}$$

$$b_j^{n+1} = \frac{-2T_j^{n+1}}{\Delta x^2}$$

$$c_j^{n+1} = \frac{\partial_x V_{j+1}^{n+1}}{2\Delta x} + \frac{T_{j+1}^{n+1}}{\Delta x^2}$$

$$a_j^n = -\frac{\partial_x V_{j-1}^n}{2\Delta x} + \frac{T_{j-1}^n}{\Delta x^2}$$

$$b_j^n = \frac{-2T_j^n}{\Delta x^2}$$

$$c_j^n = \frac{\partial_x V_{j+1}^n}{2\Delta x} + \frac{T_{j+1}^n}{\Delta x^2}$$

$$(2.27)$$

With these definitions, the Crank Nicolson scheme can be written down as follows:

$$-\frac{\Delta t}{2}a_j^{n+1}P_{j-1}^{n+1} + \left(1 - \frac{\Delta t}{2}b_j^{n+1}\right)P_j^{n+1} - \frac{\Delta t}{2}c_j^{n+1}P_{j+1}^{n+1} = a_j^n P_{j-1}^n + \left(1 + \frac{\Delta t}{2}b_j^n\right)P_j^n + \frac{\Delta t}{2}c_j^n P_{j+1}^n$$

$$(2.28)$$

This equation can be written in matrix form by defining the following matrices:

$$A = \begin{bmatrix} a_0^{n+1} & b_1^{n+1} & 0 & 0 & 0 & \dots & 0 \\ c_0^{n+1} & a_1^{n+1} & b_2^{n+1} & 0 & 0 & \dots & 0 \\ 0 & c_1^{n+1} & a_2^{n+1} & b_3^{n+1} & 0 & \dots & 0 \\ \vdots & \vdots & \ddots & \ddots & \ddots & \vdots & \vdots \\ 0 & & \dots & & c_{J-2}^{n+1} & a_{J-1}^{n+1} & b_J^{n+1} \\ 0 & & \dots & & & c_{J-1}^{n+1} & a_J^{n+1} \end{bmatrix}, \quad P^{n+1} = \begin{bmatrix} P_0^{n+1} \\ P_1^{n+1} \\ \\ \vdots \\ \\ P_{J-1}^{n+1} \\ P_J^{n+1} \end{bmatrix}$$

$$(2.29)$$

$$
B = \begin{bmatrix}
a_0^n & b_1^n & 0 & 0 & 0 & \ldots & 0 \\
c_0^n & a_1^n & b_2^n & 0 & 0 & \ldots & 0 \\
0 & c_1^n & a_2^n & b_3 n & 0 & \ldots & 0 \\
\vdots & \vdots & \ddots & \ddots & \ddots & \vdots & \vdots \\
& & & & & & \\
0 & & \ldots & & c_{J-2}^n & a_{J-1}^n & b_J^n \\
0 & & \ldots & & & c_{J-1}^n & a_J^n
\end{bmatrix}, \quad
P^n = \begin{bmatrix}
P_0^n \\
P_1^n \\
\\
\vdots \\
\\
\\
P_{J-1}^n \\
P_J^n
\end{bmatrix}
\tag{2.30}
$$

With these matrices the equation now becomes $(\mathbb{1} - \frac{\Delta t}{2} A) \cdot P^{n+1} = (\mathbb{1} - \frac{\Delta t}{2} B) \cdot P^n$, this equation can be used to step forward P. Each time that we step forward using this equation we will be out by a factor, this means that at each step we will need to renormalize using the equation $\int P(x) dx = 1$.

Likewise, we can apply the Crank Nicolson scheme to the heat equation, (eq 2.20), by looking at the right hand side of this equation, we find that

$$
F_j^i = -\alpha \left(P_j^i (\partial_x V_j^i)^2 + \frac{T_{j+1}^i - T_{j-1}^i}{2\Delta x} \partial_x V_j^i \right) + \beta \frac{T_{j+1}^i - T_j^i + T_{j-1}^i}{\Delta x^2}
\tag{2.31}
$$

Just like the discretized Smoluchowski equation, these equations can be written in matrix form. The temperature is normalized by assuming that the energy remains fixed, this will be true as long as no heat or current flows through the boundaries, i.e. $J(x = a) = 0 = J(x = b)$ and $\frac{\partial T}{\partial x}|_a = 0 = \frac{\partial T}{\partial x}|_b$. In this case, the energy is constant and is given by $E = \int P(x) V(x) dx + c_p \int T(x) dx$, so each time that we step the temperature forward, we have to calculate the potential and thermal energy and then scale the temperature so that the total energy remains fixed.

Fortunately the matrices that we are dealing with are very sparse, so the program used to solve these equations can save on memory by calling sparse matrix libraries.

Appendices

Appendix A

Testing the numerics

The idea behind finite differences is that as the discretization size goes to zero, the numerical approximation should converge on the correct analytical solution. We will compare our numerics with some known analytical results as well as performing convergence tests.

A.1 A comparison with analytical results

A.1.1 Smoluchowski equation

The Smoluchowski equation has a steady state probability density that takes on the form

$$P_{ss}(x) = N \exp\left(-\int_a^x \frac{V'(x')}{T(x')}dx'\right) \tag{A.1}$$

Although we are not able to solve the Smoluchowski equation in the dynamical sense, we are able to obtain a formula for the Kramers rate. Here we will compare our numerical results with some simulations on the Kramers rate.

A.1.2 Heat equation

The heat equation can be solved using a Fourier series technique

$$\frac{\partial T}{\partial t} = \beta \frac{\partial^2 T}{\partial x^2} \tag{A.2}$$

the initial condition for the temperature will be denoted by,

$$T(x, 0) = f(x) \tag{A.3}$$

Lets say that the boundaries are at $x = \pm\infty$ and that the derivative of the temperature is zeros at the boudaries. The solution to the heat equation is given by:

$$T(x,t) = \sum_{n=1}^{\infty} D_n \sin\left(\frac{n\pi x}{L}\right) \exp\left(\frac{-n^2\pi^2\beta t}{L^2}\right) \quad\text{(A.4)}$$

where

$$D_n = \frac{2}{L} \int_0^L f(x) \sin\left(\frac{n\pi x}{L}\right) dx \quad\text{(A.5)}$$

We can compare these analytical results to the numerical ones obtained through finite differences

A.2 Convergence tests

Here we will decrease the step size and see whether or not the numerical scheme converges on a particular result
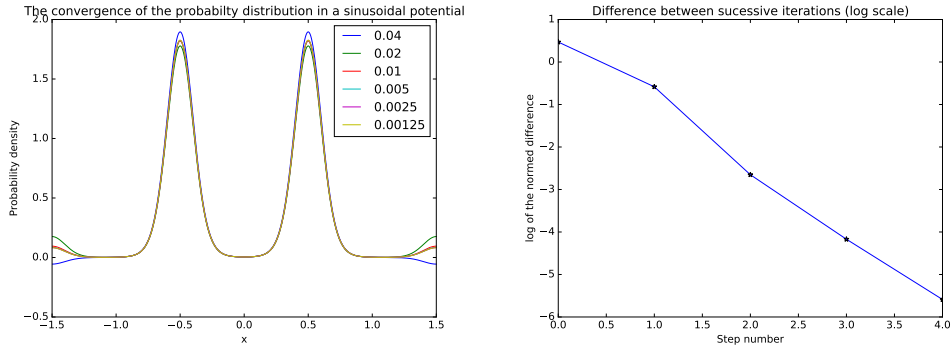

Figure A.1: The convergence of the probability distribution as Δt is decreased, the spatial discretization Δx is kept constant at 0.006.

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