Escape from a metastable state due to thermal fluctuations described by path integrals

bachelor's thesis

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Abstract

This thesis discusses the escape from a metastable state due to thermal fluctuations and how it can be described using path integrals. We investigate the probability current of a particle escaping from a potential well. Doing so, we obtain an explicit analytical expression for the probability current. Using this result, we calculate the probability current in the limit of small temperatures and large times.

Contents

Chapter 1

Introduction

For many chemical reactions, there is a timescale that determines their velocity. In 1940, Kramers modelled these reactions as the escape of a particle from a metastable potential minimum as illustrated in Fig. 1.1 to describe the reaction rates [1]. The particle is suspended in a medium, the thermal fluctuations of which drive the escape. These thermal fluctuations are also known as brownian motion. The problem has been solved by apply-

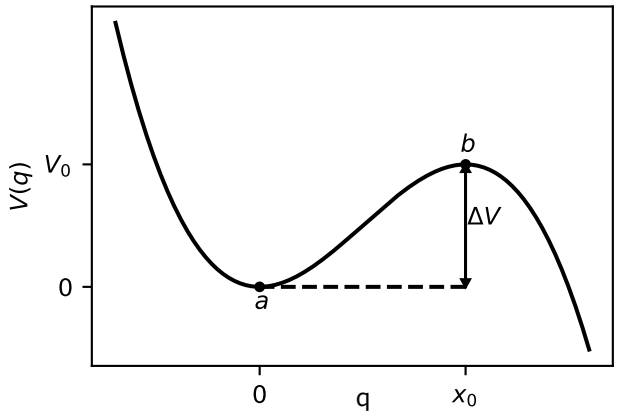

Figure 1.1: Important characteristics of the metastable minimum. The minimum is at the position $q = 0$ with the curvature $a = \frac{1}{2}V''(0)$. The probability current is the time derivative of the probability to be at the right of the maximum at $q = x_0$ with the curvature $-b = \frac{1}{2}V''(x_0)$. The potential difference between the minimum and the maximum is ΔV.

ing the Fokker Planck equations to calculate an escape rate. In this thesis, we apply the technique of path integration to Kramer's problem to obtain

a probability current out of the minimum. In Ch. 2, we introduce path integrals as a tool to describe the fluctuation. Next, we apply them to a brownian particle and calculate the upcoming fluctuation determinants. Then, Ch. 3 discusses the use of path integrals to calculate probability densities and the relaxation into a state of equilibrium. Here, we derive the well known fluctuation-dissipation theorem by comparison with results previously known from statistical mechanics. In Ch. 4, we derive a formula for the probability current. Finally, we use the formula to obtain a result for large times and low temperatures.

Chapter 2

Basic concept of path integrals

2.1 General considerations

Since we want to describe a process dictated by fluctuation, we need a method that takes into account the infinite amount of possible trajectories the particle can take. This can be achieved by calculating the integral over all paths combined with an appropriate statistical weight for each trajectory. The classical statistical weight is the exponential function of the action S along a given path. The integral over all paths that lead from a point a in space to a point b while taking the time τ is denoted by [2]

$$\int_a^b \mathcal{D}\left[q(t)\right] \mathcal{D}\left[p(t)\right] \exp\{-S\left[q(t), p(t)\right]\}. \tag{2.1}$$

The action along a path is given by

$$S = \int_0^\tau dt \left(p\dot{q} - \mathcal{H}[q, p, t]\right), \tag{2.2}$$

with $\mathcal{H}$ the Hamiltonian function of the respective problem. Each path is characterized by two functions $q(t)$ and $p(t)$, where $q(t)$ describes the position of the particle at a given time and $p(t)$ is the conjugate variable of $q(t)$. To calculate the path integral, the integral S can be written as a Riemann sum. To do so, the time axis is sliced into N intervals with length ε performing the limit $\varepsilon \to 0$ in the end, while maintaining $N\varepsilon = \tau$.

Therefore, each path can be characterized by the values of $q_n = q(n\varepsilon)$ and $p_n = p(n\varepsilon)$ at each discrete step in time as illustrated in Fig. 2.1. The integral over all paths can be calculated by performing a multiple integral over all coordinates (q_n, p_n). This does not include the endpoints. We always assume the path integral is performed in a way that is convergent and yields a real result. This means we can also integrate along an imaginary axis and choose a prefactor that ensures we obtain a real result.

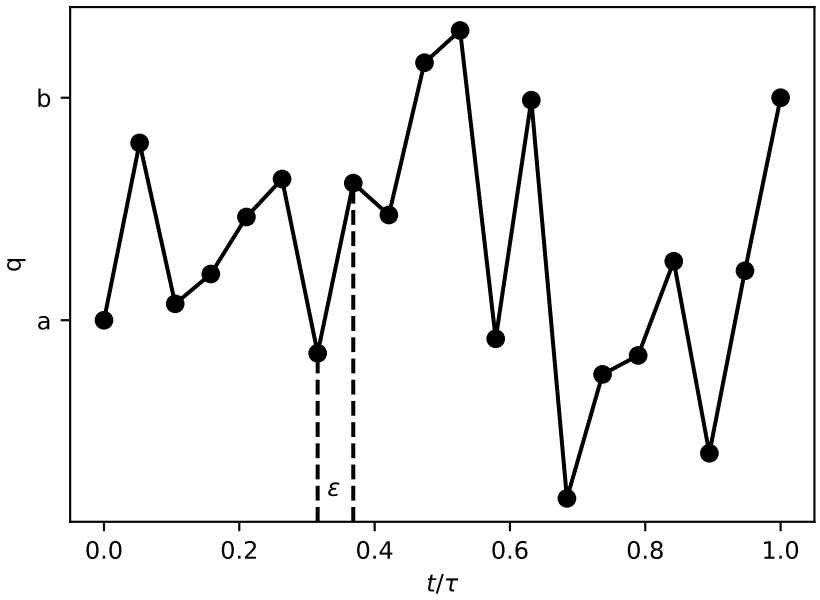

Figure 2.1: Example of a path from point a to b with a sliced time axis. The endpoints are fixed at the values a and b, while the other points can take any value. The time interval between two points is ε. To calculate a path integral, we need to integrate over all values the coordinates can take for each discrete step in time and take the limit $\varepsilon \to 0$.

To further calculate the path integral, we need to identify the paths with the biggest contribution. These paths have the property that the action is stationary, which is equivalent to $\delta S = 0$. This is fulfilled by the trajectories that satisfy the canonical equations of motion for the given Hamiltonian function [3]

$$\frac{\partial \mathcal{H}}{\partial p} = \dot{q} \qquad \text{and} \qquad -\frac{\partial \mathcal{H}}{\partial q} = \dot{p}. \tag{2.3}$$

We can map $(q, p) \mapsto (\bar{q} + q, \bar{p} + p)$ with $\bar{q}$ and $\bar{p}$ being solutions to Eq. (2.3).

The functions q and p are variations that allow us to construct every path by adding them to the trajectories of the saddlepoint. To ensure that all paths share the same endpoints we must include the condition $q(0) = q(\tau) = 0$. It is important to note that while $q(t)$ has to start at a for $t = 0$ and end at b for $t = \tau$, $p(t)$ can take any value at the endpoints of a path. With this parameterization of the paths, the action takes the form

$$S[\bar{q} + q, \bar{p} + p] \approx \bar{S} + \delta^2 S. \tag{2.4}$$

In this form, $\bar{S}$ is the action along the trajectory $(\bar{q}, \bar{p})$ and $\delta^2 S$ is the second variation of the action. This means $\delta^2 S$ is the integral over the terms of quadratic order in the variations q and p, which is given by

$$\delta^2 S = \int_0^\tau dt \left[p\dot{q} - \left.\frac{\partial^2 \mathcal{H}}{\partial p \partial q}\right|_{\bar{q},\bar{p}} pq - \frac{1}{2!}\left(\left.\frac{\partial^2 \mathcal{H}}{\partial^2 q}\right|_{\bar{q},\bar{p}} q^2 + \left.\frac{\partial^2 \mathcal{H}}{\partial^2 p}\right|_{\bar{q},\bar{p}} p^2 \right) \right]. \tag{2.5}$$

Since the action for the saddlepoint only depends on the endpoints a and b and the time τ, the integral over all paths from a to b can be written as

$$\exp\big[-\bar{S}(a, b, \tau)\big] \int_0^0 \mathcal{D}[q]\mathcal{D}[p] \exp\big(-\delta^2 S\big). \tag{2.6}$$

The remaining path integral over the variations corresponds to the contribution of the fluctuations.

2.2 Calculating fluctuation determinants

We want to calculate the contribution of the fluctuations for the special dissipative action that is used to describe the escape problem. The system is characterized by a potential $V(q)$, a constant γ, which has the dimension of an inverse viscosity and describes the damping of the system, and a constant α which describes the strength of the thermal fluctuations. The Hamiltonian function for our problem is given by

$$\mathcal{H} = \alpha p^2 - \gamma p V'(q). \tag{2.7}$$

This Hamiltonian function does not explicitly depend on time and therefore is a conserved quantity. If the fourth and higher order derivatives of $V(q)$ are sufficiently small, the expansion of the action in the way of Eq. (2.4) is

a good approximation. We turn $\delta^2 S$ into a Riemann sum assuming that p is always ahead in time relative to q. Since the path is not differentiable for a sliced time axis, we approximate the time derivative of q by the difference quotient of the discrete values. For our Hamiltonian function this leads to

$$\delta^2 S_N = \varepsilon \sum_{j=1}^{N} \Big[p_j \frac{q_j - q_{j-1}}{\varepsilon} + \gamma V''(\bar{q}_{j-1}) p_j q_{j-1} - \alpha p_j^2 + \frac{\gamma}{2} \bar{p}_j V'''(\bar{q}_{j-1}) q_{j-1}^2 \Big], \tag{2.8}$$

with $q_0 = q_N = 0$. In the calculations we want to perform, the product $\bar{p}V'''(\bar{q})$ is equal to zero and we can leave it out. It is important to note that we need to perform more integrals for p than for q, since p is not fixed at the endpoints. However, since we want p to be ahead in time of q, we do not integrate over p_0. This leaves us with only one additional integral over p_N. The sum is a quadratic form, meaning there exists a symmetric matrix M_N that, when writing the different coordinates as a vector $\vec{x} = (q_1, ..., q_{N-1}, p_1, ..., p_N)^T$, has the property $\delta^2 S_N = \frac{1}{2} \vec{x}^T M_N \vec{x}$. If the matrix is positive definite, the integral over the variations is given by [4]

$$\int_{-\infty}^{\infty} dq_1 ... dq_{N-1} dp_1 ... dp_N \exp\big(-\delta^2 S_N\big) = \sqrt{\frac{(2\pi)^{2N-1}}{\det M_N}} =: (2\pi)^{\frac{2N-1}{2}} D_N, \tag{2.9}$$

which reduces the problem to calculating the determinant of the matrix M_N. Since we always substitute our variables in a way that the integral converges, we can simply use the absolute value of $\det M_N$. M_N is a block matrix of the form

$$\left(\begin{array}{c|c} 0 & B \\ \hline B^T & C \end{array} \right). \tag{2.10}$$

Using the notation $V_n'' = V''(\bar{q}(n\varepsilon))$, the blocks of the matrix are

$$B_N = \begin{pmatrix} 1 & -1 + \varepsilon\gamma V_1'' & 0 & \dots & 0 \\ 0 & \ddots & \ddots & 0 & \vdots \\ \vdots & 0 & \ddots & \ddots & 0 \\ 0 & \dots & 0 & 1 & -1 + \varepsilon\gamma V_{N-1}'' \end{pmatrix} \in \mathbb{R}^{(N-1)\times N} \tag{2.11}$$

and

$$C_N = \begin{pmatrix} -2\varepsilon\alpha & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & -2\varepsilon\alpha \end{pmatrix} \in \mathbb{R}^{N\times N}. \tag{2.12}$$

Since C_N is proportional to the identity matrix, the block matrix determinant is given by the formula [5]

$$|\det M_N| = 2\alpha\varepsilon \det\left(B_N B_N^T\right) \tag{2.13}$$

In App. A, we derive the recurrence relation

$$\det B_N B_N^T = 1 + (1 - 2\gamma\varepsilon V''_{N-1}) \det B_{N-1} B_{N-1}^T. \tag{2.14}$$

for the determinant. We do so by utilizing a matrix with determinant one that contains $B_N B_N^T$ as a block. We can use the recurrence relation to obtain the expression

$$D_N = \sqrt{\frac{1}{|\det M_N|}} = \left\{ 2\alpha\varepsilon \left[1 + \sum_{i=1}^{N-1} \prod_{j=i}^{N-1} (1 - 2\gamma\varepsilon V''_j) \right] \right\}^{-1/2}. \tag{2.15}$$

If $V''(\bar{q}(t)) = V''$ is a constant along the chosen trajectory, the determinant becomes a geometrical sum that leads to

$$D_N = \sqrt{\frac{\gamma V'' \exp(\gamma V''\tau)}{2\alpha \sinh(\gamma V''\tau)}} \tag{2.16}$$

in the limit $\varepsilon \to 0$ while $N\varepsilon = \tau$ is kept constant.

Chapter 3

Relaxation into an equilibrium state

3.1 Results from statistical mechanics

The integral over all paths can be used to calculate probability densities and their behaviour over time. In this chapter, we want to calculate the probability density of the position of the particle for a harmonic potential $V(q) = aq^2$. We already know from statistical mechanics that, independently of the starting conditions, the system relaxes into a state of equilibrium. For the harmonic potential, we know the probability density in the equilibrium is given by the Maxwell-Boltzmann-distribution for the temperature T with k_B being the Boltzmann constant

$$f(q) = \sqrt{\frac{a}{\pi k_B T}} \exp\left(-\frac{aq^2}{k_B T}\right). \tag{3.1}$$

The relaxation into the equilibrium is associated with a timescale for the process, which is not covered by equilibrium physics. However, we can obtain this timescale by applying path integrals.

3.2 Time evolution of probability densities

In App. B, we derive a Normalization factor $\mathcal{N} = 2\pi$ that allows us to interpret the path integral towards a point q_N as a probability density. For this derivation, it is important that p is ahead in time relative to q to obtain

the correct determinant. Using Eq. (2.9), the path integral given by

$$\frac{1}{\mathcal{N}^N}\exp\big[-\bar{S}(q_N,q_0,\tau)\big](2\pi)^{\frac{2N-1}{2}}D_N=\frac{\exp\big[-\bar{S}(q_N,q_0,\tau)\big]}{\sqrt{2\pi}}D_N \tag{3.2}$$

describes the probability density of the position q_N of a particle that started at a position q_0. As always, we mean to take the limit $\varepsilon \to 0$ in the end. We can also use a probability density $P(q_0)$ for the starting position by calculating the expectation value of the path integral

$$f(q_N,\tau)=\int_{-\infty}^{\infty}dq_0P(q_0)\frac{\exp\big[-\bar{S}(q_N,q_0,\tau)\big]}{\sqrt{2\pi}}D_N. \tag{3.3}$$

By doing so, we should obtain a time dependent probability density that is $P(q_N)$ for $\tau = 0$ and approaches the equilibrium distribution. Since we know the probability density evolves towards a Maxwell-Boltzmann distribution for an arbitrary starting distribution $P(q_0)$, we can use the harmonic potential to test this assumption. We can also use the result to further determine the constants γ and α in our Hamiltonian function by comparing it to Eq. (3.1).

For the saddlepoint action, we use a trajectory that starts at an arbitrary point q_0 and ends at q_N. We calculate the action in App. C, which leads to the result

$$\bar{S}=\frac{a\gamma}{2\alpha}\frac{\exp(2a\gamma\tau)}{\sinh(2a\gamma\tau)}[q_N-q_0\exp(-2a\gamma\tau)]^2. \tag{3.4}$$

Since the second derivative of the harmonic potential is constant, we can use Eq. (2.16) with $V'' = 2a$. We obtain

$$D_N=\sqrt{\frac{a\gamma\exp(2a\gamma\tau)}{\alpha\sinh(2a\gamma\tau)}}. \tag{3.5}$$

Using these results, we find the path integral to be

$$\sqrt{\frac{a\gamma\exp(2a\gamma\tau)}{2\pi\alpha\sinh(2a\gamma\tau)}}\exp\left\{-\frac{a\gamma}{2\alpha}\frac{\exp(2a\gamma\tau)}{\sinh(2a\gamma\tau)}[q_N-q_0\exp(-2a\gamma\tau)]^2\right\}. \tag{3.6}$$

Inserting this into Eq. (3.3) gives us a time dependent function $f(q_N,\tau)$ that is normed to one for any $\tau \geq 0$. For $\tau = 0$, the path integral is equal to

$\delta(q_N - q_0)$, which gives us desired property $f(q_N, 0) = P(q_N)$. We can also see that the contribution of the starting condition q_0 decays exponentially in time with the timescale $\frac{1}{a\gamma}$. This timescale is the relaxation timescale we were unable to obtain by using the equilibrium only. In the limit $a\gamma\tau \gg 1$ the path integral becomes independent of q_0. Therefore, the equilibrium state is reached independently of the starting distribution, which is also predicted by statistical mechanics. We obtain

$$f_{eq}(q_N) = \sqrt{\frac{a\gamma}{\pi\alpha}} \exp\Big(-\frac{a\gamma}{\alpha} q_N^2\Big). \tag{3.7}$$

A comparison with Eq. (3.1) leads to

$$\alpha = \gamma k_B T, \tag{3.8}$$

which means that the strength of the thermal fluctuations is determined by the temperature, as well as the damping of the system. This result is known as the fluctuation-dissipation theorem.

The harmonic potential is also of special interest since, for sufficiently low temperatures, we can approximate every potential minimum by a harmonic well. Therefore, we expect a metastable state in the form of a Maxwell-Boltzmann distribution to occur for the potential. This state should be reached regardless of the starting distribution inside the minimum, if the temperature is low enough. Again, the initial conditions should decay on the timescale $a\gamma$, with a the curvature of the minimum given by $a = \frac{1}{2}V''(x_{min})$.

Therefore, if we want to look at the escape from a minimum at low temperatures, we can assume the starting distribution to be the a metastable Maxwell-Boltzmann distribution around the minimum.

Chapter 4

Probability currents in non-equilibrium

4.1 Deriving a formula for the probability current

For the escape problem, we are interested in the probability of the particle being to the right of a point x_0. Using Eq. (3.3), we define the probability current I as the time derivative of this probability for a given starting distribution $P(q_0)$

$$\begin{aligned} I &= \frac{d}{d\tau}\int_{x_0}^{\infty} dq_N f(q_N,\tau) \\ &= \frac{d}{d\tau}\int_{x_0}^{\infty} dq_N \int_{-\infty}^{\infty} dq_0 P(q_0)\frac{\exp\left[-\bar{S}(q_N,q_0,\tau)\right]}{\sqrt{2\pi}} D_N. \end{aligned} \tag{4.1}$$

Since we cannot calculate the integral in general, we simplify the formula by expressing the derivative by a difference quotient. We use the length of a timestep ε as the quantity we send to zero to obtain a derivative. Therefore, the difference quotient is given by the difference of two probability densities with one of them being one step ahead in time

$$I = \lim_{\varepsilon\to 0}\frac{1}{\varepsilon}\left[\int_{x_0}^{\infty} dq_{N+1} f(q_{N+1},\tau+\varepsilon) - \int_{x_0}^{\infty} dq_N f(q_N,\tau)\right]. \tag{4.2}$$

We can express the path integral that is one step ahead in time by either changing the endpoint of the paths or using the same endpoint $q_{N+1} = q_N$ while letting the paths take the time $\tau + \varepsilon$ to reach it. While both ways

should ultimately be equivalent, it is sensible to choose $q_{N+1} = q_N$. This allows us to integrate over the difference of the probability densities rather than taking the difference of the integrals as shown in Eq. (4.2). For the difference quotient of $f(q_N, \tau)$ we only need to consider the contribution of the path integrals since the integral over the starting distribution $P(q_0)$ does not depend on time. We obtain

$$\Delta = \frac{\exp\big[-\bar{S}(q_N, q_0, \tau + \varepsilon)\big]}{\sqrt{2\pi}} D_{N+1} - \frac{\exp\big[-\bar{S}(q_N, q_0, \tau)\big]}{\sqrt{2\pi}} D_N. \tag{4.3}$$

We can calculate the saddlepoint action $\bar{S}$ and the fluctuations D_N individually. For $\bar{S}$, we obtain

$$\exp\big[-\bar{S}(q_N, q_0, \tau + \varepsilon)\big] = \exp\big[-\bar{S}(q_N, q_0, \tau)\big] \left(1 - \varepsilon \frac{\partial \bar{S}}{\partial \tau}\right) + \mathcal{O}(\varepsilon^2). \tag{4.4}$$

The partial derivative of $\bar{S}$ comes from our choice to fixate the endpoint of the paths. Otherwise, we would need to use a total time derivative. We can make use of the fact that the trajectories, along which we calculate $\bar{S}$ satisfy the Hamiltonian equations of motion. This allows us to express the derivative through the Hamiltonian function $\mathcal{H}$ [3]

$$\frac{\partial \bar{S}}{\partial \tau} = -\mathcal{H}. \tag{4.5}$$

For the fluctuation, we need to consider that the saddlepoint trajectory also changes if it takes the time $\tau + \varepsilon$ to reach the endpoint. However, since the deviations are small, we can approximate the new trajectory $\bar{q}_\varepsilon(t)$ by $\bar{q}(t) + \varepsilon q_{var}(t) + \mathcal{O}(\varepsilon^2)$. This means the second derivative of the potential along the saddlepoint trajectory is given by

$$V_n''(\bar{q}_\varepsilon) = V_n''(\bar{q}) + \mathcal{O}(\varepsilon). \tag{4.6}$$

Since we always multiply V_n'' by ε in Eq. (2.15), we do not need to consider the higher orders because we are only interested in terms of order ε. Therefore, we can calculate D_{N+1} and D_N using the same saddlepoint trajectory. To take into account the additional timestep, we can use the recurrence

relation in Eq. (2.14) to express D_{N+1} in terms of D_N

$$\begin{aligned} D_{N+1} &= \left[2\alpha\varepsilon + (1 - 2\varepsilon\gamma V_N'')|\det M_N|\right]^{-1/2} \\ &= D_N + \varepsilon D_N(\gamma V_N'' - \alpha D_N^2) + \mathcal{O}(\varepsilon^2). \end{aligned} \tag{4.7}$$

We use $V_N'' = V''(q_N)$. These expansions lead to

$$\Delta = \varepsilon \frac{\exp\left[-\bar{S}(q_N, q_0, \tau)\right]}{\sqrt{2\pi}} D_N(\gamma V_N'' - \alpha D_N^2 + \mathcal{H}) + \mathcal{O}(\varepsilon^2). \tag{4.8}$$

Inserting Δ into Eq. (4.2) and applying the limit $\varepsilon \to 0$ to D_N we obtain

$$I = \int_{x_0}^{\infty} dq_N \int_{-\infty}^{\infty} dq_0 P(q_0) \frac{\exp\left[-\bar{S}(q_N, q_0, \tau)\right]}{\sqrt{2\pi}} D_N(\gamma V_N'' - \alpha D_N^2 + \mathcal{H}). \tag{4.9}$$

Since the Hamiltonian function is conserved in time, we can use any coordinates along the saddlepoint trajectory. We can also use this formula as an integral equation to determine the equilibrium distribution since we expect $I = 0$ in the equilibrium case. We can test the formula by verifying $I = 0$ for the equilibrium state in the harmonic case, which we do in App. C.

4.2 Escape from a metastable state

We want to calculate the probability current at which a particle escapes from a potential minimum with curvature a over a maximum of height ΔV with curvature $-b$. The important characteristics of the potential are shown in Fig. 4.1. Assuming sufficiently low temperatures $k_B T \ll \Delta V$, the distribution of the particle inside the minimum evolves towards a Maxwell-Boltzmann distribution with the timescale $\frac{1}{a\gamma}$. This happens due to the fact that the temperature is not high enough to reliably cause fluctuations of the positon into areas where the potential significantly deviates from a harmonic well. With this assumption, we worked out the arbitrary starting distribution and obtain

$$P(q_0) = \sqrt{\frac{a\gamma}{\pi\alpha}} \exp\Big(-\frac{a\gamma}{\alpha} q_0^2\Big). \tag{4.10}$$

If the temperature is low enough, the particle is localized at $q = 0$. Therefore, we only need to solve the equations of motion for $q_0 = 0$. In general,

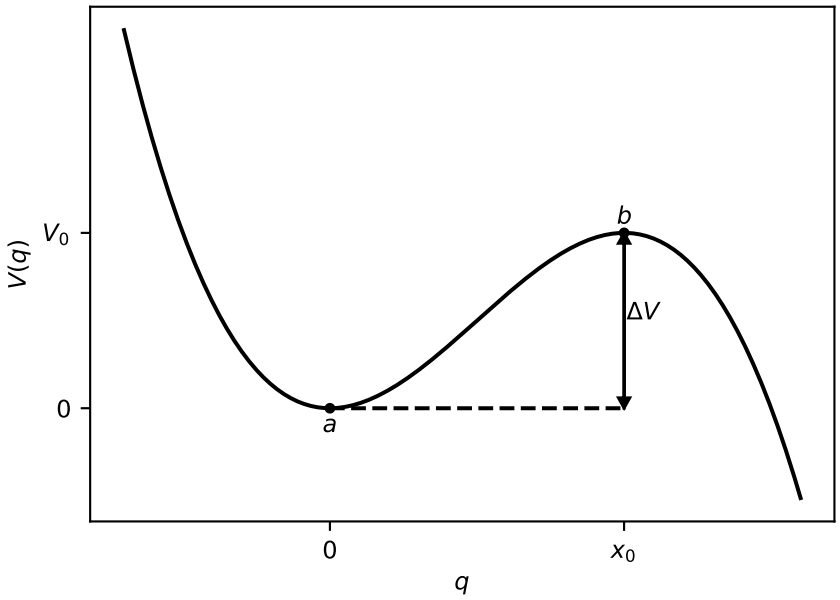

Figure 4.1: Important characteristics of the metastable minimum. The minimum is at the position $q = 0$ with the curvature $a = \frac{1}{2}V''(0)$. The probability current is the time derivative of the probability to be at the right of the maximum at $q = x_0$ with the curvature $-b = \frac{1}{2}V''(x_0)$. The potential difference between the minimum and the maximum is ΔV.

it is not possible to solve the equations of motion and therefore calculate the action of the saddlepoint. However, we can always use a trajectory with $\mathcal{H} = 0$ since, for all potentials, $\mathcal{H} = 0$ is equivalent to

$$\bar{p} = \frac{\gamma}{\alpha}V'(\bar{q}) = \frac{1}{k_B T}V'(\bar{q}). \tag{4.11}$$

Since we use $\mathcal{H} = 0$, we obtain the saddlepoint action by integrating over $\bar{p}\dot{\bar{q}}$. Using Eq. (4.11), this expression is proportional to a total time derivative of $V(q)$. The saddlepoint action is given by

$$\bar{S} = \frac{V(q_N) - V(0)}{k_B T}. \tag{4.12}$$

It is important to note that a trajectory with $\mathcal{H} = 0$ takes an infintely large time to actually reach the maximum of the potential. Therefore, the use of this saddlepoint is only valid for large times, which we assume in all following

calculations. To calculate the probability current, we simplify the trajectory by assuming the particle rests at the minimum for a the time $\tau/2$ and then rapidly moves to the maximum, where it also remains for $\tau/2$. Afterwards, the particle rapidly moves to the endpoint q_N to the right of the maximum. This means we assume V_n'' to either be $2a$ or $-2b$ along the trajectory with $\bar{p} = 0$. Therefore, we can use Eq. (2.15) to calculate the fluctuation in the limit $\varepsilon \to 0$ with $N\varepsilon = \tau$

$$D_N = \left\{ \frac{\alpha}{\gamma} \left[\frac{\exp(2b\gamma\tau) - 1}{2b} + \exp(2b\gamma\tau) \frac{1 - \exp(-2a\gamma\tau)}{2a} \right] \right\}^{-1/2}. \quad (4.13)$$

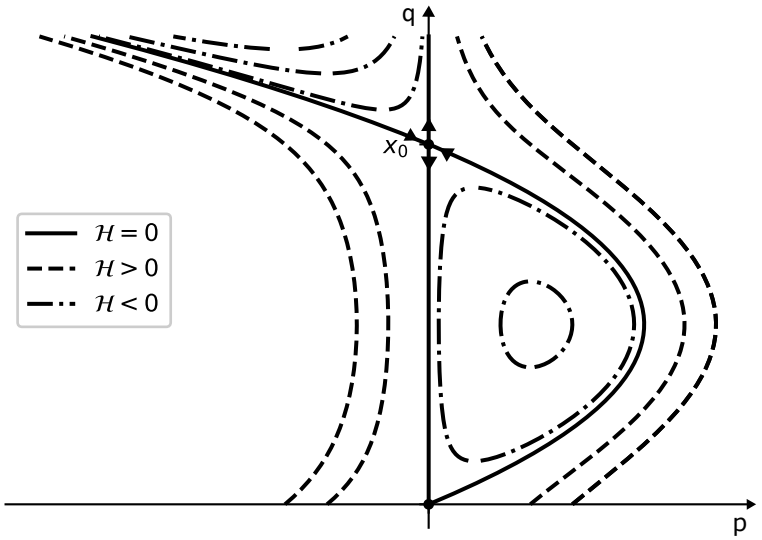

Figure 4.2: Possible trajectories in phase space. We can see that the point $(x_0, 0)$ is a saddlepoint for $\mathcal{H} = 0$. Once the particle reaches the maximum, it can either fall back into the minimum or or escape from it.

Due to the fluctuation-dissipation theorem, we know $\alpha/\gamma = k_B T$. Since we are in the case of large times, we obtain

$$D_N = \sqrt{\frac{2ab}{k_B T(a+b)}} \exp(-b\gamma\tau). \quad (4.14)$$

Since we used $\mathcal{H} = 0$, and D_N is exponentially small for large times, the

probability current is given by

$$I = \sqrt{\frac{2ab}{k_B T(a+b)}} \exp(-b\gamma\tau) \cdot \int_{x_0}^{\infty} dq_N \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{V(q_N) - V(0)}{k_B T}\right) \gamma V''(q_N). \tag{4.15}$$

We map $q_N \mapsto x_0 + \delta q$ and expand the potential up to quadratic order in δq. This leaves us with

$$I = \sqrt{\frac{2ab}{k_B T(a+b)}} \exp(-b\gamma\tau) \exp\left(-\frac{\Delta V}{k_B T}\right) \cdot \int_{0}^{\infty} \frac{d(\delta q)}{\sqrt{2\pi}} \exp\left(\frac{b\delta q^2}{k_B T}\right) (-2\gamma b). \tag{4.16}$$

To obtain a convergent integral, we substitute $\delta q \mapsto i\delta q$, which leads to an additional minus sign. The final result is

$$I = \gamma b \sqrt{\frac{a}{a+b}} \exp\left(-\frac{\Delta V}{k_B T}\right) \exp(-b\gamma\tau). \tag{4.17}$$

For large times, the probability current is exponentially small. It is also dependent on a Boltzmann factor with the height of the potential barrier, which is a rather intuitive result. Integrating this formula for the probability current in time does not yield the result one. However, this is not necessary due to the fact that the formula only holds for sufficiently large times.

Chapter 5

Conclusion and outlook

This thesis has dealt with the escape of a brownian particle from a metastable potential minimum, using path integrals to describe the thermal fluctuations. In Ch. 2, we introduced the concept of path integrals and derived an explicit formula for the fluctuation determinant in Eq. (2.15).

We discussed the relaxation into an equilibrium state for a harmonic potential in Ch. 3. In this context, we obtained the well known fluctuation-dissipation theorem, as well as the timescale of the relaxation. Furthermore, we discussed that the equilibrium state of the harmonic potential should also occur as an intermediate metastable state in a more general minimum for sufficiently low temperatures. In Ch. 4, we developed an explicit analytical expression for the probability current. Finally, we were able to use this formula to obtain the probability current of the escape from a minimum for large times and low temperatures in Eq. (4.17).

We are curious to find out whether the probability current obtained with path integration can be mapped to the previously known Kramer's escape rate [1]. For this, we could try to obtain a result for small times by using an exponentially small Hamiltonian function. We imagine, the probability current for $\tau \to 0$ should correspond to Kramer's escape rate. This would be an interesting subject for future research.

Appendix A

Derivation of the determinant formula

We want to calculate the determinant

$$|\det M_N| = 2\alpha\varepsilon \det B_N B_N^T. \tag{A.1}$$

Using Eq. (2.11), $B_N B_N^T$ is a symmetrical tridiagonal matrix that is equal to

$$\begin{pmatrix} 2-2\varepsilon\gamma V_1''+\gamma^2\varepsilon^2(V_1'')^2 & -1+\gamma\varepsilon V_1'' & 0 & 0 \\ -1+\gamma\varepsilon V_1'' & \ddots & \ddots & 0 \\ 0 & \ddots & \ddots & -1+\gamma\varepsilon V_{N-2}'' \\ 0 & 0 & -1+\gamma\varepsilon V_{N-2}'' & 2-2\varepsilon\gamma V_{N-1}''+\gamma^2\varepsilon^2(V_{N-1}'')^2 \end{pmatrix}. \tag{A.2}$$

We make use of the fact that there exists a matrix $K_N \in \mathbb{R}^{N\times N}$ of the form

$$K_N = \begin{pmatrix} 1 & 0 & \dots & 0 \\ -1+\gamma\varepsilon V_1'' & \ddots & 0 & \vdots \\ 0 & \ddots & \ddots & 0 \\ 0 & 0 & -1+\gamma\varepsilon V_{N-1}'' & 1 \end{pmatrix}, \tag{A.3}$$

which has the property that $K_N^T K_N$ is also a symmetrical tridiagonal matrix that contains $B_N B_N^T$ as a block

$$K_N^T K_N = \left(\begin{array}{ccc|c} & & & 0 \\ & B_N B_N^T & & \vdots \\ & & & 0 \\ & & & -1+\gamma\varepsilon V''_{N-1} \\ \hline 0 \ldots & 0 & -1+\gamma\varepsilon V''_{N-1} & 1 \end{array} \right). \tag{A.4}$$

We can make use of a recursive formula for the determinants of symmetrical tridiagonal matrices [6] and the fact $\det K_N = 1$ to obtain

$$1 = \det K_N^T K_N = \det B_N B_N^T - (-1+\gamma\varepsilon V''_{N-1})^2 \det B_{N-1} B_{N-1}^T. \tag{A.5}$$

By neglecting terms with factors ε^2, we obtain

$$\det B_N B_N^T = 1 + (1 - 2\gamma\varepsilon V''_{N-1}) \det B_{N-1} B_{N-1}^T. \tag{A.6}$$

We can use the recurrence relation to obtain an explicit formula

$$\begin{aligned} \det B_N B_N^T = 1 + (1 - 2\gamma\varepsilon V''_{N-1}) \Big[& 1 + (1 - 2\gamma\varepsilon V''_{N-2}) \\ & \cdot \Big[1 + \ldots \cdot [1 + ((1 - 2\gamma\varepsilon V''_1)] \ldots \Big] \Big] \end{aligned} \tag{A.7}$$

that is equivalent to

$$D_N = \sqrt{\frac{1}{|\det M_N|}} = \left\{ 2\alpha\varepsilon \left[1 + \sum_{i=1}^{N-1} \prod_{j=i}^{N-1} (1 - 2\gamma\varepsilon V''_j) \right] \right\}^{-1/2}. \tag{A.8}$$

Appendix B

Obtaining the correct normalization

To interpret the path integral towards an arbitrary position q_N as a probability density for the position of the particle, we need to ensure that the integral over all endpoints q_N equals one. To obtain the correct normalization, we can calculate the path integral in the case $V(q) = 0$. We can do so by treating q_N like an additional step with a sliced time axis and simply integrating over all (q_i, p_i) with a normalizing factor $\mathcal{N}$

$$1 \stackrel{!}{=} \frac{1}{\mathcal{N}^N} \int_{-\infty}^{\infty} dq_1 dp_1 ... dq_N dp_N \exp\left[\sum_{j=1}^{N} p_j(q_j - q_{j-1} - \varepsilon\alpha p_j)\right]. \tag{B.1}$$

The matrix M_N of the quadratic form also has the form

$$\left(\begin{array}{c|c} 0 & B \\ \hline B^T & C \end{array}\right), \tag{B.2}$$

but in this case, B and C are quadratic since we have an equal amount of q-integrals and p-integrals. Therefore, B^T and C^{-1} commute and we obtain

$$|\det M_N| = \det(C)\det\left(BC^{-1}B^T\right) = \det\left(BB^T\right) \tag{B.3}$$

In this case, B is given by

$$B = \begin{pmatrix} 1 & -1 & 0 & 0 \\ 0 & \ddots & \ddots & 0 \\ \vdots & 0 & \ddots & -1 \\ 0 & \dots & 0 & 1 \end{pmatrix}. \tag{B.4}$$

Since both B and B^T have determinant one, we obtain $\det M_N = 1$. Similarly to Eq. (2.9), we obtain

$$1 \stackrel{!}{=} \frac{(2\pi)^N}{\mathcal{N}^N} \tag{B.5}$$

and therefore $\mathcal{N} = 2\pi$.

Appendix C

Calculations for the harmonic case

C.1 Calculating the saddlepoint action

We want to calculate the action along the trajectories from q_0 to q_N that fulfill the canonical equations of motion

$$\dot{\bar{p}} = 2a\gamma\bar{p} \qquad \text{and} \qquad \dot{\bar{q}} = 2\alpha\bar{p} - \gamma V'(\bar{q}) = 2\alpha\bar{p} - 2\gamma a\bar{q}. \tag{C.1}$$

These equations have the general solution

$$\begin{aligned} \bar{q}(t) &= c_1 \frac{\alpha}{a\gamma} \sinh(2a\gamma t) + c_2 \exp(-2a\gamma t) \\ \bar{p}(t) &= c_1 \exp(2a\gamma t). \end{aligned} \tag{C.2}$$

The solutions that fulfill $\bar{q}(t=0) = q_0$ and $\bar{q}(t=\tau) = q_N$ have the constants

$$c_1 = \frac{a\gamma[q_N - q_0 \exp(-2a\gamma\tau)]}{\alpha \sinh(2a\gamma\tau)} \qquad \text{and} \qquad c_2 = q_0. \tag{C.3}$$

Using Eq. (C.1), we can simplify the action for the saddlepoint to be

$$\bar{S} = \alpha \int_0^\tau \bar{p}(t)^2 dt = \frac{a^2\gamma^2[q_N - q_0 \exp(-2a\gamma\tau)]^2}{\alpha \sinh(2a\gamma\tau)^2} \int_0^\tau \exp(4a\gamma t) dt. \tag{C.4}$$

Therefore, we obtain

$$\bar{S} = \frac{a\gamma}{2\alpha}\frac{\exp(2a\gamma\tau)}{\sinh(2a\gamma\tau)}[q_N - q_0\exp(-2a\gamma\tau)]^2. \tag{C.5}$$

C.2 Verifying zero probability current in the equilibrium state

Since we expect the probability current to be zero in the equilibrium state, we can start with the Maxwell-Boltzmann distribution to test our formula for the probability current. We use Eq. (4.9) with

$$P(q_0) = \sqrt{\frac{a\gamma}{\pi\alpha}}\exp\Big(-\frac{a\gamma}{\alpha}q_0^2\Big). \tag{C.6}$$

Since we integrate over the product of two exponential functions, we can add the arguments and complete the square to integrate over q_0. Using Eq. (C.5), we obtain

$$\begin{aligned} &-\frac{a\gamma}{\alpha}q_0^2 - \bar{S}(q_0, q_N, \tau) \\ &\qquad = -\frac{a\gamma}{\alpha}q_N^2 - \frac{a\gamma\exp(2a\gamma\tau)}{2\alpha\sinh(2a\gamma\tau)}\left[q_0 - q_N\exp(-2a\gamma\tau)\right]^2. \end{aligned} \tag{C.7}$$

Since the D_N given by Eq. (3.5) is independent of q_0 and q_N, we can treat it as a prefactor of the integral and therefore ignore it, if we just want to verify $I = 0$. We perform the integral

$$\int_{-\infty}^{\infty} dq_0 A\exp\left\{-\frac{a\gamma\exp(2a\gamma\tau)}{2\alpha\sinh(2a\gamma\tau)}\left[q_0 - q_N\exp(-2a\gamma\tau)\right]^2\right\}, \tag{C.8}$$

with A given by

$$\begin{aligned} A = (\gamma V_N'' - \alpha D_N^2 + \mathcal{H}(q_0, q_N)) &= -a\gamma\frac{\exp(-2a\gamma\tau)}{\sinh(2a\gamma\tau)} \\ - 2\frac{a^2\gamma^2}{\alpha}q_N\frac{q_N\exp(2a\gamma\tau) - q_0}{\sinh(2a\gamma\tau)} &+ a^2\gamma^2\frac{[q_0 - q_N\exp(2a\gamma\tau)]^2}{\alpha\sinh^2(2a\gamma\tau)}. \end{aligned} \tag{C.9}$$

This integral is equal to zero, which means that the probability current is zero in the equilibrium state.

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