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Confined Brownian Motion:

Fick-Jacobs Equation & Stochastic Thermodynamics

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Abstract

Brownian motion confined in a two dimensional channel with varying cross-section under the influence of an external force field is examined. In particular, a one dimensional equation approximately describing the dynamics of the Brownian particles is derived, a generalization of the well known Fick-Jacobs equation. This generalized Fick-Jacobs equation is numerically verified by Brownian dynamics simulations for a special case of the external force field. Furthermore the generalized Fick-Jacobs equation is investigated in the context of stochastic thermodynamics.

Contents

Chapter 1

Introduction

1.1 A very short historical review

In 1827 a botanist named Robert Brown was investigating grains of pollen from a plant named Clarkia pulchella. Before bursting, these grains contain 5-6 micrometer large particles. He was observing these particles immersed in water under a simple microscope. His original question was addressed to the process of fertilization. However his attention was soon drawn to another phenomena. He observed a persistent erratic motion of the particles. By repeating the experiment he was convinced that the origin of this motion was neither fluid currents nor evaporation. In 1928 he published his discovery in an article named "*A brief account of microscopical observations made in the months of June, July and August 1827, on the particles contained in the pollen of plants; and on the general existence of active molecules in organic and inorganic bodies*"[5]. In honor to Robert Brown this phenomena is still known as Brownian motion. Unfortunately he was not able to explain this strange behavior of the particles.

The problem remained unsolved for nearly a century. It was Albert Einstein who came up with a satisfying theoretical explanation in 1905. In his work [7], he argues based on the osmotic pressure, that the motion of particles immersed in a static liquid is of the same kind as the motion of the liquid particles. Namely thermal fluctuations. He then realizes that the a meaningful theoretical description requires a probabilistic approach. He shows that the probability density of the particles obeys a diffusion equation. Furthermore he realizes that the mean square displacement of the position increases linearly in time, which is typical for a diffusion process. It describes the spreading of the particles. Independently from Einstein, Marian Smoluchowski derived the same result. However he published it one year later in 1906 [30]. This linear relation is therefore known as Einstein-Smoluchowski relation.

Another cornerstone in the development of the theory of Brownian motion was laid by Paul Langevin in 1908 [12]. His approach is based on a so called stochastic differential equations, which is nowadays known as the Langevin equation. It is essentially a Newtonian like equation with a randomly fluctuating force term. It is a description on the level of a single trajectory. In contrast to Einsteins approach the Langevin equation takes into account the inertia of the particle. It will be the Langevin equation from which we start introducing the

theory of Brownian motion in section 2.2.

1.2 Brownian motion in a channel

Leaving the possible applications aside we will try to give the reader an understanding why confined Brownian motion is interesting from a physicist point of view. Since the title is rather general we will first introduce our toy model on the level of words. We have a two dimensional channel with varying cross section. The channel is filled with a static liquid. For now we assume no external forces. We take a number of spherical (Brownian) particles significantly large then the liquid particles, usually in the range of micro meters, and place all of them at a point inside the tube. We do not consider particle-particle interactions. The question is how will these particles behave?

They will undergo a diffusive process. They will spread out and interact with the wall. Mathematically, one can describe the particles with a probability density function which obeys an diffusion equation with so called reflective boundary conditions. These reflective boundary conditions make the mathematical treatment of this problem difficult. In the case of a parallel channel the probability density function is separable. The diffusion process in longitudinal direction does not influence the diffusion process in lateral direction. This is no longer the case for a channel with varying cross section. M.H. Jacobs was the first one giving this problem serious attention [9]. Using heuristic arguments he derived an approximate one dimensional equation describing the longitudinal dynamics of the particles, which is nowadays known as the Fick-Jacobs (F-J) equation. The F-J equation is an diffusion equation with an external force term effectively describing the influence of the wall. This force, let us call it the F-J force, is such that the particles tend to accumulate where the cross section of the channel is larger. In other words the particles tend to go where more space is available. In yet other words the system will gradually evolve into a macroscopic state which can be represented by the largest number of microscopic states. Here a micro state is characterized by coordinates x along and coordinates y lateral to the channel, a macro state is solely characterized by x coordinates. This of course sounds a lot like the maximum entropy principle. Thus the F-J force, although in the effective one dimensional picture appearing as a deterministic force, has a probabilistic origin. It is therefore often called an entropic force. It's a simple but nonetheless remarkable effect. Confining the phase space with a non trivial geometry leads to an effective external force.

After M.H Jacobs several other people were addressing this problem. We will list some of them.

R. Zwanzig presented an alternative more rigorous derivation of the F-J equation [32]. Furthermore he showed that introducing an effective space dependent diffusion coefficient in the F-J equation leads to a better approximation. Based on heuristic arguments he derived an analytic expression of this space dependent diffusion coefficient for a channel with constant midline i.e a symmetric channel.

D.Reguera and J.M. Rubi derived a more precise form of Zwanzigs effective space dependent diffusion coefficient using arguments based on nonequilibrium thermodynamics [21]. Furthermore they derived an F-J equation taking into

account an constant external force in lateral direction.

P. Kalinay and J. K. Percus developed a somewhat exotic perturbation method based on operator algebra allowing them to derive an even more precise expression for the space dependent diffusion coefficient of a symmetric channel. [10].

R. Bradley derived an expression of the space depended diffusion coefficient for an channel with varying midline. His derivation is based on a standard perturbation method in which the expansion parameter is defined by the ratio of two intrinsic length scales of the channel. [4].

S. Martens, G. Schmid, L. Schimansky-Geier, and P. Hänggi derived higher order corrections to the F-J equation for a three dimensional planar symmetric and periodic channel considering a constant external force in longitudinal direction [16]. They used a perturbation method similar to R. Bradley.

S. Martens, G. Schmid, L. Schimansky-Geier, AV. Straube and P. Hänggi extended their F-J equation derived in [16] considering also spatial depending external Forces [14, 17].

The derivation of a FJ-equation generalized to space dependent external forces is what we are interested in as well. In section 4.3 we present a derivation of a generalized F-J equation based on the method of multiple scales. Our equation differs to the one derived by Martens et al. in [14, 17]. In chapter 5 we numerically verify our general F-J equation by Brownian dynamics simulations.

At this point we will make a small jump to a different but related topic, namely stochastic thermodynamics. Stochastic thermodynamics was developed mainly by K. Sekimto[25], and U. Seifert [24] in the 90's and 00's. It is a framework which defines the notion of heat entropy and work on a much smaller scale, the mesoscopic scale, than classical thermodynamics. It is the scale on which the Langevin equation is valid. Quantities like entropy heat and work are no longer macroscopic ensemble averages but trajectory dependent stochastic variables. Since the F-J force has an entropic nature it seems interesting to investigate it in the context of stochastic thermodynamics. In particular the question we try to answer in chapter 6 is if the generalized FJ-equation comprise the correct stochastic thermodynamics. It turns out that for a general external force this is not the case.

Chapter 2

Brownian Motion

2.1 Stochastic processes

Before introducing the Langevin equation we will shortly discuss the concept of stochastic processes. Roughly speaking a stochastic process is a random variable $X(t)$ depending on a real parameter t. In Physics this parameter is usually time. A random variable is characterized by its probability distribution function (PDF). Similarly a stochastic process for a finite time sequence $X(t_1), X(t_2), X(t_3) \cdots X(t_n)$ is characterized by the joint PDF $p(x_1, t_1; x_2, t_2; x_3, t_3 \cdots x_n, t_n)$. We are using the standard notation big letters for random variables, small letters for their realizations. We will only encounter a particular case of stochastic processes which are called Markovian processes [8]. They obey the following property:

$$p(x_1, t_1 \mid x_2, t_2; x_3, t_3; \cdots x_n, t_n) = p(x_1, t_1 \mid x_2, t_2) \quad for \quad t_1 > t_2 > t_3 \cdots > t_n \tag{2.1}$$

In words this can be expressed in the following way. The probability of finding x_1 at time t_1 depends only on what happened at the previous time t_2. I.e. the process has no memory about the past. Using the Markovian property (2.1) we can write the joint PDF as:

$$\begin{aligned} p(x_1, t_1; x_2, t_2; x_3, t_3 \cdots x_n, t_n) =& p(x_1, t_1 \mid x_2, t_1) p(x_2, t_2 \mid x_3, t_3) \cdots \\ & p(x_{n-1}, t_{n-1} \mid x_n, t_n) p(x_n, t_n) \end{aligned} \tag{2.2}$$

The transition PDFs on the RHS can be used to fully describe the statistical properties of a Markovian process. A stochastic process of importance in the theory of Brownian motion is the so called Wiener process. Actually its transition PDF describes the simplest case of free Brownian motion, it is given by [8] :

$$p(x_1, t_1 \mid x_2, t_2) = \frac{1}{\sqrt{2\pi(t_1 - t_2)}} \exp\left[-\frac{(x_1 - x_2)^2}{2(t_1 - t_2)}\right] \tag{2.3}$$

The process depends solely on the time and space increment $\Delta t = t_1 - t_2$ and $\Delta x = x_1 - x_2$. Thus we can write the transition PDF as

$$p(\Delta x, \Delta t) = \frac{1}{\sqrt{2\pi\Delta t}} \exp\left[-\frac{\Delta x^2}{2\Delta t}\right] \tag{2.4}$$

It can be shown that the time correlation function is:

$$\langle X(t_1)X(t_2)\rangle = min(t_1, t_2) \ . \tag{2.5}$$

Another important stochastic object is Gaussian white noise, which is defined by:

$$\langle \xi(t)\rangle = 0 \qquad \langle \xi(t_1), \xi(t_2)\rangle = b\delta(t_1 - t_2) \ . \tag{2.6}$$

All higher moments are given by the rule of Gaussian processes [29]. Note we did not call it a stochastic process since it is not. There exists no well defined stochastic process with the properties of a Gaussian white noise. It is a singular object like the delta distribution. However there is a relation between the Wiener process and Gaussian white noise. Let us say $W(t)$ describes a Wiener process. Then the following is true [29]:

$$W(t) = \int_0^t \xi(s)\mathrm{d}s \ . \tag{2.7}$$

2.2 The Langevin equation

We start by considering the following system. We have a (Brownian) particle described by position x and velocity v immersed in a medium. For simplicity we consider the system to be one dimensional. The medium can be thought of as being a liquid, for example water. The Brownian particle is assumed to be significantly bigger than the medium particles, which is usually at the order of micrometers. We are interested in the trajectory of the Brownian particle. Assuming some interaction potential we could in principle solve the equations of motions of all particles numerically. However that is not what we are going to do. We want to avoid dealing with the large number of degrees of freedom needed for the description of the medium. Therefore we are going to motivate an effective equation known as the Langevin equation. The Langevin equation is neither a microscopic nor a macroscopic description. The scale on which the equation is valid is known as the mesoscopic scale. Since the Brownian particle is assumed to behave like a classical particle its dynamics is described by a Newtonian equation.

$$\dot{x}(t) = v(t) \tag{2.8}$$

$$m\dot{v}(t) = F(t) \tag{2.9}$$

The task is now to find a physical meaningful expression for $F(t)$. The only forces acting on the particle are due to the collisions of the medium particles. In order to be able to describe these collisions by the force $F(t)$, which is independent of the medium particles degrees of freedom we will have to make some simplifications.

The microscopic timescale τ_{micro} between collisions is assumed to be very small compared to mesoscopic timescale of interest τ_{meso}. In fact we will assume τ_{micro} to be infinitesimally small. On the timescale τ_{meso} the force exerted on the particle due to the collisions can then be pictured as a series of infinitely sharp and dense spikes. Furthermore we assume that on the timescale τ_{meso} a collision at time t does not influence a collision at time $t+\tau_{meso}$. I.e. the medium

has no memory. Due to the symmetry of the system on average collisions coming from the left exert the same force on the particle as collisions from the right. A suitable candidate which is statistically mimicking these properties is Gaussian white noise $\xi(t)$ defined by:

$$\langle \xi \rangle = 0 \qquad \langle \xi(t_1), \xi(t_2) \rangle = b\delta(t_1 - t_2) \ , \tag{2.10}$$

Where b is the strength of the noise. We will call ξ the random force.

Let's assume for a moment that $F(t) = \xi(t)$. Looking at the average kinetic energy leads to the following conclusion:

$$m \left\langle v(t)^2 \right\rangle = \int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2 \left\langle \xi(t_1)\xi(t_2) \right\rangle = \tag{2.11}$$

$$b \int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2 \delta(t_2 - t_1) \sim t \ . \tag{2.12}$$

The particle's average kinetic energy is increasing with time. Clearly that does not make sense physically. It seems we are missing a term responsible for slowing the particle down.

Due to the random force the particle is moving with a certain speed in a certain direction. In order to continue its motion it will have to push away medium particles which results in an asymmetric momentum transfer from the particle to the medium. There are more collisions on the front, reducing the momentum of the particle, than there are on the back increasing the momentum of the particle. We can draw the following conclusion: The faster the particle the more it will decelerate. Thus the additional force term f_{fric} should be proportional to the velocity.

We know that a macroscopic sphere in liquid experiences a frictional force $-\gamma v$. Where γ is known as the friction coefficient. Which is related to the radius r of the particle and the viscosity ν of the liquid via the stokes law $\gamma = 6\pi\nu r$. Assuming that stokes law holds at the mesoscopic scale we choose $f_{\text{fric}} = -\gamma v$. With $F(t) = -\gamma v + \xi(t)$ we arrive at the Langevin equation:

$$\dot{x}(t) = v(t) \tag{2.13}$$

$$m\dot{v}(t) = -\gamma v + \xi(t) \tag{2.14}$$

The friction force f_{fric} and the random force ξ have the same origin, namely the medium. Therefore one expects a relation between them. Indeed such a relation exists and is know as the fluctuation dissipation relation. In what follows we will sketch its derivation. The formal solution of the Langevin equation for $v(t)$ is given by:

$$v(t) = \mathrm{e}^{-\frac{\gamma t}{m}} v(0) + \int_0^t \mathrm{d}\tilde{t} \quad \mathrm{e}^{-\frac{\gamma(t-\tilde{t})}{m}} \quad \frac{\xi(\tilde{t})}{m} \ , \tag{2.15}$$

from which one can calculate the average quadratic velocity:

$$\left\langle v^2 \right\rangle = e^{-\frac{2\gamma t}{m}} v(0)^2 + \frac{b}{\gamma m}(1 - e^{-\frac{2\gamma t}{m}}) \ . \tag{2.16}$$

We know that in equilibrium i.e $t \to \infty$, the equipartition theorem $\left\langle v^2 \right\rangle_{equ} = k_{\mathrm{B}}T/m$ must hold. Using (2.16) we get:

$$\lim_{t\to\infty} \left\langle v^2 \right\rangle = \frac{b}{\gamma m} = \frac{k_{\mathrm{B}}T}{m} \tag{2.17}$$

And we arrive at the fluctuation dissipation relation:

$$b = \gamma k_{\mathrm{B}} T \tag{2.18}$$

A relation between the strength of the random force the friction coefficient and the Temperature.

Similarly to this derivation we can calculate $\langle \Delta x^2 \rangle$, where $\Delta x = \int_0^t v(\tilde{t}) \mathrm{d}\tilde{t}$.

$$\langle \Delta x^2 \rangle = 2\frac{kT}{\gamma}\left[t - \frac{m}{\gamma} + \frac{m}{\gamma}\mathrm{e}^{-\frac{\gamma t}{m}}\right] \tag{2.19}$$

For times much longer than $\frac{m}{\gamma}$ the expression reduces to:

$$\langle \Delta x^2 \rangle = 2Dt \ , \tag{2.20}$$

Where we have introduced the Diffusion coefficient $D = \frac{k_b T}{\gamma}$. This is the famous Einstein-Smoluchowski relation.

The formal solutions as presented in (2.15) is as far as we can go in solving the Langevin equation in the usual sense. Asking for an analytic expression of the trajectory $v(t)$ does not make sense since the Langevin equation is a stochastic differential equation. Due to the random force $\xi(t)$, $v(t)$ is a stochastic process. Thus any realization of the trajectory $v(t)$ will look differently. Finding the stochastic properties of $v(t)$ is what is really meant by solving the Langevin equation. This can be achieved by computing the transition probability distribution $p(v, x, t \mid v_0, x_0, t_0)$. The transition PDF for $v(t)$ is known and was first derived by Ornstein and Uhlenbeck in [28]. Not surprisingly this stochastic process is known as the Ornstein-Uhlenbeck process.

The Langevin equation can be extended by considering external deterministic forces $f^{\mathrm{ext}}(x)$ as well. The resulting equation is known as the Langevin-Kramers equation and given by:

$$\begin{aligned} \dot{x}(t) &= v(t) \\ m\dot{v}(t) &= \gamma v + f(x)^{\mathrm{ext}} + \xi(t) \end{aligned} \tag{2.21}$$

The multidimensional case of the Langevin-Kramers equation is simply given by:

$$\begin{aligned} \dot{x}_j(t) &= v_j(t) \\ m\dot{v}_j(t) &= \gamma v_j + f_j(x)^{\mathrm{ext}} + \xi_j(t) \end{aligned} \tag{2.22}$$

Where $\xi_j(t)$ are Gaussian white noises defined by:

$$\langle \xi_j \rangle = 0 \qquad \langle \xi_j(t_1)\xi_i(t_2) \rangle = b_{ij}\delta(t_1 - t_2) \tag{2.23}$$

b_{ij} is a symmetric matrix. In the presence of an external force calculating the transition PDF starting form the Langevin equation might not always be the best way. The so called Fokker Planck equation provides an alternative approach. But more on that in the next section.

2.3 The Fokker-Planck equation

The Fokker Planck equation, a second order partial differential equation, describes the time evolution of the PDF for a stochastic process described by the Langevin equation. In this section we will present a derivation of the Fokker-Planck equation starting from the Langevin equation. The derivation is based on [33] and [22] .

Generally a system of Langevin equations is given by:

$$\frac{\mathrm{d}r_j}{\mathrm{d}t} = \nu_j(r_j) + \xi_j(t) \tag{2.24}$$

where r_j are the coordinates of the phasespace, ν_j is some function depending on r_j, and ξ_j are as usual Gaussian white noises obeying

$$\langle \xi_j \rangle = 0 \qquad \langle \xi_j(t_1)\xi_i(t_2)\rangle = b_{ij}\delta(t_1 - t_2) \tag{2.25}$$

Instead of considering the trajectory we will ask for the PDF $f(r_i, t)$, which gives the probability of finding a particle in volume element of the phase space for a single realization of the random force $\xi_j(t)$. Thus $f(r_i, t)$ will still depend on the random force. For every realization of the trajectories it will look different. Since it is a PDF integration over the whole phase space gives:

$$\int f(r_i, t)\mathrm{d}r_j = 1 \ . \tag{2.26}$$

This conservation law implies a continuity equation.

$$\frac{\partial f(r_i, t)}{\partial t} = -\frac{\partial}{\partial r_j}\dot{r}_j f(r_i, t) \tag{2.27}$$

Plugging in the Langevin equation (2.24) for $\dot{r}_j$ leads to a Liouville like equation:

$$\frac{\partial f(r_i, t)}{\partial t} = -\underbrace{\frac{\partial}{\partial r_j}\nu_j}_{A} f(r_i, t) - \underbrace{\xi_j(t)\frac{\partial}{\partial r_j}}_{B} f(r_i, t) \tag{2.28}$$

We introduce the deterministic operator A and the stochastic time dependent operator B(t). Since the above equation depends on the random force it is a stochastic differential equation. Thus as mentioned before $f(r_i, t)$ is still a stochastic quantity. However we are not interested in a stochastic description therefore we will construct a differential equation for the averaged PDF:

$$p(r_i, t) = \langle f(r_i, t)\rangle \ . \tag{2.29}$$

Making the following substitution in equation (2.28)

$$f(r_i, t) = \mathrm{e}^{-At}\sigma(r_i, t) \tag{2.30}$$

leads to

$$\frac{\partial \sigma(t)}{\partial t} = -\mathrm{e}^{At}B(t)\mathrm{e}^{-At}\sigma = -L(t)\sigma(t) \ . \tag{2.31}$$

The formal solution to this equation is given by:

$$\sigma(t) = \exp\left[-\int_0^t L(t_1)\mathrm{d}t_1\right]\sigma(0) \tag{2.32}$$

Taking the average we see that $\langle\sigma\rangle$ is the characteristic function of $X(t) = i\int_0^t L(t_1)\mathrm{d}t_1$ which is again a Gaussian variable with zero mean. It's well known that the characteristic function of a Gaussian process with zero mean is $\mathrm{e}^{\frac{1}{2}\langle X(t)^2\rangle}$.

Thus we have:

$$\langle\sigma(t)\rangle = \exp\left[\frac{1}{2}\int_0^t\int_0^t \langle L(t_1)L(t_2)\rangle\,\mathrm{d}t_1\mathrm{d}t_2\right] \tag{2.33}$$

Explicitly calculating the average

$$\begin{aligned}\int_0^t\int_0^t \langle L(t_1)L(t_2)\rangle\,\mathrm{d}t_1\mathrm{d}t_2 =& b_{jk}\int_0^t\int_0^t \mathrm{e}^{At_1}\frac{\partial}{\partial r_j}\mathrm{e}^{A(t_2-t_1)}\frac{\partial}{\partial r_k}\mathrm{e}^{At_2}\delta(t_1-t_2)\mathrm{d}t_1\mathrm{d}t_2\\ =& \int_0^t \mathrm{e}^{At_1}\frac{\partial}{\partial r_j}b_{jk}\frac{\partial}{\partial r_k}\mathrm{e}^{-At_1}\mathrm{d}t_1\end{aligned} \tag{2.34}$$

we get

$$\langle\sigma(t)\rangle = \exp\left[\frac{1}{2}\int_0^t \mathrm{e}^{At_1}\frac{\partial}{\partial r_j}b_{jk}\frac{\partial}{\partial r_k}\mathrm{e}^{-At_1}\mathrm{d}t_1\right]\ . \tag{2.35}$$

Taking the time derivative we get:

$$\frac{\partial\langle\sigma(t)\rangle}{\partial t} = \frac{1}{2}\mathrm{e}^{At}\frac{\partial}{\partial r_j}b_{jk}\frac{\partial}{\partial r_k}\mathrm{e}^{-At}\langle\sigma(t)\rangle\ . \tag{2.36}$$

Resubstituting for $p(r_i,t)$ we arrive at the Fokker-Planck equation:

$$\frac{\partial p}{\partial t} = \frac{1}{2}\frac{\partial}{\partial r_j}b_{jk}\frac{\partial}{\partial r_k}p - \frac{\partial}{\partial r_j}\nu_j p\ . \tag{2.37}$$

The first term on the RHS is arising form the operator $B(t)$ it is therefore describing the effect of random force. The second term is coming from the deterministic force ν_j.

Now we can easily construct the corresponding Fokker-Planck equation also known as Kramers equation for the multidimensional Langevin-Kramers equation. It is given by:

$$\frac{\partial p}{\partial t} = \frac{1}{2}\frac{\partial}{\partial v_j}b_{jk}\frac{\partial}{\partial v_k}p + \frac{\gamma}{m}\frac{\partial}{\partial v_j}v_j p - \frac{1}{m}\frac{\partial}{\partial v_j}f_j p - \frac{\partial}{\partial x_j}v_j p\ . \tag{2.38}$$

We can interpret the Kramers equation as a transport equation.

$$\frac{\partial p}{\partial t} = -\nabla\boldsymbol{J} = -\begin{pmatrix}\partial_{x_j}\\ \partial_{v_j}\end{pmatrix}\begin{pmatrix}J_{x_j}\\ J_{v_j}\end{pmatrix}\ , \tag{2.39}$$

Where the flux $\boldsymbol{J}$ is given by:

$$\boldsymbol{J} = \begin{pmatrix} J_{x_j} \\ J_{v_j} \end{pmatrix} = \begin{pmatrix} v_j p \\ -\frac{1}{2} b_{jk} \frac{\partial}{\partial v_k} - \frac{\gamma}{m} v_j + \frac{1}{m} \frac{\partial}{\partial v_j} f_j \end{pmatrix} p \tag{2.40}$$

In order to solve the Fokker Planck equation we need to fix the initial and boundary conditions. Let us say at time t_0 all particles are in one place at x_i^0 and have v_i^0 velocity. Mathematically this is expressed by:

$$p(\tilde{x}_i, \tilde{v}_i, t_0) = \delta(\tilde{x}_i - x_i^0)\delta(\tilde{v}_i - v_i^0) \tag{2.41}$$

Since p is a PDF we have:

$$p(x_i, v_i, t) = \int \mathrm{d}\tilde{x}_i \mathrm{d}\tilde{v}_i p(x_i, v_i, t \mid \tilde{x}_i, \tilde{v}_i, t_0) p(\tilde{x}_i, \tilde{v}_i, t_0) \tag{2.42}$$

The deltas will cancel the integration and we have:

$$p(x_i, v_i, t) = p(x_i, v_i, t \mid x_i^0, v_i^0, t_0) \tag{2.43}$$

Thus the transition probability density $p(x_i, v_i, t \mid x_i^0, v_i^0, t_0)$ is a solution of the Fokker-Planck equation with initial conditions (2.41). Using (2.42) again one can then obtain a solution for any kind of initial distribution.

The choice of the boundary conditions depends on particular physical system one is looking at. Considering the phase-space to have infinite extension the natural boundary conditions are:

$$\lim_{v_i \to \pm\infty} p = \lim_{v_i \to \pm\infty} \partial_{v_i} p = 0 \tag{2.44}$$

$$\lim_{x_i \to \pm\infty} p = \lim_{x_i \to \pm\infty} \partial_{x_i} p = 0 \tag{2.45}$$

Confining the phase space would require different boundary condition. For example the so called reflective boundary conditions. Since they play a crucial role in our work we have dedicated them a section on their own (see section 4.1).

2.4 The overdamped limit

The Kramers equation is generally very hard and in most cases impossible to solve, fortunately we can reduce it's complexity by considering a physically justified limit case, namely the overdamped limit. A mesoscopic object, like a micrometer sized sphere in liquid has almost no inertia [20]. For such a system the following overdamped limit assumption is valid $\frac{m}{\gamma} << 1$.

Using this assumption we can derive an simpler Langevin respectively Fokker-Planck equation. We rewrite the Langevin equation in a slightly different form .

$$\frac{m}{\gamma} \dot{v}_i = \frac{f_i^{\text{ext}}}{\gamma} + v_i + \xi_i \ . \tag{2.46}$$

Using the overdamped limit assumption we can neglect the inertia term on LHS. The Langevin equation reduces to what we will refer as the overdamped Langevin equation:

$$\dot{x}_i = \frac{f_i^{\text{ext}}}{\gamma} + \frac{1}{\gamma}\xi_i \ . \tag{2.47}$$

The corresponding overdamped Fokker Planck equation is given by:

$$\frac{\partial}{\partial t}\rho(x_i,t) = \frac{b_{ij}}{2}\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}\rho(x_i,t) - \frac{\partial}{\partial x_j}\frac{f_j^{\text{ext}}}{\gamma}\rho(x_i,t) \ . \tag{2.48}$$

The first term on the RHS is a result of the random force and describing a diffusion process i.e a spreading of the particles. The second term is called a drift term and describing the effect of the deterministic external force. In the absence of the deterministic force f the equation reduces to the diffusion equation originally derived by Einstein [7].

Note we did not just neglect one term we actually got rid of the velocity degrees of freedom. That means an initial velocity has no effect on the dynamics of the particle anymore.

The way how we derived the overdamped equations is quiet naive. We did not formally take the limit we just set $\frac{m}{\gamma}$ to zero. A better approach is to start from the underdamped Fokker Planck equation and take the limit with the help of perturbative methods. This procedure will be presented in the next section.

2.5 The method of multiple scales

It is frequently the case that dynamical systems, relevant in nature, are consisting of several intrinsic processes running on different time and length scales [18]. A simple example is the linear damped oscillator, whose equation of motion is given by:

$$\ddot{x} + x = -2\epsilon\dot{x} \ . \tag{2.49}$$

The analytic solution is well known and given by:

$$x = a\mathrm{e}^{-\epsilon t}\cos\left[\sqrt{1-\epsilon^2}t + \phi\right] \tag{2.50}$$

Where ϕ and a are constants.

Let's assume we don't know the analytic solution. Assuming ϵ is small we can try to use a straightforward perturbation method. Expanding x in orders of ϵ, $x = x_0 + \epsilon x_1 + \epsilon x_2 \cdots$, and comparing orders of ϵ leads to the following hierarchic equations:

$$\ddot{x}_0 + x_0 = 0 \tag{2.51}$$

$$\ddot{x}_1 + x_1 = -2\dot{x}_0 \tag{2.52}$$

$$\ddot{x}_2 + x_2 = -2\dot{x}_1 \tag{2.53}$$

Solving these equations we get an approximation for x :

$$\begin{aligned} x = a\cos(t+\phi) - \epsilon a t\cos(t+\phi) \\ + \frac{1}{2}\epsilon^2 a t^2\cos(t+\phi) + \frac{1}{2}\epsilon^2 a t\sin(t+\phi) + \mathcal{O}(\epsilon^3) \ . \end{aligned} \tag{2.54}$$

However this is a very poor approximation. If t becomes of the order $\frac{1}{\epsilon}$ the second and third term becomes bigger then the first. A contradiction to the original assumption. A better approach is to use the method of multiple scales. We can identify three processes running on three different timescales. The oscillation, the exponential damping and a phase shift with characteristic timescales 1, $\frac{1}{\epsilon}$ and $\frac{1}{\epsilon^2}$. The trick of the method of multiple scales is to introduce three time variables, a fast one $t_0 = t$, an intermediate one $t_1 = \epsilon t$ and a slow one $t_2 = \epsilon^2$ by hand. x is then assumed to depend on these three time variables.

$$x(t) = x(t_0, t_1, t_2) \ . \tag{2.55}$$

And the time derivative is given by the chain rule as:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{\partial}{\partial t_0} + \epsilon \frac{\partial}{\partial t_1} + \epsilon^2 \frac{\partial}{\partial t_2} \ . \tag{2.56}$$

Which at first sight seems to be an unnecessary complication turns out ot resolve the problem encountered in the straight forward perturbation method. We will not go deeper in to the multiple scale calculation for the damped harmonic oscillator since it is not that much connected to our work. However we will present a different example. The overdamped limit can be nicely achieved using the method of multiple scales. In what follows we will present this procedure. We will closely follow [3, 2]. In contrast to the damped oscillator we are dealing with a partial differential equation, which is the Kramer equation given by:

$$\frac{\partial p}{\partial t} = \frac{\gamma}{m} \left[\frac{k_\mathrm{B} T}{m} \frac{\partial^2}{\partial v_i \partial v_i} + \frac{\partial}{\partial v_i} v_i \right] p - \left[v_i \frac{\partial}{\partial x_i} + \frac{F_i}{m} \frac{\partial}{\partial v_i} \right] p \ . \tag{2.57}$$

Note we used a special case of the Kramers equation for which the matrix b_{ij} is diagonal and all b_{ii} are equal furthermore we used the fluctuation dissipation relation. The primary goal in this case is not to get an approximate solution but to integrate out the velocity degrees of freedom which results in an effective equation. The first thing we do is to introduce dimensionless quantities.

$$v \to v v_T; \qquad x \to x l; \qquad F \to F \frac{m v_T^2}{l} \ , \tag{2.58}$$

where $v_T = \sqrt{\frac{k_\mathrm{B} T}{m}}$ is the thermal velocity and l a characteristic length scale of the process. The rescaled Kramers equation reads:

$$\frac{v_T}{l} \frac{\partial p}{\partial t} = \frac{\gamma l}{v_T m} \left[\frac{\partial^2}{\partial v_i \partial v_i} + \frac{\partial}{\partial v_i} v_i \right] p - \left[v_i \frac{\partial}{\partial x_i} + F_i \frac{\partial}{\partial v_i} \right] p \tag{2.59}$$

Note the time is still a dimensionfull quantity. The next step is to figure out the relevant timescales. In order to do so we need to gain some qualitative understanding of the system. Looking at the formal solution of the Kramers-Langevin (2.15) equation for zero force we can identify an exponential damping of the initial velocity with a characteristic timescale $\tau_d = \frac{m}{\gamma}$. Above we introduced the thermal velocity v_T its a typical velocity of the particle due to the thermal fluctuations respectively the random force. Thus we can identify a second time scale $\tau_v = \frac{l}{v_T}$ relevant for the thermal velocity of the particles. A third timescale

can be identified by looking at the Einstein-Smoluchowski relation (2.20). The relevant timescale for this spatial Diffusion process is $\tau_x = \frac{\gamma}{l^2 k_B T} = \frac{\tau_v^2}{\tau_d}$. The assumption is now that the relevant timescale for the damping of the velocity τ_d is much small than τ_v. Which is a more elaborate formulation of the over-damped limit assumption. As described in the case of the damped oscillator the trick of the multiple scale method is to artificially introduce new time variables according to the relevant timescales:

$$t_0 = \frac{t}{\tau_d}; \qquad t_1 = \frac{t}{\tau_v} \qquad t_2 = \frac{\tau_d}{\tau_v^2} t \tag{2.60}$$

Where t_0 is the fast time associated with τ_d, t_1 is the intermediate time associated with τ_v and t_2 the slow time associated with τ_x. Assuming that $p(x_i, v_i, t) = p(x_i, v_i, t_0, t_1, t_2)$, using the chain rule for the time derivative and defining a small parameter $\epsilon = \frac{\tau_d}{\tau_v}$ we get:

$$\left[\frac{1}{\epsilon}\frac{\partial}{\partial t_0} + \frac{\partial}{\partial t_1} + \epsilon\frac{\partial}{\partial t_2}\right] p = \left[\frac{1}{\epsilon}\hat{M} - \hat{L}\right] p \tag{2.61}$$

Were we have defined the operators $\hat{M}$ and $\hat{L}$ as :

$$\hat{M} = \frac{\partial^2}{\partial v_i^2} + \frac{\partial}{\partial v_i} v_i \qquad \hat{L} = v_i \frac{\partial}{\partial x_i} + F_i \frac{\partial}{\partial v_i} \tag{2.62}$$

Next we are expanding p in a power series of ϵ

$$p = p_0 + \epsilon p_1 + \epsilon^2 p_2 + \cdots \tag{2.63}$$

Plugging the series expansion back into equation (2.62) and comparing orders of ϵ gives a set of hierarchical equations.

$$\mathcal{O}\left(\epsilon^{-1}\right): \qquad \hat{M} p_0 = \frac{\partial}{\partial t_0} p_0 \tag{2.64}$$

$$\mathcal{O}\left(1\right): \qquad \hat{M} p_1 = \left[\frac{\partial}{\partial t_1} + \hat{L}\right] p_0 + \frac{\partial}{\partial t_0} p_1 \tag{2.65}$$

$$\mathcal{O}\left(\epsilon\right): \qquad \hat{M} p_2 = \frac{\partial}{\partial t_2} p_0 + \left[\frac{\partial}{\partial t_1} + \hat{L}\right] p_1 + \frac{\partial}{\partial t_0} p_2 \tag{2.66}$$

In the following we will go step by step through hierarchical equations, present their solutions and use them for the construction of the effective equation.

The $\mathcal{O}\left(\epsilon^{-1}\right)$ equation:

We are interested in the behavior of the system for times much longer than τ_v. Thus we solve the $\mathcal{O}\left(\epsilon^{-1}\right)$ equation for the stationary solution. Since $\hat{M}$ contains only derivatives with respect to v_i we can separate

$$p_0(x_i, v_i, t_1, t_2) = \rho_0(x, t_1, t_2)\omega(v, x) \ , \tag{2.67}$$

where ω is the eigenfunction of $\hat{M}$ with eigenvalue zero given by:

$$\omega(v,x) = \frac{\exp\left(-\frac{v^2}{2}\right)}{(2\pi)^{n/2}} \ . \tag{2.68}$$

And ρ_0, the marginal PDF of p_0, does not depend on t_0, however in principle it could still depend on t_1 or t_2.

The $\mathcal{O}(1)$ equation:

Before solving the $\mathcal{O}(1)$ we will integrate the equation with respect to v and use the natural boundary conditions. Which leads to

$$\frac{\partial \rho_0}{\partial t_1} = 0 \ , \tag{2.69}$$

implying that ρ is independent of t_1. Solving the $\mathcal{O}(1)$ equation then yields:

$$p_1(x_i, v_i, t_1, t_2) = \rho_1(x_i, t_1, t_2)\omega - \omega \frac{v_i}{\gamma}\left[\frac{\partial}{\partial x_i} + \frac{F_i}{T}\right]\rho_0(x_i, t_2) \ , \tag{2.70}$$

where ρ_1 is the marginal PDF of p_1.

The $\mathcal{O}(\epsilon)$ equation:

Integrating the $\mathcal{O}(\epsilon)$ equation and applying the natural boundary conditions leads to

$$\frac{\partial}{\partial t_2}\rho_0 + \frac{\partial}{\partial t_1}\rho_1 = -\int \mathrm{d}v_j \hat{L} p_1 \mathrm{d}^3 v \ . \tag{2.71}$$

Plugging in the previously calculated expression for p_1 gives:

$$\frac{\partial \rho_0}{\partial t_0} + \frac{\partial \rho_1}{\partial t_1} = \frac{\partial \rho_0}{\partial x_i \partial x_i} - \frac{\partial}{\partial x_i} F_i \rho_0 \ . \tag{2.72}$$

We don't need to solve the equation for the construction of the effective equation.

The effective equation:

Expanding the time derivative of the marginal PDF $\rho(x_i, t) = \int p(x_i, v_i, t)\mathrm{d}^3 v$ as

$$\frac{\partial}{\partial t}\rho = \left[\frac{1}{\epsilon}\frac{\partial}{\partial t_0} + \frac{\partial}{\partial t_1} + \epsilon\frac{\partial}{\partial t_2} + \cdots\right][\rho_0 + \epsilon\rho_1 + \cdots] \tag{2.73}$$

and neglecting $\mathcal{O}(\epsilon)$ terms leads to

$$\frac{\partial}{\partial t}\rho = \frac{1}{\epsilon}\frac{\partial}{\partial t_0}\rho_0 + \frac{\partial}{\partial t_0}\rho_1 + \frac{\partial}{\partial t_1}\rho_0 \ . \tag{2.74}$$

Now we collect the previously calculated expressions (2.69) and (2.72) and plug them into the above equation leading to an equation for ρ,

$$\frac{\partial \rho}{\partial t} = \frac{\partial \rho}{\partial x_i \partial x_i} - \frac{\partial}{\partial x_i} F_i \rho \ . \tag{2.75}$$

Reversing back to dimension full quantities leads to the effective equation independent of the velocity degrees of freedom which is the same as the overdamped Fokker-Planck equation:

$$\frac{\partial \rho}{\partial t} = \frac{k_b T}{\gamma} \frac{\partial \rho}{\partial x_i \partial x_i} - \frac{\partial}{\partial x_i} \frac{F_i}{\gamma} \rho \ . \tag{2.76}$$

Of course this is just an example of how the multiple scale method is applied. We did not show any rigorous proof why it is working. For a rigorous mathematical approach to the method of multiple scales for stochastic differential equations respectively partial differential equations see [19].

2.6 Ito and Stratonovich Calculus

Let us revisit the Langevin equation. For simplicity lets consider the one dimensional overdamped Langevin equation:

$$\dot{x} = \frac{f^{ext}}{\gamma} + \sqrt{2D}\xi(t) \ . \tag{2.77}$$

Note we have written the overdamped Langevin equation in a slightly different way. We used the Einstein Smoluchowski relation $b = 2D$. The correlation function of the Gaussian white noise in the above notation is given by $\langle \xi(t_1)\xi(t_2) \rangle = \delta(t_1, t_2)$. Since ξ is a singular object and therefore not definable as a stochastic process it is actually more convenient to write the Langevin equation as:

$$\mathrm{d}x = \frac{f^{ext}}{\gamma} \mathrm{d}t + \sqrt{2D} \mathrm{d}W_x \ . \tag{2.78}$$

Where $\mathrm{d}W_x$ is a Wiener process. A Wiener process is a well defined Markovian stochastic process, such that the stochastic process described by the above equation is well defined as well. Problems arise if D is not a constant but depends on x. Then the product $\sqrt{D(x)}\mathrm{d}W_x$ is no longer defined. The intuition behind this is the following. The Wiener process can be pictured as jumping process with infinitesimal small step size. The question is then where should one evaluate $D(x)$ in order to calculate the product. An additional rule is needed. Ito assigned the rule that the beginning of the step size is used. Stratonovich assigned the rule that one should use the middle of the step size. The need for this extra rule can be made mathematically visible by considering the integral $\int_{t_0}^{t_1} x(t) \cdot \mathrm{d}W_x(t)$. However we will not go any deeper into the formal treatment of these concepts. See [29, 8] for further reading. Using Ito or Stratonovich convention leads to a different Fokker Planck equation. The corresponding Fokker-Planck equation using the Ito convention is given by:

$$\frac{\partial}{\partial t} P = \frac{\partial^2}{\partial x^2} D(x) P - \frac{\partial}{\partial x} \frac{f^{ext}}{\gamma} P \ . \tag{2.79}$$

The corresponding Fokker Planck equation using the Stratonovich convention is given by:

$$\frac{\partial}{\partial t} P = \frac{\partial^2}{\partial x^2} D(x) P - \frac{\partial}{\partial x} \left(\frac{f^{ext}}{\gamma} - \frac{1}{2} D'(x) \right) P \ . \tag{2.80}$$

The difference manifests in an drift term $\frac{1}{2}D'(x)P$. For a generalization to multiple dimensions see [29, 8]. The big advantage of the Stratonovich convention is that rules of regular differential calculus apply, which is not the case for the Ito convention. Later we will use the framework of stochastic thermodynamics. Since it is based on the regular rules of differential calculus we will always use the Stratonovich convention in our calculations. We will denote the Stratonovich product by $\circ$.

Chapter 3

Stochastic Thermodynamics

3.1 Traditional thermodynamics

Before introducing the framework of stochastic thermodynamics we will give a brief summary of the first and second law of traditional thermodynamics. In thermodynamics one distinguishes between a system and its surrounding. The macroscopic properties of the system is what one is interested in. A practical example would be water in a bottle. The water is the system, everything that surrounds the water including the bottle is called the surrounding. An idealized concept is the isolated system. It's a system which can not exchange any form of energy or matter with the surrounding. If we isolate an originally not isolated system it will reach a so called equilibrium state after some time. Once the isolated system reaches this equilibrium state its macroscopic properties will not change anymore and we can describe it with a set of time independent state variables. Most people have an intuition about some of these state variables, like volume, pressure or temperature. However there are state variables which are intuitively hard to grasp like entropy. Generally these state variables are not independent from each other. A very fundamental state variable is the internal energy E. This variable will be our starting point for the introduction of the first law of thermodynamics. Assume we can add energy in the form of mechanical work W_{ad} to an "isolated" system without letting the system interact with its surrounding. So strictly speaking it is no longer an isolated system. Such a system that can exchange energy only in the form of mechanical work is called an adiabatic system. The system will be driven out of equilibrium. After some time we will stop adding energy and it will relax to an equilibrium state again which is generally different from the original equilibrium state. Experiments show that the work W_{ad} needed to go from one equilibrium state to another for an adiabatic system is independent of the type of work and independent of the path. Since the only source of energy is W_{ad} the difference of the internal energy ΔE between the two equilibrium states is

$$\Delta E = W_{ad} \ . \tag{3.1}$$

And for infinitesimal changes we have:

$$\mathrm{d}E = \mathrm{d}W_{ad} \ . \tag{3.2}$$

Since W_{ad} is path independent so is the internal energy. Thus E can be used as a state variable. If we also allow the system to exchange energy with the surrounding we need to modify the law. Some of the energy transfered to the system by doing work is lost to the surrounding. The energy exchanged with the surrounding is called heat and denoted by Q. It is defined by $Q = W_{ad} - W$, which leads to the first law of thermodynamics:

$$\Delta E = Q + W \ . \tag{3.3}$$

In differential form it reads

$$\mathrm{d}E = \mathrm{d}Q + \mathrm{d}W \ . \tag{3.4}$$

It is basically a statement of energy conservation. In contrary to Newtonian mechanics, where energy conservation is a consequence of the underlaying dynamical equations, the first law is a postulate based on empirical observations. We only talked about one state variable, the internal energy, so far. Heat and work are path dependent and therefore not suitable to describe the state of the system. Another important state variable is the entropy S. There are different approaches to justify the necessity of such a state variable. We will focus on the microscopical approach which might be the physically most illuminating one.

Let us start with a simple demonstrative example. We have a one dimensional lattice with N lattice sites. Each lattice site can either be occupied or unoccupied. A microscopic state is then characterized by knowing which lattice site is empty an which is not. If N is very large a vast amount of numbers is needed to describe a micro state, which is not very practical. A better approach is to use fewer macroscopic variables. We define the internal energy of the system as $E_1 = N_{oc}$, the number of occupied lattice sites. The number of microstates Ω_1, called the multiplicity, for a given internal energy is then given by the binomial coefficient

$$\Omega_1 = \binom{N}{E_1} = \frac{N!}{E_1!\,(E_1 - N)!} \tag{3.5}$$

Now we consider another system of the same kind but with internal energy E_2 an bring it into contact with the E_1 system. By contact we mean that they can exchange energy. The total energy $E = E_1 + E_2$ is fixed, but E_1 and E_2 can change. After some time the combined system will reach an equilibrium state, meaning E_1 and E_2 stop changing. The question is then, what are the values of E_1 and E_2 of this equilibrium state? The multiplicity of the total system Ω is given by:

$$\Omega = \Omega_1\Omega_2 = \frac{N!N!}{E_1!E_2!\,(N - E_1)!\,(N - E_2)!} \tag{3.6}$$

$$= \frac{N!N!}{E_1!\,(E - E_1)!\,(N - E_1)!\,(N + E_1 - E)!} \tag{3.7}$$

Figure (3.1) shows a plot of the multiplicity $\Omega(E_1, E, N)$ as a function of E_1 for E =100 and N=10 000. One can see a single peak with a maximum at $E_1 = 50$. We assign a probability to every microstate and assume that in equilibrium all micro states have equal probability. The most probable macro state is then at $E_1 = E_2 = 50$. Upon this observation we will make the following postulate:

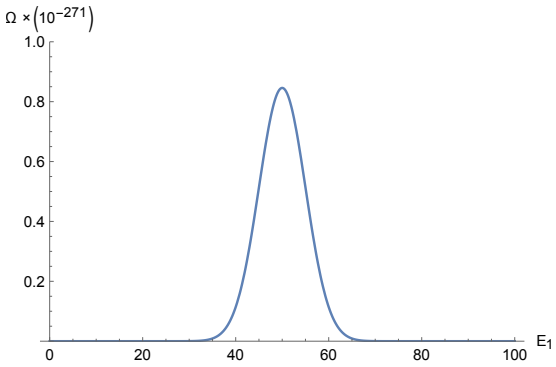

Figure 3.1: Number of microstates as a function of E_1 for E=100, N=10 000,

The system will evolve into a macrostate for which the multiplicity takes on a maximum. This is a way how to state the second law of thermodynamics. We have now discovered another state variable the multiplicity. However In practice the multiplicity is not a very handy quantity. It is better to use the entropy S defined by:

$$S = k_{\mathrm{B}} \ln(\Omega) \ . \tag{3.8}$$

The entropy has the advantages of being smaller and additive We can reformulate the second law in terms of the entropy. A system in equilibrium has maximum entropy. Gibbs generalized the notion of entropy introducing:

$$S_{Gibbs} = -k_{\mathrm{B}} \sum_i P_i \ln P_i \ . \tag{3.9}$$

Where P_i denotes the probability of a microstate. For the case in which P_i is uniformly distributed S_{Gibbs} reduces to S. For continuous states space the Gibbs entropy reads:

$$S_{Gibbs} = -k_{\mathrm{B}} \int p(x) \ln p(x) \mathrm{d}x \ . \tag{3.10}$$

3.2 Stochastic energetics

As discussed in the previous section, the first law of thermodynamics is a statement about energy exchange between a system and its surrounding. It is valid on the macroscopic scale. Stochastic energetics is a similar concept but valid on the mesoscopic scale. In this section we will give a short introduction of this field. We will follow Sekimotos work [25].

We start with the Langevin-Kramers equation. For simplicity we consider a one dimensional system:

$$\begin{aligned} \dot{x}(t) &= v(t) \\ m\dot{v}(t) &= -\gamma v + f(x,\lambda)^{\mathrm{ext}} + \xi(t) \ . \end{aligned}$$

Where λ is a parameter controlled by an external agent. The evolution of this parameter is not determined by the Langevin equation itself. The other quantities are defined as in equation (2.14). In analogy to classical thermodynamics we can identify the Brownian particle as the system and the medium as the surrounding. The first task is to define the heat. Therefore we reshuffle the Langevin equation:

$$m\dot{v}(t) - f^{ext}(x,\lambda) = -\gamma v + \xi(t) \ .$$

The RHS is describing a force acting on the particle due to the collisions of the medium particles. If the action reaction principle holds, as Sekimotos assumes in [25] we can look at the system from the perspective of the medium and say $-(-\gamma\dot{x} + \xi(t))$ is the force acting on the medium due to the motion of the particle. We denote $\mathrm{d}x(t)$ as an infinitesimal increment along the trajectory $x(t)$. Then $(-\gamma\dot{x} + \xi(t)) \circ \mathrm{d}x(t)$ is the work done on the particle by the medium. And $-(-\gamma\dot{x} + \xi(t)) \circ \mathrm{d}x(t)$ is the work done on the medium by the Brownian particle. Due to the action reaction principle changing the perspective results only in a change of the sign. Finally we define heat as the energy transfer from the medium to the particle :

$$\mathrm{d}Q = [-\gamma\dot{x} + \xi(t)] \circ \mathrm{d}x(t) \ . \tag{3.11}$$

We used the Stratonovich convention in order to use the regular rules of differential calculus. We assume that $f^{\mathrm{ext}}(x,\lambda)$ has a potential $f(x,\lambda) = -\frac{\partial U^{\mathrm{ext}}(x,\lambda)}{\partial x}$. Since the underdamped Langevin equation holds we can write the heat as:

$$\mathrm{d}Q = \left[\frac{\partial U(x,\lambda)}{\partial x} + m\dot{v}(t)\right] \circ \mathrm{d}x(t) \ . \tag{3.12}$$

We define the internal energy as :

$$E = \frac{mv^2}{2} + U(x,\lambda) \tag{3.13}$$

The change of the kinetic Energy part along a trajectories is given by :

$$\mathrm{d}\left(\frac{mv^2}{2}\right) = m\dot{v}\mathrm{d}t = m\dot{v}\mathrm{d}x(t) \ . \tag{3.14}$$

Similarly the change of the potential part is given by:

$$\mathrm{d}U = \frac{\partial U}{\partial x}\mathrm{d}x(t) + \frac{\partial U}{\partial \lambda}\mathrm{d}\lambda \ . \tag{3.15}$$

Identifying the work done by the external agent as :

$$\mathrm{d}W = \frac{\partial U}{\partial \lambda}\mathrm{d}\lambda \tag{3.16}$$

We get an energy balance equation similar to the first law in classical thermodynamics:

$$\mathrm{d}E = \mathrm{d}Q + \mathrm{d}W \ . \tag{3.17}$$

However, in contrary to classical thermodynamics we did not postulate the energy balance equation. We derived it from the underlying equations of motion, the Langevin-Kramers equation, and the assumption that the action reaction principle holds.

A similar calculation can be done for the overdamped Langevin equation which leads to the same energy balance equation. The only difference in the calculation is that the inertia term is zero.

3.3 Stochastic thermodynamics

Stochastic energetics succeeded in finding an analogous of the first law on the mesoscopic scale. The natural next step is to find an analogous to the second law on the mesoscopic scale. Pioneering work in this field was done by Seifert, in [24]. The second law in classical thermodynamics is based on the notion of entropy. Thus in order to be able to develop the second law on the mesoscopic scale one first needs to define entropy on the mesoscopic scale . Seifert proposed such a definition. We will closely follow his work.

Due to the dissipated heat Q into the medium the entropy of the medium changes. One identifies the entropy change of the medium along a trajectory as

$$\Delta s[x(t)] := \frac{\Delta Q[x(t)]}{T} \ . \tag{3.18}$$

Furthermore one defines the trajectory dependent entropy of the system as :

$$s_{sys}[x(t)] := -k_{\mathrm{B}} \ln p(x(t), t) \ , \tag{3.19}$$

Where $p(x(t))$ is the solution of the Fokker Planck equation evaluated at the trajectory $x(t)$. Since the system entropy depends on $p(x, t)$ it will depends on the whole ensemble of trajectories. These definitions become meaningful due to the following observations:

The average of $s(t)$ is the usual definition of the Gibbs entropy.

$$S_{Gibbs}(t) = -\int \mathrm{d}x p(x, t) \ln p(x, t) = \langle s_{sys}(t) \rangle \tag{3.20}$$

and the total entropy change

$$\Delta s_{tot} := \Delta s + \Delta s_{sys} \tag{3.21}$$

obeys an integral fluctuation theorem:

$$\left\langle \exp^{-\Delta s_{tot}} \right\rangle = 1 \ , \tag{3.22}$$

form which follows that

$$< \Delta s_{tot} > \geqslant 0 \tag{3.23}$$

This can be seen as the mesoscopic equivalent of the second law of thermodynamics. It should be mentioned that this integral fluctuation theorem is not a proof of the second law of thermodynamics since the Langevin equation is already time irreversible. Stochastic energetics and thermodynamics should be seen as a separate framework.

Chapter 4

Confined Brownian Motion

4.1 Reflective boundary conditions

In this section we will introduce the reflective boundary conditions for the over-damped Fokker-Planck equation. Usually these boundary conditions are introduced by stating that the flux normal to the boundary is zero [8]. Which implies that the number of particles enclosed by the boundary is constant. However we developed a different and more fundamental approach.

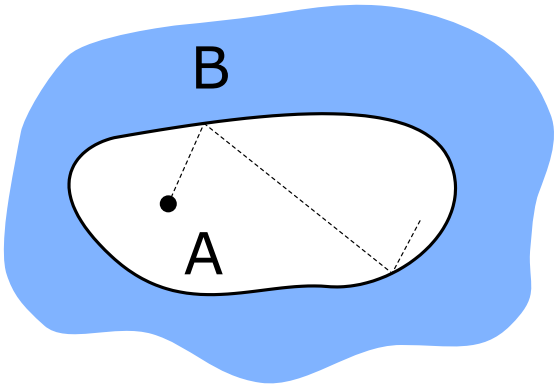

Figure 4.1: Particle enclosed by reflective walls.

We start with a simple Newtonian particle confined in a region A (see figure 4.1). Region A is enclosed by a boundary ∂A. The boundary is assumed to be a hard wall characterized by a reflection law. If the particle hits the wall its velocity component normal to the boundary changes the sign. Mathematically we can express this as follows. If the particle has velocity v_i before the collision, the velocity v_i' after the collision is given by:

$$v_i' = v_i - 2v_j n_j n_i \ , \tag{4.1}$$

where n_j is the normal vector of the boundary. It is easy to show that the collision conserves kinetic energy ${v'}^2 = v^2$. The trajectory can be calculated by using Newtonian equations of motions assuming initial velocity and position .

If the particle hits the wall relation (4.1) is used to get a new initial velocity which is then used to solve the equations of motion and so on.....

Of course we are not really interested in this deterministic classical system. We want to know how this reflection law can be introduced for a particle described by the Langevin Kramers equation. In principle the reflection law should stay the same. However there is one essential problem. The Langevin-Kramers equation is a coarse grained equation, meaning below a certain finite timescale it is not valid anymore. But the collisions with the wall are instantaneous. Therefore it does not make any sense to introduce them for the Langevin-Kramers equation in the same way as we did in (4.1) for the Newtonian particle. We will never be able to calculate the exact collision time using the Langevin equation. However this problem can be bypassed by considering the PDF $p(r_i, v_i, t)$ of the Brownian particles and not a single trajectory. Then we just need to know the implications of the reflection law on $p(r_i, v_i, t)$. In order to figure this out, we will look at the system in a slightly different way. We assume the medium and the Brownian particles are in region A as well as in region B, where region B is just the outside of region A (see Figure 4.1). From this point of view the reflection law can be seen as a condition on the Brownian particles. For every particle going from A to B and having a particular velocity v_i at a particular time and at a particular point on the boundary, there must be one particle going from B to A and having velocity v_i' at the exact same time and on the exact same point. If we just look at the region A without the boundary we can not distinguish whether there are new particles coming in from B or particles are reflected. We can draw the following conclusion: The probability of finding a particle with v_i or v_i' in an infinitesimal small neighborhood of a point on the boundary is the same. Thus we have:

$$p(r_i, v_i, t)_{|\partial A} = p(r_i, v_i', t)_{|\partial A} \ . \tag{4.2}$$

These are the reflective boundary condition for the Kramers equation. It is intuitively clear that this condition preserves the number of particles in A. Let us prove it nevertheless. We want to show that:

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_A \int_{-\infty}^{\infty} p \, \mathrm{d}^n x \, \mathrm{d}^n v = 0 \ , \tag{4.3}$$

where n is the dimension of the space. We can interchange the time derivative with the integrals and use the Fokker Planck equation (2.39) :

$$\int_A \int_{-\infty}^{\infty} \partial_t p \, \mathrm{d}^n x \, \mathrm{d}^n v = \int_A \int_{-\infty}^{\infty} \partial_{x_i} J_{x_i} \, \mathrm{d}^n x \, \mathrm{d}^n v + \int_A \int_{-\infty}^{\infty} \partial_{v_i} J_{v_i} \, \mathrm{d}^n x \, \mathrm{d}^n v \tag{4.4}$$

The second integral on the RHS vanishes due to the natural boundary conditions $\lim_{v_i \to \pm\infty} p = \lim_{v_i \to \pm\infty} \partial_{v_i} p = 0$. We can switch the order of integration of the first integral and apply gauss theorem which gives:

$$\int_{-\infty}^{\infty} \int_{\partial A} p v_i n_i \, \mathrm{d}S \, \mathrm{d}^n v = \int_{\partial A} \int_{-\infty}^{\infty} p v_i n_i \, \mathrm{d}^n v \, \mathrm{d}S \tag{4.5}$$

Now we rename v_i with v_i' and make a variable transformation according to (4.1). The Jacobian determinant $\mathcal{J}(x_i)$ is independent of v_i since the transformation

is linear in v_i. Due to the boundary condition (4.2) , p is unaffected by the transformation. And it follows that

$$\int_{-\infty}^{\infty} v_i p \, \mathrm{d}^n v = -\mathcal{J} \int_{-\infty}^{\infty} v_i p \, \mathrm{d}^n v \ . \tag{4.6}$$

Thus (4.3) holds.

Since later we will only deal with the overdamped Fokker-Planck equation we want to know the overdamped reflective boundary condition. In section 2.5 we already discussed the procedure of deriving the overdamped Fokker-Planck equation starting form the Kramers equation. The procedure was based on a perturbative multiscale method where we expanded p in orders of a small parameter ϵ: $p = p_0 + \epsilon p_1 + \epsilon^2 p_2 + ...$. We used p_0 and p_1 for the construction of the overdamped equation. The derivation basically stays the same except that we have additional boundary condition (4.2). Since p has to obey the boundary condition, p_0 and p_1 have to obey it as well. For p_0 and p_1 we had (see equation (2.67) and (2.70)).

$$p_0 = \rho_0 \omega \tag{4.7}$$

$$p_1 = \rho_1 \omega - \omega v_i \left[\frac{\partial}{\partial x_i} + F_i \right] \rho_0 \ , \tag{4.8}$$

where ω is given by:

$$\omega(v) = \frac{\exp\left(-\frac{v^2}{2}\right)}{(2\pi)^{n/2}} \ . \tag{4.9}$$

Since $v'^2 = v^2$ we have $\omega(v) = \omega(v')$. Thus p_0 obeys the boundary condition everywhere. $p_1(v_i)_{|\partial A} = p_1(v_i')_{|\partial A}$ leads to:

$$\omega v_j n_j n_i \left[\frac{\partial}{\partial x_i} + F_i \right] \rho_{0|\partial A} = 0 \ . \tag{4.10}$$

$v_j n_j$ is generally not zero thus we have:

$$n_i \left[\frac{\partial}{\partial x_i} + F_i \right] \rho_{0|\partial A} = 0 \ , \tag{4.11}$$

reverting back to dimensionfull quantities and neglecting terms of order ϵ ($\rho \approx \rho_0$) we get

$$n_i \underbrace{\left[D \frac{\partial}{\partial x_i} + \frac{F_i}{\gamma} \right]}_{-J_i} \rho_{|\partial A} = 0 \ . \tag{4.12}$$

This is the reflective boundary condition for the overdamped Fokker Planck equation. Note that the expression inside the brackets is just the flux J_i of the overdamped Fokker-Planck equation.

$$\frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial x_i} J_i \ . \tag{4.13}$$

Conclusion:

We have established the reflective boundary conditions for the Kramers equation by using heuristic arguments based on the classical reflection law. Using the perturbative multi-scale method we derived the reflective boundary conditions for the overdamped Fokker-Planck equation. As expected, the overdamped boundary condition states that the flux normal to the boundary vanishes.

4.2 Brownian motion in a two dimensional tube and the Fick-Jacobs approach

In this section we introduce the main model of this thesis. We have noninteract-

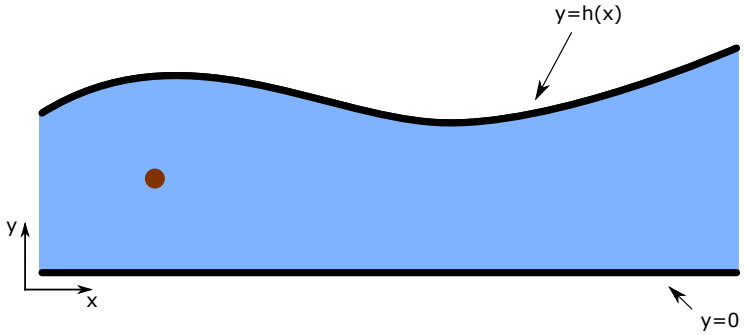

Figure 4.2: Brownian particle (brown) inside a two dimensional channel with upper boundary at $y = h(x)$ and lower boundary at $y = 0$.

ing Brownian particles in a two dimensional channel with reflecting walls. The upper boundary is considered to be at $y = h(x)$. Where $h(x)$ is a continuous function bigger than zero and bounded from above. For simplicity the lower boundary is assumed to be at $y = 0$. For now we do not assume any external deterministic forces. Furthermore we assume the overdamped limit is valid. The dynamics of the system is then described by the following overdamped Fokker-Planck equation and reflecting boundary conditions:

$$\partial_t \rho(x,y,t) = D\big[\partial_x^2 + \partial_y^2\big]\rho(x,y,t) \tag{4.14}$$

$$\begin{aligned} \partial_y \rho(x,y,t)_{|_h} &= h' \partial_x \rho(x,y,t)_{|_h} \\ \partial_y \rho(x,y,t)_{|_0} &= 0 \end{aligned} \tag{4.15}$$

where D is the diffusion coefficient. $'$ denotes a partial derivative with respect to x. Note the reflective boundary conditions as written above can be derived by stating that the flux normal to the walls vanishes.

$$n_i^{\text{up}} J_{i_{|_h}} = 0 \tag{4.16}$$

$$n_i^{\text{low}} J_{i_{|_0}} = 0 \tag{4.17}$$

$$\tag{4.18}$$

where n_i^{up} is the normal vector of the upper and n_i^{lo} of the lower wall given by:

$$n_i^{\text{up}} = \begin{pmatrix} -h' \\ 1 \end{pmatrix} \qquad n_i^{\text{low}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{4.19}$$

and the flux J_i is given by:

$$J_i = -D \begin{pmatrix} \partial_x \rho \\ \partial_y \rho \end{pmatrix} \tag{4.20}$$

For a general $h(x)$ the exact solution of this boundary value problem is not known and might be impossible to find. Thus we need to use other methods to make the physical effects hidden in the above equation qualitatively and quantitatively visible. The Fick-Jacobs approximation is such a method. The core essence of this approach is to create an effective one dimensional equation, known as the Fick-Jacobs equation, by integrating out the y degrees of freedom. In that sense it is similar to the overdamped limit, where we integrated out the velocity degrees of freedom. In what follows we will give a short informal derivation of the Fick-Jacobs equation similar but not the same as presented in [32].

The aim is to create an approximate equation for the marginal PDF $P(x,t) = \int_0^{h(x)} \rho(x,y,t)\mathrm{d}y$. The first step is to integrate equation (4.14) with respect to y from 0 to $h(x)$ which gives :

$$\partial_t P = D \left[\int_0^{h(x)} \partial_x^2 \rho \mathrm{d}y + \partial_y \rho \mid_0^{h(x)} \right] . \tag{4.21}$$

Using the boundary conditions (4.15) we get:

$$\partial_t P(x,t) = D \left[\int_0^{h(x)} \partial_x^2 \rho(x,y,t) \mathrm{d}y + h^{'} \partial_x \rho_{|_h} \right] . \tag{4.22}$$

Using the Leibniz integral rule

$$\partial_x \int_{a(x)}^{b(x)} f(x,y)\mathrm{d}y = \int_{a(x)}^{b(x)} \partial_x f(x,y)\mathrm{d}y + b(x)^{'} f(x,b(x)) - a(x)^{'} f(x,a(x))$$

gives

$$\partial_t P(x,t) = D \left[\partial_x^2 P(x,t) - \partial_x h^{'} \rho(x,h(x),t) \right] . \tag{4.23}$$

(4.23) is almost our desired equation. The problem is that the equation still depends on $\rho(x,h(x),t)$. We need to find a relation between $\rho(x,h(x),t)$ and $P(x,t)$. Here the so called local equilibrium approximation is coming into play. It is based on the assumption that during the time the system reaches equilibrium in y direction almost nothing is happening in x direction. We will go into detail under which conditions this assumption is valid in the next section. If it is valid we can make an approximation and say that the system is instantaneously in equilibrium in y direction and therefore uniformly distributed along the y axis. Thus we can write ρ as:

$$\rho(x,y,t) \approx P_{eq}(y \mid x) P(x,t) = \frac{P(x,t)}{h(x)} . \tag{4.24}$$

Where $P_{eq}(y \mid x)$ is the local equilibrium distribution. Plugging this relation into (4.23) we arrive at the Fick-Jacobs equation.

$$\partial_t P(x,t) = D\left[\partial_x^2 P(x,t) - \partial_x \frac{h'}{h} P(x,t)\right] \ . \tag{4.25}$$

Not only is this equation easier to solve we have also gained qualitative insight. We can see an additional drift term. The force $F_{\mathrm{FJ}} = k_{\mathrm{B}}T\frac{h'}{h}$ is clearly an effect of the confinement. Let us try to understand this force a bit better. It is positive/negative if the slope of $h(x)$ is positive/negative. The force is smaller if the width of the channel is bigger. This means that there is a tendency for the particles to go where there is more space available (see figure 4.3).

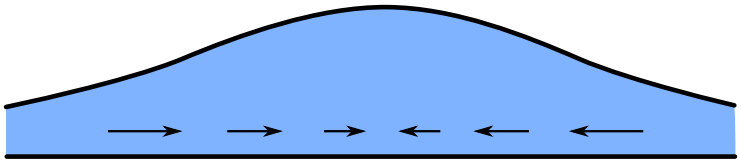

Figure 4.3: Schematical picture of F_{FJ}(black arrows).

This is not surprising if we look at the origin of the force. Although it can be interpreted as a deterministic force in the effective picture its nature is entropic. To make that clear we look at the free energy functional. It is a functional who has a minimum at the stationary distribution [23]. Thus solving the overdamped Fokker-Planck equation for the stationary solution is equivalent in finding a minimum of the free energy functional. For a general overdamped Fokker-Planck equation confined by hard reflective walls it is given by:

$$G[\rho(\vec{r},t)] = \int \mathrm{d}\vec{r}\,[k_{\mathrm{B}}T\rho(\vec{r},t)\ln\rho(\vec{r},t) + U(\vec{r})\rho(\vec{r},t)] \ . \tag{4.26}$$

The expression inside the integral is a density, the free energy density. The first term is the entropic term it is basically the Gibbs entropy times temperature. And the second term is coming from the deterministic external force, where $U(\vec{r})$ is a potential. Since there are no external forces present in our model the functional reduces to

$$G[\rho(x,y,t)] = k_{\mathrm{B}}T\int_{-\infty}^{\infty}\int_{0}^{h}\mathrm{d}x\mathrm{d}y\rho(x,y,t)\ln\rho(x,y,t) \ . \tag{4.27}$$

Using the local equilibrium approximation we get:

$$G[P(x,t)] = k_{\mathrm{B}}T\int_{-\infty}^{\infty}\int_{0}^{h}\mathrm{d}x\mathrm{d}y\frac{P(x,t)}{h(x)}\ln P(x,t) \tag{4.28}$$

$$-k_{\mathrm{B}}T\int_{-\infty}^{\infty}\int_{0}^{h(x)}\mathrm{d}x\mathrm{d}y\frac{P(x,t)}{h(x)}\ln h(x) \tag{4.29}$$

Performing the y integration we get:

$$G[P(x,t)] = k_{\mathrm{B}}T\int_{-\infty}^{\infty}\mathrm{d}x P(x,t)\ln P(x,t) \tag{4.30}$$

$$-k_b T\int_{-\infty}^{\infty}\mathrm{d}x P(x,t)\ln h(x) \tag{4.31}$$

The free energy density is then given by:

$$g(x,t) = T \underbrace{k_{\mathrm{B}} P(x,t) \ln P(x,t)}_{s_{1\mathrm{d}}} - P(x,t) \underbrace{k_{\mathrm{B}} T \ln h}_{U_{\mathrm{FJ}}} \tag{4.32}$$

Where U_{FJ} is the potential of F_{FJ} and $s_{1\mathrm{d}}$ is the entropy density of the effective one dimensional system. One can conclude that U_{FJ} is arising from the entropy density of the original two dimensional system. This makes the entropic origin of F_{FJ} visible.

As mentioned in the introduction, people tried to improve the Fick-Jacobs approximation by either calculating corrections or extending the equation to additional deterministic forces. The latter is what we do as well but in the next section.

4.3 Derivation of a general Fick-Jacobs equation

In the previous section we derived the Fick-Jacobs equation for particles freely diffusing in a 2d tube. But what if we consider an additional deterministic force $\vec{F}(x,y)$. Can we use a similar approach and derive an effective one dimensional equation? The short answer is, yes we can. But we need a more elaborate method. Due to the time scale separation between diffusive process in x and y direction the method of multiple scales seems to be a natural candidate.

As in the previous section we start with the Fokker-Planck equation and its no-flux boundary conditions, which are given by:

$$\partial_t \rho = D\big[\partial_x^2 + \partial_y^2\big]\rho - \frac{1}{\gamma}\big[\partial_x F_x + \partial_y F_y\big]\rho$$

$$\begin{aligned} \big[D\partial_y - \frac{F_y}{\gamma}\big]\rho_{|_h} &= h'\big[D\partial_x - \frac{F_x}{\gamma}\big]\rho_{|_h} \\ \big[D\partial_y - \frac{F_y}{\gamma}\big]\rho_{|_0} &= 0 \end{aligned} \tag{4.33}$$

$F_x(x,y)$ is a force in x and $F_y(x,y)$ a force in y direction. All other quantities are labeled as in the previous section. Note the reflective boundary conditions as written above can be derived in the same manner as we discussed in the previous section except that now the flux J_i is given by:

$$J_i = -\begin{pmatrix} D\partial_x - F_x/\gamma \\ D\partial_y - F_y/\gamma \end{pmatrix} \rho \ . \tag{4.34}$$

In order to apply the method of multiple scales we need to treat the local equilibrium approximation with more care. The crucial part is to figure out the relevant length and time scales of the system.

Let us blend out the drift term for a moment. We can identify two relevant length scales L_y and L_x due to the channel like geometry of $h(x)$. L_y is related to the width of the channel. L_x is related to the scale on which $h(x)$ varies significantly e.g. the periodic length of a channel. We require $\epsilon = \frac{L_y}{L_x} << 1$, meaning $h(x)$ is approximately constant on the scale L_y. These two different

spatial scales imply a time scale separation of the diffusive process in x and y direction. The characteristic timescale for the diffusion process on the scale L_y is $\tau_y = \frac{L_y^2}{D}$ and $\tau_x = \frac{L_x^2}{D}$ on the scale L_x . We have $\frac{\tau_y}{\tau_x} = \epsilon^2$. which corresponds to the local equilibrium assumption. For small ϵ the equilibrium in y direction will be reached much faster then in x direction. It essentially means that at timescales τ_y the channel looks straight for the particles in the sense that they do not spread enough to see variations in $h(x)$.

Upon these observations/assumptions we can draw the following qualitative picture. We stretch the x axis by scaling $x \to L_x x$ and shrink the y axis by scaling $y \to L_y y$. Then for timescales τ_y we see a diffusion process in y direction and almost no dynamics in x direction . For timescales τ_x we see a diffusion process in x direction however in y direction we already reached equilibrium long time ago.

Let us also consider the drift now. The force in x direction F_x gives the particle an additional velocity $v_x = \frac{F_x}{\gamma}$. In order to not violate the local equilibrium assumption we need to require $\frac{F_x}{\gamma}\tau_y = \mathcal{O}(L_y)$. This means that the displacement of the particles during the time τ_y resulting from the force in x direction must be of $\mathcal{O}(L_y)$, so that the particles still do not see the variations of the channel at the timescale τ_y. It follows that $F_x = \mathcal{O}(\frac{k_B T}{L_y})$. The timescale for which the effect of v_x becomes relevant on the length scale L_x is $\tau_{v_x} = \frac{L_x L_y}{D}$, which follows from considering $\frac{k_B T}{L_y}\frac{1}{\gamma}\tau_{v_x} = L_x$. It's natural to consider F_x and F_y being of the same order, $F_y = \mathcal{O}(\frac{k_B T}{L_y})$. Then the timescale for which $v_y = \frac{F_y}{\gamma}$ becomes relevant on the scale L_y is $\tau_{v_y} = \tau_y = \frac{L_y^2}{D}$.

We can complete the qualitative picture from before. Again we stretch the x axis and shrink the y axis as before. At the timescale τ_y there is a drift and an diffusive process in y direction and almost no motion in x direction. At timescales τ_{v_y} there is a drift in x direction in y direction the system is already in equilibrium. At timescales τ_x the diffusive process in x direction becomes relevant.

We have determined all relevant time and length scales. The next step of the method of multiple scales is to introduce new time variables according to the relevant time scales.

$$t_0 = \frac{t}{\tau_y}, \qquad t_1 = \frac{t}{\tau_{v_x}}, \qquad t_2 = \frac{t}{\tau_x}, \tag{4.35}$$

where t_0 is a fast, t_1 an intermediate and t_2 a slow time. $\rho(x, y, t_1, t_2, t_3)$ is now assumed to depend on these times independently. Using the chain rule the time derivative reads:

$$\partial_t = \frac{D}{L_x^2}\partial_{t_2} + \frac{D}{L_x L_y}\partial_{t_1} + \frac{D}{L_y^2}\partial_{t_0} \ .$$

Furthermore we scale the Diffusion equation and its boundary conditions as

follows:

$$y \to L_y y, \quad x \to L_x x, \quad h \to L_y h$$
$$F_x \to \frac{k_\mathrm{B}T}{L_y} F_x, \quad F_y \to \frac{k_\mathrm{B}T}{L_y} F_y$$

Using $\epsilon = \frac{L_y}{L_x}$ the dimensionless Fokker-Plank equation and boundary conditions reads :

$$\left[\partial_{t_2} + \frac{1}{\epsilon}\partial_{t_1} + \frac{1}{\epsilon^2}\partial_{t_0}\right] \rho = \frac{1}{\epsilon^2}\left[\partial_y^2 - \partial_y F_y\right] \rho - \frac{1}{\epsilon}\partial_x F_x \rho + \partial_x^2 \rho$$

$$\frac{1}{\epsilon^2}\left[\partial_y - F_y\right] \rho_{|_h} = h^{'} \left[\partial_x - \frac{1}{\epsilon} F_x\right] \rho_{|_h} \tag{4.36}$$
$$\left[\partial_y - F_y\right] \rho_{|_0} = 0 \ . \tag{4.37}$$

Expanding ρ in orders of ϵ

$$\rho = \rho_0 + \epsilon\rho_1 + \epsilon^2\rho_2 + \cdots \tag{4.38}$$

and comparing orders of ϵ leads to a set of hierarchic equations. For the Fokker Planck equation we get:

$$\mathcal{O}\left(\epsilon^{-2}\right): \quad \left[\partial_y^2 - \partial_y F_y\right] \rho_0 = \partial_{t_0} \rho_0 \tag{4.39}$$

$$\mathcal{O}\left(\epsilon^{-1}\right): \quad \left[\partial_y^2 - \partial_y F_y\right] \rho_1 = \left[\partial_{t_1} + \partial_x F_x\right] \rho_0 + \partial_{t_0} \rho_1 \tag{4.40}$$

$$\mathcal{O}\left(\epsilon^{0}\right): \quad \left[\partial_y^2 - \partial_y F_y\right] \rho_2 = \left[\partial_{t_2} - \partial_x^2\right] \rho_0 + \left[\partial_{t_1} + \partial_x F_x\right] \rho_1 + \partial_{t_0} \rho_2 \tag{4.41}$$

For the boundary condition at $y = h$ we get:

$$\mathcal{O}\left(\epsilon^{-2}\right): \quad \left[\partial_y - F_y\right] \rho_0 = 0 \tag{4.42}$$

$$\mathcal{O}\left(\epsilon^{-1}\right): \quad \left[\partial_y - F_y\right] \rho_1 = -h^{'} F_x \rho_0 \tag{4.43}$$

$$\mathcal{O}\left(\epsilon^{0}\right): \quad \left[\partial_y - F_y\right] \rho_2 = -h^{'} F_x \rho_1 + h^{'} \partial_x \rho_0 \tag{4.44}$$

The boundary condition at y=0 is independent of ϵ, therefore we simply have

$$\left[\partial_y - F_y\right] \rho_n = 0 \qquad n \in \mathcal{N} \tag{4.45}$$

at any order. With the help of the first three equations we will construct the one dimensional effective equation. We will go step by step through the equations.

The $\mathcal{O}\left(\epsilon^{-2}\right)$ equation:

The $\mathcal{O}\left(\epsilon^{-2}\right)$ equation depends on x only in a parametric way such that we can interpret it as a one dimensional equation. There is no dynamics in x direction. In fact it describes a one dimensional Brownian motion confined by reflective "point" walls at $y = 0$ and $y = h$. This precisely coincides with the qualitative picture drawn earlier. We are interested in the long time behavior $\tau >> \mathcal{O}\left(\tau_{v_x}\right)$ of the system, therefore we solve for the stationary solution. The stationary solution of the equation subjected to the boundary conditions is given by:

$$\rho_0 = \frac{\chi(x,y)P_0(x,t_1,t_2)}{n(x)} \ , \tag{4.46}$$

where P_0 is the zeroth order marginal distribution

$$P_0(x,t_1,t_2) = \int_0^h \rho_0 \mathrm{d}y \ . \tag{4.47}$$

χ is given by:

$$\chi(x,y) = \exp\big[\int_0^y F_y(x,u)du\big] \tag{4.48}$$

and n is a normalization factor

$$n(x) = \int_0^h \chi(x,y)dy \ . \tag{4.49}$$

The $\mathcal{O}\left(\epsilon^{-1}\right)$ equation:

The LHS of the equation still describes the same one dimensional system as before. The first term on the RHS can be interpreted as a source term depending on ρ_0 which is mimicking the effect of F_x. As before we are interested in the long time behavior thus $\partial_{t_0}\rho_1 = 0$. Before solving the equation we will do something different. We integrate it with respect to y from 0 to h. Using the Leibniz integration rule and the boundary conditions leads to the following equation for P_0:

$$\partial_{t_1}P_0 = -\partial_x \int_0^h \frac{F_x\chi}{n}\mathrm{d}yP_0 = -\partial_x\overline{F}_xP_0 \ . \tag{4.50}$$

Where $\overline{F}_x(x) = \int_0^h \frac{F_x\chi}{n}\mathrm{d}y$ is the force F_x averaged over the channel width. As we will see later this is one contribution of the effective equation. This equation again supports our qualitative picture from before that at timescales τ_{v_x} the deterministic force F_x is relevant but not the diffusive process in x direction.

Now we solve the $\mathcal{O}\left(\epsilon^{-1}\right)$ equation. Inserting (4.46) and equation (4.50) into the $\mathcal{O}\left(\epsilon^{-1}\right)$ equation gives:

$$\big[\partial_y^2 - \partial_y F_y\big]\rho_1 = -\frac{\chi}{n}\partial_x \overline{F}_x P_0 + \partial_x \frac{\chi F_x}{n} P_0 \tag{4.51}$$

Integrating the above equation with respect to y gives:

$$\begin{aligned}\big[\partial_y - F_y\big]\rho_1 = \int_0^y \big[-\frac{\chi(x,u)}{n(x)}\partial_x \overline{F}_x(x) P_0(x) + \partial_x \frac{\chi(x,u)F_x(x,u)}{n(x)} P_0(x)\big]\mathrm{d}u \\ -\big[\partial_y - F_y\big]\rho_{1|_0}\ .\end{aligned} \tag{4.52}$$

Due to the boundary condition at $y = 0$ the boundary term on the RHS has to vanish. It is easy to show that the boundary condition at $y = h$ is fulfilled. It is advantageous to rewrite the above equation as follows:

$$\begin{aligned}\left[\partial_y - F_y\right]\rho_1 = &\int_0^y \big[\frac{\chi(x,u)}{n(x)}(F_x(x,u) - \overline{F}_x(x))' + \left(\frac{\chi(x,u)}{n(x)}\right)' F_x(x,u)\big]\mathrm{d}u\ P_0 \\ &+ \int_0^y \frac{\chi(x,u)}{n(x)}\left(F_x(x,u) - \overline{F}_x(x)\right)\mathrm{d}u\ \partial_x P_0\ .\end{aligned} \tag{4.53}$$

Due to the frequent appearance of the expression $F_x(x,y) - \overline{F_x}$, which is just the deviation from the averaged force $\overline{F}_x$, we introduce the abbreviate notation $\Delta F_x = F_x(x,y) - \overline{F_x}$.

Solving equation (4.53) gives:

$$\begin{aligned}\rho_1 = &\left[\chi(x,y)\int_0^y \frac{\int_0^v \big[\frac{\chi(x,u)}{n(x)}\Delta F_x'(x,u) + \left(\frac{\chi(x,u)}{n(x)}\right)' F_x(x,u)\big]\mathrm{d}u}{\chi(x,v)}\mathrm{d}v\right] P_0 \\ &+\left[\chi(x,y)\int_0^y \frac{\int_0^v \frac{\chi(x,u)}{n(x)}\Delta F_x(x,u)\mathrm{d}u}{\chi(x,v)}\mathrm{d}y\right]\partial_x P_0 + \chi(x,y)\ \rho_1(x,0)\ .\end{aligned} \tag{4.54}$$

The boundary term can be determined by using the normalization condition $\int_0^h \rho_1 dy = P_1$. This leads to the desired solution:

$$\begin{aligned}\rho_1 = &\left[\chi(x,y)\int_0^y \frac{\int_0^v \big[\frac{\chi(x,u)}{n(x)}\Delta F_x'(x,u) + \left(\frac{\chi(x,u)}{n(x)}\right)' F_x(x,u)\big]\mathrm{d}u}{\chi(x,v)}\mathrm{d}v\right] P_0 \\ &-\left[\frac{\chi(x,y)}{n(x)}\int_0^h \chi(x,y)\int_0^y \frac{\int_0^v \big[\frac{\chi(x,u)}{n(x)}\Delta F_x'(x,u) + \left(\frac{\chi(x,u)}{n(x)}\right)' F_x(x,u)\big]\mathrm{d}u}{\chi(x,v)}\mathrm{d}v\mathrm{d}y\right] P_0 \\ &+\left[\chi(x,y)\int_0^y \frac{\int_0^v \frac{\chi(x,u)}{n(x)}\Delta F_x(x,u)\mathrm{d}u}{\chi(x,v)}\mathrm{d}y\right]\partial_x P_0 \\ &-\left[\frac{\chi(x,y)}{n(x)}\int_0^h \chi(y)\int_0^y \frac{\int_0^{x,v} \frac{\chi(x,u)}{n(x)}\Delta F_x(x,u)\mathrm{d}u}{\chi(x,v)}\mathrm{d}v\mathrm{d}y\right]\partial_x P_0 + \frac{\chi(x,y)}{n(x)}P_1\ .\end{aligned} \tag{4.55}$$

The $\mathcal{O}\left(\epsilon^0\right)$ equation:

The first term on the RHS of the $\mathcal{O}\left(\epsilon^0\right)$ is a source term describing the diffusion in x direction. Thus, as previously discussed, at timescales $\mathcal{O}(\tau_x)$ the diffusion process in x direction becomes relevant. We do not need to solve this equation for the construction of the effective equation. We will integrate it with respect to y from 0 to h. Using the Leibniz integration rule and the boundary conditions we find:

$$\partial_{t_2} P_0 + \partial_{t_1} \int_0^h \rho_1 \mathrm{d}y = -\partial_x \int_0^h F_x \rho_1 \mathrm{d}y + \partial_x^2 P_0 - \partial_x \frac{h' \chi_{|_h}}{n} P_0 \tag{4.56}$$

Inserting the previously calculated expression for ρ_1 we get an equation which will be the second contribution to the effective equation. It's suitable to split the first term of the RHS into an diffusion and drift term.

$$\partial_{t_2} P_0 + \partial_{t_1} P_1 = \partial_x \left[1 + \kappa_{\text{tay}}\right] \partial_x P_0 - \partial_x \left[\frac{h^{'} \chi(x,h)}{n} + F_{\text{tay}}\right] P_0 + \partial_x \overline{F}_x P_1 \tag{4.57}$$

Where F_{tay} and κ_{tay} is given by:

$$\kappa_{\text{tay}} = -\int_0^h \Delta F_x(x,y)\chi(x,y) \int_0^y \frac{\int_0^v \frac{\chi(x,u)}{n(x)} \Delta F_x(x,u) \mathrm{d}u}{\chi(x,v)} \mathrm{d}v \mathrm{d}y$$

$$F_{\text{tay}} = \int_0^h \Delta F_x(x,y)\chi(x,y) \int_0^y \frac{\int_0^v \left[\frac{\chi(x,u)}{n(x)} \Delta F_x'(x,u) + \left(\frac{\chi(x,u)}{n(x)}\right)' F_x(x,u)\right] \mathrm{d}u}{\chi(x,v)} \mathrm{d}v \mathrm{d}y$$

Performing a partial integration these expressions can be brought in a more convenient form:

$$\kappa_{\text{tay}} = \int_0^h \frac{\chi(x,y)}{n(x)} \left[\int_0^y \frac{\chi(x,s)}{\chi(x,y)} \Delta F_x(x,s) \mathrm{d}s\right]^2 \mathrm{d}y \tag{4.58}$$

$$\begin{aligned} F_{\text{tay}} = &\int_0^h \frac{\chi(x,y)}{n(x)} \left[\int_0^y \frac{\chi(x,s)}{\chi(x,y)} \Delta F_x'(x,s) \mathrm{d}s\right] \left[\int_0^y \frac{\chi(x,s)}{\chi(x,y)} \Delta F_x(x,s) \mathrm{d}s\right] \mathrm{d}y \\ &+ \int_0^h \frac{\chi(x,y)}{n(x)} \left[\int_0^y \frac{\chi(x,s)'}{\chi(x,y)} F_x(s) \mathrm{d}s\right] \left[\int_0^y \frac{\chi(x,s)}{\chi(x,y)} \Delta F_x(x,s) \mathrm{d}s\right] \mathrm{d}y \\ &- \int_0^h \frac{\chi(x,y)}{n(x)} \left[\int_0^y \frac{\chi(x,s)}{\chi(x,y)} \frac{n'(x)}{n(x)} F_x(x,s) \mathrm{d}s\right] \left[\int_0^y \frac{\chi(x,s)}{\chi(x,y)} \Delta F_x(x,s) \mathrm{d}s\right] \mathrm{d}y \end{aligned} \tag{4.59}$$

The effective equation:

From equations (4.50) and (4.57) we are able to construct an effective 1d equation valid up to order ϵ^0. Meaning we do not take terms of order ϵ into account. First we expand $P \approx P_0 + \epsilon P_1$. Writing the time derivative of the marginal PDF $P(x,t)$ as

$$\tau_x \partial_t P(x,t) = \left[\partial_{t_2} + \frac{1}{\epsilon}\partial_{t_1} + \frac{1}{\epsilon^2}\partial_{t_0}\right] P(x,t_1,t_2) \ , \tag{4.60}$$

expanding P in orders of ϵ and neglecting terms of order ϵ and higher gives

$$\tau_x \partial_t P = \partial_{t_2} P_0 + \partial_{t_1} P_1 + \frac{1}{\epsilon}\partial_{t_1} P_0 \ . \tag{4.61}$$

Collecting the contributions (4.50) and (4.57) leads to :

$$\tau_x \partial_t P = \partial_x \left[1 + \kappa_{\text{tay}}\right] \partial_x P_0 - \partial_x \left[\frac{h'\chi(x,h)}{n} + F_{\text{tay}}\right] P_0 + \frac{1}{\epsilon}\partial_x \overline{F}_x \left[P_0 + \epsilon P_1\right] \ . \tag{4.62}$$

Using the ϵ expansion of P we get:

$$\tau_x \partial_t P = \partial_x \left[1 + \kappa_{\text{tay}}\right] \partial_x P - \partial_x \left[\frac{h'\chi(x,h)}{n} + F_{\text{tay}}\right] P + \frac{1}{\epsilon}\partial_x \overline{F}_x P \ . \tag{4.63}$$

Scaling back to dimensionfull quantities we finally arrive at the effective equation:

$$\partial_t P = \partial_x D \left[1 + \kappa_{\text{tay}}\right] \partial_x P - \partial_x \frac{1}{\gamma} \left[F_{\text{FJG}} + F_{\text{tay}} + \overline{F}_x\right] P \tag{4.64}$$

Where:

$$\kappa_{tay} = \frac{1}{(k_{\text{B}}T)^2} \int_0^h \frac{\chi(x,y)}{n(x)} \left[\int_0^y \frac{\chi(x,s)}{\chi(x,y)} \Delta F_x(x,s) \mathrm{d}s\right]^2 \mathrm{d}y \tag{4.65}$$

$$F_{\text{FJG}} = \frac{k_{\text{B}}T h'\chi(x,h)}{n(x)} \tag{4.66}$$

$$\begin{aligned}
F_{tay} = {} & \frac{1}{k_{\text{B}}T} \int_0^h \frac{\chi(x,y)}{n(x)} \left[\int_0^y \frac{\chi(x,s)}{\chi(x,y)} \Delta F'_x(x,s) \mathrm{d}s\right] \left[\int_0^y \frac{\chi(x,s)}{\chi(x,y)} \Delta F_x(x,s) \mathrm{d}s\right] \mathrm{d}y \\
& + \frac{1}{k_{\text{B}}T} \int_0^h \frac{\chi(x,y)}{n(x)} \left[\int_0^y \frac{\chi'(x,s)}{\chi(x,y)} F_x(x,s) \mathrm{d}s\right] \left[\int_0^y \frac{\chi(x,s)}{\chi(x,y)} \Delta F_x(x,s) \mathrm{d}s\right] \mathrm{d}y \\
& - \frac{1}{k_{\text{B}}T} \frac{\int_0^h \chi'(x,y) \mathrm{d}y}{n(x)} \int_0^h \frac{\chi(x,y)}{n(x)} \left[\int_0^y \frac{\chi(x,s)}{\chi(x,y)} F_x(x,s) \mathrm{d}s\right] \left[\int_0^y \frac{\chi(x,s)}{\chi(x,y)} \Delta F_x(x,s) \mathrm{d}s\right] \mathrm{d}y \\
& - \frac{1}{k_{\text{B}}T} \frac{h' \chi_{|h}}{n} \int_0^h \frac{\chi(x,y)}{n} \left[\int_0^y \frac{\chi(x,s)}{\chi(x,y)} F_x(x,s) \mathrm{d}s\right] \left[\int_0^y \frac{\chi(x,s)}{\chi(x,y)} \Delta F_x(x,s) \mathrm{d}s\right] \mathrm{d}y
\end{aligned} \tag{4.67}$$

and

$$\chi = \exp\left[\int_0^y \frac{F_y(x,s)}{k_{\mathrm{B}}T}\mathrm{d}s\right] \tag{4.68}$$

$$n = \int_0^h \chi(x,y)\mathrm{d}y \tag{4.69}$$

$$\overline{F}_x = \int_0^h \frac{\chi(x,y)}{n(x)}F_x(x,y)\mathrm{d}y \tag{4.70}$$

$$\Delta F_x(x,y) = F_x(x,y) - \overline{F}_x(x)\ . \tag{4.71}$$

Conclusion and Discussion:

The effective equation (4.64) is a generalized version of the Fick-Jacobs equation. It is valid for times larger than τ_{v_x} for forces of $\mathcal{O}(\frac{k_bT}{L_x})$ and of course for $\epsilon << 1$.
Let us look at some special cases of our generalized F-J equation.

For $F_x = F_y = 0$ it is easy to see that $\kappa_{\mathrm{tay}} = F_{\mathrm{tay}} = \overline{F}_x = 0$, $\chi = 1$ and $n(x) = h(x)$. Thus we have

$$F_{\mathrm{FJG}} = F_{\mathrm{FJ}} = \frac{k_{\mathrm{B}}Th'}{h}\ . \tag{4.72}$$

And our generalized F-J equation reduces to the simple F-J equation derived in the previous section (see equation (4.25)). The F_{FJG} term can be seen as generalization of the F_{FJ} to non uniform local equilibrium distributions.

For the case where $F_y = 0$ and $F_x = F_x(x)$ one can show that $\overline{F}_x = F_x$ thus $\Delta F_x = 0$ from which follows that $\kappa_{\mathrm{tay}} = F_{\mathrm{tay}} = 0$ and the generalized F-J equation reduces to

$$\partial_t P = D\partial_x^2 P - \partial_x \frac{1}{\gamma}\left[F_{\mathrm{FJ}} + F_x\right]P\ . \tag{4.73}$$

Which coincides with the equation P.Kalinay derived in [11].

For the case where $F_x = 0$ and $F_y = F = const$ we have $\kappa_{\mathrm{tay}} = F_{\mathrm{tay}} = \overline{F}_x = 0$. Furthermore one can show that

$$F_{\mathrm{FJG}} = \frac{Fh'}{1 - e^{-\frac{Fh}{k_{\mathrm{B}}T}}}\ , \tag{4.74}$$

and our generalized F-J equation reduces to:

$$\partial_t P = D\partial_x^2 P - \frac{F}{\gamma}\partial_x \frac{h'}{1 - e^{-\frac{Fh}{k_{\mathrm{B}}T}}}P\ . \tag{4.75}$$

As mentioned in the introduction D.Reguera and J.M. Rubi derived a Fick-Jacobs equation for this special case however they considered a symmetric channel [21]. Our model is a bit simpler since the lower boundary is at $y = 0$ and not at $y = -h(x)$. It is straightforward to apply their derivation to our model the resulting equation coincides with equation (4.75).

The F-J equation which resembles our generalized F-J equation the most is probably the one derived by Martens et al. in [17, 14, 15]. They considered space dependent external forces as well, however their channel is three dimensional with constant height in z direction and periodic walls at $y = h(x)$ and $y = -h(x)$. Despite those differences we claim their equation should contain similar terms than ours, however there is no analogous term to the κ_{tay} and F_{tay} term in their equation. The reason for that is most likely due to their different perturbative approach. They start from the stationary overdamped Fokker-Planck equation with reflecting boundary conditions use a standard perturbative method with an expansion parameter similar to ours but a different scaling approach for the external force. They do not use the method of multiple scales which would not make sense anyways since they start from a stationary equation.

Since the κ_{tay} and F_{tay} terms are the new terms we will try to give them a physical interpretation.

We start with the κ_{tay} term. In contrast to the other terms this is a diffusive term. κ_{tay} is an effective space dependent diffusion coefficient. It is easier to understand the effect if we imaginary switch of the diffusion process in x direction. Let us consider one particle. It will have an average velocity $\frac{\overline{F}_x}{\gamma}$ and diffuse in y direction. The average velocity alone is a poor description. Due to the diffusive/random motion of the particle in y direction and the y dependence of $F_x(x, y)$ it will randomly change the velocity in x direction. Sometimes it has a velocity bigger than $\frac{\overline{F}_x}{\gamma}$ and sometimes smaller than $\frac{\overline{F}_x}{\gamma}$. If we give the particle enough time to discover the space in y direction it will effectively look like an random force in x direction is acting on it. Or in other words the local equilibrium distribution gets torn apart by the y dependent force in x direction. That is what κ_{tay} describes. Terms containing the deviation from the average force ΔF_x are typical for this effect (see figure 4.4 for a visualization of ΔF_x).

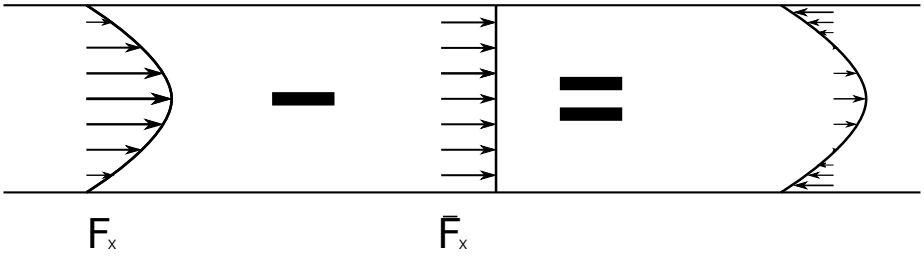

Figure 4.4: Schematical visualization of ΔF_x.

This effect is not that new. It is known as Taylor dispersion [13, 27]. However to the best of our knowledge other people did not consider x and y dependent forces in x direction as well as x and y dependent forces y direction in combi-

nation with a curvy channel.

The F_{tay} term is less understood. F_{tay} contains ΔF_x as well. Thus there must be a connection with κ_{tay}. At first sight one would assume that $F_{tay} \sim \partial_x \kappa_{\text{tay}}$ and that F_{tay} is a Stratonovich drift, however this can be disproved by considering a special case of the external force. Another thing we can see is that $F_{tay} = 0$ if it is independent of x. The first term of F_{tay} in 4.67 is zero if F_x is independent of x. The second and the third if F_y is independent of x. And the fourth one if h is independent of x. The only vague interpretation we have is the following. Due to the x dependence of h, F_x and F_y the Taylor dispersion effect changes with x as well which leads to an asymmetric diffusion process which in return leads to a Drift term.

Chapter 5

Comparison with numerical simulations

In this chapter we will numerically verify the general Fick-Jacobs equation by Brownian dynamics simulations.

5.1 Brownian dynamics simulations in a 2d tube

In this section we will explain how to simulate trajectories from Langevin equations in the presence of a hard wall. Let's start with the one dimensional overdamped Langevin equation.

$$\dot{x} = \frac{f(x)}{\gamma} + \sqrt{2D}\xi(t) \ . \tag{5.1}$$

Integration leads to:

$$x(t+\Delta t) = x(t) + \frac{1}{\gamma}\int_t^{t+\Delta t} \mathrm{d}t_1 f(x(t_1)) + \sqrt{2D}\int_t^{t+\Delta t} \mathrm{d}t_1 \xi(t_1) \ . \tag{5.2}$$

For a sufficiently small Δt we can approximate the second term on the RHS by:

$$\int_t^{t+\Delta t} \mathrm{d}t_1 f(x(t_1)) \approx f(x(t))\Delta t \ , \tag{5.3}$$

meaning $f(x(t))$ stays approximately constant during the time interval Δt. This approximation does not work for the random force term, since $\xi(t)$ is varying drastically even for arbitrary small Δt. But we know the PDF of $\Delta W = \int_t^{t+\Delta t} \mathrm{d}t_1 \xi(t_1)$. It is a Wiener process. Thus we can just draw a random number from

$$p(\Delta W, \Delta t) = \frac{1}{\sqrt{2\pi\Delta t}} \exp\left[-\frac{\Delta W^2}{2\Delta t}\right] \ . \tag{5.4}$$

More conveniently we can write:

$$x(t+\Delta t) = x(t) + \frac{1}{\gamma} f(x(t))\Delta t + \sqrt{2D}\mathcal{N}(0,1)\sqrt{\Delta t} \ , \tag{5.5}$$

where $\mathcal{N}(0,1)$ denotes a standard Gaussian random variable. This integration algorithm is known as the Euler Maruyama method. In practise one simulates a large number of trajectories from which relevant statistical quantities can be computed.

Next we consider a reflective wall at $x = 0$. The question is how to include the wall-particle interaction in the algorithm? This problem was resolved by Eichhorn and Behringer in [1]. In what follows we will present the essential points of their work.

Looking at the case where f is constant will be helpful later. The Fokker-Planck equation is then given by:

$$\partial_t p(x,t \mid x_0,t_0) = D\partial_x^2 p(x,t \mid x_0,t_0) - \partial_x \frac{f}{\gamma} p(x,t \mid x_0,t_0) \ . \tag{5.6}$$

The reflective boundary conditions are $[\partial_x - f/\gamma]\, p_{|_0} = 0$. The solution to this problem is well known and was first derived by Smoluchowski in [31]. It is given by:

$$p(x,t \mid x_0,t_0) = p_1(x,t \mid x_0,t_0) + p_2(x,t \mid x_0,t_0) + p_3(x,t \mid x_0,t_0) \ , \tag{5.7}$$

where the individual contributions are:

$$p_1(x,t \mid x_0,t_0) = \frac{1}{\sqrt{4\pi D\Delta t}} \exp\left[-\frac{\left(x - x_0 - \frac{f}{\gamma}\Delta t\right)^2}{4D\Delta t} \right] \tag{5.8}$$

$$p_2(x,t \mid x_0,t_0) = \frac{\exp\left(-\frac{f x_0}{\gamma D}\right)}{\sqrt{4\pi D\Delta t}} \exp\left[-\frac{\left(x + x_0 - \frac{f}{\gamma}\Delta t\right)^2}{4D\Delta t} \right] \tag{5.9}$$

$$p_2(x,t \mid x_0,t_0) = -\frac{f}{2D\gamma} \exp\left(\frac{f}{D\gamma}\right) \operatorname{erfc}\left(\frac{x + x_0 + \frac{f}{\gamma}\Delta t}{\sqrt{4D\Delta\ .t}} \right) \tag{5.10}$$

Now back to the case where f is not constant. Assume we start at $t = t_0$ at position $x_0 > 0$. Using (5.5) we get a new position $x(t_0 + \Delta t)$. If the particle has not been interacting with the wall during Δt i.e. $x(t_0 + \Delta t) > 0$ we can accept this position as the new one. If $x(t_0 + \Delta t) < 0$ the new position is clearly unphysical, since the particle is not allowed to cross the wall. We need to include the particle wall interaction to get the correct position. Let us call the correct position $\tilde{x}(t_0 + \Delta t)$. If we manage to find the transition PDF $p_w(\tilde{x}, t \mid x_0, t_0)$ we can simply draw $\tilde{x}(t_0 + \Delta t)$ from it. In the algorithm it is assumed that $f(x(t))$ is approximately constant during the time interval Δt. Thus we need to find $p_w(\tilde{x}, t \mid x_0, t_0)$ for constant f. That is where the solution (5.7) comes into play. $p_1(x,t \mid x_0,t_0)$ can be identified as a contribution describing the free diffusion. $p_2(x,t \mid x_0,t_0)$ and $p_3(x,t \mid x_0,t_0)$ are contributions describing the wall particle interaction. Thus it is intuitively clear that:

$$p_w(\tilde{x},t \mid x_0,t_0) = \frac{p_2(\tilde{x},t \mid x_0,t_0) + p_2(\tilde{x},t \mid x_0,t_0)}{\int_0^\infty \mathrm{d}x\, (\tilde{x},t \mid x_0,t_0) + p_2(\tilde{x},t \mid x_0,t_0))} \ . \tag{5.11}$$

For a proof see [1]. In summary the algorithm goes as follows:

1. Start at x_0 and t_0. Compute a new position $x(t_0 + \Delta t)$ using (5.5).

2a. If $x(t_0 + \Delta t) > 0$ accept the new position.

2b. If $x(t_0 + \Delta t) < 0$ generate new position from p_w.

Our model is in two dimensions. Thus we need a generalized version of the algorithm. Our model has reflective walls at $y = 0$ and $y = h(x)$. Then the algorithm goes as follows:

1. Start at (x_0, y_0) and t_0.
   Compute a new position $(x(t_0 + \Delta t), y(t_0 + \Delta t))$ using (5.5).

2a. If $0 < y(t_0 + \Delta t) < h(x(t_0 + \Delta t))$ accept the new position.

2b. If $y(t_0 + \Delta t)) < 0$ generate new position $\tilde{y}$ from $p_w(\tilde{y}, t \mid y_0, t_0)$.

2c. If $y(t_0 + \Delta t) > h(x(t_0 + \Delta t))$ compute new $\tilde{x}$ and $\tilde{y}$ from:

   $\vec{\tilde{r}} = \vec{r}_0 + \Delta\vec{\tilde{r}} = \vec{r}_0 + \Delta\vec{r} + (q - q_0 - \vec{n}\Delta\vec{r})\,\vec{n}$
   q is generated from $p_w(q, t \mid q_0, t_0; f_\perp)$.
   $f_\perp = \vec{n}\vec{f}$ is the normal component of $\vec{f}$.
   $\vec{n}$ is the normal vector passing though $\vec{r}_0$.
   q_0 the distance from the wall.

For justification of the algorithm see [1]. It is valid if the the particle wall distance q_0 is small enough such that the wall appears locally flat for the particle. For our model this is always fulfilled in the limit $\epsilon = \frac{L_y}{L_x} \to 0$.

5.2 Stokes flow in a 2d tube

In order to use the Brownian dynamics simulation we need to specify the force $\vec{F}(x, y)$. We can interpret $\vec{v}(x, y) = \frac{\vec{F}(x,y)}{\gamma}$ as the velocity the particle gets either due to the deterministic force or by advection of the medium/liquid. The latter is what we consider. By advection we mean that if the liquid is moving with velocity $\vec{v}(x, y)$ the Brownian particles is moving with velocity $\vec{v}(x, y)$ as well. A hydrodynamic flow in a tube can be induced in various different ways. The one, we will be focusing on is pressure driven stationary Stokes flow. The velocity field $\vec{v} = (v_x, v_y)$ is obtained by solving Stokes equation and the continuity equation:

$$\nu \left(\partial_x^2 + \partial_y^2\right) v_x = \partial_x \mathcal{P}, \tag{5.12}$$

$$\nu \left(\partial_x^2 + \partial_y^2\right) v_y = \partial_y \mathcal{P} \tag{5.13}$$

$$\partial_x v_x + \partial_y v_y = 0 \tag{5.14}$$

where ν is the viscosity of the liquid and $\mathcal{P}$ the pressure. At the walls the velocity is assumed to vanishes $\vec{v} = 0$ at $y = 0$ and $y = h(x)$. This boundary condition is called the no slip boundary condition. An exact analytical expression for $\vec{v}$ is not known. However a perturbative methods is well established [26, 13]. Like the Fick-Jacobs approach it makes use of the two intrinsic spatial scales L_x and L_y. We will shortly sketch this perturbative method. We introduce the following scaling:

$$x \to L_x x \qquad y \to L_y y \qquad v_x \to v_x \frac{Q_0}{L_y} \qquad v_y \to \frac{Q_0}{L_x}$$

$$\mathcal{P} \to \mathcal{P}\Delta\mathcal{P} = \mathcal{P}\frac{\nu Q_0 L_x}{L_y^3} \ ,$$

where we have denoted the constant flow rate per unit width as Q_0. The dimensionless Stokes and continuity equations are then given by:

$$\nu \left(\epsilon^2 \partial_x^2 + \partial_y^2\right) v_x = \partial_x \mathcal{P} \tag{5.15}$$

$$\nu \left(\epsilon^4 \partial_x^2 + \epsilon^2 \partial_y^2\right) v_y = \partial_y \mathcal{P} \tag{5.16}$$

$$\partial_x v_x + \partial_y v_y = 0 \ , \tag{5.17}$$

where we have introduced the expansion parameter $\epsilon = \frac{L_x}{L_y}$. It is the same as in the Fick-Jacobs approach. Expanding the velocity field and the pressure in powers of ϵ and comparing orders of ϵ leads to set of hierarchic equations. We are only interested in the zeroth order approximation since that is the limit for which our generalized Fick Jacobs equation holds. The zeroth order equations are given by:

$$\partial_x v_x + \partial_y v_y = 0 \tag{5.18}$$

$$\frac{\partial_x^2 v_x}{\partial y^2} = \frac{\partial \mathcal{P}_0}{\partial_x} \tag{5.19}$$

$$\frac{\partial \mathcal{P}_0}{\partial_y} = 0 \tag{5.20}$$

Solving these equations for v_x and v_y using the no slip boundary condition and the constant flow rate condition $\int_0^{h(x)} v_x \mathrm{d}y = 1$ gives the following dimensionfull solution [26]:

$$\begin{aligned} v_x &= Q_0 \frac{6}{h(x)^3} \left(hy - y^2\right) \\ v_y &= Q_0 \left[2y^3 \left(\frac{1}{h^3}\right)' - 3y^2 \left(\frac{1}{h^2}\right)'\right] \end{aligned} \tag{5.21}$$

Now we apply this velocity field to our generalized FJ-equation. The generalized FJ-equation has the following form:

$$\partial_t P = \partial_x D_{\text{eff}}(x) \partial_x P - \partial_x F_{\text{eff}}(x) P \ . \tag{5.22}$$

We consider the upper reflective wall to be periodic $h(x) = h(x + L)$ with period length L. Then the velocity field is periodic as well and so are $D_{\text{eff}}(x)$

and $F_{\text{eff}}(x)$. Solving for $P(x,t)$ is still next to impossible. But we can solve for the time independent stationary distribution $P_{\text{stat}}(x)$. In order for $P_{\text{stat}}(x)$ to exist we need to introduce non trivial boundary conditions. Due to the periodic nature of the system it's natural to introduce periodic boundary conditions $P_{\text{stat}}(x) = P_{\text{stat}}(x+L)$.
We need to solve:

$$\partial_x D_{\text{eff}}(x)\partial_x P_{\text{stat}} - \partial_x F_{\text{eff}}(x) P_{\text{stat}} = 0 \ . \tag{5.23}$$

Integration leads to:

$$\partial_x P_{\text{stat}} - \frac{F_{\text{eff}}}{D_{\text{eff}}} P_{stat} = -\frac{J}{D_{\text{eff}}} \ , \tag{5.24}$$

Where J is an integration constant. We define the Potential like function

$$V(x) := -\int_0^x \frac{F_{\text{eff}}(\tilde{x})}{D_{\text{eff}}(\tilde{x})} \mathrm{d}\tilde{x} \ . \tag{5.25}$$

Note although F_{eff} and D_{eff} are periodic $V(x)$ is not necessary periodic since the integral form zero to x of a constant is not periodic. We can write equation (5.23) as :

$$\partial_x \mathrm{e}^{-V} P_{\text{stat}} = -\frac{J}{D_{\text{eff}}(x)} \mathrm{e}^{-V} \tag{5.26}$$

Integration from x to $x+L$ and using the periodic boundary conditions leads to the solution.

$$P_{stat} = \frac{1}{N} \mathrm{e}^{V(x)} \int_x^{x+L} \frac{e^{-V(\tilde{x})}}{D_{\text{eff}}(\tilde{x})} \mathrm{d}\tilde{x} \tag{5.27}$$

Where N is a normalization constant given by:

$$N = \int_0^L \left[\mathrm{e}^{V(x)} \int_x^{x+L} \frac{e^{-V(\tilde{x})}}{D_{\text{eff}}(\tilde{x})} \mathrm{d}\tilde{x} \right] \mathrm{d}x \tag{5.28}$$

We have arrived at a formal solution. The question is if we can solve the integrals hidden in D_{eff} and F_{eff} analytically. Unfortunately we can not. We need to solve them numerically. Already $n(x)$ needs to be computed numerically. The integral in (5.27) is constant if $V(x)$ is periodic which can be achieved by adding an appropriate constant force to F_{eff}. By doing so we are canceling out the flux J as well. There is two practical reasons why we are doing this: The numerical integration of the nested integrals is time consuming. Zero flux will make the comparison with the Brownian dynamics simulations easier.

Of course this constant force should have some physical representative however we will not care about it here. We denote this constant force by K. We can determine its value in the following way. We define a new potential $\tilde{V}$ by:

$$\tilde{V}(x) = -\int_0^x \frac{F_{\text{eff}}(\tilde{x}) - K}{D_{\text{eff}}(\tilde{x})} \mathrm{d}\tilde{x} \ . \tag{5.29}$$

For $\tilde{V}(x+L)$ we have:

$$\begin{aligned}\tilde{V}(x+L) &= -\int_0^{x+L} \frac{F_{\text{eff}}(\tilde{x}) - K}{D_{\text{eff}}(\tilde{x})} \mathrm{d}\tilde{x} \\ &= \tilde{V}(x) - \int_x^{x+L} \frac{F_{\text{eff}}(\tilde{x})}{D_{eff}(\tilde{x})} \mathrm{d}\tilde{x} + K \int_x^{x+L} \frac{1}{D_{\text{eff}}(\tilde{x})} \mathrm{d}\tilde{x} \ . \end{aligned} \tag{5.30}$$

Demanding $\tilde{V}(x+L) = \tilde{V}(x)$ we get :

$$K = \frac{\int_x^{x+L} \frac{F_{\text{eff}}(\tilde{x})}{D_{\text{eff}}(\tilde{x})} \mathrm{d}\tilde{x}}{\int_x^{x+L} \frac{1}{D_{\text{eff}}(\tilde{x})} \mathrm{d}\tilde{x}} \ . \tag{5.31}$$

And the stationary solution reduces to:

$$P_{\text{stat}} = \frac{1}{\tilde{N}} \mathrm{e}^{\tilde{V}(x)} \ , \tag{5.32}$$

where $\tilde{N}$ is a normalization constant given by:

$$\tilde{N} = \int_0^L \mathrm{e}^{\tilde{V}(x)} \mathrm{d}x \ . \tag{5.33}$$

5.3 Numerical results

In order to do the numerical integration and the Brownian dynamics simulation we have to choose a specific $h(x)$. We choose:

$$h(x) = \sin\left(\frac{2\pi}{100} x\right) + 2 \ . \tag{5.34}$$

The length units are chosen to be μm. We can identify $L_y = 3\mu m$ and $L_x = 50\mu m$. Thus $\epsilon = 0.06 << 1$ and the generalized F-J equation is applicable. The Force F_x and F_y are chosen according to (5.21):

$$\begin{aligned} F_x &= Q_0 \gamma \frac{6}{h} \left(\frac{1}{h} - \frac{y^2}{h^2}\right) - K\gamma \\ F_y &= Q_0 \gamma \left[2y^3 \left(\frac{1}{h^3}\right)' - 3y^2 \left(\frac{1}{h^2}\right)'\right] \ . \end{aligned}$$

In order for the FJ-equation to be applicable $F_x = \mathcal{O}(\frac{k_b T}{L_y})$. Then $K = \mathcal{O}(\frac{k_B T}{L_y})$ as well. We introduce a parameter $A := \frac{3Q_0\gamma}{2k_B T}$ which allows us to keep track of the order of the force in terms of $\frac{k_B T}{L_y}$. The forces then read:

$$\begin{aligned} F_x &= 4A \cdot k_B T \frac{1}{h} \left(\frac{1}{h} - \frac{y^2}{h^2}\right) - K \\ F_y &= 4A \cdot k_B T \left[y^2 \frac{h'}{h^3} - y^3 \frac{h'}{h^4}\right] \end{aligned}$$

If $A = \mathcal{O}(1)$ the generalized FJ-equation is valid. However it is more interesting to test the equation for bigger A. Another interesting aspect are the effects of the F_{tay} and D_{tay} terms since they are not seen in Martens generalized F-J equation[14, 17]. The figures 5.1-5.4 show P_{stat} for different values of A. The green line is P_{stat} without the F_{tay} and D_{tay} terms the red line is P_{stat} numerically calculated from our generalized FJ equation. The blue histogram in the background is made from 100 000 trajectories computed via Brownian dynamics simulations. The evolution time of the trajectories was chosen to be 10000 sec. The constants were chosen as follows: $k_{\text{B}}T = 4.11\,\text{fN}\mu\text{m}$ and $\gamma = \frac{6\pi}{10}\,\frac{\text{sec}\cdot\text{fN}}{\mu\text{m}}$. For the Code of the Brownian dynamics simulation see Appendix A, and for the code of the numerical integration see Appendix B.

Conclusion and Discussion:

We numerically solved the generalized time independent FJ-equation for a stationary pressure driven stokes flow. Furthermore we compared the semi-analytical solution (red line) with the PDF (blue histogram) obtained by Brownian dynamics simulations for different values of A. It shows a good agreement for $A = 5$ and $A = 15$ see figure 5.1 and 5.2. For $A = 30$ and $A = 50$ the deviation from the PDF (blue histogram) obtained by Brownian dynamics simulations becomes significant. Which is what we expect since the generalized FJ equation is applicable for forces of $\mathcal{O}(\frac{k_{\text{B}}T}{L_y})$. If we compare the semi-analytical solution of the generalized FJ-equation (red line) with the semi-analytical solution of the generalized FJ-equation without the F_{tay} and κ_{tay} terms (green line) we can see that the effect of these terms is bigger for bigger A . That is due to the fact that F_{tay} and κ_{tay} scales with A^2 and the other drift terms with A. At $A = 15$ the effect of these terms are significant. In summery the numerical results show that the generalized FJ-equation works well in its regime of validity and that the new terms F_{tay} and κ_{tay} are significant.

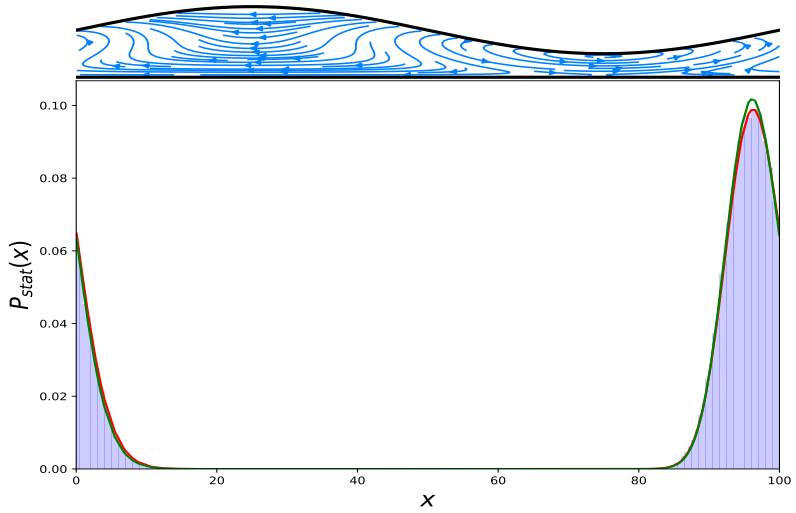

Figure 5.1: P_{stat} for A=5, green line is the semi-analytical solution without Taylor effects, red line is the semi analytical solution with Taylor effects, blue histogram is from Brownian dynamics simulations.

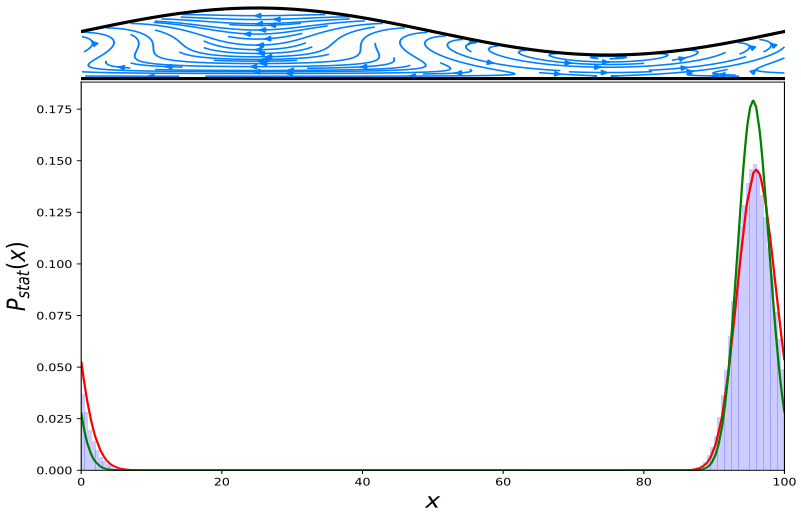

Figure 5.2: P_{stat} for A=15, green line is the semi-analytical solution without Taylor effects, red line is the semi analytical solution with Taylor effects, blue histogram is from Brownian dynamics simulations.

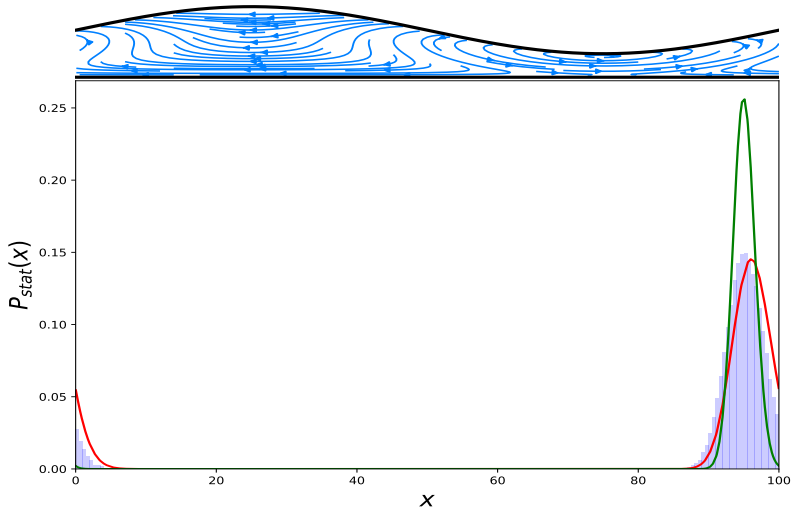

Figure 5.3: P_{stat} for A=30, green line is the semi-analytical solution without Taylor effects, red line is the semi analytical solution with Taylor effects, blue histogram is from Brownian dynamics simulations.

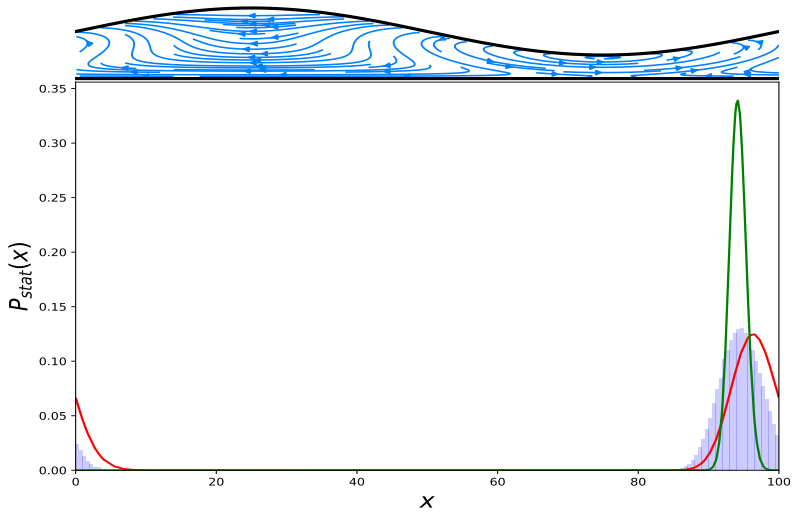

Figure 5.4: P_{stat} for A=50, green line is the semi-analytical solution without Taylor effects, red line is the semi analytical solution with Taylor effects, blue histogram is from Brownian dynamics simulations.

Chapter 6

Stochastic thermodynamics and the Fick-Jacobs approach

In the limit $\epsilon \to 0$ the generalized F-J equation (see equation (4.64)) correctly describes the dynamics of our system and its corresponding Langevin equation the trajectory of a particle. The question is if the entropy produced along this trajectory, in the sense of stochastic thermodynamics, is correctly representing the entropy production of the original two dimensional system? It is known for other approximations that the effective equation fails to predict the entropy production. One such case is the overdamped Fokker-Planck equation for a space dependent temperature [6]. The conclusion is that for some limit cases of systems there are processes which are not visible in the dynamics but still produce entropy. This phenomena is called anomalous entropy production.

The procedure which we will use to answer the above question is similar to the method of multiple scales for the dynamics (see section 4.3). For simplicity we will only consider a force in x direction $F_x(x, y)$.

6.1 Stochastic entropy production of the generalized Fick-Jacobs equation.

As mentioned before we will consider the special case for which $F_y(x, y) = 0$. In that case the generalized F-J equation (see equation (4.64)) reads

$$\partial_t P = D\partial_x \left[1 + \kappa_{\text{tay}}\right] \partial_x P - \frac{1}{\gamma}\partial_x \left[\frac{k_{\text{B}} T h'}{h} + F_{\text{tay}} + \overline{F}_x\right] P \ , \qquad (6.1)$$

where:

$$\kappa_{\text{tay}}(x) = \frac{1}{(k_{\text{B}}T)^2}\int_0^h \frac{1}{h}\left[\int_0^y \Delta F_x(x,y)\mathrm{d}s\right]^2 \mathrm{d}y \tag{6.2}$$

$$\begin{aligned} F_{\text{tay}}(x) = &\frac{1}{k_{\text{B}}T}\int_0^h \frac{1}{h}\left[\int_0^y \Delta F'_x(x,s)\mathrm{d}s\right]\left[\int_0^y \Delta F_x(x,s)\mathrm{d}s\right]\mathrm{d}y \\ &- \frac{h'}{h}\int_0^h \frac{1}{h}\left[\int_0^y F_x(x,s)\mathrm{d}s\right]\left[\int_0^y \Delta F_x(x,s)\mathrm{d}s\right]\mathrm{d}y \end{aligned} \tag{6.3}$$

$$\overline{F}_x(x) = \int_0^h \frac{F_x(x,y)}{h}\mathrm{d}y \tag{6.4}$$

$$\Delta F_x(x,y) = F_x(x,y) - \overline{F}_x(x)\ . \tag{6.5}$$

The corresponding Langevin equation in the Stratonovich sense is given by:

$$\begin{aligned} \mathrm{d}x^{1d} = &\frac{1}{\gamma}\left[\frac{k_{\text{B}}Th'}{h} + F_{tay} + \overline{F}_x - \frac{k_{\text{B}}T\kappa'_{\text{tay}}}{2}\right]\mathrm{d}t \\ &+\sqrt{2D\left(1-\kappa_{\text{tay}}\right)}\circ \mathrm{d}W_{x^{1d}}\ . \end{aligned} \tag{6.6}$$

$x^{1d}(t)$ is the trajectory of the effective one dimensional system. The entropy production in the effective one dimensional medium is then given by (see section 3.3 for definition):

$$\mathrm{d}s^{1d} = \frac{\mathrm{d}Q[x(t)]}{T} = \frac{1}{T}\left[\frac{k_{\text{B}}Th'}{h} + F_{tay} + \overline{F}_x - \frac{k_{\text{B}}T\kappa'_{\text{tay}}}{2}\right]\circ \mathrm{d}x^{1d} \tag{6.7}$$

The Entropy production in the medium, of the two dimensional original system is given by:

$$\mathrm{d}s = \frac{F_x}{T}\circ \mathrm{d}x \tag{6.8}$$

Where $x(t)$ is the (x coordinate) trajectory from the original two dimensional system. Due to the way how we derived the generalized FJ-equation it is obvious that in the limit $\epsilon \to 0$ $\mathrm{d}x$ coincide with $\mathrm{d}x^{1d}$. However it is by far not obvious that in the limit $\epsilon \to 0$ $\mathrm{d}s$ coincide with $\mathrm{d}s^{1d}$. Meaning it is not obvious that the generalized F-J equation inherits the correct stochastic thermodynamics. We need to take the limit for the stochastic Entropy in the same manner as we did for the stochastic dynamics in section 4.3. This will be done in the next section.

6.2 Stochastic entropy production in the F-J limit.

In this section we will formally take the F-J limit for the stochastic entropy production in the medium and in the system. We consider the special case

$F_y = 0$. We start with the overdamped Langevin equations of the original 2d system given by:

$$dx = \frac{F_x}{\gamma}\mathrm{d}t + \sqrt{2D}\mathrm{d}W_x \tag{6.9}$$

$$dy = \sqrt{2D}\mathrm{d}W_y \ . \tag{6.10}$$

The infinitesimal entropy produced in the medium along a trajectory is given by:

$$ds = \frac{F_x}{T}dx = \frac{F_x^2}{T\gamma}dt + \frac{F_x\sqrt{2D}}{T}dW_x \ . \tag{6.11}$$

Where we have used the x Langevin equation in the second equality sign. The equation for s can be interpreted as a Langevin equation. Together with the Langevin equation for motion in x and y direction we have a set of equations. Using the Stratonovich convention we can write down the Fokker-Planck equation for the joint PDF $\rho(x, y, s, t)$:

$$\begin{aligned}\partial_t\rho = D\left[\partial_x^2 + \partial_y^2 + \frac{F_x^2}{T}\partial_s^2 + \partial_x\frac{F_x}{T}\partial_s + \frac{F_x}{T}\partial_x\partial_s\right]\rho \\ -\frac{1}{\gamma}\left[\partial_x F_x + \frac{F_x^2}{T^2}\partial_s\right]\rho \ .\end{aligned} \tag{6.12}$$

The flux $\vec{J}$ can be identified as:

$$\vec{J} = \begin{bmatrix} D\partial_x + \frac{F_x}{T}\partial_s - \frac{F_x}{\gamma} \\ D\partial_y \\ \frac{DF_x^2}{T^2}\partial_s + \frac{F_x}{\gamma}\partial_x + \frac{F_x^2}{\gamma T}\end{bmatrix}\rho \tag{6.13}$$

The vector normal to the boundary is given by $\vec{n} = (-h^{'}, 1, 0)$. Thus the no flux boundary condition $\vec{n}\vec{J} = 0$ leads to:

$$D\left[\partial_y\rho\right]_{|_h} = h^{'}\left[D\partial_x\rho + \frac{F_x}{T}\partial_s\rho - \frac{F_x}{\gamma}\rho\right]_{|_h} \tag{6.14}$$

$$D\left[\partial_y\rho\right]_{|_0} = 0 \ . \tag{6.15}$$

We introduce the following scaling:

$$x \mapsto L_x x \qquad y \mapsto L_y y \qquad s \mapsto k_\mathrm{B}\frac{L_x}{L_y}s \tag{6.16}$$

$$F_x \mapsto \frac{k_\mathrm{B}T}{L_y}F_x \qquad h \mapsto L_y h \tag{6.17}$$

This is essentially the same scaling as we used for the generalized FJ-equation (see section 4.3), except for s which is scaled in a not obvious way. It is justified by realizing that $ds = \left[k_{\mathrm{B}} \frac{Lx}{Ly}\right] \frac{F_x}{T} dx$ for dimensionless quantities, meaning the variable s is of order $k_{\mathrm{B}} \frac{Lx}{Ly}$. Since we want everything to be of order one we have to scale s in this manner. The relevant timescales are the same as those for the dynamics. Therefore we introduce three different time variables. A fast one t_0 an intermediate one t_1 and a slow one t_2.

$$t_2 = \frac{D}{L_x^2} t \qquad t_1 = \frac{D}{L_x L_y} t \qquad t_0 = \frac{D}{L_y^2} t \tag{6.18}$$

Defining a small parameter $\epsilon = \frac{L_y}{L_x}$ and scaling the Fokker-Planck equation and its boundary conditions as discussed above gives:

$$\begin{aligned}\left[\partial_{t_2} + \frac{1}{\epsilon}\partial_{t_1} + \frac{1}{\epsilon^2}\partial_{t_0}\right]\rho =& \frac{1}{\epsilon^2}\partial_y^2 \rho - \frac{1}{\epsilon}\left[\partial_x F_x + F_x^2 \partial_s\right]\rho \\ &+ \left[\partial_x^2 + F_x^2 \partial_s^2 + \partial_x F_x \partial_s + F_x \partial_x \partial_s\right]\rho \ .\end{aligned} \tag{6.19}$$

$$\begin{aligned}\frac{1}{\epsilon^2}\left[\partial_y \rho\right]_{|_h} =& -\frac{1}{\epsilon} h^{'} \left[F_x \rho\right]_{|_h} \\ &+ h^{'} \left[\partial_x \rho + F_x \partial_s \rho\right]_{|_h}\end{aligned} \tag{6.20}$$

Expanding ρ in orders of ϵ, $\rho = \rho_0 + \epsilon\rho_1 + \epsilon^2\rho_2 + \cdots$ and comparing the orders of ϵ leads to a hierarchic set of equations.

In what follows we will go step by step through the first three hierarchic equations and use them for constructing the effective equation.

The $\mathcal{O}\left(\epsilon^{-2}\right)$ equation:

The $\mathcal{O}\left(\epsilon^{-2}\right)$ equation and its corresponding boundary condition are given by:

$$\partial_y^2 \rho_0 = \partial_{t_0} \rho_0 \qquad \left[\partial_y \rho_0\right]_{|_{h \wedge 0}} = 0 \ . \tag{6.21}$$

We are interested in the long time behaviour therefore we solve for the stationary PDF ($\partial_{t_0}\rho_0 = 0$). The solution is obtained by integrating the equation twice with respect to y. Using the boundary condition and the normalization condition $P_0(x) = \int_0^h \rho_0(x,y)\mathrm{d}y$ gives:

$$\rho_0 = \frac{P_0}{h} \ . \tag{6.22}$$

The $\mathcal{O}\left(\epsilon^{-1}\right)$ equation:

The order $\mathcal{O}\left(\epsilon^{-1}\right)$ equation and its corresponding boundary condition are given by:

$$\partial_{t_1}\rho_0 = \partial_y^2 \rho_1 - \left[\partial_x F_x + F_x^2 \partial_s\right]\rho_0 \tag{6.23}$$

$$\left[\partial_y \rho_1\right]_{|_h} = -h^{'}\left[F_x \rho_0\right]_{|_h} \tag{6.24}$$

$$\left[\partial_y \rho_1\right]_{|_0} = 0 \ , \tag{6.25}$$

where we already assumed $\partial_{t_0}\rho_1 = 0$. Integration of equation (6.23) with respect to y from 0 to h and using the boundary conditions leads to:

$$\partial_{t_1} P_0 = -\left[\partial_x \overline{F}_x + \overline{F^2}_x \partial_s\right] P_0 \tag{6.26}$$

$\overline{F}_x = \int_0^h \frac{F_x}{h} \mathrm{d}y$ is the force in x direction averaged over the channel width. Similarly $\overline{F^2}_x = \int_0^h \frac{F_x^2}{h} \mathrm{d}y$ is the the square of the force averaged over the channel width. Equation (6.26) will be used later for the construction of the effective equation. From now on we will solve equation (6.26). We plug $\rho_0 = \frac{P_0}{h}$ and equation (6.26) into equation (6.23). We integrate the resulting equation twice with respect to y. The two boundary terms can be determined by using the boundary conditions and the normalization condition $\int_0^h \rho_1 \mathrm{d}y = P_1$. This leads to :

$$\rho_1 = \frac{P_1}{h} + \left[\tilde{D}\partial_x P_0 + \tilde{F} + \tilde{S}\partial_s\right] P_0 \ . \tag{6.27}$$

$\tilde{D}, \tilde{F}$ and $\tilde{S}$ are given by:

$$\tilde{D}(x,y) = \int_0^y \int_0^v \frac{1}{h} \Delta F_x(x,u) \mathrm{d}u\mathrm{d}v - \frac{1}{h}\int_0^h \int_0^y \int_0^v \frac{1}{h} \Delta F_x(x,u) \mathrm{d}u\mathrm{d}v\mathrm{d}y \tag{6.28}$$

$$\tilde{S}(x,y) = \int_0^y \int_0^v \frac{1}{h} \Delta F_x^2(x,u) \mathrm{d}u\mathrm{d}v - \frac{1}{h}\int_0^h \int_0^y \int_0^v \frac{1}{h} \Delta F_x^2(x,u) \mathrm{d}u\mathrm{d}v\mathrm{d}y \tag{6.29}$$

$$\begin{aligned}\tilde{F}(x,y) = &\int_0^y \int_0^v \left[\frac{1}{h}\Delta F_x'(x,u) + F_x\left(\frac{1}{h}\right)'\right] \mathrm{d}u\mathrm{d}y \\ &- \frac{1}{h}\int_0^h \int_0^y \int_0^v \left[\frac{1}{h}\Delta F_x'(x,u) + F_x\left(\frac{1}{h}\right)'\right] \mathrm{d}u\mathrm{d}v\mathrm{d}y \ ,\end{aligned} \tag{6.30}$$

where we introduced the abbreviate notation $\Delta F_x = F_x - \overline{F}_x$ and $\Delta F_x^2 = F_x^2 - \overline{F^2}_x$.

The $\mathcal{O}\left(\epsilon^0\right)$ equation:

The $\mathcal{O}\left(\epsilon^0\right)$ equation and its corresponding boundary condition are given by:

$$\begin{aligned}\partial_{t_2}\rho_0 + \partial_{t_1}\rho_1 = \partial_y^2\rho_2 &- \left[\partial_x F_x + F_x^2\partial_s\right]\rho_1 \\ &+ \left[\partial_x^2 + F_x^2\partial_s^2 + \partial_x F_x \partial_s + F_x\partial_x\partial_s\right]\rho_0\end{aligned} \tag{6.31}$$

$$\left[\partial_y\rho_2\right]_{|_h} = -h^{'}\left[F_x\rho_1\right]_{|_h} + h^{'}\left[\partial_x\rho_0 + F_x\partial_s\rho_0\right]_{|_h} \tag{6.32}$$

$$\left[\partial_y\rho_2\right]_{|_0} = 0 \tag{6.33}$$

Integrating equation (6.32) from 0 to h with respect to y and using the boundary conditions leads to:

$$\partial_{t_2} P_0 + \partial_{t_1} P_1 = \left[\partial_x^2 + \partial_x \overline{F}_x \partial_s + h\overline{F}_x \partial_s \partial_x \frac{1}{h} + \overline{F_x^2}\partial_s^2\right] P_0 - \left[\partial_x \int_0^h F_x \rho_1 \mathrm{d}y + \int_0^h F_x^2 \partial_s \rho_1 \mathrm{d}y\right] - \partial_x \frac{h'}{h} P_0 \ . \tag{6.34}$$

Plugging in the previously calculated expression for ρ_1 and slightly rearranging the equation gives:

$$\begin{aligned}\partial_{t_2} P_0 + \partial_{t_1} P_1 = {} & \partial_x \left[1 - \int_0^h F_x \tilde{D} \mathrm{d}y\right] \partial_x P_0 + \left[\overline{F^2}_x - \int_0^h F_x^2 \tilde{S} \mathrm{d}y\right] \partial_s^2 P_0 \\ & + \partial_x \left[\overline{F}_x - \int_0^h F_x \tilde{S} \mathrm{d}y\right] \partial_s P_0 + \left[\overline{F}_x - \int_0^h F_x^2 \tilde{D} \mathrm{d}y\right] \partial_s \partial_x P_0 \\ & - \partial_x \left[\frac{h'}{h} + \int_0^h F_x \tilde{F} \mathrm{d}y\right] P_0 - \left[\frac{\overline{F}_x h'}{h} + \int_0^h F_x^2 \tilde{F} \mathrm{d}y\right] \partial_s P_0 \\ & - \left[\partial_x \overline{F}_x + \overline{F^2}_x \partial_s\right] P_1 \ .\end{aligned} \tag{6.35}$$

That is the second equation we are going to use for the construction of the effective equation.

The effective equation:

To get the effective equation we expand P to first order in ϵ: $P \approx P_0 + \epsilon P_1$. We write the time derivative as follows:

$$\frac{L_x^2}{D}\partial_t = \partial_{t_2} + \frac{1}{\epsilon}\partial_{t_1} + \frac{1}{\epsilon^2}\partial_{t_0} \ . \tag{6.36}$$

Applying the time derivative on P and neglecting terms of order ϵ and higher gives:

$$\frac{L_x^2}{D}\partial_t P \approx \partial_{t_2} P_0 + \frac{1}{\epsilon}\partial_{t_1} P_0 + \partial_{t_1} P_1 \ . \tag{6.37}$$

Plugging equations (6.26) and (6.35) into (6.37) gives:

$$\begin{aligned}\frac{L_x^2}{D}\partial_t P = {} & \partial_x \left[1 - \int_0^h F_x \tilde{D} \mathrm{d}y\right] \partial_x P + \left[\overline{F^2}_x - \int_0^h F_x^2 \tilde{S} \mathrm{d}y\right] \partial_s^2 P \\ & + \partial_x \left[\overline{F}_x - \int_0^h F_x \tilde{S} \mathrm{d}y\right] \partial_s P + \left[\overline{F}_x - \int_0^h F_x^2 \tilde{D} \mathrm{d}y\right] \partial_s \partial_x \ P \\ & - \partial_x \left[\frac{h'}{h} + \int_0^h F_x \tilde{F} \mathrm{d}y\right] P - \left[\frac{\overline{F}_x h'}{h} + \int_0^h F_x^2 \tilde{F} \mathrm{d}y\right] \partial_s P \\ & - \frac{L_x}{L_y} \left[\partial_x \overline{F}_x + \overline{F^2}_x \partial_s\right] P \ .\end{aligned} \tag{6.38}$$

Note we used $P_0 \approx P - \epsilon P_1$ and neglected the order ϵ terms. Reverting to dimensionfull quantities finally gives the effective equation:

$$\begin{aligned}
\partial_t P = &\partial_x \left[D - \frac{1}{kT\gamma} \int_0^h F_x \tilde{D} \mathrm{d}y \right] \partial_x P + \left[\frac{D}{T^2} \overline{F^2}_x - \frac{1}{kT^3\gamma} \int_0^h F_x^2 \tilde{S} \mathrm{d}y \right] \partial_s^2 P \\
&+ \partial_x \left[\frac{D}{T} \overline{F}_x - \frac{1}{kT^2\gamma} \int_0^h F_x \tilde{S} \mathrm{d}y \right] \partial_s P + \left[\frac{D}{T} \overline{F}_x - \frac{1}{kT^2\gamma} \int_0^h F_x^2 \tilde{D} \mathrm{d}y \right] \partial_s \partial_x P \\
&- \partial_x \left[\frac{D h^{'}}{h} + \frac{1}{kT\gamma} \int_0^h F_x \tilde{F} \mathrm{d}y + \frac{\overline{F}_x}{\gamma} \right] P \\
&- \left[\frac{D \overline{F}_x h^{'}}{Th} + \frac{1}{kT^2\gamma} \int_0^h F_x^2 \tilde{F} \mathrm{d}y + \frac{\overline{F^2}_x}{\gamma T} \right] \partial_s P
\end{aligned} \tag{6.39}$$

In order to get the functional for the entropy production in the medium we need to read of the corresponding Langevin equations from the above effective Fokker Planck equation.

For the following general Langevin equations

$$\begin{bmatrix} \mathrm{d}x \\ \mathrm{d}s \end{bmatrix} = \begin{bmatrix} F_1 \\ F_2 \end{bmatrix} \mathrm{d}t + \sqrt{2} \begin{bmatrix} a(x) & b(x) \\ c(x) & d(x) \end{bmatrix} \circ \begin{bmatrix} \mathrm{d}W_x \\ \mathrm{d}W_s \end{bmatrix} \tag{6.40}$$

the corresponding Fokker-Planck equation in the stratonovich sense can be written as:

$$\begin{aligned}
\partial_t P = &\partial_x \left[a^2 + b^2 \right] \partial_x P + \left[c^2 + d^2 \right] \partial_s^2 P \\
&+ \partial_x \left[ac + bd \right] \partial_s P + \left[ac + bd \right] \partial_x \partial_s P \\
&- \partial_x \left[F_1 - a a^{'} - b b^{'} \right] P - \left[F_2 - c a^{'} - d b^{'} \right] \partial_s P
\end{aligned} \tag{6.41}$$

By comparing equation (6.39) with equation (6.41) we can determine a,b,c, and d.

Since $\mathrm{d}W_s$ did not show up in the original Langevin equations (6.9), (6.10), (6.11) it seems natural to assume that $b = d = 0$. That would lead to the following expressions for a and c:

$$a = \sqrt{D - \frac{1}{kT\gamma} \int_0^h F_x \tilde{D} \mathrm{d}y} \tag{6.42}$$

$$c = \sqrt{\frac{D}{T^2} \overline{F^2}_x - \frac{1}{kT^3\gamma} \int_0^h F_x^2 \tilde{S} \mathrm{d}y} \tag{6.43}$$

$$ac = \frac{D}{T} \overline{F}_x - \frac{1}{kT^2\gamma} \int_0^h F_x \tilde{S} \mathrm{d}y \tag{6.44}$$

In addition the following must hold:

$$\sqrt{D - \frac{1}{kT\gamma}\int_0^h F_x \tilde{D}\mathrm{d}y} \cdot \sqrt{\frac{D}{T^2}\overline{F^2}_x - \frac{1}{kT^3\gamma}\int_0^h F_x^2 \tilde{S}\mathrm{d}y} = \\ = \frac{D}{T}\overline{F}_x - \frac{1}{kT^2\gamma}\int_0^h F_x \tilde{S}\mathrm{d}y \ . \tag{6.45}$$

This is not the case as can be proven by considering one special of F_x for which it is not true. It can be shown that already for $F_x \sim y$ equation (6.45) is not fulfilled. $b \neq 0$ would make no sense since then $\mathrm{d}W_s$ would appear in the Langevin equation for $\mathrm{d}x$.

So let us assume $b = 0$ and $d \neq 0$. We find that:

$$a = \sqrt{D - \frac{1}{kT\gamma}\int_0^h F_x \tilde{D}\mathrm{d}y} \tag{6.46}$$

$$c = \left[\frac{D}{T}\overline{F}_x - \frac{1}{kT^2\gamma}\int_0^h F_x \tilde{S}\mathrm{d}y\right] \cdot \left[D - \frac{1}{kT\gamma}\int_0^h F_x \tilde{D}\mathrm{d}y\right]^{-\frac{1}{2}} \tag{6.47}$$

$$d = \left[\left[\frac{D}{T^2}\overline{F^2}_x - \frac{1}{kT^3\gamma}\int_0^h F_x^2 \tilde{S}\mathrm{d}y\right] - \right. \\ \left. \left[\frac{D}{T}\overline{F}_x - \frac{1}{kT^2\gamma}\int_0^h F_x \tilde{S}\mathrm{d}y\right]^2 \cdot \left[D - \frac{1}{kT\gamma}\int_0^h F_x \tilde{D}\mathrm{d}y\right]^{-1}\right]^{\frac{1}{2}} \tag{6.48}$$

$$F_1 = \frac{Dh'}{h} + \frac{1}{kt\gamma}\int_0^h F_x \tilde{F}\mathrm{d}y - \frac{1}{2kT\gamma}\left(\partial_x \int_0^h F_x \tilde{D}\mathrm{d}y\right) + \frac{\overline{F}_x}{\gamma} \tag{6.49}$$

$$F_2 = \frac{D\overline{F}_x h'}{Th} + \frac{1}{kT^2\gamma}\int_0^h F_x^2 \tilde{F}\mathrm{d}y + \frac{\overline{F^2}_x}{\gamma T} \\ + \frac{1}{2}\left[\frac{D}{T}\overline{F}_x - \frac{1}{kT^2\gamma}\int_0^h F_x \tilde{S}\mathrm{d}y\right] \cdot \left[D - \frac{1}{kT\gamma}\int_0^h F_x \tilde{D}\mathrm{d}y\right]^{-1} \\ \cdot \partial_x \left[\frac{1}{kT\gamma}\int_0^h F_x \tilde{D}\mathrm{d}y\right] \ . \tag{6.50}$$

Which can be written in a different form by performing a partial integration:

$$a = \sqrt{D + \frac{1}{kT\gamma}\int_0^h \frac{1}{h}\left[\int_0^y \Delta F_x(u)\mathrm{d}u\right]^2 \mathrm{d}y} \tag{6.51}$$

$$c = \frac{\frac{D}{T}\overline{F}_x - \frac{1}{kT^2\gamma}\int_0^h \frac{1}{h}\int_0^y \Delta F_x(u)\mathrm{d}u \int_0^y \Delta F_x^2(u)\mathrm{d}u\mathrm{d}y}{\sqrt{D - \frac{1}{kT\gamma}\int_0^h \frac{1}{h}\left[\int_0^y \Delta F_x(u)\mathrm{d}u\right]^2 \mathrm{d}y}} \tag{6.52}$$

$$d = \left\{ \left[\frac{D}{T^2}\overline{F^2}_x - \frac{1}{kT^3\gamma}\int_0^h \frac{1}{h}\left[\int_0^y \Delta F_x^2(u)\mathrm{d}u\right]^2 \mathrm{d}y\right] - \frac{\left[\frac{D}{T}\overline{F}_x - \frac{1}{kT^2\gamma}\int_0^h \frac{1}{h}\int_0^y \Delta F_x(u)\mathrm{d}u \int_0^y \Delta F_x^2(u)\mathrm{d}u\mathrm{d}y\right]^2}{D - \frac{1}{kT\gamma}\int_0^h \frac{1}{h}\left[\int_0^y \Delta F_x(u)\mathrm{d}u\right]^2 \mathrm{d}y} \right\}^{\frac{1}{2}} \tag{6.53}$$

$$\begin{aligned} F_1 = &\frac{Dh^{'}}{h} + \frac{1}{kT\gamma}\int_0^h \frac{1}{h}\int_0^y \Delta F_x(u)\mathrm{d}u \int_0^y [\Delta F_x(u)^{'} - \frac{h^{'}}{h}F_x(u)]\mathrm{d}u\mathrm{d}y \\ &- \frac{1}{2kT\gamma}\partial_x \int_0^h \frac{1}{h}\left[\int_0^y \Delta F_x(u)\mathrm{d}u\right]^2 \mathrm{d}y + \frac{\overline{F}_x}{\gamma} \end{aligned} \tag{6.54}$$

$$\begin{aligned} F_2 = &\frac{D\overline{F}_x h^{'}}{Th} + \frac{1}{kT^2\gamma}\int_0^h \frac{1}{h}\int_0^y \Delta F_x^2(u)\mathrm{d}u \int_0^y [\Delta F_x(u)^{'} - \frac{h^{'}}{h}F_x(u)]\mathrm{d}u\mathrm{d}y + \frac{\overline{F^2}_x}{\gamma T} \\ &+ \frac{\frac{D}{T}\overline{F}_x - \frac{1}{kT^2\gamma}\int_0^h \frac{1}{h}\int_0^y \Delta F_x(u)\mathrm{d}u \int_0^y \Delta F_x^2(u)\mathrm{d}u\mathrm{d}y}{\sqrt{D - \frac{1}{kT\gamma}\int_0^h \frac{1}{h}\left[\int_0^y \Delta F_x(u)\mathrm{d}u\right]^2 \mathrm{d}y}} \cdot \partial_x \left[\frac{1}{kT\gamma}\int_0^h F_x \tilde{D}\mathrm{d}y\right] . \end{aligned} \tag{6.55}$$

Note we did not explicitly write the x arguments of the quantities. The entropy production in the medium in the limit $\epsilon \to 0$ is then given by.

$$ds = F_2\mathrm{d}t + \sqrt{2}\left[c \circ \mathrm{d}W_x + d \circ \mathrm{d}W_s\right] . \tag{6.56}$$

Likewise the Langevin equation for the x dynamics in the limit $\epsilon \to 0$ is given by:

$$dx = F_1\mathrm{d}t + \sqrt{2}\left[a \circ \mathrm{d}W_x\right] . \tag{6.57}$$

To complete the picture of the stochastic entropy we have to also consider the entropy of the system itself in the limit $\epsilon \to 0$. The system entropy of the original two dimensional system is given by:

$$s_{sys} = -k\ln\rho(x(t), y(t), t) \tag{6.58}$$

Where $\rho(x, y, t)$ obeys equations (4.33). Expanding ρ in orders of ϵ gives

$$s_{sys} = -k\ln\left(\rho_0 + \mathcal{O}(\epsilon)\right) = -k\ln(\rho_0) + \mathcal{O}(\epsilon) , \tag{6.59}$$

where the second equality sign follows from a Taylor expansion of the logarithm. Neglecting terms of order ϵ and using the expression for ρ_0 derived in section 4.3 we get:

$$\lim_{\epsilon \to 0} s_{sys} = -k \ln \left(\frac{P_0(x(t))}{h(x(t))} \right) = -k \ln P_0(x(t)) + k \ln h(x(t)) \ . \tag{6.60}$$

Conclusion and Discussion

The result for the entropy production in the medium is quite messy and we have to admit that we do not really understand it yet. The reason why we wrote the results in two different ways is due to the hope of finding a more compact underlying structure which makes it easier to interpret the results. Despite our lack of understanding the result we can observe some other interesting things. As expected $\mathrm{d}x$ in the limit $\epsilon \to 0$, given by equation (6.57) coincides with $\mathrm{d}x^{1d}$ given by equation (6.6). However the corresponding $\mathrm{d}s$ in the limit $\epsilon \to 0$, given by equation (6.56) does not coincide with $\mathrm{d}s^{1d}$ given by equation (6.7). The peculiar thing is the Wiener process $\mathrm{d}W_s$ which has to be there according to the effective Fokker-Planck equation (6.39). It seems the Wiener process $\mathrm{d}W_x$ alone is not enough to describe the entropy production in the effective one dimensional medium. The additional stochastic process $\mathrm{d}W_s$ is not visible in the dynamics however it produces entropy. It might be another case of anomalous entropy production similar to what people already observed in [6], however our level of understanding is too low to make any concrete statements.

Another interesting observation can be made by considering the special case for which F_x solely depends on x. In that case the equations simplify a lot. If we are just given the generalized F-J equation without knowing about the original system we would identify the Entropy production in the medium from equation (6.6) as

$$\mathrm{d}s^{1d} = \left[\frac{Dh^{'}}{Th} + \frac{F_x}{T} \right] \circ \mathrm{d}x \ , \tag{6.61}$$

and the Entropy production of the system as:

$$s^{1d}_{sys} = k_b \ln P(x(t)) \ . \tag{6.62}$$

The total Entropy produced along a trajectory is then given by:

$$\Delta s^{1d}_{tot} = \ln P(x(t_0)) - \ln P(x(t_1)) + \int_{t_0}^{t_1} \left[\frac{Dh^{'}}{Th} + \frac{F_x}{T} \right] \circ \mathrm{d}x(t) \ . \tag{6.63}$$

However if we start from the two dimensional system and formally take the limit, as we did in this section, the entropy production in the medium given by equation (6.56) is :

$$\mathrm{d}s = \frac{F_x}{T} \left[\left(\frac{Dh^{'}}{h} + F_x \right) \mathrm{d}t + \sqrt{D} \mathrm{d}W_x \right] \tag{6.64}$$

Note since $d = 0$ the Wiener process $\mathrm{d}W_s$ disappears. The corresponding Langevin equation for the dynamics (6.57) is given by:

$$\mathrm{d}x = \left[\frac{Dh^{'}}{h} + F_x \right] \mathrm{d}t + \sqrt{D} \mathrm{d}W_x \tag{6.65}$$

Thus we can write $\mathrm{d}s$ as:

$$\mathrm{d}s = \frac{F_x}{T} \circ \mathrm{d}x \tag{6.66}$$

The total entropy production along a trajectory is then given by

$$\begin{aligned}
\Delta s_{tot} &= \Delta s_{sys} + \Delta s \\
&= \ln P(x(t_0)) - \ln P(x(t_1)) + \ln h(x(t_1)) - \ln h(x(t_0)) + \int_{t_0}^{t_1} \frac{F_x}{T} \circ \mathrm{d}x(t) \\
&= \ln P(x(t_0)) - \ln P(x(t_1)) + \int_{t_0}^{t_1} \left[\frac{Dh^{'}}{Th} + \frac{F_x}{T} \right] \circ \mathrm{d}x(t)
\end{aligned} \tag{6.67}$$

The total entropy Δs_{tot}^{1d} and Δs_{tot} coincide. The above calculation shows a transfer of the $\ln(h)$ term. In the original two dimensional system the term was part of the system entropy but in the effective one dimensional system it is part of the medium entropy. Something like that is actually what we expected due to the entropic nature of the F-J force. However it is still interesting that stochastic thermodynamics describes the entropic nature of the F-J force by a transfer of entropy form the system to the medium.

Chapter 7

Summary and Outlook

We will give a quick summary of all results and discuss possible future goals.

In section 4.1 we derived the reflective boundary conditions starting from an classical reflection law, a more fundamental approach than usually presented in the literature [29, 8]

In section 4.3 we derived an effective one dimensional equation describing the dynamics of Brownian particles in a two dimensional tube in the presence of a space dependent external force. This equation is a generalized version of the F-J equation. The most interesting thing about the equation is that it contains terms describing Taylor dispersion [13] in a quite general way, however there is still much room for improvement. We only considered the case where the upper boundary varies and the lower one does not. One could first extend the model to the case where the upper and lower boundaries vary symmetrically, which should be straightforward, and then to arbitrary varying upper and lower boundaries. Another extension would be to consider a 3d channel, a radial symmetric channel should be possible as well as planar channel with very small height. Another aspect is the derivation of higher order correction terms. Yet another possible extension is to consider an anisotropic temperature, which might allow for a better tuning of the Taylor dispersion terms. Instead of spherical particles one could also consider ellipsoidal particles. One can see the possibilities to improve the model seems to be endless.

In chapter 6 we investigated the generalized F-J equation in the context of stochastic thermodynamics. In particular we wanted to know whether the generalized F-J equation inherits the correct entropy production of the original two dimensional system. We found that generally it does not. Due to simplicity we just considered a space dependent external force in x direction. In the case for which the force solely depends on x we found that the effective one dimensional model correctly describes the total entropy production. However the system and medium entropy in the one dimensional and two dimensional description are different. Thus we concluded that the F-J approximation causes a transfer of entropy from the system to the medium entropy. In the one dimensional effective model this transfer manifests in the form of an entropic force F_{FJ}. There is only one possible future goal here: Understand the results derived in section 6.2.

Appendices

Appendix A

C++ Code for Brownian Dynamics Simulation

```
#include <iostream>
#include <stdio.h>
#include <math.h>
#include <gsl/gsl_rng.h>
#include <time.h>
#include "brent.h"
#include "brent1.h"
#include <fstream>
#include <gsl/gsl_randist.h>
#include <string>
using namespace std;
// Am=15 f=-12.6077433664, Am=50 f=-42.4412722187, Am=5 f
    =-4.19895037306
//upper boundary
inline double h(double x,double Lx, double Ly)
{

  return (sin(x/Lx)+2)*Ly;
}

//derivative of upper boundary
inline double dh(double x,double Lx, double Ly)
{

  return (Ly/Lx)*cos(x/Lx);
}

//velocity in x direction
double vx(double x, double y, double Amplitude, double Lx, double
    Ly)
{
  double L=1/h(x,Lx,Ly);

  return Amplitude*(h(x,Lx,Ly)-y)*y*L*L*L -42.4412722187;
}
//velocity in y direction
double vy(double x, double y, double Amplitude, double Lx, double
    Ly)
{
  double L=1/h(x,Lx,Ly);
```

```
38
39    return Amplitude*(h(x,Lx,Ly)-y)*y*y*dh(x,Lx,Ly)*L*L*L*L;
40  }
41
42  int main (void)
43  {
44    //characteristic lengthscales for the tube
45    double Lx=100/(2*M_PI);
46    double Ly=1;
47    //Diffusion coefficent and kT
48    double kT=4.11;
49    double gamma=6*M_PI/10;
50    double D=kT/gamma;
51    //Amplitude of velocity
52    int Am=50;
53    double Amplitude=4*Am*D;
54    //time increment
55    double dt=0.001;
56    //end time
57    int t=10000;
58    int nend=t/dt;
59    //realizations
60    int Mend=100000;
61      //particle initial positions
62    double x=0;
63    double y=0.5;
64    double xb=0;
65    double yb=0;
66    //simplifications
67    double alpha=sqrt(4*D*dt);
68    double betha=sqrt(2*D*dt);
69    //distnace from wall
70    double q_0=0;
71    // point on boundary
72    double x_s=0;
73    double h_xs=0;
74    double dh_xs=0;
75    // norm of normal vector
76    double norm=0;
77    //correction
78    double q=0;
79    //random number for brent
80    double r=0;
81    //normal velocity to the wall
82    double v=0;
83    double v_x=0;
84    double v_y=0;
85    //prÃodic length
86    double L = 100 ;
87    // array for collecting end points
88    double *xend = new double[nend];
89    double *yend = new double[nend];
90    //Initialize random number generator
91    const gsl_rng_type * T;
92    gsl_rng * ran1;
93    gsl_rng * ran2;
94    gsl_rng * ran3;
95    gsl_rng_env_setup();
96    T = gsl_rng_taus;
97    ran1=gsl_rng_alloc (T);
98    ran2=gsl_rng_alloc (T);
99    ran3=gsl_rng_alloc(T);
```

```
100   gsl_rng_set (ran1, time(NULL));
101   gsl_rng_set (ran2, time(NULL)+1);
102   gsl_rng_set (ran3, time(NULL)+2);
103   //realization loop
104   for (int M=0; M<Mend;M++){
105     x=50; y=0.5;
106     //trajectory loop
107     for (int n=0; n<nend;n++)
108     {
109       //previous position
110       xb=x;
111       yb=y;
112       //velocity in x and y direction
113       v_x=vx(xb,yb,Amplitude,Lx,Ly);
114       v_y=vy(xb,yb,Amplitude,Lx,Ly);
115       // random walk integration
116       x=x+v_x*dt+betha*gsl_ran_gaussian_ziggurat(ran1,1);
117       y=y+v_y*dt+betha*gsl_ran_gaussian_ziggurat(ran2,1);
118         //particle hits lower wall
119         if(y <= 0)
120         {
121           r=gsl_rng_uniform(ran3);
122           //distance form wall
123           q_0=yb;
124           //generating valid positionS
125           q=brent(Ly ,q_0, dt, D, r, v_y ,alpha);
126           //new position
127           y=q;
128         }
129         //particle hits upper wall
130         if (y >= h(x,Lx,Ly))
131         {
132           r=gsl_rng_uniform(ran3);
133           // x_s is  a point  on the boundary such that a line thru
      (x_s,h(x_s)) and (xb,yb) is normal to the boundary.
134           x_s = brent1(xb, yb, Lx, Ly);
135           h_xs=h(x_s,Lx,Ly);
136           dh_xs=dh(x_s,Lx,Ly);
137           //distance from the wall
138           q_0=sqrt((xb-x_s)*(xb-x_s)+(h_xs-yb)*(h_xs-yb));
139           //norm of vector normal to the boundary
140           norm=1/(sqrt(dh_xs*dh_xs+1));
141           //velocity normal to the boundary
142           v= norm*(dh_xs*v_x-v_y);
143           //corretction q
144           q=brent(Ly ,q_0, dt, D, r, v ,alpha);
145           // new valid positions
146           x=x+(q-q_0-norm*(dh_xs*(x-xb)+(yb-y)))*norm*dh_xs;
147           y=y+(q-q_0-norm*(dh_xs*(x-xb)+(yb-y)))*-norm;
148
149         }
150       //periodic boundary conditions
151       x=fmod(fmod(x,L)+L ,L);
152     }
153     //counter
154     cout << M << endl;
155     // end point array
156     xend[M]=x;
157     yend[M]=y;
158
159   }
160 // Dumping data
```

```
161  ofstream fout("Forcexy1_Am=50_Ly=2_t=10000_no_flux.txt");
162  for (int k=0; k<Mend; k++)
163  {
164    fout <<xend[k] << "\n" << yend[k] << "\n";
165  }
166  fout.close();
167
168  return 0 ;
169 }
```

Listing A.1: Main program for the Brownian dynamics simulation

```
#include <iostream>
#include <gsl/gsl_roots.h>
#include <math.h>
#include <gsl/gsl_sf_erf.h>

struct Params { double q_0, dt, D, r, v,alpha;};

// Function F(q)-r where F(q) is the cummulative ditribution of the
     wall interaction part and r is a unform random number
inline double f(double q, void *param)
{

  Params* p = (Params*)param;
  double q_0 =  (p->q_0);
  double dt =  (p->dt);
  double D =  (p->D);
  double r =  (p->r);
  double alpha = (p->alpha);
  double v =  (p->v);

  return (1-r)*gsl_sf_erfc((q_0+v*dt)/alpha)-gsl_sf_erfc((q+q_0+v*
    dt)/alpha)*exp(v*q/D);

}
//Brent algorithm for computing the roots of F(q)-r i.e generates a
     random variable q.
inline double brent(double Ly , double q_0, double dt, double D,
    double r, double v, double alpha)
{
  double x_lo=0;
  double x_hi=3;
  Params args = {q_0, dt, D, r,v, alpha};
  gsl_root_fsolver* solver;
  gsl_function fwrapper;
  solver=gsl_root_fsolver_alloc(gsl_root_fsolver_brent);
  fwrapper.function=f;
  fwrapper.params=&args;
  gsl_root_fsolver_set(solver, &fwrapper, x_lo, x_hi);
  int status = 1;
  double x_rt=0;
  for (int iter=0; status and iter <100; ++iter)
  {
    gsl_root_fsolver_iterate(solver);
    x_rt = gsl_root_fsolver_root(solver);
    double x_lo = gsl_root_fsolver_x_lower(solver);
    double x_hi = gsl_root_fsolver_x_upper(solver);
    status = gsl_root_test_interval(x_lo,x_hi,0.000001,0);

  }
  gsl_root_fsolver_free(solver);
  return x_rt;

}
```

Listing A.2: Header for generating the random variable needed for the correct treatment of the wall particel interaction

```
#include <iostream>
#include <gsl/gsl_roots.h>
#include <math.h>


struct Params1 { double x,y,Lx,Ly ;};


//Function for calculating point on the wall for which a line thru
    (x_s,h(x_s)) and (xb,yb) is normal to the boundary.
inline double nfun(double x_s, void *param)
{
  Params1* p = (Params1*)param;

  double x =  (p->x);
  double y =  (p->y);
  double Lx =  (p->Lx);
  double Ly =  (p->Ly);


  return x_s-x+((sin(x_s/Lx)+2)*Ly-y)*Ly/Lx*cos(x_s/Lx);

}

//Computing minimum of nfun which gives the desired point x_s
inline double brent1(double x , double y, double Lx, double Ly)
{

  double x_lo=x-0.5;
  double x_hi=x+0.5;
  Params args = {x, y, Lx, Ly};
  gsl_root_fsolver* solver;
  gsl_function fwrapper;
  solver=gsl_root_fsolver_alloc(gsl_root_fsolver_brent);
  fwrapper.function=nfun;
  fwrapper.params=&args;
  gsl_root_fsolver_set(solver, &fwrapper, x_lo, x_hi);
  int status = 1;
  double x_rt=0;
  for (int iter=0; status and iter <100; ++iter)
  {
    gsl_root_fsolver_iterate(solver);
    x_rt = gsl_root_fsolver_root(solver);
    double x_lo = gsl_root_fsolver_x_lower(solver);
    double x_hi = gsl_root_fsolver_x_upper(solver);
    status = gsl_root_test_interval(x_lo,x_hi,0.000001,0);

  }
  gsl_root_fsolver_free(solver);
  return x_rt;

}
```

Listing A.3: Header for computing the refernce point on the wall

Appendix B

Python Code for Numerical Integration

```
from __future__ import division
import scipy.integrate
import numpy as np
import matplotlib.pyplot as plt
from settingx import c
from settingx import p_


# Period length
L=100
#=============================================================
# Calculating effective force and diffusion coefficent
#=============================================================

def Feff(x):
    setx=c(x)
    Feff=scipy.integrate.quad(setx.feffI,0,setx.h)
    return Feff[0]

def Deff(x):
    setx=c(x)
    Deff=scipy.integrate.quad(setx.deffI,0,setx.h)
    return c.D-Deff[0]/(c.kT*c.gamma)
#=============================================================
# Calculating Potnetial
#=============================================================

#Integrand of potential
def v(x):
    setx=c(x)
    Fe=scipy.integrate.quad(setx.feffI,0,setx.h)
    De=scipy.integrate.quad(setx.deffI,0,setx.h)
    Force=setx.D*setx.dh*setx.chi(setx.h)/setx.n+setx.Fm/setx.gamma
    +Fe[0]/(c.gamma*c.kT)
    Diffusion=c.D-De[0]/(c.kT*c.gamma)
    return Force/Diffusion
#Potential
def V(x):
    I=scipy.integrate.quad(v,0,x)

```

```
    return -I[0]
#=============================================================
# Adding a constant force such that the flux is 0
# ie. the potnetial Vtilde is periodic
#=============================================================

def overDeff(x):
    return 1/Deff(x)

I1=scipy.integrate.quad(v,0,L)[0]
I2=scipy.integrate.quad(overDeff,0,L)[0]

f=-I1/I2
print f

def vtilde(x):
    setx=c(x)
    Fe=scipy.integrate.quad(setx.feffI,0,setx.h)
    De=scipy.integrate.quad(setx.deffI,0,setx.h)
    Force=(setx.D*setx.dh*setx.chi(setx.h)/setx.n+
        setx.Fm/setx.gamma+Fe[0]/(c.gamma*c.kT)+f)
    Diffusion=c.D-De[0]/(c.kT*c.gamma)
    return Force/Diffusion
#Potential

def Vtilde(x):
    I=scipy.integrate.quad(vtilde,0,x)

    return -I[0]

#=============================================================
# Claclulating the stationary PDF for zero flux
#=============================================================

def P(x):
    I=np.e**(-Vtilde(x))
    print 'a'
    p_.p=np.append(p_.p,I)
    p_.u=np.append(p_.u,x)
    return I

def N():

    Ninverse=scipy.integrate.quad(P,0,L)
    return 1/(Ninverse[0])
#=============================================================
# plotting and sving PDF
#=============================================================

N_=N()

p_.p=N_*p_.p

plt.plot(p_.u,p_.p,color='blue',label='Potential')
np.savetxt('Pd x Am=%s_Ly=%s no flux'%(c.Am,c.Ly),p_.u)
np.savetxt('Pd  Am=%s_Ly=%s no flux'%(c.Am,c.Ly),p_.p)
```

Listing B.1: Program for numerical computation of P_{stat}

```
from __future__ import division
import scipy.integrate
import numpy as np

#=============================================================
# c is  a class which serves for the calculation
#of functions relevant for the integration.
#All functions solely depending on x are saved as
# variables when an instance
#of the class is generated (see __init__ constructor)
#=============================================================

class c:
    Lx=100
    Ly=2
    a=1
    kT=4.11
    gamma=6*np.pi/10
    D=kT/gamma
    Am=50
    Amplitude=4*Am*kT
    Am_3=Am/3

    def __init__(self,x):

        self.Sin1=np.sin(2*np.pi*x/c.Lx)
        self.Cos1=np.cos(2*np.pi*x/c.Lx)
        self.h=(self.Sin1*c.a+c.Ly)
        self.h_3=1/(self.h*self.h*self.h)
        self.h_4=self.h_3*(1/self.h)
        self.h_5=self.h_4*(1/self.h)
        self.dh=self.a*2*np.pi*(self.Cos1)/c.Lx
        self.dh_2=self.dh*self.dh
        self.ddh=-c.a*4*np.pi*np.pi*(self.Sin1)/(c.Lx*c.Lx)
        self.n=scipy.integrate.quad(self.chi,0,self.h)[0]
        self.n_1=1/self.n
        self.dn=scipy.integrate.quad(self.dchi,0,self.h)[0]+self.dh
    *self.chi(self.h)
        self.Fm=scipy.integrate.quad(self.Fxchi,0,self.h)[0]/self.n
        self.I1=scipy.integrate.quad(self.dFxchi,0,self.h)
        self.I2=scipy.integrate.quad(self.Fxchi,0,self.h)
        self.dFm=(self.I1[0]-self.dn*self.I2[0]/self.n+(self.dh*
    self.Fx(self.h)*self.chi(self.h)))/self.n

    def Fx(self,y):
        return self.Amplitude*(self.h*y-y*y)*self.h_3


    def Fy(self,y):
        return self.Amplitude*y*y*(self.h-y)*self.dh*self.h_4

    def dFx(self,y):

        return self.Amplitude*y*(3*y-2*self.h)*self.dh*self.h_4

    def chi(self,y):

        exponent=(self.Am_3*y*y*y)*(4*self.h-3*y)*self.dh*self.h_4
        return np.e**exponent

    def dexponent(self,y):

```

```
61          dexponent=(self.Am_3*self.h_5*y*y*y)*(12*(y-self.h)*self.
    dh_2+self.h*(4*self.h-3*y)*self.ddh)
62          return dexponent
63
64      def dchi(self,y):
65
66          dexponent=(self.Am_3*self.h_5*y*y*y)*(12*(y-self.h)*self.
    dh_2+self.h*(4*self.h-3*y)*self.ddh)
67          return self.chi(y)*dexponent
68
69      def Fxchi(self,y):
70          return self.chi(y)*self.Fx(y)
71
72
73      def dFxchi(self,y):
74          return self.dFx(y)*self.chi(y)+self.Fx(y)*self.dchi(y)
75
76      def ideff(self,y) :
77          return self.chi(y)*(self.Fx(y)-self.Fm)
78
79
80      def deff(self,y):
81
82
83          I=scipy.integrate.quad(self.ideff,0,y)
84
85          return I[0]/self.n
86
87      def ifeff(self,y):
88
89
90          ifeff=self.chi(y)*self.n_1*(self.dFx(y)-self.dFm+(self.
    dexponent(y)-(self.dn*self.n_1))*self.Fx(y))
91          return ifeff
92
93      def feff(self,y):
94
95          I=scipy.integrate.quad(self.ifeff,0,y)
96          return I[0]
97
98
99      def i1(self,y):
100             return self.feff(y)/self.chi(y)
101
102     def i2(self,y):
103             return self.deff(y)/self.chi(y)
104
105     def feffI(self,y):
106         I1=scipy.integrate.quad(self.i1,0,y)
107         return I1[0]*self.chi(y)*(self.Fx(y)-self.Fm)
108
109     def deffI(self,y):
110         I2=scipy.integrate.quad(self.i2,0,y)
111         return I2[0]*self.chi(y)*(self.Fx(y)-self.Fm)
112
113
114 class p_:
115     p=np.array([])
116     u=np.array([])
```

Listing B.2: Class which computes relevant functions for the integration

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