BEN-GURION UNIVERSITY OF THE NEGEV
FACULTY OF ENGINEERING SCIENCES
DEPARTMENT OF BIOMEDICAL ENGINEERING

Diffusion in Periodic Systems

Thesis submitted in partial fulfilment of the requirements for the M.Sc. degree

By: Matan Sivan

May, 2019

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Chairman of Graduate Studies Committee:.....Date:.....

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Abstract

Brownian motion in a periodic potential constitutes one of the fundamental problems of particle transport with numerous applications in various fields of science and technology. Despite being studied extensively throughout the years (see review in Riskens' book, "The Fokker-Planck Equation" - chapter 11), the general solution of the Smoluchowski (diffusion) equation for motion in periodic potentials is generally unknown. In this thesis, we close this gap in the literature and present (in chapter 2) a systematic way to derive the asymptotic (at large times) solution of the time-dependent equation for any periodic even function $U(x)$. The leading term of this solution is the well known solution to the simple time-dependent diffusion equation, namely a Gaussian function with an effective diffusion coefficient D^*, multiplied by Boltzmann's factor corresponding to the periodic potential. We present a method for finding the corrections to the leading term, and derive the first two corrections, thus obtaining a solution which is asymptotically correct up to terms decaying faster than $\sim t^{-3/2}$. The effective diffusion coefficient of the periodic Brownian motion is given by the Lifson-Jackson formula, which we also recover independently as part of the derivation of the solution. We conduct Langevin dynamics based simulations, that show excellent agreement between the analytical solution and the numerical results. The simulations demonstrate that for small periodic wavelengths and for high potential barriers, the Lifson-Jackson formula does not hold and, instead, an Arrhenius-Kramer behaviour is observed.

In chapter 3 we address the problem of diffusion in two dimensional (2D) periodic channels, and attempt to map it into an effective 1D Fick-Jacobs equation, which is a Smoluchowski equation with an entropic potential. In order to improve the fit to the 2D description, a periodic, spatially-dependent diffusion coefficient $D(x)$ is added, which significantly enhances the agreement between Fick-Jacobs 1D simulation results and the results of 2D channel simulations. We obtain a series of approximations for $D(x)$, and numerically compare them to previously derived expressions and note that to leading order in the derivative of the height function of the channel, $A'(x) = dA/dx$, they all have the same form: $D(x)/D \sim 1 - A'^2/3$. Notably, our first order expression coincides with the formula suggested by Zwanzig. Our results show that the choice of a space dependent diffusion coefficient indeed does improve the 1D fit dramatically, although for short periodic wavelengths

λ, the series of approximations of $D(x)$ does not converge properly, and the 1D description may still be quite inaccurate.

In summary, we derive an asymptotic solution to the fundamental problem of single particle diffusion in 1D periodic potentials. We then use this solution in order to map the problem of diffusion in a 2D periodic channel into a 1D description, which includes finding a periodic $D(x)$ in order to improve the agreement to the exact solution of the 2D problem.

Contents

Chapter 1

Introduction

1.1 The Smoluchowski Equation

Brownian motion is the movement of particles due to thermal collisions with solvent molecules that cause the particles to exhibit random motion, also known as single-particle diffusion. It is named after the botanist Robert Brown who, while looking through a microscope at pollen grains and dust particles, noticed that they move erratically through the water [1]. In 1905 (the "miracle year"), Albert Einstein published a paper that explained precisely how the motion that Brown observed was a result of the pollen grains colliding with water molecules [2]. Fifty years earlier in 1855, Adolf Fick introduced Fick's laws of diffusion, which govern the spontaneous transport of mass through a medium [3]. Instead of considering the motion of individual particles, Fick's laws provide a continuum description to the same process in which the net flow of particles is in accordance to the concentration gradient (i.e., from high to low concentration).

Particle transport via diffusion is an important phenomenon in many fields of science, ranging from biophysics (e.g., diffusion of polymers [4]), biology (e.g., diffusion of Oxygen and Carbon Dioxide in the lungs [5], particle transport through the cell membrane [6]), chemistry, mechanical engineering (e.g., heat transfer [7]), etc. As a more broad definition, diffusion could be also referred to how something is widely distributed or spreads across, and is also used to describe many social processes such as diffusion of innovations [8] and populations [9], cultural diffusion [10], and changes in income [11]. In this thesis, we address

the physical problem of mass transport which is described mathematically by Fick's laws.

Fick's first law of diffusion describes the relationship between the flux of particles $J(\mathbf{r},t)$, and the probability distribution function (PDF) of the particles $P(\mathbf{r},t)$[1]:

$$\vec{J}(\mathbf{r},t) = -D(\mathbf{r})\vec{\nabla}P(\mathbf{r},t), \tag{1.1}$$

where $\mathbf{r}$ represents the space coordinates, t is the time, and $D(\mathbf{r})$ is the diffusion coefficient which may coordinate-dependent. If the particle experiences a potential $U(\mathbf{r})$, then the flux also features a drift term and reads:

$$\vec{J}(\mathbf{r},t) = -D(\mathbf{r})\vec{\nabla}P(\mathbf{r},t) - \mu(\mathbf{r})P(\mathbf{r},t)\vec{\nabla}U(\mathbf{r}), \tag{1.2}$$

where $\mu(\mathbf{r})$ is the mobility, which is related to the diffusion coefficient via Einstein's relation [12]

$$D(\mathbf{r}) = k_B T\mu(\mathbf{r}), \tag{1.3}$$

where k_B is Boltzman's factor, and T is the temperature.

The continuity equation describes the relation between the temporal derivative of the $P(\mathbf{r},t)$ and the spatial derivative of the flux:

$$\frac{\partial P(\mathbf{r},t)}{\partial t} = -\vec{\nabla}\cdot\vec{J}(\mathbf{r},t). \tag{1.4}$$

Substituting Eq. (1.1) in Eq. (1.4) leads to Fick's second law of diffusion:

$$\frac{\partial P(\mathbf{r},t)}{\partial t} = \vec{\nabla}\cdot[D(\mathbf{r})\vec{\nabla}P(\mathbf{r},t)]. \tag{1.5}$$

The solution of Eq. (1.5) with delta-function initial condition $P(\mathbf{r},t=0) = \delta(\mathbf{r})$ and constant D is a Gaussian function: $P(\mathbf{r},t) = (4\pi Dt)^{-d/2}\exp[-\mathbf{r}^2/4Dt]$, where d is the space dimensionality. The mean displacement of the particle $\langle\Delta\mathbf{r}\rangle = 0$, and the mean square

[1]The same law is often written with other quantities like the concentration $c(\mathbf{r},t)$ or the mass $m(\mathbf{r},t)$ which are proportional to the PDF.

displacement (MSD) satisfies:

$$\langle \Delta \mathbf{r}^2 \rangle = 2dDt. \tag{1.6}$$

In the presence of a potential $U(\mathbf{r})$, Eq. (1.2) should be substituted into Eq. (1.4), leading to the Smoluchowski equation [13]:

$$\frac{\partial P(\mathbf{r},t)}{\partial t} = \vec{\nabla} \cdot [D(\mathbf{r})\vec{\nabla} P(\mathbf{r},t)] + \vec{\nabla} \cdot [\mu(\mathbf{r}) P(\mathbf{r},t) \vec{\nabla} U(\mathbf{r})]. \tag{1.7}$$

An alternative form of this equation is:

$$\frac{\partial P(\mathbf{r},t)}{\partial t} = \vec{\nabla} \cdot \left\{ D(\mathbf{r}) e^{-\beta U(\mathbf{r})} \vec{\nabla} \left[e^{\beta U(\mathbf{r})} P(\mathbf{r},t) \right] \right\}, \tag{1.8}$$

where $\exp[-\beta U(\mathbf{r})]$ is Boltzmann's factor and $\beta = 1/k_B T$. In case of a constant force $\mathbf{f} = -\vec{\nabla} U = const$, and constant diffusivity D, the solution to this equation is a "running" Gaussian function: $P(\mathbf{r},t) = (4\pi D t)^{-d/2} \exp[(\mathbf{r} - \mu \mathbf{f} t)^2 / 4Dt]$.

1.2 Langevin's Equation

An alternative route for describing the dynamics of a Brownian particle is the Langevin equation of motion [2] [14]

$$m\frac{dv(t)}{dt} = -\alpha(x)v(t) + f(x) + \xi(t), \tag{1.9}$$

which is Newton's second law describing the motion of a particle of mass m, where in addition to the conservative force, $f(x)$, the particle experiences two forces originating from collisions with the medium molecules. These include a friction force $-\alpha(x)v$, where $v(t)$ is the velocity of the particle and $\alpha(x)$ is the friction coefficient which may depend on the coordinate, and a stochastic white noise with the following statistical properties:

$$\langle \xi(t) \rangle = 0 \tag{1.10}$$

[2] In this section we consider for simplicity the one-dimensional case. In $d > 1$ dimensions, the equation can be decoupled into d one-dimensional Langevin equations.

$$\langle \xi(t)\xi(t')\rangle = \Gamma\delta(t-t'). \tag{1.11}$$

For constant α and f, the solution to this stochastic differential equation is:

$$v(t) = v_0 e^{-\alpha t/m} + \frac{f}{\alpha}\left(1 - e^{-\alpha t/m}\right) + \frac{1}{m}\int_0^t \xi(t')e^{-(t-t')\alpha/m}dt', \tag{1.12}$$

where v_0 denotes the initial velocity of the particle.

In order to find the relation between the diffusion coefficient D and the friction coefficient α, we consider the special case of $f = 0$ [3], and calculate the velocity's autocorrelation function (ACF):

$$\begin{aligned}\langle v(t')v(t'')\rangle &= \langle v_0^2\rangle e^{-\alpha(t'+t'')/m} + \frac{1}{m^2}\int_0^{t'}\int_0^{t''}\langle \xi(t_1)\xi(t_2)\rangle e^{-\alpha(t'+t''-t_1-t_2)/m}dt_1dt_2 \\ &= e^{-\alpha(t'+t'')/m}\left[\langle v_0^2\rangle - \frac{\Gamma}{2\alpha m}\right] + \frac{\Gamma}{2\alpha m}e^{-\alpha|t'-t''|/m}.\end{aligned} \tag{1.13}$$

Substituting $t' = t'' = t$ into Eq. (1.13), and arrive at:

$$\left\langle v^2\right\rangle = e^{-2\alpha t/m}\left[\left\langle v_0^2\right\rangle - \frac{\Gamma}{2\alpha m}\right] + \frac{\Gamma}{2\alpha m}. \tag{1.14}$$

In order to find Γ, we apply the equipartition theorem which states that the internal energy of a system composed of a large number of particles at thermal equilibrium will distribute itself evenly among the degrees of freedom. Specifically, the theorem implies that:

$$\left\langle \frac{1}{2}mv^2\right\rangle_{eq} = \frac{1}{2}k_BT. \tag{1.15}$$

As follows, the equilibrium variance satisfies:

$$\left\langle v^2\right\rangle_{eq} = \frac{k_BT}{m}. \tag{1.16}$$

Now, by taking the limit of $t \to \infty$ in Eq. (1.14), and by using Eq. (1.16), we arrive at:

$$\langle v^2\rangle_{eq} = \frac{\Gamma}{2\alpha m} = \frac{k_BT}{m}, \tag{1.17}$$

[3] It is assumed that the white noise statistics (i.e. Γ) is independent of the determinant force.

which leads to $\Gamma = 2\alpha k_B T$, and the noise autocorrelation function [Eq. (1.11)] reads:

$$\langle \xi(t)\xi(t')\rangle = 2\alpha k_B T \delta(t-t'). \tag{1.18}$$

Eq. (1.18) describes the relationship between the thermal fluctuations and the friction of the medium in accordance to the *fluctuation-dissipation theorem*. Notice that if the initial velocity is drawn from the equilibrium Maxwell-Boltzmann distribution, i.e., satisfies Eq. (1.16), then the first term on the r.h.s. of Eq. (1.13) cancels out. Assuming that this is indeed the case then the velocity's ACF satisfies:

$$\langle v(t')v(t'')\rangle = \frac{k_B T}{m} e^{-\alpha|t'-t''|/m}. \tag{1.19}$$

From Eq. (1.19), we can identify the time scale in which a particle's velocity becomes uncorrelated, which is known as the *balistic time* $\tau_b \sim m/\alpha$. Time scales much shorter (longer) than τ_b are referred to as the ballistic (diffusive) dynamic regimes.

The particle displacement $\Delta x(t)$ is related to the velocity by integration:

$$\Delta x(t) = x(t) - x_0 = \int_0^t v(t')dt', \tag{1.20}$$

and from Eq.(1.10) we find that $\langle \Delta x\rangle = 0$. By squaring Eq. (1.20) and averaging over all the noise realizations, we arrive at:

$$\langle \Delta x^2\rangle = \int_0^t \int_0^t \langle v(t')v(t'')\rangle dt'dt''. \tag{1.21}$$

Substituting Eq. (1.19) into Eq. (1.21) gives:

$$\langle \Delta x^2\rangle = \frac{k_B T}{m}\int_0^t \int_0^t e^{-\frac{|t'-t''|}{\tau_b}} dt'dt'' = \frac{2k_B T}{\alpha}\left[t - \frac{m}{\alpha}\left(1 - e^{-t/\tau_b}\right)\right]. \tag{1.22}$$

Eq. (1.22) can be divided into two regions of interest:

$$\langle \Delta x^2\rangle = \begin{cases} \dfrac{k_B T}{m} t^2 = \left\langle v_0^2\right\rangle_{eq} t^2 & t \ll \tau_b \quad (1.23) \\ \dfrac{2k_B T}{\alpha} t & t \gg \tau_b \quad (1.24) \end{cases}$$

Eqs. (1.23)-(1.24) show that the dynamics are diffusive (i.e., $\langle \Delta x^2 \rangle \sim t$) only at the large time scales of the diffusive regime. Only in this regime the Langevin and Smoluchowski descriptions of the dynamics are equivalent, and can be derived from one another [15]. By comparing Eq. (1.24) to Eq. (1.6) with $d = 1$ we arrive at Einstein's relation:

$$D = \frac{k_B T}{\alpha} = k_B T \mu, \tag{1.25}$$

where the friction α and the mobility μ are inversely related: $\alpha = 1/\mu$.

In the balistic regime ($t \ll \tau_b$) $\Delta x \simeq v_0 t$ and, thus, $\Delta x^2 \simeq (v_0 t)^2$. In Eq. (1.23) it is assumed that the initial velocity is drawn from the equilibrium Maxwell-Boltzmann distribution, i.e., satisfies Eq. (1.16).

1.3 Numerical Integration

1.3.1 The G-JF algorithm

In most cases, the Smoluchowski equation [Eq. (1.8)] is either unsolvable analytically or may require many approximations in order to simplify the problem and make it analytically solvable. A useful way to obtain or verify such solutions is to use the correspondence between the diffusion equation and the associated Langevin equation. The PDF that solves the Smoluchowski equation can be calculated numerically, by simulating an ensemble of Langevin dynamics trajectories. In order to generate such trajectories, an algorithm for numerically integrating the Langevin equation (1.9) is required. Here we use the algorithm of Grønbech-Jensen and Farago (G-JF) [16, 17],which is known for producing accurate configurational equilibrium sampling of molecular systems. The method is based on the underdamped Langevin equation [i.e., including the inertial term on the l.h.s. of Eq. (1.9)], and (as discussed above) generates statistics that are equivalent to the overdamped Smlochowsky equation in the diffusive region ($t \gg \tau_b$), i.e., after the short time scale inertial effects have been decayed. The G-JF algorithm advances the system each time by one time step from t_n to $t_{n+1} = t_n + dt$. Every time step the position and velocity of the particle at time t_n, denoted by x^n and v^n respectively, are calculated using the following set of discrete-time

equations:

$$x^{n+1} = x^n + bdtv^n + \frac{bdt^2}{2m} f^n + \frac{bdt}{2m}\xi^{n+1} \tag{1.26}$$

$$v^{n+1} = av^n + \frac{dt}{2m}\left(af^n + f^{n+1}\right) + \frac{b}{m}\xi^{n+1}, \tag{1.27}$$

where $f^n = f\left(x^n\right)$ is the *deterministic* force acting on the particle, ξ^{n+1} is a Gaussian random number satisfying

$$\langle \xi^n \rangle = 0 \; ; \; \left\langle \xi^n \xi^l \right\rangle = 2\alpha k_B T dt \delta_{n,l}, \tag{1.28}$$

and the dampening coefficients of the algorithm are

$$b = \left[1 + (\alpha dt/2m)\right]^{-1} \; ; \; a = \left[1 - (\alpha dt/2m)\right] b. \tag{1.29}$$

1.3.2 Simulating a coordinate dependent friction $\alpha(x)$

If the friction varies in space, $\alpha(x)$, the above equations (1.26) and (1.27) must be complemented with a convention for choosing the value of α to be used in Eqs. (1.28)-(1.29) at each time step. Choosing the appropriate convention is known in the literature as the "Itô-Stratonovich dilemma" after the two most commonly used conventions - the one of Itô [18] which uses the value of α at the beginning of the time step, and the one of Stratonovich [19] which takes the average of the friction function at the initial and the end points. In the overdamped limit of the Langevin equation (i.e., when the left-hand side of Eq. (1.9) vanishes), neither of these two interpretations reproduce the equilibrium Boltzmann distribution. It is Hänggi's (isothermal) convention [20], in which the friction is chosen from the end of the time step, which generates the correct equilibrium statistics.

For the underdamped Langevin equation, all (reasonable) conventions lead to the correct equilibrium description in the limit of $dt \to 0$[4]. Here, we use the recently proposed inertial convention [12, 21] that assigns to α^{n+1} the value of the spatial average of α along

[4]This is because the underdamped Langevin equation is second order in x, while the overdamped approximation is a first order equation. In the latter (overdamped) equation, the velocity is a stochastic (noisy) variable rather than a physical one.

the inertial trajectory from x^n to $\tilde{x}^{n+1} = x^n + v^n dt$

$$\alpha^{n+1} = \frac{\int_{x^n}^{\tilde{x}^{n+1}} \alpha(x)dx}{\tilde{x}^{n+1} - x^n} \approx \frac{\alpha(\tilde{x}^{n+1}) + \alpha(x^n)}{2}, \tag{1.30}$$

where the approximation in the r.h.s. is acceptable for slowly varying friction coefficients. The advantage of using the inertial convention is that it produces accurate computational results even for time steps that are not extremely small.

1.4 Periodic Systems

Brownian motion in a periodic systems constitutes one of the fundamental problems of particle transport with numerous applications in various fields of science and technology. Many classical examples of diffusion in periodic systems are found in the area of condensed matter physics, including diffusion of atoms in and on the surface of lattices [22, 23], and fluctuations of Josephson supercurrent through a tunneling junction [24]. In many situations, e.g., the cases of superionic conductors [25] and rotating dipoles in external fields [26], a constant force which biases the stochastic dynamics in a given direction is also present. In such scenarios, often referred to as diffusion in a *tilted* periodic potential, different types of dynamics are observed in the overdamped (high friction) regime depending on whether the total potential energy (the sum of periodic and linear potentials) has minima or not [27]. In the former case, the particle moves from one minimum to another and the solution is termed "locked"; in the latter case, the particle moves down the corrugated potential gradient and the solution in termed "running" [28].

The problem of diffusion in periodic systems is also relevant to the study of thermal ratchets [29]. Thermal ratchets employ a time-varying spatially-asymmetric periodic potential that drives isothermal systems out of equilibrium and allows for the rectification of the thermal noise in the form of a directed probability (particle) flux. Thermal ratchets attracted much renewed interest in the 1990s' as possible models for motor proteins [30]. Advances in various experimental techniques, most notably in optical trapping ("tweezers") devices, have led to novel experimental setups where some of the new theoretical concepts were tested [31]. Another closely-related problem attracting considerable recent attention is diffusion in cor-

rugated channels [32]. Understanding Brownian motion in confined geometries is important for the study of transport of materials in, e.g., zeolites [33] and microfluidic channels [34]. Such dynamics can be studied by considering a 1D Fick-Jacobs diffusion equation of a particle moving in the presence of an effective potential of mean force arising from the variations in the cross-sectional area of the channel [35, 36].

When describing the dynamics of a particle, one of the most interesting features is the effective diffusion coefficient defined by:

$$D^* = \lim_{t\to\infty} \frac{\langle \Delta x^2 \rangle}{2t}. \tag{1.31}$$

In periodic systems, D^* can be found by using the Lifson-Jackson (LJ) formula [37]:

$$D^* = \frac{D}{\langle e^{-\beta U(x)} \rangle \langle e^{\beta U(x)} \rangle}. \tag{1.32}$$

The effective diffusion coefficient D^* is smaller or equal to the medium diffusion coefficient D, since the particles tend to linger at the minima of the potential, which slows down their diffusivity. As the potential function flattens (i.e., the force $f \to 0$), D^* approaches the medium coefficients $D^* \to D$. Eq. (1.32) applies for the special case of a constant diffusion coefficient. When generalizing to the case of a preiodic space dependent $D(x)$, the correct equation is the modified Lifson-Jackson equation (MLJ):

$$D^* = \frac{D}{\langle e^{-\beta U(x)} \rangle \langle e^{\beta U(x)}/D(x) \rangle}. \tag{1.33}$$

The LJ and MLJ formulas, which are derived from the Smoluchowski equation (1.8), are valid only when the potential barrier, $\Delta U = U_{\max} - U_{\min}$ is not too high. In the high barrier limit, $\beta\Delta U \gg 1$, the particle only rarely escapes the vicinity of a potential minimum, and it advances to a neighboring cell with a characteristic time that scales as $\tau \sim \exp(\beta\Delta U)$. In this limit, the effective diffusion coefficient is expected to follow an Arrhenius-Kramer behavior [38]: $D^* \sim De^{-\beta\Delta U}$.

1.5 Thesis Outline

This thesis is organized as follows. In chapter 2 we discuss the problem of single particle diffusion in a 1D medium with periodic potential and constant diffusion coefficient D. We present the asymptotic (at long times) solution to the Smoluchowski equation (1.8), and evaluate the effective diffusion coefficient D^* in the limits $\Delta U \gg k_B T$ and $\Delta U \ll k_B T$. In chapter 3, we address the problem of diffusion in a two-dimensional (2D) periodic channel which is unbounded in the x direction, and restricted in the orthogonal direction $0 < y < A(x)$, where $A(x)$ is a periodic function. This situation can be mapped into a 1D diffusion equation of a particle moving under the action of a periodic potential of mean force $U(x) = -k_B T \ln[A(x)]$ with a (periodic as well) space-dependent diffusion coefficient $D(x)$. Chapter 4 summarizes the research work.

Chapter 2

Diffusion in Periodic Potentials

2.1 Introduction

We consider 1D overdamped diffusion with constant diffusion coefficient D. The probability distribution function, $P(x,t)$, of finding the particle at coordinate x at time t can be found by solving the Smoluchowski equation (1.8)

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial}{\partial x}\left\{e^{-\beta U(x)}\frac{\partial}{\partial x}\left[e^{\beta U(x)}P(x,t)\right]\right\}. \tag{2.1}$$

Throughout this work, we assume that $U(x)$ is an even periodic function with period λ and consider a particle initially located at the origin, i.e., $P(x,t=0)=\delta(x)$, where δ is the Dirac delta-function. From symmetry considerations, the mean displacement of the particle vanishes identically, $\langle x\rangle = 0$. The mean-squared displacement does not vanish but rather exhibits, at asymptotically large times, a linear growth with time characterizing the diffusive nature of the dynamics.

Despite the extensive theoretical literature on the problem of diffusion in periodic potentials, the general solution of Eq. (2.1) subject to the delta-function initial condition is not known. In this chapter, we close this gap in the literature and find an asymptotic (at large times) solution for the Smoluchowski equation for any even periodic potential function $U(x)$. We use Langevin dynamics simulations of a case-study to demonstrate excellent agreement between our analytical solution and the computed PDF. As part of our derivation, we independently arrive at the LJ formula (1.32), derived from Eq. (2.1), for the effective

diffusion coefficient D^*.

As discussed in section (1.2), Langevin dynamics are inertial at time scales much smaller than the ballistic time $\tau_b = m/\alpha$, during which the particle moves a characteristic distance $l_b \sim v_{\rm th}\tau_b$, where $v_{\rm th} = \sqrt{k_B T/m}$ is the thermal velocity of the particle. The dynamics becomes diffusive at length scales much larger than l_b. Moreover, the Smoluchowski Eq. (2.1) correctly describes the dynamics only if the spatial variations of the deterministic force $f = -dU/dx$ on length scales of the order of l_b are much smaller than the characteristic friction force, i.e., for $(m/\alpha^2)|df/dx| \ll 1$ [40]. In the case of a periodic force $|df/dx| \sim \Delta U/\lambda^2$, where λ is the periodicity, implying that Eq. (2.1) may not be valid when the periodic length of the potential becomes comparable to the ballistic length, or in the case when $\Delta U \gg k_B T$. We will later see that, indeed, in these limits, the LJ formula derived from Eq. (2.1) fails to depict correctly the effective diffusion coefficient D^*.

We notice that if $U(x)$ is periodic then the Boltzmann's weight $\exp[-\beta U(x)]$ is also a periodic function. We thus define the periodic function $\eta(x)$

$$1 + \epsilon\eta(x) = \frac{e^{-\beta U(x)}}{\left\langle e^{-\beta U(x)}\right\rangle}, \tag{2.2}$$

with the variable

$$\epsilon = 1 - \frac{e^{-\beta U_{max}}}{\left\langle e^{-\beta U(x)}\right\rangle} \tag{2.3}$$

satisfying $0 \leq \epsilon < 1$. The function $\eta(x)$ has the following properties: (i) $\langle\eta(x)\rangle = 0$, and (ii) min[$\eta(x)$]=-1. With the definition of ϵ and $\eta(x)$, the Smoluchowski equation (2.24) takes the form

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial}{\partial x}\left\{[1+\epsilon\eta(x)]\,\frac{\partial}{\partial x}\frac{P(x,t)}{[1+\epsilon\eta(x)]}\right\}, \tag{2.4}$$

and LJ formula (1.32) reads

$$D^* = \frac{D}{\left\langle [1+\epsilon\eta(x)]^{-1}\right\rangle}. \tag{2.5}$$

In the high barrier limit $\epsilon \to 1$, we expect the Arrhenius-Kramer law which takes the form

$$D^* \sim D(1-\epsilon). \tag{2.6}$$

2.2 Langevin dynamics simulations

We simulate the dynamics of a particle of unity mass $m = 1$ moving in a system with friction coefficient $\alpha = 1$ at constant temperature $k_B T = 1$. For this choice of parameters the ballistic time $\tau_b \sim m/\alpha = 1$ and ballistic length $l_b \sim \sqrt{m k_B T}/\alpha = 1$. As a numerical example, we consider the case where $\eta(x) = \cos(2\pi x/\lambda)$ ($f(x) = -U'(x) = k_B T \epsilon \eta'(x)/[1 + \epsilon\eta(x)]$). The particle's trajectory begins at $x = 0$ with initial velocity which is drawn from the equilibrium Maxwell-Boltzmann distribution, and is numerically integrated using the G-JF algorithm with $dt = 0.1$, which is an order of magnitude smaller than τ_b. The numerical results presented here are based on statistical averages of 2×10^8 independent trajectories. Fig. 2.1(a) shows the ratio between $\langle x^2 \rangle$ and $2t$ [see Eq. (1.31)] as a function of t for $\epsilon = 0.5$ and $\lambda = 50 \gg l_b$. At asymptotically large times, this ratio converges to the effective diffusion coefficient $D^* \simeq 0.863$ which is indeed smaller than the medium diffusion coefficient $D = k_B T/\alpha = 1$. The open circles in Fig. 2.1(b) show our computational results for D^*/D as a function of ϵ, for $\lambda = 50$. The results exhibit excellent agreement with the solid line depicting the LJ formula (2.5) which, for the specific choice of $\eta(x)$ discussed here, gives $D^*/D = \sqrt{1-\epsilon^2}$. Very small deviations from the LJ formula are observed for $\epsilon > 0.6$ when the potential barrier becomes larger [$\exp(-\beta\Delta U) \lesssim 0.17$]. In contrast, the results for $\lambda = 2$, which are plotted in Fig. 2.1(c), exhibit agreement with LJ formula only for $\epsilon < 0.1$. This behavior is expected since LJ formula is derived from the Smoluchowski equation, but the latter becomes invalid when λ is comparable to the ballistic length l_b. For $\epsilon \to 1$, we observe that D^*/D diminishes like $(1-\epsilon)$, in accordance with Eq. (2.6).

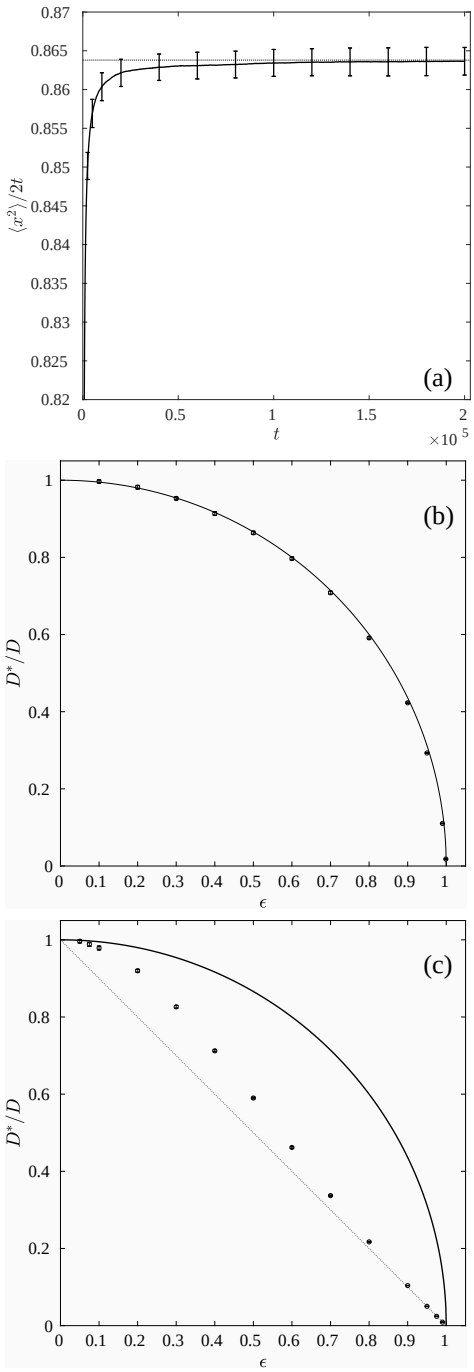

Figure 2.1: (a) The ratio between the mean squared displacement and twice the time, $D^* = \langle x^2 \rangle / 2t$, as a function of t for $\epsilon = 0.5$ and $\lambda = 50$. At large times this ratio converges to $D^* \simeq 0.863$ that matches the value for the effective diffusion coefficient D^* predicted by the LJ formula. (b) The effective diffusion coefficient D^* (normalized by the medium diffusion coefficient D) as a function of ϵ for $\lambda = 50$. Circles - simulation results, solid curve - the LJ formula. (c) Same as (b) for $\lambda = 2$. The dashed line depicts the function $(1 - \epsilon)$.

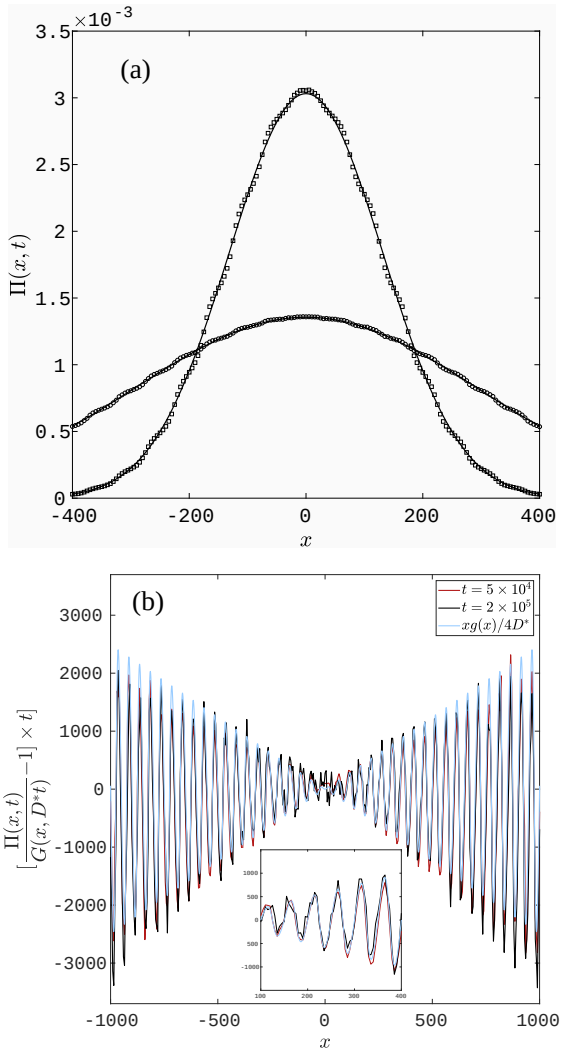

Figure 2.2: (a) The function $\Pi(x,t)$ as a function of x for $\epsilon = 0.5$ and $\lambda = 50$, at $t = 10^4$ (squares) and and $t = 5\times10^4$ (circles). The solid curves depict the Gaussian form $G(x, D^*t) = \exp(-x^2/4D^*t)/\sqrt{4\pi D^*t}$ with $D^* = 0.863$. (b) The function $t\,[\Pi(x,t)/G(x,D^*t) - 1]$ as a function of x for $t = 5 \times 10^4$ (red) and $t = 2 \times 10^5$ (black). The light blue curve is the analytical approximation $xg(x)/(4D^*)$ with $g(x)$ given by Eq. (2.15). The inset shows a magnification of the region with the best agreement between the analytical approximation and numerical results.

Fig. 2.2(a) shows the PDF normalized by the Boltzmann factor, $\Pi(x,t) = P(x,t)/[1 + \epsilon\eta(x)]$, for $\epsilon = 0.5$ and $\lambda = 50$ at $t = 10^4$ (squares) and $t = 5 \times 10^4$ (circles). The graphs indicate that at large times, the function $\Pi(x,t)$ is very well approximated by a Gaussian form (solid lines) $G(x, D^*t) = \exp(-x^2/4D^*t)/\sqrt{4\pi D^*t}$, where $D^* = 0.863$ is the

effective diffusion coefficient for the corresponding values of ϵ and λ (see above). This, however, is only an approximation, and it is straightforward to check that $P(x,t) = [1 + \epsilon\eta(x)]G(x, D^*t)$ is *not* a solution of Eq. (2.4). Careful inspection of Fig. 2.2(a) reveals small undulations of $\Pi(x,t)$ with wavelength λ around the Gaussian form. We thus speculate that the Gaussian form is the leading term in an expression including additional terms, and write $P(x,t) = [1 + \epsilon\eta(x)]G(x, D^*t)\,[1 + q_0(x) + q_1(x,t)]$, where $q_0(x)$ and $q_1(x,t)$ denote, respectively, static and time-decaying corrections exhibiting oscillations with periodicity λ. The static term can be ruled out based on the simple argument that it contributes a term equal to $G(x, D^*t)\, d\{[1 + \epsilon\eta(x)]q_0'(x)\}/dx$ on the right hand side of Eq. (2.4), and this term dominates the asymptotic behavior of $\partial_t P(x,t)$ at long times. Since the Gaussian function $G(x, D^*t)$ is positive, it follows that the long time limit of $\partial_t P(x,t)$ has the same sign as the *static* function $d\{[1+\epsilon\eta(x)]q_0'(x)\}/dx$ that oscillates between positive and negative values [1]. This, however, is impossible because the particle propagates to further distances with time and the probability density cannot accumulate at any point in space. Stated differently, for any x_0, the probability density $P(x_0,t)$ must decay at large times, namely $\partial_t P(x_0,t) < 0$ for some $t > t_0$. This property of $P(x,t)$ precludes the possibility of a static correction $q_0(x)$ and allows only a time-decaying term $q_1(x,t)$.

Insight into the form of the time-decaying correction can be gained from Fig. 2.2(b) where we plot the function $t\,[\Pi(x,t)/G(x, D^*t) - 1] = tq_2(x,t)$ as a function of x for $\epsilon = 0.5$ and $\lambda = 50$, at $t = 5 \times 10^4$ (red) and $t = 2 \times 10^5$ (black). While the collapse of the data for the different times is not perfect, it seems to indicate that the time-decaying correction may have the form $q_1(x,t) \sim (x/t)g(x)$, where $g(x)$ is a scaling function with periodicity λ. This term decays at a rate $t^{1/2}$ faster than the leading Gaussian form because of the scaling $x \sim (D^*t)^{1/2}$. (Larger values of x need not be considered because for $x^2 \gg D^*t$ the PDF is practically zero.) The solution can be further refined by introducing a series of corrections $P(x,t) = [1 + \epsilon\eta(x)]G(x, D^*t)\,[1 + q_1(x,t) + q_2(x,t) + \cdots]$, with each term decaying $t^{1/2}$ faster than the previous one. Here, we attempt to find the first two leading

[1] The last statement is incorrect when $q_0'(x) = [1 + \epsilon\eta(x)]^{-1}$. However, this possibility can be ruled out since in this case the average slope of q_0 does not vanish, which implies that $q_0(x)$ and, therefore, also the probability density $P(x,t)$ obtain large negative values for some x.

corrections and, therefore, consider the following form [2]

$$P(x,t) = \left\{ [1+\epsilon\eta(x)]\, G(x,D^*t) \left[1 + \frac{\lambda x g(x)}{4D^*t} Q_1\left(\frac{x^2}{4D^*t}\right) + \frac{\lambda^2 h(x)}{4D^*t} Q_2\left(\frac{x^2}{4D^*t}\right) \right] \right\}, \quad (2.7)$$

where $g(x)$ and $h(x)$ are two dimensionless functions with periodicity λ, while Q_1 and Q_2 are polynomials in $x^2/4D^*t$. This solution constitutes the *asymptotic* solution to Smoluchowski equation (2.4) at large times $t \gg \tau_b$, up to order $G(x,D^*t)/t \sim 1/t^{3/2}$.

2.3 The probability distribution:

We consider a symmetric system with an even function $\eta(x)$, which implies that the PDF is symmetric and, therefore, $g(x)$ must be an odd function while $h(x)$ is even. Both scaling functions are periodic with periodicity λ and have a finite amplitude. Thus, $\eta'(x)$, as well as $g'(x)$ and $h'(x)$, are all of order $1/\lambda$. With this in mind, we substitute the solution (2.7) into Eq. (2.4). On the right hand side, we find terms that scale as like $G(x,D^*t)(x/\lambda t)$. These terms must cancel each other, which occurs provided that (i) $Q_1 = const$ (which, by a proper definition of $g(x)$, can be arbitrarily set to unity), and (ii) the scaling function $g(x)$ satisfies the ordinary differential equation

$$[1+\epsilon\eta(x)]\,\lambda g''(x) + \epsilon\eta'(x)\,[\lambda g'(x) - 2] = 0. \quad (2.8)$$

Taking into account that $g(x)$ is an odd function and therefore $g(0) = 0$, we readily arrive at the solution

$$\lambda g(x) = kI\left[\frac{1}{1+\epsilon\eta(x)}\right] + 2x, \quad (2.9)$$

where $I[y(x)]$ denotes the primitive function of $y(x)$ with $I(x=0) = 0$. The constant k can be found from the requirement that $g(x)$ is periodic. Thus, $\int_0^\lambda g'(x)dx = g(\lambda) - g(0) = 0$,

[2] We note that (because $g(x)$ is a periodic function which also assumes negative values) the solution (2.7) becomes negative for some $x \gg D^*t/\lambda$,which is obviously impossible. At large times, this regime is found at the tail of the distribution function where PDF is, anyhow, negligible.

which gives

$$k = -\frac{2}{\left\langle [1+\epsilon\eta(x)]^{-1} \right\rangle}. \tag{2.10}$$

We now proceed and find the function $h(x)$ and the polynomial Q_2 by comparing terms of the form $G(x, D^*t)(x^2/4D^*t)^n/t$ (where n is an integer), on both sides of Eq. (2.4). From this comparison, we readily conclude that $Q_2\left(x^2/4D^*t\right) = [1 + bx^2/(4D^*t)]$. This leaves us with two different differential equations for the scaling function $h(x)$ which cannot be solved simultaneously unless we set $b = -2$, in which case the equations coincide and read

$$\begin{aligned} &(1+\phi)\,[1+\epsilon\eta(x)]\left[\lambda^2 h''(x) + 2\lambda g'(x)\right] + \\ &(1+\phi)\,\epsilon\eta'(x)\left[\lambda^2 h'(x) + \lambda g(x)\right] = 2\phi\,[1+\epsilon\eta(x)]\,, \end{aligned} \tag{2.11}$$

where $\phi = D/D^* - 1$. By defining the function $\tilde{h}(x) = [1+\epsilon\eta(x)]\,[\lambda^2 h'(x) + \lambda g(x)]$, we arrive at the simple equation

$$\tilde{h}'(x) = -\left[\frac{2}{1+\phi} + k\right] - \frac{2\epsilon\eta(x)}{1+\phi}, \tag{2.12}$$

which can be integrated once to yield $\tilde{h}(x)$, from which the scaling function $h(x)$ can be derived by performing yet another integration in x. Importantly, the fact that $h(x)$ is an even periodic function with a finite amplitude imposes the relationship $2/(1+\phi) + k = 0$ from which D^* can be deduced. Using Eq. (2.10) we find

$$D^* = \frac{D}{1+\phi} = -\frac{kD}{2} = \frac{D}{\left\langle [1+\epsilon\eta(x)]^{-1} \right\rangle}, \tag{2.13}$$

which is identical to the LJ formula (2.5). The scaling function $h(x)$ is given by

$$\lambda^2 h(x) = kI\left\{\frac{I\,[\epsilon\eta(x)]}{1+\epsilon\eta(x)} - I\left[\frac{1}{1+\epsilon\eta(x)}\right]\right\} - x^2 + \lambda^2 C, \tag{2.14}$$

where the constant C is determined by the normalization condition $\int_{-\infty}^{\infty} P(x,t)dx = 1$ (which must be satisfied up to an order of $1/t$).

Returning to our simulation results above for $\eta(x) = \cos(2\pi x/\lambda)$, the corresponding

scaling function $g(x)$ can be found

$$g(x) = -\frac{2}{\pi}\arctan\left[\sqrt{\frac{1-\epsilon}{1+\epsilon}}\tan\left(\frac{\pi x}{\lambda}\right)\right] + \frac{2x}{\lambda}, \tag{2.15}$$

where the arctan function is interpreted such that it returns a value between $-\pi/2$ and $\pi/2$ which is then shifted by an integer number of π in order that $g(\lambda/2+n\lambda) = 0$ (where n is an integer). We were unable to find the scaling function $h(x)$; however, we take advantage of the fact that it represents a correction to the Gaussian form of $\Pi(x,t)$ which is asymptotically smaller than the one involving the function $g(x)$ [see Eq. (2.7)], and use the approximation $t\,[\Pi(x,t)/G(x,D^*t) - 1] \simeq xg(x)/(4D^*)$. This approximation, which is plotted in Fig. 2.2(b) in light blue, shows a good fit to the simulation results. The deviations, which can be attributed to the higher order correction term in Eq. (2.7), are particularly small for $x^2 \simeq 2D^*t$ - see inset in Fig. 2.2(b).

2.4 Coordinate-dependent diffusion coefficient

Let us now consider the same system, but with a space-dependent diffusion periodic function, $D(x)$, with periodicity λ similar to that of $\eta(x)$. In the next chapter we will discuss the connection of this 1D equation to the problem of diffusion in 2D periodic channels. We now need to solve the Smoluchowski equation (1.8), the solution of which has the same general form as in Eq. (2.7). Focusing on the leading time-decaying term, we write

$$P(x,t) = [1+\epsilon\eta(x)]G(x,D^*t)\left[1+\frac{\lambda x g(x)}{4D^*t}\right], \tag{2.16}$$

which is correct up to order $\mathcal{O}(G/t^{1/2}) \sim \mathcal{O}(1/t)$ provided that the correct function $g(x)$ is found. This is done by substituting the solution (2.7) into Eq. (1.8) and comparing terms that scale like $G(x,D^*t)(x/t)$, which yields the following differential equation

$$\{D(x)[1+\epsilon\eta(x)](g'-2)\}' = 0. \tag{2.17}$$

Integrating this equation once with respect to x gives

$$g' = 2 + \frac{c_1}{[1+\epsilon\eta(x)]D(x)}. \tag{2.18}$$

The constant c_1 can be determined by acknowledging that $g(x)$ is periodic and, therefore,

$$0 = g(\lambda) - g(0) = \int_0^\lambda g'(x)dx = 2\lambda + c_1 \int_0^\lambda \frac{dx}{[1+\epsilon\eta(x)]D(x)}. \tag{2.19}$$

Thus, the constant c_1 is given by:

$$c_1 = -\frac{2}{\langle\{[1+\epsilon\eta(x)]D(x)\}^{-1}\rangle}. \tag{2.20}$$

Integrating Eq. (2.18) once again with respect to x gives

$$g(x) = 2x - \frac{2}{\langle\{[1+\epsilon\eta(x)]D(x)\}^{-1}\rangle} I\left[\frac{1}{D(x)[1+\epsilon\eta(x)]}\right], \tag{2.21}$$

which reduces to (2.9) when $D(x) = const.$ Notice that when the diffusion coefficient depends on the coordinate x, the effective diffusion coefficient D^* is given by the modified Lifson Jackson (MLJ) formula (1.33), which in terms of $\eta(x)$ reads

$$D^* = \frac{1}{\langle D(x)[1+\epsilon\eta(x)]\rangle} \tag{2.22}$$

which reduces to (2.5) when $D(x) = const$, and allows one to also write

$$g(x) = 2x - 2D^* I\left[\frac{1}{D(x)[1+\epsilon\eta(x)]}\right]. \tag{2.23}$$

2.5 Diffusion in a tilted periodic potential

Another interesting problem is when a particle diffuses in a medium with constant diffusivity D, under the action of both a periodic potential $U(x)$ and a constant force f, the

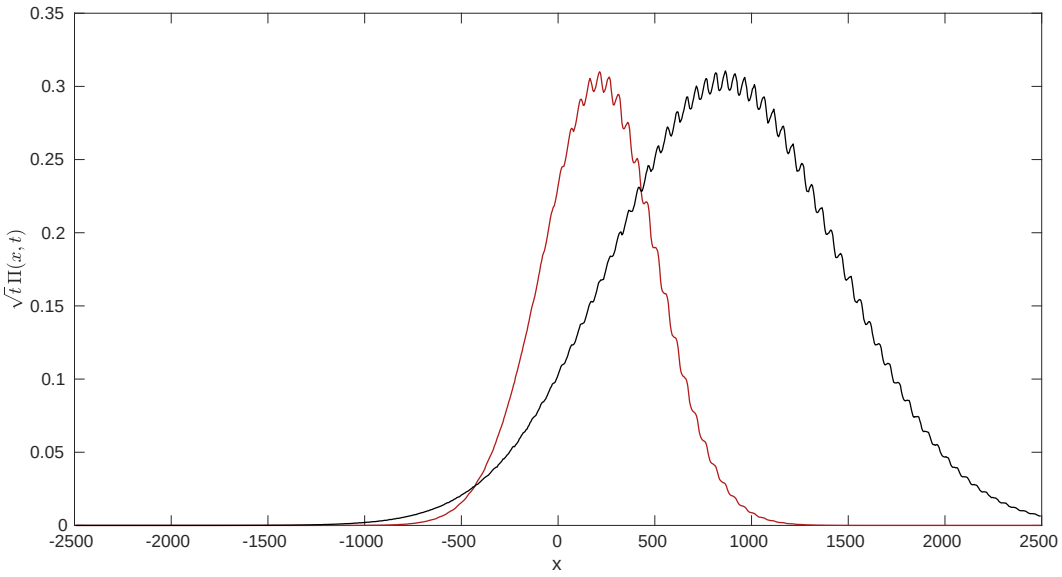

Figure 2.3: The function $\sqrt{t}\Pi(x,t)$ vs. x for $\eta(x) = \cos(2\pi x)$, $\epsilon = 0.5$, $\lambda = 50$ and $f = 0.005$, at $t = 5 \times 10^4$ (red) and $t = 2 \times 10^5$ (black).

Smoluchowski equation reads

$$\begin{aligned}\frac{\partial P(x,t)}{\partial t} &= D\frac{\partial}{\partial x}\left\{e^{-\beta(U(x)-fx)}\frac{\partial}{\partial x}\left[e^{\beta(U(x)-fx)}P(x,t)\right]\right\} \\ &= -\mu f\frac{\partial P}{\partial x} + D\frac{\partial}{\partial x}\left\{\left[1+\epsilon\eta(x)\right]\frac{\partial}{\partial x}\frac{P(x,t)}{\left[1+\epsilon\eta(x)\right]}\right\},\end{aligned} \tag{2.24}$$

where $\mu = D/k_BT$, while $\eta(x)$ and ϵ are defined similarly to Eq. (2.2).

In Fig. 2.3, we present Langevin dynamics simulations results of the same system as in Fig. 2.2 of the non-tilted potential with an additional constant force $f = 0.005$. The graph shows $\sqrt{t}\Pi(x,t) = \sqrt{t}P(x,t)/[1+\epsilon\eta(x)]$ as a function of x at different times [$t = 5 \times 10^4$ (red) and $t = 2 \times 10^5$ (black)]. The two main differences with respect to the case $f = 0$ considered previously: (i) The Gaussian "moves" at constant velocity $f\mu^*$, where $\mu^* \neq \mu$ is the effective mobility coefficient satisfying $\mu^* \to D^*/k_BT$ for $f \to 0$ [41]. (ii) The oscillations of the PDF around the Gaussian form do not decay with time and have the periodicity λ of the potential $U(x)$. This implies that the corrections to the Gaussian form also include a static term $q_0(x)$ missing when $f = 0$. Thus, we speculate that the solution takes the form

$$P(x,t) = \left[1+\epsilon\eta\left(x\right)\right]G\left(x-\mu^* ft, D^*t\right)\left[1+q_0(x)+q_1(x,t)+q_2(x,t)+\cdots\right], \tag{2.25}$$

where $G(x-\mu^* ft, D^* t) = \exp[-(x-\mu^* ft)^2/4D^* t]/\sqrt{4\pi D^* t}$ denotes the "running" Gaussian, while q_1 and q_2 are the time decaying corrections of order $1/t^{1/2}$ and $1/t$, respectively, having the same general form as in Eq. (2.7).

Upon substituting the solution (2.25) into Eq. (2.24) and comparing terms of similar order, we first arrive at the following differential equation for the static term $q_0(x)$

$$\frac{\partial}{\partial x}\left\{\left[1+\epsilon\eta\left(x\right)\right]\left[\beta f+\beta f q_0\left(x\right)-q_0'\left(x\right)\right]\right\}=0. \tag{2.26}$$

From the requirements that (i) $q_0(x)$ does not diverge exponentially for $x \to \infty$, and that (ii) $P(x,t)$ is normalized to unity at any time (including for $t \to \infty$, when the time-decaying terms become irrelevant), we arrive at

$$q_0(x) = \beta f e^{\beta f x} I\left[e^{-\beta f x}\left(\frac{c_1}{1+\epsilon\eta(x)}+1\right)\right], \tag{2.27}$$

and

$$c_1 = \left\{\beta f\left\langle\left[1+\epsilon\eta\left(x\right)\right]e^{\beta f x} I\left[\frac{e^{-\beta f x}}{1+\epsilon\eta(x)}\right]\right\rangle\right\}^{-1}. \tag{2.28}$$

The first time-decaying correction $q_1(x)$ can be now found by solving the equation obtained from the terms that scale as $1/t^{1/2}$. This equation involves the already found static scaling function $q_0(x)$. Then, the second correction, $q_2(x)$, can be found from the equation corresponding to the terms proportional to $1/t$, which involves $q_0(x)$ and $q_1(x)$ (and so on). Notice that the form of q_0 (2.27) does not give any information on the effective parameters μ^* and D^*. These will be found from the equations for q_1 and q_2, respectively.

2.6 Summary

In this chapter, we derived an asymptotic (at large times) expression for the PDF of a particle diffusing in a periodic potential energy landscape $U(x)$. The solution, which is given by Eq. (2.7), is correct to order $O(t^{-3/2})$. Faster decaying corrections can, in principle, be systematically derived by comparing, on both sides of Eq. (2.4), terms of order $O(t^{-2})$, $O(t^{-5/2})$ .... This will require solving increasingly complicated differential equations in-

volving the scaling functions of slower decaying terms. We continued by showing that this approach can also be applied to the case of a coordinate dependent diffusion coefficient $D(x)$, a fact that we will take advantage of in the next chapter in order to project the problem of a 2D channel into an effective 1D description. Finally, we have briefly examined the question of diffusion in a tilted periodic potential, and how our approach can be modified to solve such problems.

Chapter 3

Diffusion in Periodic Channels

3.1 Introduction

In this chapter we address the problem of diffusion in a 2D corrugated channel, which is a special class of periodic systems where there is in fact no potential [42]. We consider a particle moving in an open channel whose long axis lies along the x-direction ($-\infty < x < \infty$). In the perpendicular y direction, the channel is bounded between $0 \leq y \leq A(x)$, where $A(x)$ is a periodic function with wavelength λ. The 2D problem may be mapped onto an effective 1D picture of a particle diffusing in an effective potential of mean force. This potential is derived from the collisions with the reflecting walls of the channel [as depicted by fig. (3.1)], and satisfies $\langle f_x \rangle = -dU_{ent}/dx$. Fig. (3.1) illustrates a periodic channel, where the mean force $\langle f_x \rangle$ biases the dynamics of the particle and forces it towards the areas where the channel height is maximal. (The arrows indicate the direction in which the mean force pushes the particles.) The entropy S, is related to the number of possible states Ω by $S = k_B \ln(\Omega)$, and Ω is proportional to the height of the channel $\Omega \sim A(x)$. Therefore, the entropy scales as

$$S = k_B \ln[A(x)]. \tag{3.1}$$

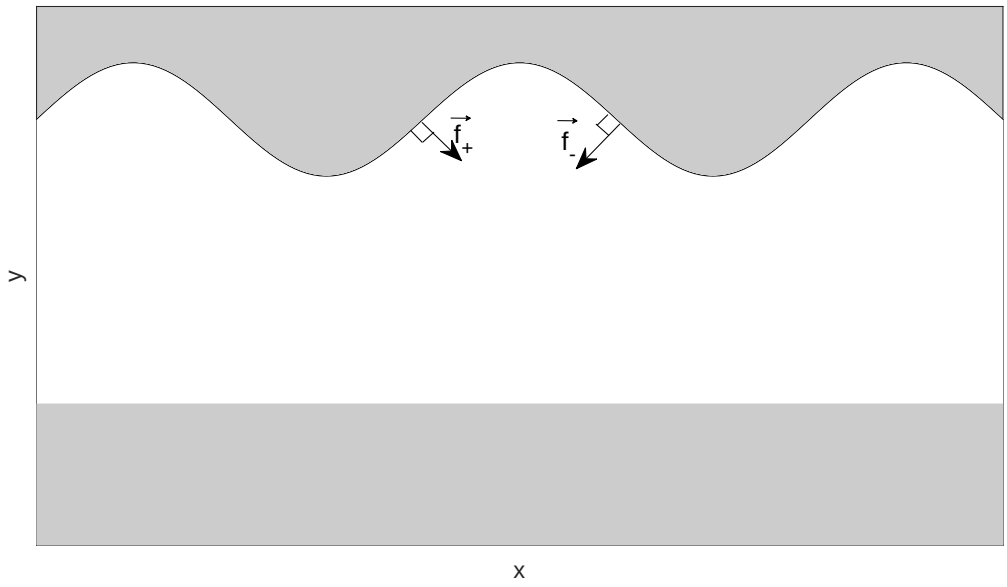

Figure 3.1: An illustration of a two dimensional periodic channel. The arrows indicate the direction of the mean force f_+ and f_- respectively (which is perpendicular to the reflecting wall). f_+ (f_-) is the force where the slope of the wall is most positive (negative) and thus the absolute value of the x coordinate of the mean force f_x is maximal.

In order to take into account the entropy, we calculate the Helmholtz free energy, which satisfies [43]:

$$F(x) = U(x) - TS(x) = U(x) - k_B T \ln[A(x)]. \tag{3.2}$$

When no potential exists in the channel, $U(x) = 0$, we identify the entropic potential as follows:

$$U_{ent}(x) = F(x) = -k_B T \ln[A(x)]. \tag{3.3}$$

The 2D probability density, $\rho(x, y, t)$ [1], satisfies the diffusion equation

$$\frac{\partial \rho(x, y, t)}{\partial t} = D\nabla^2 \rho(x, y, t). \tag{3.4}$$

[1] In chapter 1 we noted the multi-dimensional PDF as $P(\mathbf{r}, t)$. In this chapter we refer to the 2D PDF as $\rho(x, y, t)$, and use $P(x, t)$ to denote the projected 1D PDF.

Equation (3.4) must be solved subject to reflecting (Neumann) boundary conditions on the walls of the channel (see Fig. 3.1)

$$\frac{\partial \rho(x,y,t)}{\partial y}|_{y=0} = 0 \tag{3.5}$$

and

$$\frac{\partial \rho(x,y,t)}{\partial y}|_{y=A(x)} = A'(x)\frac{\partial \rho(x,y,t)}{\partial x}. \tag{3.6}$$

As the motion is limited to the longitudinal x-direction, one is naturally interested in the 1D PDF

$$P(x,t) = \int_0^{A(x)} \rho(x,y,t)\, dy. \tag{3.7}$$

It has been suggested that $P(x,t)$ may be found by solving the 1D Smoluchowski equation describing Brownian dynamics under the action of an entropic potential of mean force as describes by Eq. (3.3)

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial}{\partial x}\left\{e^{-\beta U_{ent}(x)}\frac{\partial}{\partial x}\left[\frac{P(x,t)}{e^{-\beta U_{ent}(x)}}\right]\right\} = D\frac{\partial}{\partial x}\left\{A\left(x\right)\frac{\partial}{\partial x}\left[\frac{P(x,t)}{A\left(x\right)}\right]\right\}. \tag{3.8}$$

This is Eq. (2.4) with $A(x)/A_0 = 1+\epsilon\eta(x)$, and the mean hight of the channel $A_0 = \langle A(x)\rangle = (\lambda)^{-1}\int_0^{\lambda} A(x)dx$. Eq. (3.8) is also known as Fick-Jacobs (FJ) equation [47]. Strictly speaking, the 1D description provided by the FJ equations holds only when the two-dimensional probability density is uniform along the y-direction, i.e., when $\rho(x,y,t) = P(x,t)/A(x)$, which is generally not the case. Since the agreement between the solution of FJ equation (3.8) and simulation results may be quite poor [48,49], a modified version of the FJ equation with a coordinate-dependent diffusion coefficient, $D(x)$, has been considered

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left\{D(x)A(x)\frac{\partial}{\partial x}\left[\frac{P(x,t)}{A(x)}\right]\right\}, \tag{3.9}$$

which is Eq. (1.8) in 1D with $\exp[-\beta U(x)] = A(x)$, and $D(x)$ is supposedly a function of

$A(x)$ and its derivatives [2].

Eq. (3.9) was first derived by Zwanzig [32], by analyzing the temporal evolution of the deviations in the local density from uniformity, $\delta\rho(x,y,t) = \rho(x,y,t) - P(x,t)/A(x)$. From the analysis, Zwanzig concluded that the introduction of a spatially-dependent diffusion coefficient can improve the agreement between the 2D and 1D descriptions, and he proposed the following expression for $D(x)$

$$D_{\rm Z}(x) = \frac{D}{1 + A'^2(x)/3}. \tag{3.10}$$

Notice that the reduction of the 2D diffusion equation (3.4) to an effective 1D equation (3.9) cannot yield exact results since the 2D diffusion process projected onto the x direction is not Markovian and thus cannot be described by a 1D diffusion equation with local diffusion coefficient $D(x)$ [50]. Nevertheless, Zwanzig's framework of Eq. (3.9) for depicting transport in corrugated channels has become popular and other expressions for $D(x)$ have been proposed, for instance,

$$D_{\rm RR}(x) = \frac{D}{[1 + A'^2(x)]^{1/3}}, \tag{3.11}$$

and

$$D_{\rm KP}(x) = D\frac{\arctan\left[A'(x)\right]}{A'(x)}, \tag{3.12}$$

which were suggested, respectively, by Reguera and Rubi (RR) [35] and by Kalinay and Percus (KP) [36]. All the above three formulas for $D(x)$ (i) satisfy $D(x)/D \sim 1 - A'^2(x)/3$ for $A'(x) \ll 1$, and (ii) ignore the higher order derivatives of $A(x)$. The latter property of these expressions is not mathematically well justified. In fact, the expression of KP (3.12) was derived using a mapping formalism [51] that generates a series of expressions that include increasingly higher order derivatives of $A(x)$. Unfortunately, the formalism involves a complicated differential operator containing derivatives of all orders, which makes it rather impractical. An alternative analytical approach has been more recently introduced, which is

[2] The framework of Eq. (3.9) employing a local diffusion coefficient is applicable for continuous functions $A(x)$ only, see discussion in M. Mangeat, T. Guérin and D. S. Dean, J. Chem. Phys. **149** 124105 (2018).

based on formulation of the 2D problem in the complex plane [52]. The derivation, via this route, of expressions for $D(x)$ that take higher order derivatives into account is still highly non-trivial; however, the method has been recently exploited successfully for the derivation of a series of expressions for the effective diffusion coefficient D^* in periodic channels [50].

In this chapter, we consider dynamics in channels with periodic cross-sectional area $A(x)$. We derive a series of approximations for $D(x)$, successively taking into account higher order derivatives of $A(x)$. In contrast to almost all previous studies of the problem (an exception is ref. [53]), our derivation is not based on calculations of the steady-state PDF, but rather on the solution of the time-dependent Smoluchowski equation with delta-function initial conditions $P(x,0) = \delta(x)$. Similarly to [36], each new term in the series of expressions for $D(x)$ requires the calculation of an exponentially increasing number of derivatives of functions of $A(x)$; but in contrast to [36], the differentiations that need to be performed at each step are clearly expressed and not formulated with differential operators that are hard to interpret. The leading approximation coincides with Zwanzig's formula (3.10). We explicitly give expressions for $D(x)$ up to the fourth approximation involving the 7th derivative of $A(x)$. Finally, we use computer simulations of a case study to evaluate the importance of the higher order corrections. For slowly varying (long wavelength) channels, the contribution of the higher order derivatives appear to be rather small and unimportant, and the agreement between the 1D and 2D simulations is excellent. As the periodicity decreases, the higher order corrections may exhibit instability, leading, locally, to $D(x) > D$, and stronger deviations are found between the effective diffusion coefficient computed in the 1D and 2D simulations.

This chapter is organized as follows: In section 3.2 we consider the 2D problem. First, in subsection 3.2.1, we derive an expression for the 2D density, $\rho(x,y,t)$, in the form of an expansion in even powers in y. Then, in subsection 3.2.2, the 2D density is projected onto the x direction, and by comparison with the PDF derived in section 2.4, we arrive at the expansion for $D(x)$ in subsection 3.2.3. The first few terms in this expansion are calculated in subsection 3.2.4. In section 3.3, we use computer simulations to test the newly derived approximations for $D(x)$, and in section 3.4 we summarize our results.

3.2 Diffusion in a two-dimensional periodic channel

3.2.1 The two-dimensional density

In section 2.4 we presented the solution of the modified FJ equation for a *given* diffusion function $D(x)$. It is given by Eq. (2.16) [with D^* and $g(x)$ given by Eqs. (1.33) and (2.23), respectively], and it is correct up to order $\sim \mathcal{O}(1/t)$ at large times. The goal now is to find an expression for $D(x)$, for which this solution provides the best approximation to the true projected PDF. The latter is obtained, via Eq. (3.7), from the 2D density, $\rho(x, y, t)$, that solves the 2D diffusion equation (3.4) with the reflecting boundary conditions (3.5) and (3.6) at the walls of the channel. The fact that the projected 1D PDF takes the asymptotic (large t) form of Eq. (2.16) implies that the 2D density has following asymptotic form

$$\rho(x, y, t) = \frac{G(x, D^*t)}{A_o} \left[1 + \frac{\lambda x}{4D^*t} \sum_{n=0}^{\infty} f_n(x) y^{2n}\right], \tag{3.13}$$

where $f_n(x)$ are some functions to be determined. Only even powers of y are included in this expression due to the invariance of the equation and the boundary conditions with respect to reflection around the x axis ($y \leftrightarrow -y$).

We note here that although Eqs. (2.16) and (3.13) represent solutions that are only asymptotically correct and that they miss higher order time-decaying terms, these forms are sufficient for the sake of the task in hand which is to find the best choice of $D(x)$. This is because, as hinted by Eq. (2.21), the information needed for the determination of $D(x)$ is encompassed in the leading asymptotic correction.

We proceed by first noting that expression (3.13) satisfies automatically the boundary condition (3.5) at $y = 0$. We then follow a route similar to the one presented in section 2.4 for the determination of $g(x)$, and substitute expression (3.13) in Eq. (3.4). By comparing terms of the form $G(x, D^*t)(xy^{2n}/t)$ on both sides of the equation we arrive at the following recurrence relation (for $n \geq 1$)

$$f''_{n-1}(x) + 2n(2n-1) f_n(x) = 0, \tag{3.14}$$

which can be successively solved to yield

$$f_n(x) = \frac{(-1)^n}{(2n)!} f_0^{(2n)}(x), \tag{3.15}$$

where (throughout this thesis) $f_0^{(m)}(x)$ denotes the derivative of order m of the function $f_0(x)$.

The function f_0 [from which all other functions f_n can be derived via relation (3.15)] can be found from the remaining boundary condition at $y = A(x)$. This is done by substituting expression (3.13) in (3.6) and, again, comparing only terms proportional to $G(x, D^*t)(x/t)$. This leads to the following equation

$$\sum_{n=1}^{\infty} 2n f_n(x) \left[A(x)\right]^{2n-1} = A'(x) \left\{ -\frac{2}{\lambda} + \sum_{n=0}^{\infty} f_n'(x) \left[A(x)\right]^{2n} \right\}, \tag{3.16}$$

which by using relation (3.15) can be also written in the form

$$\sum_{n=1}^{\infty} \frac{(-1)^n f_0^{(2n)}(x) \left[A(x)\right]^{2n-1}}{(2n-1)!} = A'(x) \left\{ -\frac{2}{\lambda} + \sum_{n=0}^{\infty} \frac{(-1)^n f_0^{(2n+1)}(x) \left[A(x)\right]^{2n}}{(2n)!} \right\}, \tag{3.17}$$

involving only the function $f_0(x)$. Finally, we define the function

$$\psi(x) = f_0'(x) - \frac{2}{\lambda}, \tag{3.18}$$

and rewrite Eq. (3.17) as

$$\sum_{n=1}^{\infty} \frac{(-1)^n \psi^{(2n-1)}(x) \left[A(x)\right]^{2n-1}}{(2n-1)!} = A'(x) \left[\sum_{n=0}^{\infty} \frac{(-1)^n \psi^{(2n)}(x) \left[A(x)\right]^{2n}}{(2n)!} \right]. \tag{3.19}$$

3.2.2 The projected one-dimensional PDF

By using Eqs. (3.13) and (3.15) in Eq. (3.7) we arrive at

$$P(x,t) = \int_0^{A(x)} \rho(x,y,t) dy = \frac{G(x, D^*t) A(x)}{A_0} \left\{ 1 + \frac{\lambda x}{4D^*t} \sum_{n=0}^{\infty} \frac{(-1)^n f_0^{(2n)}(x) \left[A(x)\right]^{2n}}{(2n+1)!} \right\}. \tag{3.20}$$

This form has to be compared to Eq. (2.16) with $1+\epsilon\eta(x) = A(x)/A_0$:

$$P(x,t) = \frac{G(x,D^*t)A(x)}{A_0}\left[1+\frac{\lambda x g(x)}{4D^*t}\right]. \tag{3.21}$$

From the comparison we conclude that

$$g(x) = \sum_{n=0}^{\infty}\frac{(-1)^n f_0^{(2n)}(x)\left[A(x)\right]^{2n}}{(2n+1)!}. \tag{3.22}$$

3.2.3 The spatially-dependent diffusion coefficient

The coordinate-dependent diffusivity $D(x)$ can be now identified by writing the function $g(x)$ in Eq. (3.22) in the form of Eq. (2.23). Thus, we wish to find the function $D(x)$ satisfying

$$\sum_{n=0}^{\infty}\frac{(-1)^n f_0^{(2n)}(x)\left[A(x)\right]^{2n}}{(2n+1)!} = 2x - 2A_0D^*I\left[\frac{1}{D(x)A(x)}\right]. \tag{3.23}$$

Differentiating Eq. (3.23) with respect to x gives

$$\frac{2A_0D^*}{A(x)D(x)} = 2 - \left\{\sum_{n=0}^{\infty}\frac{(-1)^n f_0^{(2n)}(x)\left[A(x)\right]^{2n}}{(2n+1)!}\right\}', \tag{3.24}$$

and by using Eq. (3.18) we may also write

$$\frac{2A_0D^*}{A(x)D(x)} = -\psi(x) - \left\{\sum_{n=1}^{\infty}\frac{(-1)^n \psi^{(2n-1)}(x)\left[A(x)\right]^{2n}}{(2n+1)!}\right\}'. \tag{3.25}$$

By reciprocating Eq. (3.25) we finally arrive at

$$D(x) = -\frac{2A_0D^*}{A(x)\left[\psi(x) + \left\{\sum_{n=1}^{\infty}\frac{(-1)^n\psi^{(2n-1)}(x)[A(x)]^{2n}}{(2n+1)!}\right\}'\right]}. \tag{3.26}$$

In order to find $D(x)$ from Eq. (3.26), we now need to find the function $\psi(x)$ by solving Eq. (3.19). Unfortunately, this equation involves derivatives of $\psi(x)$ of any order and, therefore, cannot be solved. In what follows we present a set of approximations for $\psi(x)$ and $D(x)$. Notice, that Eq. (3.19) is a homogeneous differential equation and, therefore, the

function $\psi(x)$ can be determined up to a multiplicative constant. Therefore, we will rewrite Eq. (3.26)

$$D(x) = \frac{A_0 \mathcal{D}}{A(x)\left[\psi(x) + \left\{\sum_{n=1}^{\infty} \frac{(-1)^n \psi^{(2n-1)}(x)[A(x)]^{2n}}{(2n+1)!}\right\}'\right]}, \tag{3.27}$$

where $\mathcal{D}$ is some diffusion coefficient that depends on the choice of the multiplicative constant in the definition of $\psi(x)$. The diffusion constant $\mathcal{D}$ will be determined by other considerations.

3.2.4 Series expansion

The function $\psi(x)$ is periodic with wavelength λ. Introducing the dimensionless parameter $\omega = A_0/\lambda \sim A'$ which becomes vanishingly small for narrow and slowly varying channels, we can formally write the function $\psi(x)$ as an expansion in terms of increasing orders of ω, namely

$$\psi(x) = \psi_0(x) + \psi_1(x) + \psi_2(x) + \cdots \ , \tag{3.28}$$

where

$$\psi_n(x) \sim \omega^{2n} \tag{3.29}$$

The scaling behavior (3.29) follows from the fact to be shown henceforth that $\psi_{n+1} \sim A^2 \psi_n'' \sim A^2 \psi_n/\lambda^2 \sim \omega^2 \psi_n$.

In order to obtain the n-th function $\psi_n(x)$, we need to identify the terms in Eq. (3.19) of order ω^{2n+1}.

3.2.4.1 The zeroth approximation.

In this approximation $\psi(x) = \psi_0(x)$, and only the first terms in the sums on both sides of Eq. (3.19) are kept. Thus we have the equation

$$-\psi_0'(x)A(x) = \psi_0(x)A'(x), \tag{3.30}$$

with terms of order $\sim \omega$ on both sides, and with the solution

$$\psi_0(x) = \frac{A_0}{A(x)}. \tag{3.31}$$

Notice that in order to keep the function ψ dimensionless, we pick A_0 as our choice for the "arbitrary" multiplicative constant in its definition [see discussion around Eq. (3.27) above].

The zeroth approximation of $D(x)$ is obtained by substituting $\psi = \psi_0(x)$ in Eq. (3.27) and keeping only the leading term in the square brackets in the denominator. This gives

$$D(x) = \frac{A_0 \mathcal{D}}{A(x)\psi_0(x)} = \mathcal{D}. \tag{3.32}$$

Since the zeroth approximation of $D(x)$ must converge to the correct value in the limit $\omega \to 0$, which corresponds to the case of a flat channel, we must set $\mathcal{D} = D$. Let us denote the n-th approximation of $D(x)$ by $D_n(x)$. Thus, to zero order in ω

$$D_0(x) = D_0 = D, \tag{3.33}$$

which upon substitution in the modified FJ equation (3.9), reduce it to the form of the original FJ equation (3.8). To highlight that the zeroth approximation coincides with the medium diffusion coefficient, we will henceforth denote the latter as D_0.

3.2.4.2 The first approximation

To a first approximation, $\psi(x) = \psi_0(x) + \psi_1(x)$, where $\psi_0(x)$ is given by Eq. (3.31). The function $\psi_1(x)$ is found by solving the following equation

$$-\psi_1'(x)A(x) + \frac{1}{3!}\psi_0^{(3)}(x)A^3(x) = A'(x)\left[\psi_1(x) - \frac{1}{2!}\psi_0''(x)A^2(x)\right]. \tag{3.34}$$

This equation is derived by: (i) writing Eq. (3.19) for $\psi = \psi_0 + \psi_1$ with only two terms in each sum on both sides (i.e., one term more than in the zeroth approximation), and (ii) isolating the terms that scale $\sim \omega^3$. (The terms scaling $\sim \omega$ constitute the already solved Eq. (3.30), and the terms scaling $\sim \omega^5$ are discarded.) Since Eq. (3.34) can be also written

as

$$[\psi_1(x)A(x)]' = \frac{[\psi_0''(x)A^3(x)]'}{3!}, \tag{3.35}$$

we immediately find that

$$\psi_1(x) = \frac{\psi_0''(x)A^2(x)}{3!}. \tag{3.36}$$

The first approximation, $D_1(x)$, is derived by substituting $\psi(x) = \psi_0(x) + \psi_1(x)$ in the leading term in the square brackets, and $\psi(x) = \psi_0(x)$ in the first term in the sum ($n = 1$). Thus, to first approximation

$$D_1(x) = \frac{A_0 D_0}{A(x)\left[\{\psi_0(x) + \psi_1(x)\} - \{\psi_0'(x)A^2(x)/3!\}'\right]}, \tag{3.37}$$

which is correct to order ω^2. (In general, $D_n(x)$, is correct to order ω^{2n}.) By using Eq. (3.36), we can also write the alternative form for (3.37)

$$D_1(x) = \frac{A_0 D_0}{A(x)\left[\psi_0(x) - 2\psi_0'(x)A(x)A'(x)/3!\right]}. \tag{3.38}$$

By using Eq. (3.31) in Eq. (3.38) we arrive at

$$D_1(x) = \frac{D_0}{1 + \left[A'(x)\right]^2/3}, \tag{3.39}$$

which is the Zwanzig formula (3.10).

3.2.4.3 The second approximation

Similarly, the second approximation for the function ψ reads $\psi = \psi_0 + \psi_1 + \psi_2$, and the latter term can be found from the equation for the terms in (3.19) scaling $\sim \omega^5$. The equation reads

$$-\psi_2' A + \frac{1}{3!}\psi_1^{(3)} A^3 - \frac{1}{5!}\psi_0^{(5)} A^5 = A'\left[\psi_2 - \frac{1}{2}\psi_1'' A^2 + \frac{1}{4!}\psi_0^{(4)} A^4\right], \tag{3.40}$$

which can be also written as

$$(\psi_2 A)' = \left[-\frac{1}{5!}\psi_0^{(4)} A^5 + \frac{1}{3!}\psi_1'' A^3 \right]'. \tag{3.41}$$

Thus,

$$\psi_2 = -\frac{1}{5!}\psi_0^{(4)} A^4 + \frac{1}{3!}\psi_1'' A^2. \tag{3.42}$$

The second approximation, $D_2(x)$, is derived by truncating the sum in the denominator at $n = 2$, and keeping only terms up to order ω^4. This yields,

$$D_2(x) = \frac{A_0 D_0}{A\left[\{\psi_0 + \psi_1 + \psi_2\} - \{(\psi_0' + \psi_1')\, A^2/3!\}' + \left\{\psi_0^{(3)} A^4/5!\right\}'\right]}. \tag{3.43}$$

Using Eqs. (3.31), (3.36), and (3.42) in Eq. (3.43), we arrive at the second approximation for $D(x)$

$$D_2(x) = \frac{D_0}{1 + A'^2/3 + (A^2 A' A^{(3)} - A A'^2 A'' - 4A'^4)/45}. \tag{3.44}$$

3.2.4.4 Higher order corrections

Following the same scheme, one can readily find that the ψ_n can be obtained recursively via the relation

$$\psi_n = \sum_{k=0}^{n-1} \frac{(-1)^{n-k-1} \psi_k^{(2n-2k)} A^{2n-2k}}{(2n-2k+1)!}, \tag{3.45}$$

with $\psi_0 = A_0/A$ (3.31). The n-th approximation, $D_n(x)$ is given by

$$D_n(x) = \frac{A_0 D_0}{A\left[\sum_{k=0}^{n} \psi_k + \sum_{k=1}^{n} \frac{(-1)^k}{(2k+1)!} \left\{\sum_{l=0}^{n-k} \psi_l^{(2k-1)} A^{2k}\right\}'\right]}. \tag{3.46}$$

A more "user-friendly" expression can be wrtiten for the n-th approximation of the friction coefficient $1/D_n(x)$

$$\frac{1}{D_n(x)} = \frac{A}{A_0 D_0}\left[\sum_{k=0}^{n}\psi_k + \sum_{k=1}^{n}\frac{(-1)^k}{(2k+1)!}\left\{\sum_{l=0}^{n-k}\psi_l^{(2k-1)}A^{2k}\right\}'\right], \tag{3.47}$$

which can be decomposed into two contributions as follows:

$$\begin{aligned}\frac{1}{D_n(x)} &= \frac{A}{A_0 D_0}\left[\sum_{k=0}^{n-1}\psi_k + \sum_{k=1}^{n-1}\frac{(-1)^k}{(2k+1)!}\left\{\sum_{l=0}^{(n-1)-k}\psi_l^{(2k-1)}A^{2k}\right\}'\right] \\ &+ \frac{A}{A_0 D_0}\left[\psi_n + \left\{\sum_{k=1}^{n}\frac{(-1)^k}{(2k+1)!}\psi_{n-k}^{(2k-1)}A^{2k}\right\}'\right] \\ &= \frac{1}{D_{n-1}(x)} + \frac{A}{A_0 D_0}\left[\psi_n + \left\{\sum_{k=1}^{n}\frac{(-1)^k}{(2k+1)!}\psi_{n-k}^{(2k-1)}A^{2k}\right\}'\right].\end{aligned} \tag{3.48}$$

By using Eq. (3.45) and changing the index of summation in (3.48) from k to $l = n-k$, we arrive at

$$\frac{1}{D_n} = \frac{1}{D_{n-1}} + \frac{AA'}{A_0 D_0}\sum_{l=0}^{n-1}\frac{(-1)^{n-l}(2n-2l)}{(2n-2l+1)!}\psi_l^{(2n-2l-1)}A^{2n-2l-1}. \tag{3.49}$$

Using Eqs. (3.45) and (3.49), we calculate the third approximation

$$\begin{aligned}\frac{1}{D_3} &= \frac{1}{D_2} + \frac{1}{945 D_0}\left[2A^4A'A^{(5)} + 8A^3A'^2A^{(4)} - 12A^3A'A''A^{(3)}\right. \\ &- \left. 27A^2A'^3A^{(3)} - 58A^2A'^2A''^2 + 31AA'^4A'' + 44A'^6\right],\end{aligned} \tag{3.50}$$

and the fourth approximation

$$\begin{aligned}\frac{1}{D_4} &= \frac{1}{D_3} + \frac{1}{14175 D_0}\left[3A^6A'A^{(7)} + 39A^5A'^2A^{(6)} + 5A^5A'A''A^{(5)}\right. \\ &+ 74A^4A'^3A^{(5)} - 53A^5A'A^{(3)}A^{(4)} - 412A^4A'^2A''A^{(4)} - 118A^3A'^4A^{(4)} \\ &- 911A^4A'^2[A^{(3)}]^2 - 682A^3A'^3A''A^{(3)} + 451A^2A'^5A^{(3)} - 467A^4A'A''^2A^{(3)} \\ &+ \left. 157A^3A'^2A''^3 + 1956A^2A'^4A''^2 - 555AA'^6A'' - 428A'^8\right].\end{aligned} \tag{3.51}$$

In principle one can proceed and derive the higher order approximations $D_n(x)$ in the

same manner, but in practice the number of differentiations that need to be carried grows exponentially with n and the calculations become tedious. The same feature complicates the calculation of the series of $D_n(x)$ in ref. [36], but the approach in that work "suffers" from an extra complication which is the use of differential operators containing derivatives of all orders that are very hard to identify. The use of Eqs. (3.45) and (3.49) clearly offers a far more tractable route to finding the higher order terms. The expressions for D_1, D_2, and D_3 given here by Eqs. (3.39), (3.44), and (3.50), respectively, are different from their counterparts in ref. [36] [see Eq. (13) therein]. However, if we Taylor expand the former and leave in the expansion only terms up to order ω^{2n} than the latter are recovered. It is reasonable to speculate that this also holds true for $n > 3$.

3.3 Simulation results

As a case study, we consider diffusion in a channel with cross sectional area given by $A(x) = h_0 + \Delta[(2x/\lambda)^2 - 1]^2$ for $x \in [-\lambda/2, \lambda/2]$ and repeated periodically outside of this interval. We set the parameters $h_0 = 3$ (minimum channel opening) and $\Delta = 12$ (amplitude of channel height oscillations), and take the channel periodicity to be either $\lambda = 90$ or $\lambda = 30$. The average height of the channel is $A_0 = \langle A(x) \rangle = 8\Delta/15 + h_0 = 9.4$. Therefore, the corresponding values of $\omega = A_0/\lambda$ are 0.10 and 0.31 for $\lambda = 90$ and $\lambda = 30$, respectively. We set the medium diffusion coefficient D_0 to unity. Fig. 2.1 shows the first three approximations $D_n(x)$ [$n = 1, 2, 3$ in Eqs. (3.39), (3.44), and (3.50), respectively], as well as the expression of Kalinay and Percus (KP) [Eq. (3.12)] which is the limit ($n \to \infty$) expression when all the derivatives of $A(x)$, except for the first one, are set to zero. In Fig. 3.2 (a) we plot the diffusion functions corresponding to the channel with the long wavelength $\lambda = 90$. All the expressions look remarkably identical, which is not surprising since the variable ω in the power expansion in section 3.2.4 is indeed small in this case and the higher order corrections are expected to vanish rapidly. In contrast, for the case of a short wavelength channel with $\lambda = 30$ depicted in Fig. 3.2 (b), significant variations between the different expressions are observed. This is the regime where for some values of x, $|A'(x)| > 1$, and the series expansion fails to converge. Particular notice should be given to the fact that truncating the expansion at a finite n may locally lead to $D(x) > D_0 = 1$ [see, e.g., $D_3(x)$ in Fig. 3.2 (b)], which best

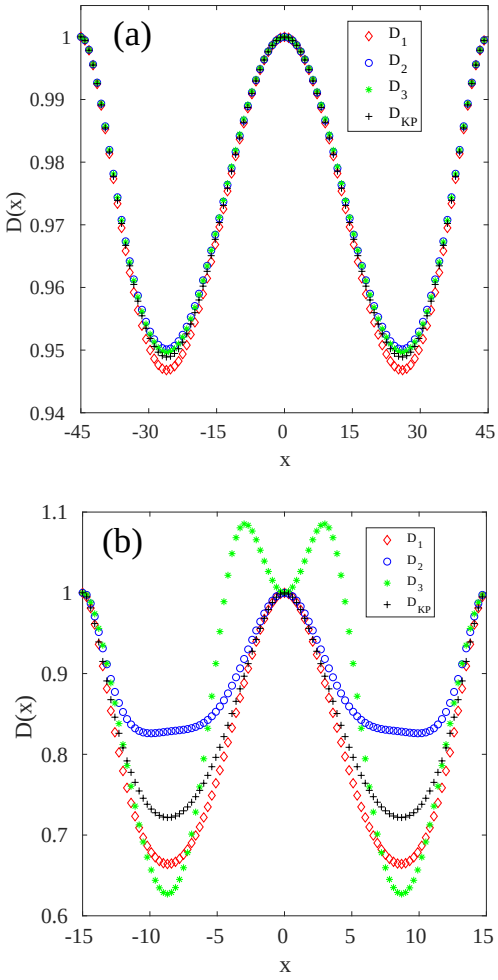

Figure 3.2: The coordinate-dependent diffusion coefficients D_1 (red diamonds), D_2(blue circles), D_3(green stars), and KP expression $D_{\rm KP}$ (black pluses) for the case studies discussed in the text. The periodicity of the channel is $\lambda = 90$ ($\omega = 0.10$) in (a) and $\lambda = 30$ ($\omega = 0.31$) in (b).

demonstrates that the higher order corrections may become increasingly large.

To further test the accuracy of the 1D effective description of the dynamics, we performed Langevin dynamics simulations of both 2D channels with a height profile $A(x)$ and a constant diffusion coefficient $D = 1$ (case 1), and of 1D systems with a periodic potential $U(x) = -k_B T \ln [A(x)]$ and various periodic diffusion functions $D(x)$, including $D_0 = 1$ (case 2), our expressions for D_1, D_2, D_3 (cases 3-5), and $D_{\rm KP}$ (case 6). In each case, we measured the effective diffusion coefficient D^* via Eq. (1.31), by simulating 5×10^8 long trajectories of particles starting at the origin. The trajectories were computed using the G-JF integrator, and the spatial variations in $D(x)$ were accounted for using the "inertial convention" [see dis-

cussion in 1.3.2]. Our results are summarized in tables 3.1 and 3.2 which give the simulation values, along with the corresponding values derived from the MLJ formula (1.33) for 1D periodic systems. Table. 3.1 shows the results for a channel of wavelength $\lambda = 90$. As can be deduced from the table, the first order diffusion coefficient $D_1(x)$ [Zwanzig's expression (3.10)] gives remarkably precise results when compared to the 2D case. The higher order corrections, which in Fig. 3.2 (a) appear rather small, are unnecessary and do not yield any further improvement in the results. Furthermore, the data confirms that for slowly varying channels, The MLJ formula gives values of D^* that are identical to the numerical counterparts (see discussion in [54]). In contrast, table 3.2 reveals that for $\lambda = 30$, the agreement of the 1D simulations results with the 2D case is far from perfect. The first order diffusion coefficient D_1 exhibits significant improvement compared to the zeroth approximation D_0, but D_2 is no better than D_1. Both D_3 and D_{KP} appear to give D^* that is quite close to the value measured in the 2D simulations, but this is clearly coincidental. Once the series expansion fails to converge (as demonstrated by the strong variations between the successive approximations exhibited in Fig 3.2), the accuracy of the 1D effective picture of the dynamics becomes highly questionable. The MLJ results follow the trends exhibited by their corresponding numerical values, albeit with a lesser degree of accuracy than for $\lambda = 90$.

Table 3.1: Effective diffusion coefficients for channels with $\lambda = 90$

Case studied	Simulation results	MLJ formula
(1) 2-dim	0.7340(5)	
(2) D_0	0.7543(5)	0.7564
(3) D_1	0.7344(3)	0.7367
(4) D_2	0.7353(5)	0.7377
(5) D_3	0.7351(3)	0.7376
(6) D_{KP}	0.7346(3)	0.7372

Table 3.2: Effective diffusion coefficients for channels with $\lambda = 30$

Case studied	Simulation results	MLJ formula
(1) 2-dim	0.6276(3)	
(2) D_0	0.7419(5)	0.7564
(3) D_1	0.6022(2)	0.6093
(4) D_2	0.6624(4)	0.6716
(5) D_3	0.6213(4)	0.6283
(6) $D_{\rm KP}$	0.6244(3)	0.6325

With the above said, we can clearly see from table 3.2 that the zeroth approximation of a constant diffusion coefficient $D(x) = D_0$ gives far worse results for D^* than all the proposed expressions for coordinate-dependent $D(x)$. This observation supports Zwanzig's idea that the modified FJ equation (3.9) provides a better effective 1D description of the 2D diffusion problem than the simple FJ equation (3.8). To further support this conclusion, we plot in fig 3.3 the function $\Pi(x,t) = P(x,t)A_0/A(x)$ for $\lambda = 30$ at $t = 2 \times 10^4$. The plot shows the function Π computed from simulations of the 2D channel (blue circles), along with those computed from 1D FJ simulations with D_0 (green stars), $D_1(x) = D_{\rm Z}(x)$ (Zwanzig's formula - red diamonds), and $D_{\rm KP}(x)$ (Kalinay-Percus formula - black pluses). The degree of agreement between the function Π of the 2D simulations and the approximations corresponding to D_0 (very poor agreement), D_1 (significantly improved agreement), and $D_{\rm KP}$ (nearly perfect agreement), is clearly in accord with the results for D^* in table 3.2 showing precisely the same trends. We do not show the PDF for the higher order approximations (D_2, D_3) since, as evident from fig. 3.2 (b), these expressions are derived from a non-converging series expansion (see discussion in the previous paragraph). In contrast, both $D_1 = D_{\rm Z}$ and $D_{\rm KP}$ satisfy $0 < D(x)/D_0 \leq 1$ [for any periodic function $A(x)$], which precludes strong oscillations in $D(x)$ like the ones exhibited by $D_3(x)$ in fig. 3.2 (b). We thus conclude that although the 1D projection method becomes less accurate for higher values of ω, there is still a significant improvement in the accuracy of the PDF when $D_1(x) = D_{\rm Z}(x)$ and $D_{\rm KP}(x)$ are used instead

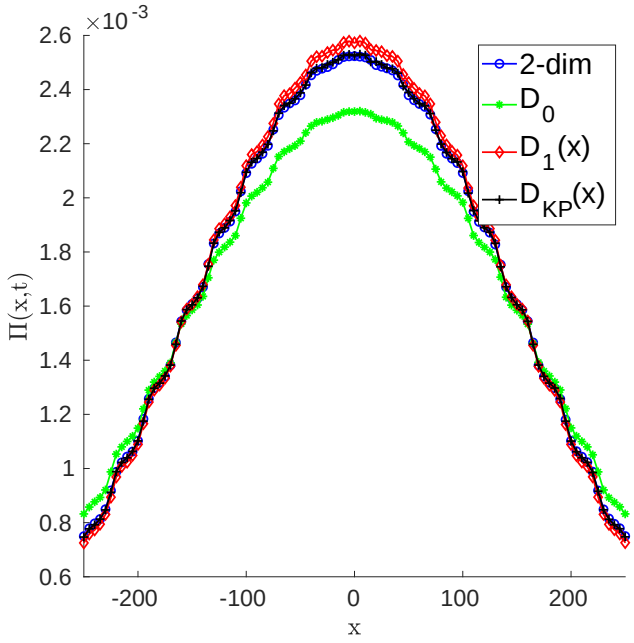

Figure 3.3: The numerical results for the function $\Pi(x,t) = P(x,t)A_0/A(x)$ computed from 2D channel simulation (blue circles), and from 1D FJ simulations with D_0 (green stars), $D_1(x)$ (red diamonds), and $D_{\rm KP}(x)$ (black pluses) for $\lambda = 30$. The data is collected at $t = 2 \times 10^4$.

of the constant D_0.

3.4 Summary

In this chapter we revisited the problem of describing diffusive dynamics along 2D periodic corrugated channels via a 1D FJ equation with a spatially-dependent diffusion coefficient. In contrast to previous attempts to derive expressions for $D(x)$ which were based on steady state solutions, here we consider the non-stationary state of a particle moving in an open channel. Similarly to the work in ref. [36], the expression derived here for $D(x)$ is in the form of a series expansion in the parameter ω associated with the aspect ratio of the channel; but in contrast to that work, the formalism presented herein does not involve complicated differnetal operators that are very hard to identify. The first order approximation, $D_1(x)$, coincides with Zwanzig's formula for $D(x)$, and for long wavelength channels (small ω) it yields results that are in perfect agreement with the 2D description. The agreement is lost when ω is not sufficiently small, reflecting two problems of the method. The first problem is a mathematical one: When ω is not small, the series expansion does not converge

properly and cannot be truncated. The second problem is physical. The 1D description via FJ equation assumes a Markovian diffusion process, which is only the case in the limit of fast relaxation of the probability density in the transverese direction, i.e., for nearly flat thin channels. Therefore, one should not be surprised by the disagreement between the Langevin dynamics simulations of 1D periodic systems and the 2D simulation results for short wavelength channels. In fact, in this regime the 1D simulation results for the effective diffusion coefficient do not even agree with the Lifson-Jackson formula, which highlights yet another problem of the FJ equation - its overdamped nature. FJ is a Smoluchowski equation which is applicable only if, at length scale of the ballistic distance of the dynamics, the variations in the force associated with the entropic potential are much smaller than the characteristic friction force (see discussion in [54]) . This requirement is also not fulfilled for short wavelength channels.

Finally, we point out that the derivation of a series expansion for $D(x)$ presented here for 2D channels can be extended to three-dimensional (3D) geometries with cylindrical symmetry. In order to do so, we assume that the 3D density, $\rho(x, r, t)$, has the same form as the 2D density (3.13) but with y replaced by r, and then substitute this form in the 3D diffusion equation written in cylindrical coordinates. The resulting recurrence relation, which is different than Eq. (3.14) for the 2D problem, needs now to be solved, and the steps of the derivation presented in section 3.2 should be followed.

Chapter 4

Summary and Conclusions

Diffusion of particles in periodic systems is a prominent phenomena whose understanding is essential to a broad spectrum of fields of science and engineering. In this thesis, we have presented a method that can be used to solve a variety of different diffusion equations in the presence of a periodic potential $U(x)$. The method is based on the fact that, at asymptotically large times, the leading term of the solution to the Smoluchowski equation (2.1) is the known solution to the basic diffusion problem, i.e. the Gaussian function $G(x, D^*t)$, with an effective diffusion coefficient D^*, multiplied by Boltzmann's factor $\exp[-\beta U(x)]$. The solution is written as a series of corrections to the leading term, where each correction decays $t^{-1/2}$ faster than the previous one. The terms are found successively by substitution into the Smoluchowski equation and solving a differential equation that involves the previously found (lower order) terms.

By following this method, we found an asymptotic solution to the 1D Smoluchowski equation (2.1) for any periodic, even potential function $U(x)$ up to the second correction (which scales $\sim t^{-3/2}$). Our solution has been verified by numerical simulations via the highly accurate and robust G-JF algorithm [16]. These results show excellent fit to the analytical solution as seen in Fig. (2.2). The effective diffusion coefficient D^* can also be determined via this approach by solving for the second correction, by which we independently derived the LJ formula (1.32). Since the Smoluchowski equation is valid only in large time scales (i.e. $t \gg m/\alpha$), and only when the spatial variations in the force are rather slow, our solution is also limited accordingly. Furthermore, as we have shown numerically, when the potential

barrier is high (i.e. $\beta\Delta U \gg 1$), the effective diffusion coefficient D^* no longer follows the LJ formula, but rather follows the Arrhenius-Kramer law, scaling as $D^* \sim D\exp(-\beta\Delta U)$.

In Chapter 3, we use this method in order to map the problem of diffusion in a 2D periodic channel, into a 1D description. This mapping is done by using the FJ equation (3.9), and adding a space dependent diffusion coefficient $D(x)$. We present a systematic method for finding $D(x)$ in a form of a series expansion in $\omega \sim 1/\lambda$, where λ is the periodic length of the channel. By truncating this expression up to order of ω^{2n}, we arrive at the nth approximation $D_n(x)$. To zeroth approximation, $D_0(x) = D$, where D is the medium diffusion coefficient. The first order expression $D_1(x)$ is identical to Zwanzig's expression (3.10). Based on our simulation results, we find that there is a delicate trade off between the stability of the expansion, and the contribution of the higher order expressions to the fit to the 2D results. On the one hand, when the periodicity λ is too small, the series expansion does not converge properly and thus the truncated expressions are not reliable. This fact is not surprising since as the periodicity approaches the ballistic length l_b, the validity of the FJ equation diminishes. On the other hand, when the periodicity λ is too large, the contribution of higher order terms is quite small.

We numerically compared results of the 1D FJ equation with (i) our series of expressions for $D(x)$ and (ii) the expression of Kalinay and Percus, with 2D channel simulations. We conclude that the expression of Kalinay and Percus matches best the 2D simulation results. Although there is an instability problem for low values of ω, we find that the first approximation D_1 significantly improves the fit to the 2D simulation results compared to constant diffusion coefficient D_0. (see Tables 3.2,3.1).

In a future work, it would be interesting to compare the 1D Fick-Jacobs equation to simulations of diffusion in confined non-periodic 2D channels with a random profile and in open wedges. In random channels, we expect the leading term of the solution to be a Gaussian function multiplied by Boltzmann's factor corresponding to the entropic potential associated with the channels' profile. It would be interesting to see if one can find corrections to this leading term or, at least, a new formula for the effective diffusion coefficient of the random channel.

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