Proton Dynamics in Cavities

Dominik Wille

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1 Introduction

2 Brownian Dynamics

The motion of a particle such as a proton in a fluid is primarily caused by collisions with other particles. This motion firstly was described by Robert Brown who observed the motion of minute particles of pollen in water and is widely known as **brownian motion**.

2.1 Langevin Symulation

2.1.1 Priciple

The principle of a Langevin simulation generally is to consider collisions with other particles as a random force. And propergate the position of a particle over small time steps δt.

2.1.2 Physical background

An approach to describe situations with brownian motion was suggested by Paul Langevin who added the random force $\mathbf{Z}(t)$ in newtons equation of motion. This stochastic term represents the collision driven force. His equation, the Langevin equation reads:

$$m\ddot{\mathbf{r}} = -\lambda\dot{\mathbf{r}} + \mathbf{Z}(t) \tag{1}$$

where m is the mass of the particle, $\mathbf{r}$ the position of the particle and λ The friction constant.

Brownian dynamics can be represented with the so called **overdamped langevin equation** where the $m\ddot{\mathbf{r}}$ term is neglected. The equation for the prevailing situation therefore is:

$$\lambda\dot{\mathbf{r}} = \mathbf{Z}(t) \tag{2}$$

In order to get an iterable expression this expression is discretesated in time intervals Δt:

$$\int_t^{t+\delta t} \dot{\mathbf{r}}(t')\,dt' = \int_t^{t+\Delta t} \frac{\mathbf{Z}(t')}{\lambda}\,dt' \tag{3}$$

$$\mathbf{r}(t+\delta t) - \mathbf{r}(t) = \frac{1}{\lambda}\int_t^{t+\Delta t} \mathbf{Z}(t)\,dt' \tag{4}$$

$$\mathbf{r}(t+\delta t) - \mathbf{r}(t) \cong \boldsymbol{\zeta}(t,\varepsilon) \tag{5}$$

In the discussed 1–dimensional case ε is the step size and $\boldsymbol{\zeta}(t,\varepsilon)$ will be ε or $-\varepsilon$ with a chance of 50% each.

The position of a particle at time $t+\Delta t$ can easily derived from its position at time t.

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \boldsymbol{\zeta}(t,\varepsilon) \tag{6}$$

2.2 Connection to diffusion

The motion which is performed in the langevin simulation is widely known as a **random walk**. The probability $p(x,n)$ that a random walk comes to a position x after n steps. Is given by:

$$p(x,n) = \frac{\text{Number of ways to position } x}{\text{Total number of ways}} = \frac{N_x}{N} \tag{7}$$

Since there are 2 possible successors for every position the total number of ways doubles every step.

$$N = 2^n \tag{8}$$

The number of ways to the position x after n steps can be obtained by **Pascal's triangle**.

$$N_x = \binom{n}{k} \tag{9}$$

$$\text{with} \quad k = \frac{1}{2}\left(\frac{x}{\varepsilon} + n\right) \tag{10}$$

Therefore $p(x,n)$ follows as:

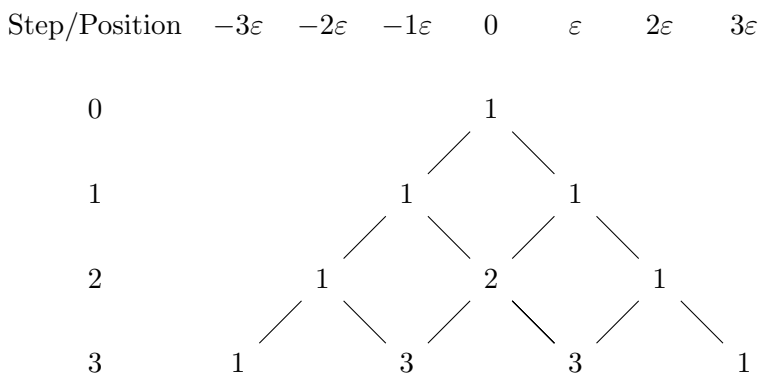


Figure 1: Number of ways to different distances

$$p(x,n) = \binom{n}{k} \cdot 2^{-n} \tag{11}$$

A consequence of the **de Moivre–Laplace theorem** is that for large numbers of steps ($n \to \infty$) this expression can be approximated with the following gaussian curve:

$$p(x,n) \cong \sqrt{\frac{2}{n\pi}} \exp\left(\frac{-x^2}{2\varepsilon^2 n}\right) \tag{12}$$

The probability function $p(x,n)$ has valid values only for values

$$x \in \{x \mid x = z \cdot 2\varepsilon + \varepsilon\,(n \bmod 2),\ z \in \mathbb{Z} \wedge |x| \leq n\varepsilon\} \tag{13}$$

For other values x the probability is 0. This means that there is only one value per 2ϵ interval, therefore the probability density function $\rho(x,n)$ is:

$$\rho(x,n) = \frac{1}{2\varepsilon}\, p(x,n) = \frac{1}{\varepsilon\sqrt{2\pi n}} \exp\left(\frac{-x^2}{2\varepsilon^2 n}\right) \tag{14}$$

Which is the normal distribution with $\mu = 0;\ \ \sigma = \varepsilon\sqrt{n}$.

The probability density function of a **random walk** fulfills the diffusion equation (*Note:* $n = {}^{t}/_{\delta t}$):

$$\frac{\partial}{\partial t}\rho(x,t) = D\frac{\partial^2}{\partial x^2}\rho(x,t) \tag{15}$$

$$\text{with}\ \ D = \frac{\varepsilon^2}{2\delta t} \tag{16}$$

What means that a random walk can also be seen as a diffusion process.

2.3 Mean square distance

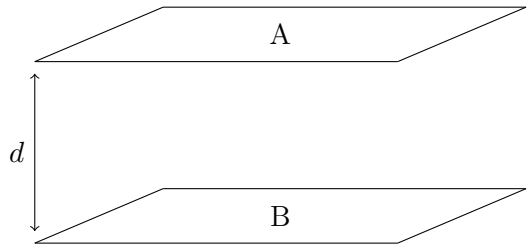
Obviously the expectation value for x after n steps $\langle x_n \rangle = 0$. What can be derived from:

$$\langle x_n \rangle = \int_{-\infty}^{\infty} x \cdot \rho(x,t)\, dx = 0 \tag{17}$$

But the **Mean Square Distance** $\langle x_n^2 \rangle$ (MSD) fulfills the following expression:

$$\langle x_n^2 \rangle = \int_{-\infty}^{\infty} x^2 \cdot \rho(x,t)\, dx = 2Dt \tag{18}$$

3 Implementation of the langevin simulation



4 Comparision to the analytical Calculation

4.1 Free particle

A very simple test is to check if the simulation of a particle without any barriers has a linear growing MSD in time steps. *Figure 3* shows the average squared distance x_n^2 for different numbers of runs compared to the analytic expression. The parameters were:

Parameter	Value
D	0.1
δt	20
$x(n=0)$	0
$n_{\max}$	400

Note that ε is determined by *Equation 16*.

The expectation is that for large numbers of runs the mean square converges against the following analytic expression derived from *Equation 18*:

$$\langle x_n^2 \rangle(t) = 2Dt \tag{19}$$

$$\Rightarrow \langle x_n^2 \rangle(n) = 2D\delta t \cdot n \tag{20}$$

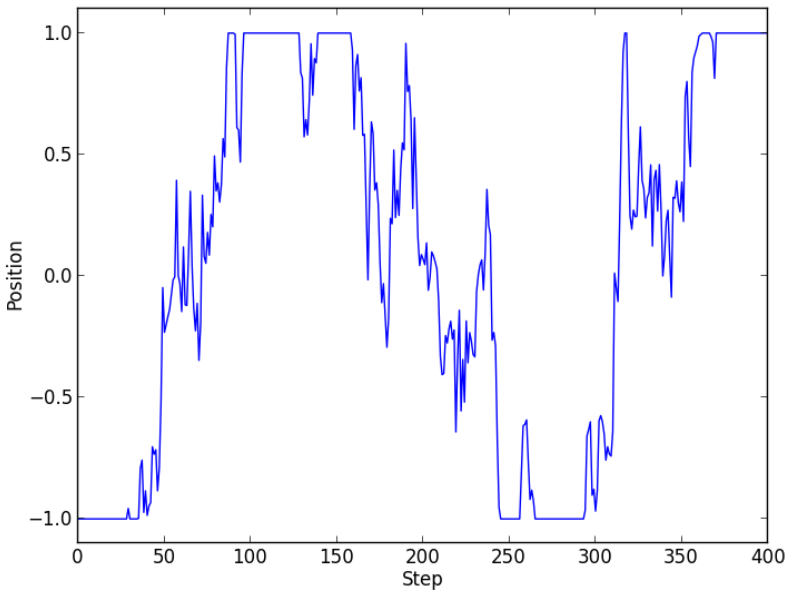


Figure 2: Position of an ion

4.2 Correlation functions

Since there is an analytic expression for the Correlation functions $C_{AA}(t)$ and $C_{AB}(t)$ which represent the probability for an ion to be absorbed at time t on plate A/B given that it is absorbed on plate A at time $t = 0$.

These correlation functions can easily be obtained from the langevin simulation by noting if and where the particle is absorbed over the time.

Afterwards the values of the correlation function $C_{AA}(t)$ can be calculated as the number of time intervals with length t where the ion is absorbed on plate A at the beginning and at the end over the total number of intervals.

Similarly the values of the correlation function $C_{AB}(t)$ can be calculated as the number of time intervals with length t where the ion is absorbed on plate A at the beginning and on plate B at the end over the total number of intervals.

The test was performed with the following parameters:

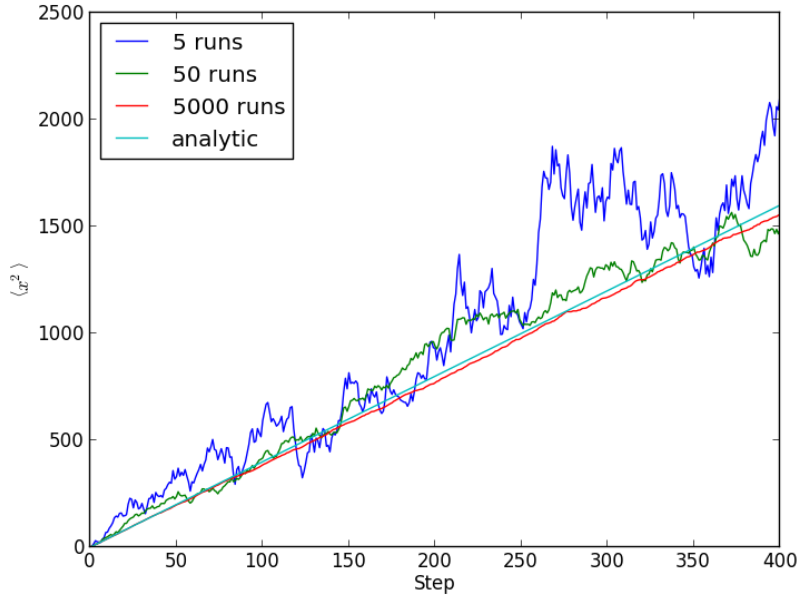


Figure 3: MSD over time for different numbers of runs

Parameter	Value
D	0.2
δt	0.1
τ	1
p	0.3
s	2.0

where D the diffusion constant, δt the step size, τ the exponential decay constant for the desorbtion probability, p the probability that a particle at the boundary absorbs and s is the plate distance.

In order to compare these correlation functions with its analytic equivalents they need to be Laplace transformed. To obtain easy expressions for the Laplace transformed functions they are fitted with the following functions:

$$C_{AA}(n) = a \cdot e^{-n \cdot b} + c \cdot e^{-n \cdot d} + f \cdot e^{-n \cdot g} + h \tag{21}$$

$$C_{AB}(n) = j \cdot e^{-n \cdot k} + l \tag{22}$$

The parameters were determined as:

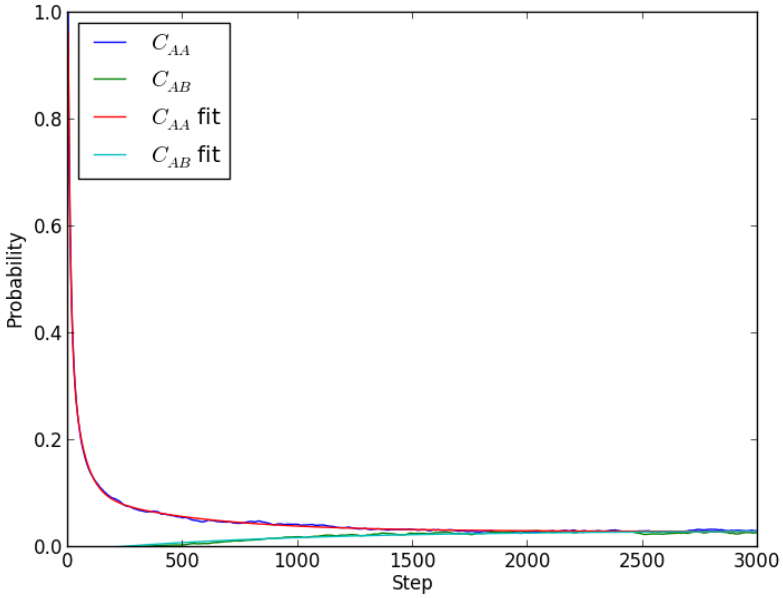


Figure 4: Correlation Functions and its fits

Parameter	Value
a	0.07712867
b	0.00204063
c	0.55760507
d	0.10309138
f	0.30010113
g	0.01889753
h	0.02938739
j	-3.83406062e-02
k	1.078311976e-03
l	3.11126910e-02

Since for a simple exponential expression the Laplace transformed expression is given by:

$$F(x) = A \cdot e^{B \cdot x} \tag{23}$$

$$\widetilde{F}(\omega) = \int_0^\infty A \cdot e^{B \cdot x} \cdot e^{-\omega \cdot x} \, dx \tag{24}$$

$$= \frac{A}{B + \omega} \tag{25}$$

The Laplace transformed correlation functions are:

$$\widetilde{C}_{AA}(\omega) = \frac{a}{b+\omega} + \frac{c}{d+\omega} + \frac{f}{g+\omega} + \frac{h}{\omega} \tag{26}$$

$$\widetilde{C}_{AB}(\omega) = \frac{j}{k+\omega} + \frac{l}{\omega} \tag{27}$$