Proton Dynamics in Cavities

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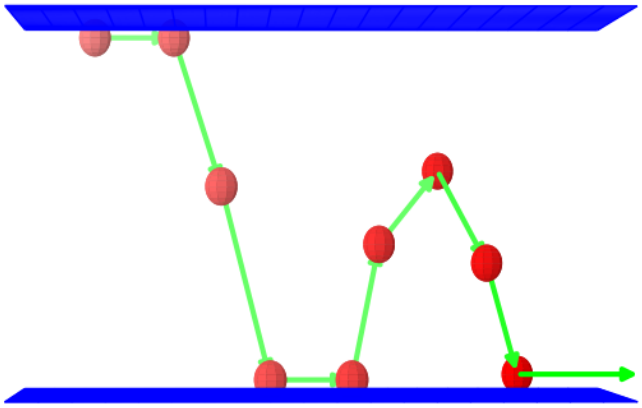
October 23, 2014



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1 Introduction

Proton- or generally ion dynamics in fluids directly imply fluctuations in the potential and conductivity of surrounded nano–scaled structures. The major processes which influence these measurable properties and which are considered here are **absorption** and **desorption** processes. The amount of mobile ions which are contained in the fluid are proportional to the fluids conductivity. An experimental way to detect this conductivity is by measuring the ionic current. And since ions carry charges, absorption of ions causes changes of the potential.

Since such fluctuations, could bring hints to extract physical, chemical or even geometrical information concerning the system, they are part of current investigations. But today many of these fluctuations are not satisfactorily explained[1].

In this document the motion of one particle is considered as a brownian motion. Even though ions and especially protons are not necessarily smaller than the fluid molecules which is the reason why the diffusion constant does not fulfill EINSTEINS formula[2], the general assumption that the motion is caused by random strokes is fulfilled for smaller particles as well. In this document a **Langevin-Simulation** of a particle is used to determine correlations of the absorption–desorption processes, which can be indirectly measured as conductivity and potential.

The simulations are based on previous analytic calculations by ROLAND NETZ which obtain these correlation functions for infinite cylindrical and planar geometries[3]. To determine the correctness of the **Langevin-Simulation** it is tested for these limiting cases as well as simple simulations for a free particle. Moreover the most important processes which take effect in the correlation functions and methods to describe and implement these in the simulation are briefly summarized and explained.

The title image shows one visualized particle on a random walk between two plates in 2-d for different times. The time increases from left to right.

[1] [3] Simon Gravelle and Bocquet "Pink noise of ionic current, theory and modelisation" 2014
[2] [2] "Notes on Brownian Motion" 2011
[3] [1] Netz and Bocquet "Conductivity Fluctuations in Cylindrical Pores" 2014

2 Analytic calculations

In this document some properties of the

For a single surface this means[4]:

$$C_{AA}(t) = \sum_{i,l=0}^{\infty} \left\{ \int_0^{\infty} \mathrm{d}t_e \, Q_A(t_e) \prod_{j=1}^{i} \left[\int_0^{\infty} \mathrm{d}t_j \, P_A(t_j) \int_0^{\infty} \mathrm{d}t'_j \, J_{AA}(t'_j) \right] \right.$$
$$\left. \delta \left(\sum_{k=1}^{i} (t_k + t'_k) + t_e - t \right) \right\} \tag{1}$$

[4][1] Netz and Bocquet "Conductivity Fluctuations in Cylindrical Pores" 2014

3 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**.

3.1 Langevin Symulation

3.1.1 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.

3.1.2 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:

$$m\ddot{\mathbf{r}} = -\lambda\dot{\mathbf{r}} + \mathbf{Z}(t) \tag{2}$$

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:

$$\lambda\dot{\mathbf{r}} = \mathbf{Z}(t) \tag{3}$$

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

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

$$\mathbf{r}(t+\delta t) - \mathbf{r}(t) = \frac{1}{\lambda}\int_t^{t+\Delta t} \mathbf{Z}(t)\,dt' \tag{5}$$

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

In the discussed 1–dimensional case ε is the mean step size and $\boldsymbol{\zeta}(t,\varepsilon)$ is one random vector. For a simple random walk with unique step size this will be ε or $-\varepsilon$ with a chance of 50% each. For a gaussian random walk this will be some value s with a probability:

$$P(s) = \frac{1}{\varepsilon\sqrt{2\pi}} e^{-s^2/2\varepsilon^2} \tag{7}$$

The position of a particle at time $t+\Delta t$ can easily derived from its position[5] at time t.

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \boldsymbol{\zeta}(t,\varepsilon) \tag{8}$$

3.2 Connection to diffusion

The probability density function for both mentioned types of **random walks** fulfill the diffusion equation (*Note:* $n = {}^{t}/_{\delta t}$):

$$\frac{\partial}{\partial t}\rho(x,t) = D\frac{\partial^2}{\partial x^2}\rho(x,t) \quad * \tag{9}$$

$$\text{with} \quad D = \frac{\varepsilon^2}{2\delta t} \tag{10}$$

What means that a random walk can also be seen as a diffusion process. The exact form of the probability density functions is discussed below.

3.2.1 Fixed step size

The motion which is performed in the langevin simulation is widely known as a **random walk**. The simplest variant is as mentioned before to choose ε or $-\varepsilon$ with a chance of 50% each. The probability $p(x,n)$ that a random walk with discrete steps of length ε comes to a position x after n steps. Is given by:

[5] [3] Simon Gravelle and Bocquet "Pink noise of ionic current, theory and modelisation" 2014

$$p(x,n) = \frac{\text{Number of ways to position } x}{\text{Total number of ways}} = \frac{N_x}{N} \tag{11}$$

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

$$N = 2^n \tag{12}$$

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

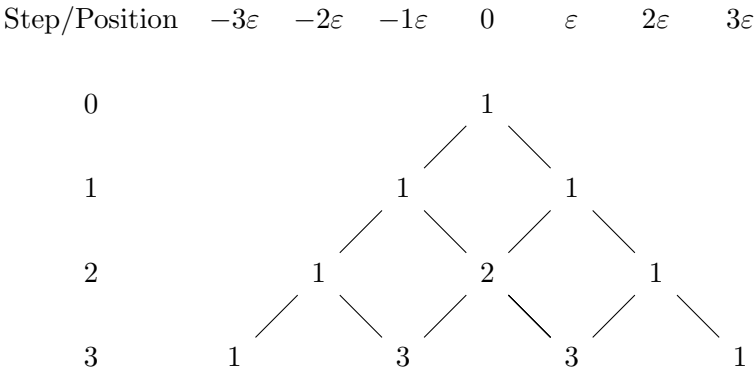

Figure 1: Number of ways to different distances

$$N_x = \binom{n}{k} \tag{13}$$

$$\text{with} \quad k = \frac{1}{2}\left(\frac{x}{\varepsilon} + n\right) \tag{14}$$

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

$$p(x,n) = \binom{n}{k} \cdot 2^{-n} \tag{15}$$

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:

$$p(x,n) \cong \sqrt{\frac{2}{n\pi}} e^{-x^2/2\varepsilon^2 n} \quad * \tag{16}$$

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

$$x \in \{x \mid x = z \cdot 2\varepsilon + \varepsilon\,(n \bmod 2),\ z \in \mathbb{Z} \wedge |x| \leq n\varepsilon\} \tag{17}$$

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:

$$\rho(x,n) = \frac{1}{2\varepsilon}\, p(x,n) = \frac{1}{\varepsilon\sqrt{2\pi n}} e^{-x^2/2\varepsilon^2 n} \tag{18}$$

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

3.2.2 Gaussian random walk

The probability density function for a gaussian random walk with mean step size ε has exactly the same form as the for fixed step size ε.

$$\rho(x,n) = \frac{1}{\varepsilon\sqrt{2\pi n}} e^{-x^2/2\varepsilon^2 n} \tag{19}$$

This can easily be shown with a mathematical induction for $p(x,n)$. Note that because every position is possible the probability

$$p(x,n) = 0 \tag{20}$$

because that means that the number of possible positions is infinite.

Base case $(n = 1)$**:**

$$\rho(x,1) = \frac{1}{\varepsilon\sqrt{2\pi}} e^{-x^2/2\varepsilon^2} \tag{21}$$

Which is exactly the expression of a gaussian distributed 1–dimensional random vector with ε variance. ✓

Inductive step $(n+1)$**:**

$$\rho(x,n+1) = \int_{-\infty}^{\infty} \frac{1}{\varepsilon\sqrt{2n\pi}}\, e^{-x'^2/2n\varepsilon^2} \cdot \frac{1}{\varepsilon\sqrt{2\pi}}\, e^{-(x\,-\,x')^2/2\varepsilon^2}\, \mathrm{d}x' \tag{22}$$

$$= \frac{1}{\varepsilon\sqrt{2(n+1)\pi}}\, e^{-x^2/2(n\,+\,1)\varepsilon^2} \quad * \tag{23}$$

and since the calculated $\rho(x,n+1)$ is the same as $\rho(x,n)$ in *Equation 19* the expression is proofed. ✓

3.3 Mean square distance

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

$$\langle x_n \rangle = \int_{-\infty}^{\infty} x \cdot \rho(x,t)\,\mathrm{d}x = 0 \tag{24}$$

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

$$\langle x_n^2 \rangle = \int_{-\infty}^{\infty} x^2 \cdot \rho(x,t)\,\mathrm{d}x = 2Dt \quad * \tag{25}$$

4 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 2* 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 10*.

The expectation is that for large numbers of runs the mean square converges against the following analytic expression derived from *Equation 25*:

$$\langle x_n^2 \rangle(t) = 2Dt \tag{26}$$

$$\Rightarrow \langle x_n^2 \rangle(n) = 2D\delta t \cdot n \tag{27}$$

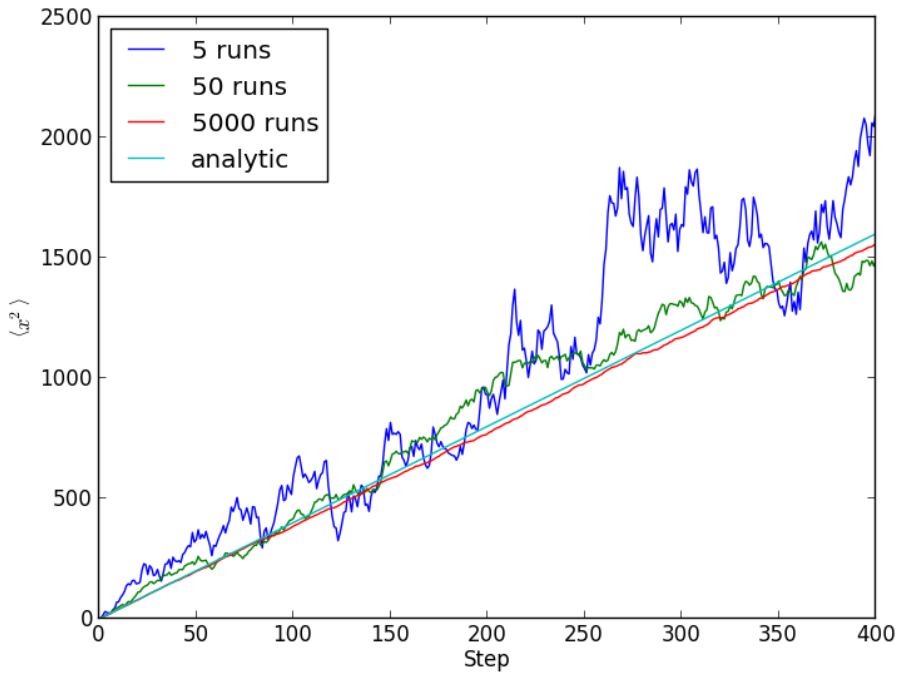

Figure 2: MSD over time for different numbers of runs

5 Infinite plates

The system which is simulated consists of two infinite plates A and B with distance H. Between the two plates is some fluid which surrounds the simulated ion. The ion absorbs at the surface of the two plates with the probability p and desorbs with an exponential decaying probability $P(t)$ given by:

$$P(t) = \frac{1}{\tau} e^{-t/\tau} \tag{28}$$

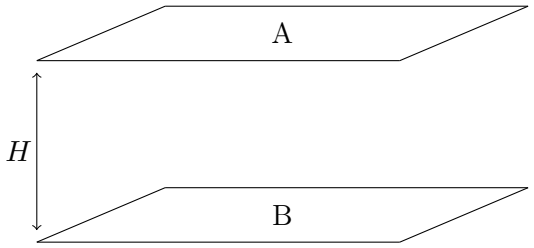

Figure 3: Schematic structure of the system

5.1 Simple random walk vs. Gaussian random walk

For all relevant simulations a gaussian random walk was used. Even if the distribution becomes equivalent for large numbers of steps the gauss distribution represents a much more natural motion of the particle. Moreover much smaller step sizes what means more steps in the simulation are necessary to allow small motions of the particle. And since performance of the simulation is not an issue the gaussian random walk therefore is just superior the simple random walk.

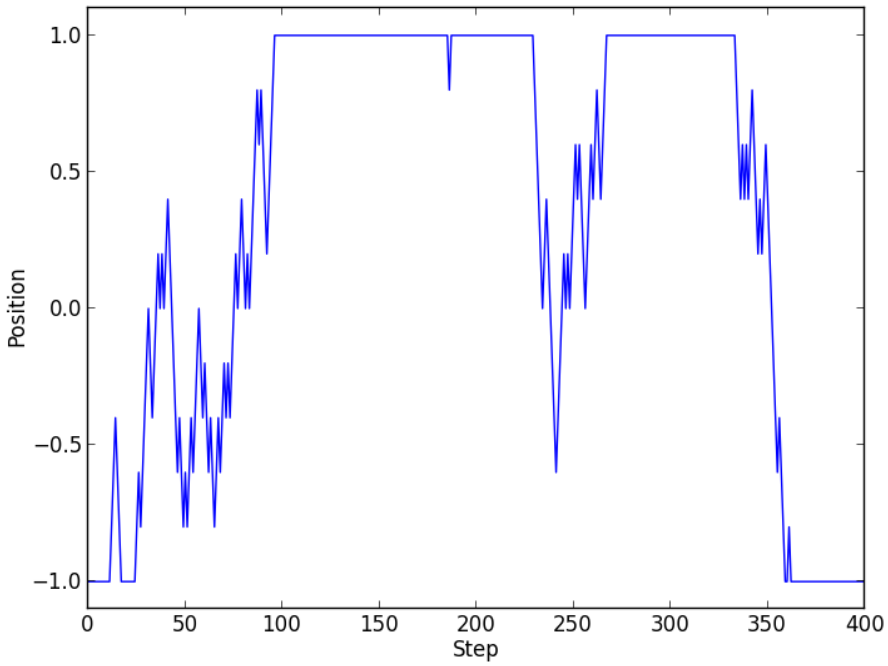

Figure 4: Position of a particle on a simple random walk

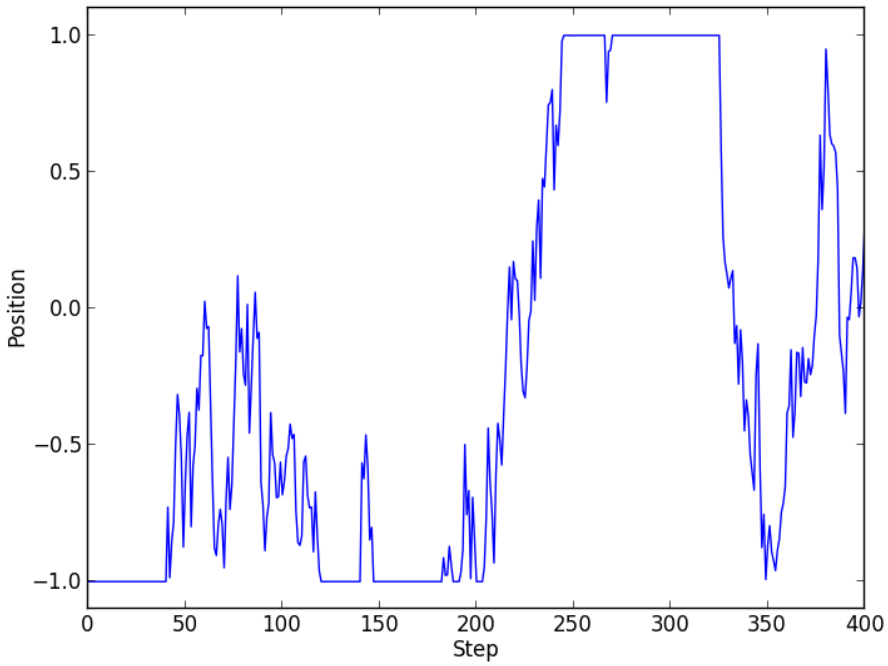

Figure 5: Position of a particle on a gaussian random walk

5.2 Probability density

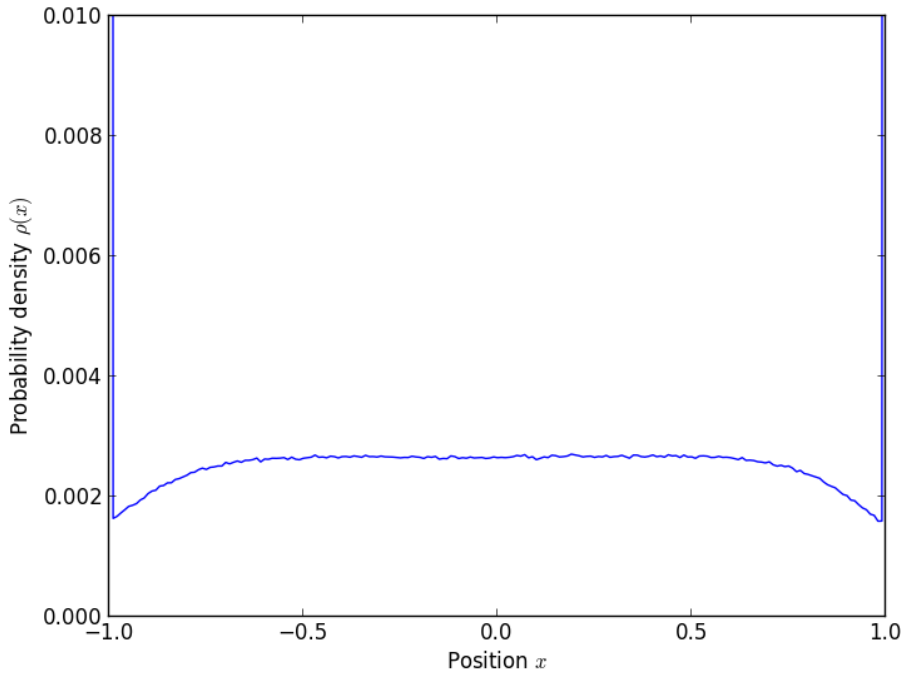

Figure 6: Probability density

5.3 Correlation functions

For a geometry with two plates there is a 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 correlation functions were obtained out of 1 simulation. For all correlation functions the values of the correlation function $C(t)$ for different times t were calculated as:

$$C_{ij}(t) = \frac{\int_0^{t_{max}-t} S_i(t') \cdot S_j(t'+t)\,\mathrm{d}t'}{\int_0^{t_{max}-t} S_i(t')\,\mathrm{d}t'} \tag{29}$$

Where $S_{i/j}(t) = 1$ if the particle has the state of interest at the beginning/end of an interval and $S_{i/j}(t) = 0$ otherwise.

5.4 Parameters of the simulation

The run for the comparison was performed with the following parameters:

Parameter	Value
D	0.1
δt	0.1
τ	1.0
p	1.0
H	1.0

where D the diffusion constant, δt the step size, τ the exponential decay constant for the desorption probability, p the probability that a particle at the boundary absorbs and s is the plate distance. The start position for this lagevin–simulation is not relevant for the correlation functions.

5.5 Interpretation

Also the behavior of the correlation functions in *Figure 7* is easily explainable. Obviously $C_{AA}(t)$ starts from 1 because after its definition it is definitely absorbed at time $t = 0$ on Plate A. $C_{AB}(t)$ and $C_{AD}(t)$ start from 0 because if a particle is absorbed on plate A it is neither possible that it is absorbed on plate B nor it is desorbed. For $t \to \infty$ the absorbed–desorbtion–state wont depend on the state at time $t = 0$ therefore the correlation functions $C_{AA}(t)$ and $C_{AB}(t)$ become stationary on some finite probability. Also the relation $C_{AD}(t) = 1 - C_{AA}(t) - C_{AB}(t)$ is fulfilled what implies that $C_{AD}(t)$ becomes stationary for $t \to \infty$ as well.

5.6 Comparison

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 functions of the following type:

$$C(t) = \sum_{i=0}^{n} c_i \cdot e^{b_i \cdot t} \tag{30}$$

To determine the constants c_i and b_i the `scipy.optimize.curve_fit` in Phython was used which uses non-linear least squares to fit a function[6]. For C_{AA} 4 terms of the and for C_{AB} 2 terms of *Equation 30* function were used.

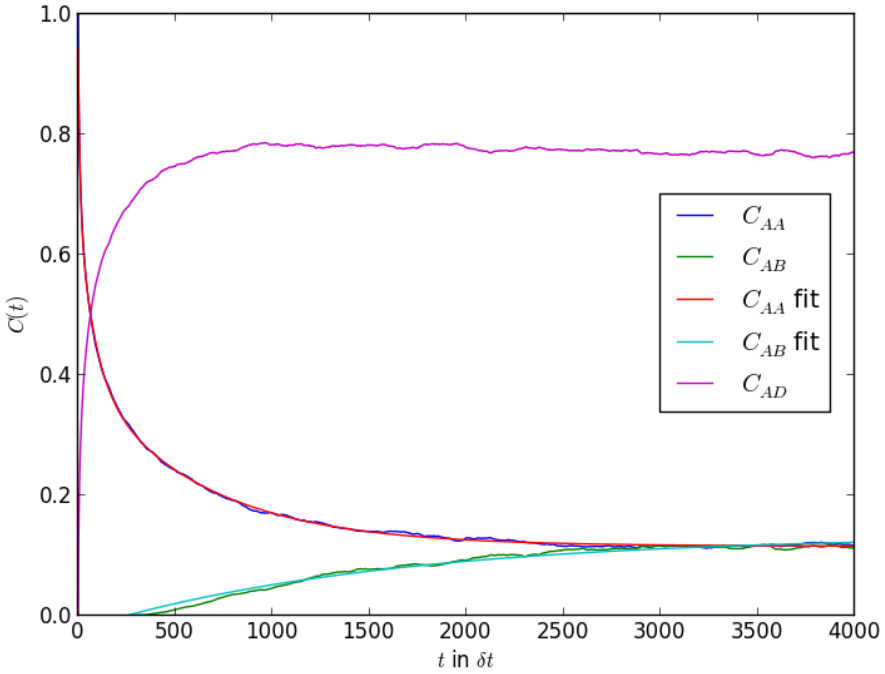

Figure 7: Correlation Functions and its fits

For the simple exponential expression in *Equation 30* the Laplace transformed can be obtained via:

$$F(t) = c_i \cdot e^{b_i \cdot t} \tag{31}$$

$$\widetilde{F}(\omega) = \int_0^\infty c_i \cdot e^{b_i \cdot x} \cdot e^{-\omega \cdot t} \, \mathrm{d}t \tag{32}$$

$$= \frac{ci}{\omega - b_i} \quad \text{(only for } \; b_i > \omega) \tag{33}$$

[6][4] *scipy.optimize.curve_fit* 2014

The Laplace transform correlation functions follow as:

$$\widetilde{C}(\omega) = \sum_{i=0}^{n} \frac{c_i}{\omega - b_i} \tag{34}$$

The comparision between that and the analytic result for $\widetilde{C}_{AA}(\omega)$ is shown on the log–log–plot below:

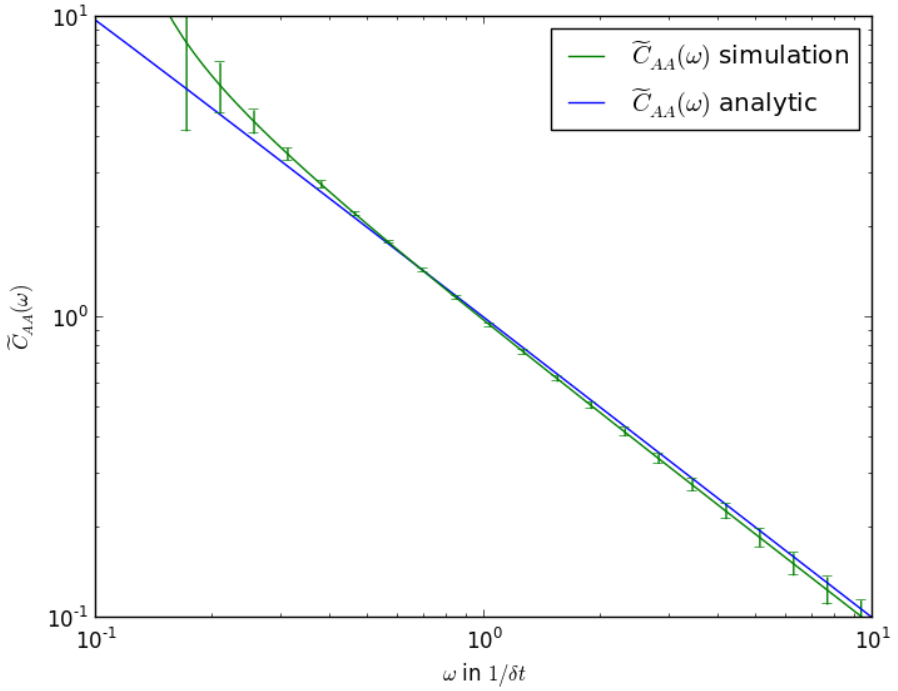

Figure 8: Comparsion of the laplace transform correlation function $\widetilde{C}_{AA}(\omega)$

The errorbars in the figure above are obtained from the variance of the fitting parameters c_i and b_i. It makes clear that in the uncertainty of the fitting curve the result is identical. Note that for $\omega \to b_i$ The fitting function is not properly defined (See *Equation 33*). That means that the divergence at these values is only caused by the fitting method.

6 Finite plates

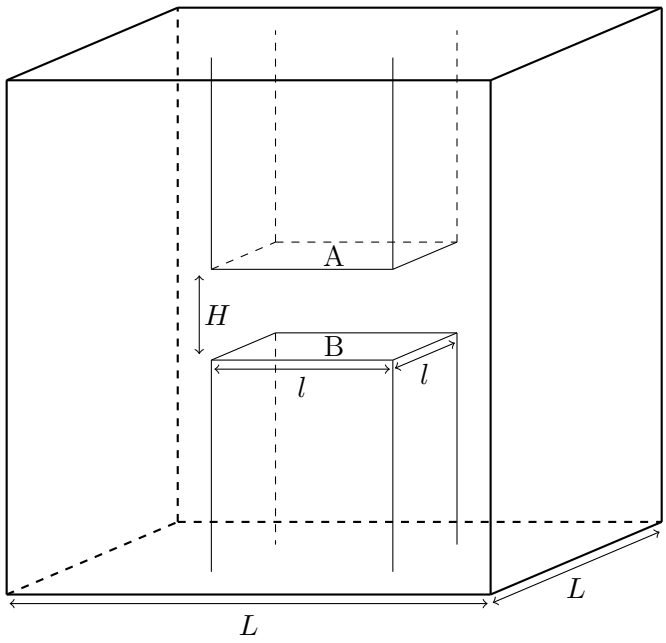

Figure 9: Schematic structure of the finite plate system

7 Conclusion

8 Annex

Equation 9

$$\rho(x,t) = \frac{1}{\varepsilon\sqrt{2\pi^t/\delta t}}\, e^{-\frac{x^2\delta t}{2\varepsilon^2 t}} \tag{35}$$

$$\frac{\partial}{\partial t}\rho(x,t) = -\frac{1}{2t}\rho(x,t) + \frac{x^2\delta t}{\varepsilon^2 t^2}\rho(x,t) \tag{36}$$

$$= \frac{1}{2}\left(\frac{x^2\delta t}{\varepsilon^2 t^2} - \frac{1}{t}\right)\rho(x,t) \tag{37}$$

$$\frac{\partial^2}{\partial x^2}\rho(x,t) = \frac{\partial}{\partial x}\left(-\frac{x\delta t}{\varepsilon^2 t}\right)\rho(x,t) \tag{38}$$

$$= -\frac{\delta t}{\varepsilon^2 t}\rho(x,t) + \frac{x^2\delta t^2}{\varepsilon^4 t^2}\rho(x,t) \tag{39}$$

$$= \frac{\delta t}{\varepsilon^2}\left(\frac{x^2\delta t}{\varepsilon^2 t^2} - \frac{1}{t}\right)\rho(x,t) \tag{40}$$

$$\frac{\partial}{\partial t}\rho(x,t) = D\frac{\partial^2}{\partial x^2}\rho(x,t) \tag{41}$$

$$\Rightarrow \frac{1}{2} = D \cdot \frac{\delta t}{\varepsilon^2} \tag{42}$$

$$\Leftrightarrow D = \frac{\varepsilon^2}{2\delta t} \tag{43}$$

Equation 16

$$p(x,n) = \binom{n}{k} \cdot 2^{-n} \quad \text{with} \quad k = \frac{1}{2}\left(n + \frac{x}{\varepsilon}\right) \tag{44}$$

$$= \frac{n!}{k!(n-k)!} \cdot 2^{-n} \tag{45}$$

$$\text{with} \quad n! \cong \sqrt{2\pi n}\, n^n e^{-n} \qquad \text{(Stirling's formula)}$$

$$\Rightarrow \quad p(x,n) \cong \frac{\sqrt{2\pi n}\, n^n e^{-n}}{\sqrt{2\pi k}\, k^k e^{-k} \sqrt{2\pi(n-k)}\, (n-k)^{n-k} e^{k-n}} \cdot 2^{-n} \tag{46}$$

$$= \left(\frac{\sqrt{2\pi n}}{\sqrt{2\pi k}\, \sqrt{2\pi(n-k)}}\right) \underbrace{\left(\frac{e^{-n}}{e^{-k}\, e^{k-n}}\right)}_{=1} \left(\frac{n^n}{k^k (n-k)^{n-k}}\right) \cdot 2^{-n} \tag{47}$$

$$= \sqrt{\frac{2n}{\pi(n + {}^{x}\!/\!_{\varepsilon})(n - {}^{x}\!/\!_{\varepsilon})}} \cdot \left(\frac{n}{2}\right)^k \cdot \left(\frac{n}{2}\right)^{n-k}$$

$$\cdot \left(\frac{1}{2}\,(n + {}^{x}\!/\!_{\varepsilon})\right)^{-\frac{1}{2}(n+{}^{x}\!/\!_{\varepsilon})} \cdot \left(\frac{1}{2}\,(n - {}^{x}\!/\!_{\varepsilon})\right)^{-\frac{1}{2}(n-{}^{x}\!/\!_{\varepsilon})} \tag{48}$$

$$= \sqrt{\frac{2n}{\pi\left(n^2 - ({}^{x}\!/\!_{\varepsilon})^2\right)}} \cdot \left(\frac{n}{n + {}^{x}\!/\!_{\varepsilon}}\right)^{-\frac{1}{2}(n+{}^{x}\!/\!_{\varepsilon})} \cdot \left(\frac{n}{n - {}^{x}\!/\!_{\varepsilon}}\right)^{-\frac{1}{2}(n-{}^{x}\!/\!_{\varepsilon})} \tag{49}$$

$$= \sqrt{\frac{2n}{\pi\left(n^2 - ({}^{x}\!/\!_{\varepsilon})^2\right)}} \cdot \left(1 + \frac{x}{\varepsilon n}\right)^{-\frac{1}{2}(n+{}^{x}\!/\!_{\varepsilon})} \cdot \left(1 - \frac{x}{\varepsilon n}\right)^{-\frac{1}{2}(n-{}^{x}\!/\!_{\varepsilon})} \tag{50}$$

$$\text{use} \quad x = e^{\ln(x)} \tag{51}$$

$$\Rightarrow \quad p(x,n) \cong \sqrt{\frac{2}{\pi n\left(1 - \left(\frac{{}^{x}\!/\!_{\varepsilon}}{n}\right)^2\right)}}$$

$$\cdot \exp\left\{-\frac{n}{2}\left(1 + \frac{{}^{x}\!/\!_{\varepsilon}}{n}\right) \ln\left(1 + \frac{{}^{x}\!/\!_{\varepsilon}}{n}\right) - \frac{1}{2}(n - {}^{x}\!/\!_{\varepsilon}) \ln\left(1 - \frac{{}^{x}\!/\!_{\varepsilon}}{n}\right)\right\} \tag{52}$$

$$\text{for} \quad n \to \infty \;\Rightarrow\; \alpha \to 0 \quad \alpha := \frac{{}^{x}\!/\!_{\varepsilon}}{n} \tag{53}$$

$$\Rightarrow \quad 1 - \alpha^2 \to 1 + ... \tag{54}$$

$$\text{and} \quad \ln(1+\alpha) \to \alpha - \frac{1}{2}\alpha^2 + ... \tag{55}$$

$$\Rightarrow \quad p(x,n) \cong \sqrt{\frac{2}{n\pi}} \cdot \exp\left\{-\frac{n}{2}\left[(1+\alpha)\left(\alpha - \frac{1}{2}\alpha^2\right) + (1-\alpha)\left(-\alpha - \frac{1}{2}\alpha^2\right)\right]\right\} \tag{56}$$

$$= \sqrt{\frac{2}{n\pi}} \cdot \exp\left\{-\frac{n}{2}\left[\alpha - \frac{1}{2}\alpha^2 + \alpha^2 - \alpha - \frac{1}{2}\alpha^2 + \alpha^2 + \mathcal{O}(\alpha^3)\right]\right\} \tag{57}$$

$$\cong \sqrt{\frac{2}{n\pi}} \cdot \exp\left\{-\frac{n}{2}\left[\alpha^2\right]\right\} \tag{58}$$

$$= \sqrt{\frac{2}{n\pi}} \cdot e^{-x^2/2\varepsilon^2 n} \tag{59}$$

Equation 23

$$p(x,n+1) = \int_{-\infty}^{\infty} \frac{1}{\varepsilon\sqrt{2n\pi}}\, e^{-x'^2/2n\varepsilon^2} \cdot \frac{1}{\varepsilon\sqrt{2\pi}}\, e^{-(x\,-\,x')^2/2\varepsilon^2}\, \mathrm{d}x' \tag{60}$$

$$= \frac{1}{\varepsilon^2\sqrt{4\pi^2 n}} \int_{-\infty}^{\infty} e^{-\frac{x'^2+x^2n-2xx'n+x'^2n}{2n\varepsilon^2}}\, \mathrm{d}x' \tag{61}$$

$$= \frac{1}{\varepsilon^2\sqrt{4\pi^2 n}} \int_{-\infty}^{\infty} e^{-\frac{(n+1)x'^2-2xx'n+x^2n^2/(n\,+\,1)+x^2n-x^2n^2/(n\,+\,1)}{2n\varepsilon^2}}\, \mathrm{d}x' \tag{62}$$

$$= \frac{1}{\varepsilon^2\sqrt{4\pi^2 n}} \int_{-\infty}^{\infty} e^{-\frac{(\sqrt{n+1}x-xn/\sqrt{n\,+\,1}')^2}{2n\varepsilon^2}} \cdot e^{-\frac{x^2-x^2n/(n\,+\,1)}{2\varepsilon^2}}\, \mathrm{d}x' \tag{63}$$

$$\text{let} \quad \alpha = \frac{\sqrt{n+1}x' - {}^{xn}\!/_{\sqrt{n\,+\,1}}}{\sqrt{2n}\varepsilon} \quad \Rightarrow \quad \mathrm{d}\alpha = \sqrt{\frac{n+1}{2n\varepsilon^2}}\, \mathrm{d}x'$$

$$p(x,n+1) = \frac{1}{\varepsilon^2\sqrt{4\pi^2 n}} \sqrt{\frac{2n\varepsilon^2}{n+1}} \cdot e^{-\frac{(n+1)x^2-x^2n}{2(n+1)\varepsilon^2}} \int_{-\infty}^{\infty} e^{-\alpha^2}\, \mathrm{d}\alpha$$

$$= \frac{1}{\varepsilon\sqrt{2(n+1)\pi}} \cdot e^{-\frac{x^2}{2(n+1)\varepsilon^2}}$$

Equation 25

$$\langle x_n^2 \rangle = \int_{-\infty}^{\infty} x^2 \cdot \frac{1}{\varepsilon\sqrt{2\pi n}}\, e^{-x^2/2\varepsilon^2 n}\, \mathrm{d}x \tag{64}$$

$$= \frac{1}{\varepsilon\sqrt{2\pi n}} \int_{-\infty}^{\infty} x^2 \cdot e^{-x^2/2\varepsilon^2 n}\, \mathrm{d}x \tag{65}$$

$$\text{let} \quad \alpha = \frac{x}{\sqrt{2\varepsilon^2 n}} \quad \Rightarrow \quad dx = \sqrt{2\varepsilon^2 n}\, \mathrm{d}\alpha \tag{66}$$

$$\langle x_n^2 \rangle = \frac{\sqrt{2\varepsilon^2 n}}{\varepsilon\sqrt{2\pi n}} \int_{-\infty}^{\infty} 2\varepsilon^2 n\alpha^2\, e^{-\alpha^2}\, \mathrm{d}\alpha \tag{67}$$

$$= \frac{2\varepsilon^2 n}{\sqrt{\pi}} \int_{-\infty}^{\infty} \alpha^2\, e^{-\alpha^2}\, \mathrm{d}\alpha \tag{68}$$

$$= \frac{\varepsilon^2 n}{\sqrt{\pi}} \int_{-\infty}^{\infty} \alpha \cdot 2\alpha\, e^{-\alpha^2}\, \mathrm{d}\alpha \tag{69}$$

$$= \frac{\varepsilon^2 n}{\sqrt{\pi}} \left(-\alpha e^{-\alpha^2} \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} 1 \cdot \left(-e^{-\alpha^2} \right) \mathrm{d}\alpha \right) \tag{70}$$

$$= \frac{\varepsilon^2 n}{\sqrt{\pi}} \left(0 + \sqrt{\pi} \right) \tag{71}$$

$$= \varepsilon^2 n \tag{72}$$

$$= 2D\delta t n \tag{73}$$

$$= 2Dt \tag{74}$$

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