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Confined Brownian Motion

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Abstract

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MSD Mean Squared Displacement

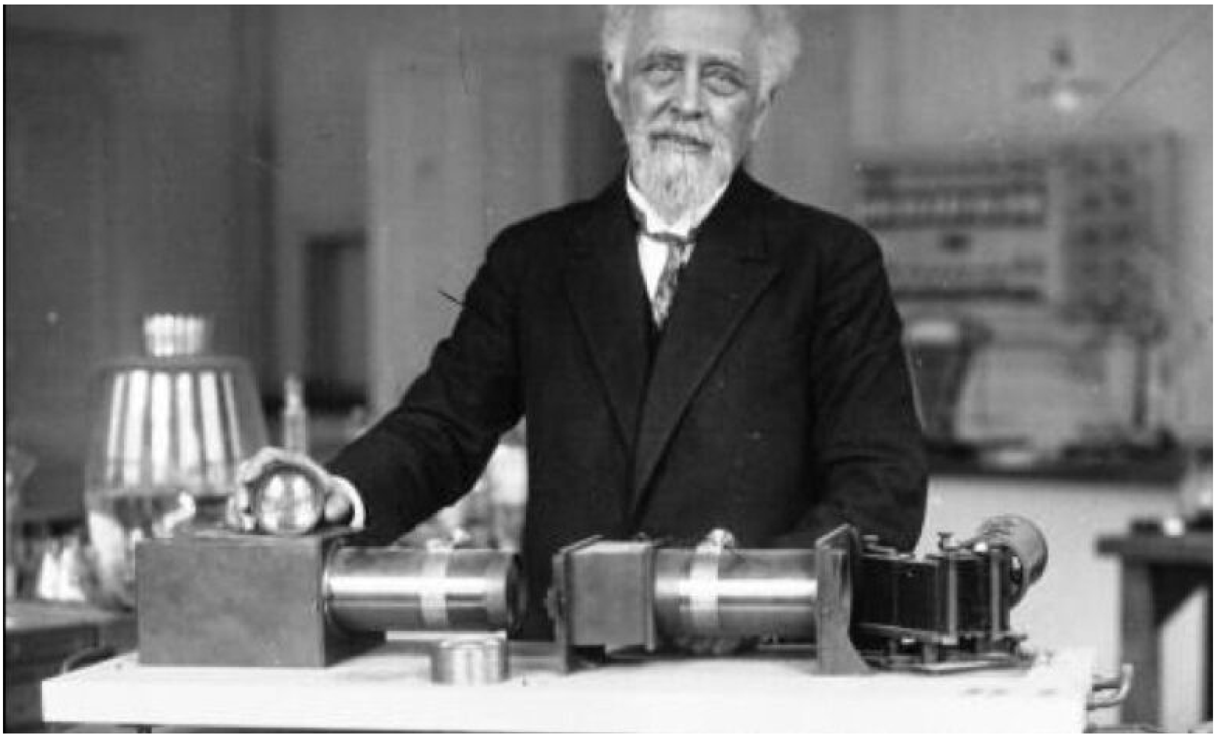
1 Introduction

Since the observations of Gordon Moore in the 60's we know that the technological progress is bound to our ability to miniaturize. It's indeed due to the miniaturization that we are able to have more computational power leading to the rise of knew technologies like the Deep Learning that showed the need of large computational capabilities by having the computer program *AlphaGo* beating *Lee Sedol* one of the greatest player of *Go* in 2016. Since this powerful demonstration AIs using the same technologies are showing up in every field, from the language translator to autonomous cars and is know starting to be extensively used in physics with in 2020 the first focus session on machine learning at the *March Meeting* that continued this year with presentations at every sessions. The success of Deep learning is not due to the fact that it's new and fancy algorithm since it known for several decade but only the fact that the miniaturization permitted to do the stunning amount of computation needed to have a smart AI. Our ability to use this technologies is finally bound to our ability to understand the surface physics at the manometer scale.

On another side we have microfluidic since the 80s which is an incredible multidisciplinary field involving chemistry, engineering, soft matter physics and also biotechnology. Microfluidic permitted the development of daily life technologies like the ink-jet printers or more advanced tools such as DNA chips or lab-on-a-chip technology. The ability to compose with a lot of different system to build microfluidic systems is a wonderful playground for physicists which gave a lot of complex systems in confinement to study and understand how different boundaries can change the dynamic properties of a system. At a time of miniaturization and nanotechnologies, the need of tools permitting the systematic study of complex confined system is a key.

In order to address these challenges my work in the past three years focused on using the confined Brownian motion. Brownian Motion is a central paradigm in modern science. It has implications in fundamental physics, biology, and even finance, to name a few. By understanding that the apparent erratic motion of colloids is a direct consequence of the thermal motion of surrounding fluid molecules, pioneers like Einstein and Perrin provided decisive evidence for the existence of atoms, Specifically, free Brownian motion in the bulk us characterized by a typical spatial extent evolving as the square root of time, as well as Gaussian displacements. At a time of miniaturization and interfacial science, and moving beyond the idealized bulk picture, it is relevant to consider the added roles of boundaries to the above context. Indeed, Brownian motion at interfaces and in confinement is a widespread practical situation in microbiology and nanofluidics. In such case, surface effects become dominant and alter drastically the Brownian statistics, with key implications towards: i) the understanding and smart control of the interfacial dynamics of microscale entities; and ii) high-resolution measurements of surfce forces at equilibrium. Intertingly, a confined colloid will exhibit non-Gaussian statistics in displacements, due to the presence of multiplicative noises induced by the hindered mobility near the wall. Besides, the particle can be subjected to electrostatic or Van der Waals forces exerted by the interface, and might experience slippage too. Considering the two-body problem, the nearby boundary can also induce some effective interaction. Previous studies have designed novel methods to measure the diffusion coefficient of confined colloids, or to infer surface forces.

In the the first part of the manuscript I will present the history of the Brownian motion and it's basic theory. In a second part I will present particle tracking using Mie holography and our experimental setup. Then the third part will focus on one trajectory analysis in order to infer the surface induced effects on the Brownian motion. In a last chapter I will present more complex inference.



2 Brownian motion

2.1 The Brownian motion discovery

In 1827 the Scottish botanist Robert Brown published a paper [1] on his observation on the pollen of *Clarkia pulchella* with a lot of details on his taught processes. His experiments was made to understand the flower reproduction, but, as he was looking through the microscope he observed some minute particles ejected from the pollen grains. At first, he thought this movement was a test to of the male organ, then looking at grains Mosses and *Equiseta* which had been dried up for one hundred years, he was surprised to see this "peculiar" movement and since he was able to increase the number of particle by bruising ovula or seeds of *Equisetum* he abandoned his supposition. Interestingly each time that he encountered a material that he was able to reduce to a fine enough powder to be suspended in water, he observed a constant motion, although, he never guessed the origin of the particles movement.

The difficulty at this time to observe and capture this movement made the study of what we called today Brownian motion quite difficult and the first work on erratic movement was actually done by Louis Bachelier in 1900 in his PhD thesis "The theory of speculation", where he describe a stochastic analysis of the stock and option market. The mathematical description is still a used in the modern development of tools for the economic industry.

It's finally in 1905 that Albert Einstein describe that "bodies of microscopically visible size suspended in a liquid will perform movements of such a magnitude that they can be easily observed in a microscope". [2]. A nice remark to make here is that in 1948 Einstein wrote a letter to one of his friend where he stated having deduced the Brownian motion "from mechanics, without knowing that anyone had already observed anything of the kind" [3].

It's in 1908 that Jean Perrin published his experimental work on the Brownian motion, that way he was able to measure the Avogadro number and prove the kinetic theory that Einstein developed. I would also cite M. Chaudesaigues and M. Dabrowski, who helped J. Perrin to track the particles by hand, half-minutes by half-minutes, for more than 3000 displacements (25 hours) and several particles. This impressive and daunting work is highly detailed in "Mouvement brownien et molécules" [4]. This is partly due to this work than J. Perrin received the nobel award in 1926.

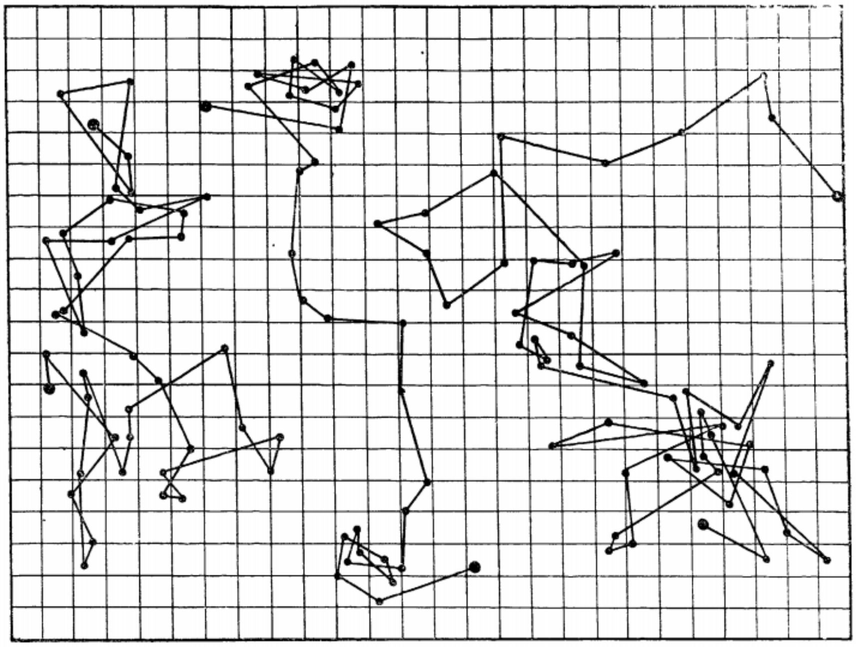


Figure 1: Brownian motion of 1 μm particle in water tracked by hand by Jean Perrin and his colleagues, each point are timely space by 30 seconds and 16 divisions represents 50 μm the mean square value of was the first prove of the Einstein's kinetic theory

2.2 The Einstein Brownian theory

In this section we will derive the main characteristic of the bulk Brownian motion in the manner of Einstein in 1905 by summarizing the section 4 of [2]. We will then examine the random motion of particles suspended in a liquid and their relation to diffusion, caused bu thermal molecular motion. We assume that each particle motion is independent of other particles; also. the motion of one particle at different time interval as to to be taken independent process as long as the time interval is not too small. We know introduce a time interval τ which as to be small compered to the observation time but small enough so that the displacement between two consecutive time intervals τ may be taken as independent events (ie. the over damped regime).

For simplicity, we will here look only at the Brownian motion of n particles in 1D along the x axis. In a time interval τ the position of each individual particle will increase by a displacement Δ, positive or negative and different for all the particles. The number of particle dn experiencing a displacement lying between Δ and $\Delta + d\Delta$ in a time interval τ is written as:

$$dn = n\varphi(\Delta)d\Delta, \tag{2.2.1}$$

where

$$\int_{-\infty}^{\infty} \varphi(\Delta) d\Delta = 1, \tag{2.2.2}$$

and φ is nonzero only for very small displacement Δ and satifies $\varphi(\Delta) = \varphi(-\Delta)$.

Let $f(x,t)$ be the number of particles per unit volume. From the definition of the function $\varphi(\Delta)$ we can obtain the distribution of particles found at time $t+\tau$ from their distribution at a time t, we obtain:

$$f(x, t+\tau)dx = dx \int_{\Delta=-\infty}^{\Delta=+\infty} f(x+\Delta, t)\varphi(\Delta)d\Delta \tag{2.2.3}$$

Since τ is very small, we have:

$$f(x, t+\tau) = f(x,t) + \tau\frac{\partial f}{\partial t} \tag{2.2.4}$$

On the other side we can Taylor expend $f(x+\Delta, t)$ in powers of Δ since only small values of Δ contribute. We obtain:

$$f(x+\Delta, t) = f(x,t) + \Delta\frac{\partial f(x,t)}{\partial x} + \frac{\Delta^2}{2!}\frac{\partial^2 f(x,t)}{\partial x^2}... \tag{2.2.5}$$

Putting all together, in Eq.2.2.3 we obtain:

$$f + \frac{\partial f}{\partial t}\tau = f\int_{-\infty}^{+\infty} \varphi(\Delta)d\Delta + \frac{\partial f}{\partial x}\int_{-\infty}^{+\infty} \Delta\varphi(\Delta)d\Delta + \frac{\partial^2 f}{\partial x^2}\int_{-\infty}^{+\infty} \frac{\Delta^2}{2}\varphi(\Delta)d\Delta... \tag{2.2.6}$$

On the right-hand side, since $\varphi(x) = \varphi(-x)$ all even terms will vanish and all the odd terms will be very small compared to the precedent. If we take into account 2.2.2 and only the first and third term of the right hand side, by putting:

$$\frac{1}{\tau}\int_{-\infty}^{+\infty} \frac{\Delta^2}{2}\varphi(\Delta)d\Delta = D, \tag{2.2.7}$$

the Eq.2.2.6 finally becomes:

$$\frac{\partial f}{\partial t} = D\frac{\partial^2 f}{\partial x^2}. \tag{2.2.8}$$

We can here recognize a differential equation for the diffusion with D the diffusion coefficient. We will now initiate the same position $x = 0$ for all the particle at $t = 0$ as in the Fig. and $f(x,t)dx$ now denoting the number of particles whose position as increased between the times $t = 0$ and $t = t$ by a quantity lying between x and $x + dx$ such that we must have:

$$f(x \neq 0, t = 0) = 0 \text{ and } \int_{-\infty}^{+\infty} f(x,t)dx = n. \tag{2.2.9}$$

The solution of this equation is known and the same as the heat equation and is given by the Gaussian:

$$f(x,t) = \frac{1}{\sqrt{4\pi D}} \frac{\exp^{\frac{-x^2}{4Dt}}}{\sqrt{t}} \tag{2.2.10}$$

From this solution we can see that the mean value of the displacement of all the particles along the x axis is equal to 0 and the square root of the arithmetic mean of the squares of displacements (that we commonly call Mean Square displacement (MSD)) is given by:

$$\lambda_x = \sqrt{2Dt} \tag{2.2.11}$$

The mean displacement is thus proportional to the square root of time, this result is generally the first behavior that we check when we study for the first time experimental Brownian motion. We can further suppose that in 3D, the square root of the MSD will be given by $\lambda_x\sqrt{3}$

Previously in his paper, in the chapter 3, he had found by writing the thermodynamic equilibrium of a suspension of particles that the diffusion coefficient of a particle should be written:

$$D = \frac{RT}{N_A}\frac{1}{6\pi\eta a} \tag{2.2.12}$$

with R the gas constant, T the temperature, N_A the Avogadro number and η the fluid viscosity. Thus an experimental observation measurement could lead to a measurement of the Avogadro number and the true size of the atoms since:

$$N_A = \frac{t}{\lambda_x^2} \frac{RT}{3\pi\eta a} \tag{2.2.13}$$

Finally he ends up is paper [2] by saying *"Let us hope that a researcher will soon succeed in solving the problem posed here, which is of such importance in the theory of heat!"*. I'd like here to emphasize on the importance of solving this problem in very beginning of th 19's. At this time two theory about the fundamental component existed, ones seeing only energy and a second one especially supported by Boltzmann and his kinetic theory of gases, here used by Einstein. Thus, an experimental proof of Eq.2.2.12 would prove the existence of atoms and molecules. Due to a lot of theoretical misunderstanding of the theory and experimental error scientist such as Svedberg or Henri thought that Eintein's theory was false [5] by even proving that the statistical properties of the Brownian motion was changing with the pH of the solution. It's finally in 1908 that Chaudesaigues and Perrin published all the evidence to prove Einstein's theory mainly by their ability to create particle emulsion of well controlled radius.

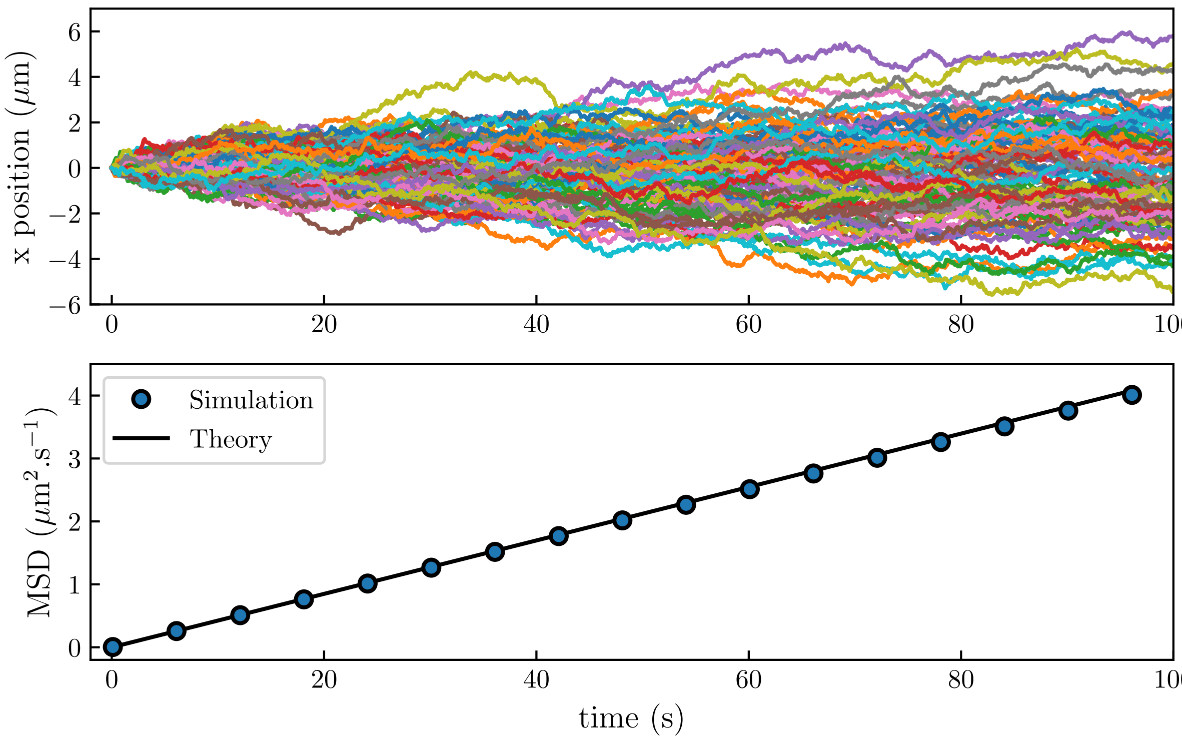


Figure 2: Simulation of bulk Brownian motion of 1 μm particles in water. On the top each line represents the trajectory of a Brownian particle over 100 seconds a total of 100 trajectories or shown. On the bottom, bullets represents the MSD computed from the simulated trajectories. The black plain line represents the Einstein's theory, which is computed from the square of Eq.2.2.11

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