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Confined Brownian Motion

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Abstract

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Nomenclature

| | |
|------------------|--|
| α | Noise amplitude |
| ℓ_B | Boltzmann length |
| ℓ_B | Debye length |
| η | Fluid viscosity |
| η_\perp | Viscosity orthogonal to a wall, see Eq.2.4.1 |
| η_\parallel | Viscosity parrallel to a wall, see Eq.2.4.2 |
| γ | Friction coefficient |
| ρ_F | Fluid density |
| ρ_P | Particle density |
| B | Amplitude of the electrostatic interactions |
| D | Diffusion coefficient, see Eq.2.2.12 |
| g | Gravity constant |
| k_B | Boltzmann Constant |
| m | Mass of a particle |
| N_A | Avogrado constant |
| R | Gas constant |
| T | Temperature |
| V_t | Velocity of a particle |
| X_t | Particle position, see Eq.2.3.13 |

List of Abbreviations

| | |
|------------|-----------------------------------|
| fps | Frames per second |
| MSD | Mean Squared Displacement |
| SDE | Stochastic Differential Equations |

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 new 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 now 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 nanometer 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 is 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 surface forces at equilibrium. Interestingly, 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 were 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 ovule 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 particle's 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 his PhD thesis "The theory of speculation", where he describes 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.

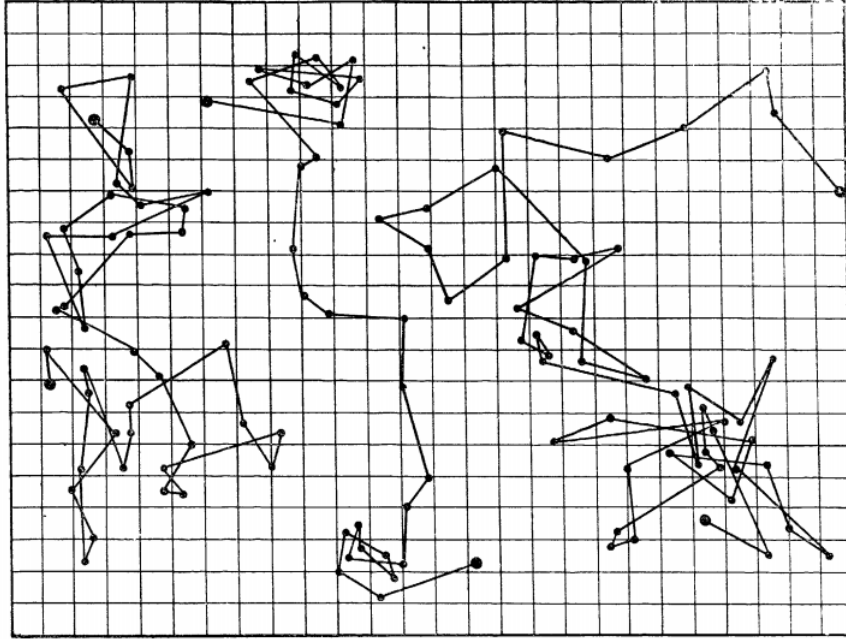


Figure 1: Brownian motion of $1 \mu\text{m}$ particle in water tracked by hand by Jean Perrin and his colleagues, each point are timely space by 30 seconds and 16 divisions represents $50 \mu\text{m}$ the mean square value of was the first prove of the Einstein's kinetic theory

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 by 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 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 compared to the observation time but small enough so that the displacement between two consecutive time intervals τ may be taken as independent events (i.e. 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:

$$dn = n\varphi(\Delta)d\Delta, \quad (2.2.1)$$

where

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

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

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:

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

Since τ is very small, we have:

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

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

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

Putting all together, in Eq.2.2.3 we obtain:

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

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:

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

the Eq.2.2.6 finally becomes:

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2}. \quad (2.2.8)$$

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.2 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:

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

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

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

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:

$$\lambda_x = \sqrt{2Dt} \quad (2.2.11)$$

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:

$$D = \frac{RT}{N_A} \frac{1}{6\pi\eta a} \quad (2.2.12)$$

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:

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

Finally, he ends up in 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 the 19's. At this time two theory about the fundamental component existed, one's 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 Einstein'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.

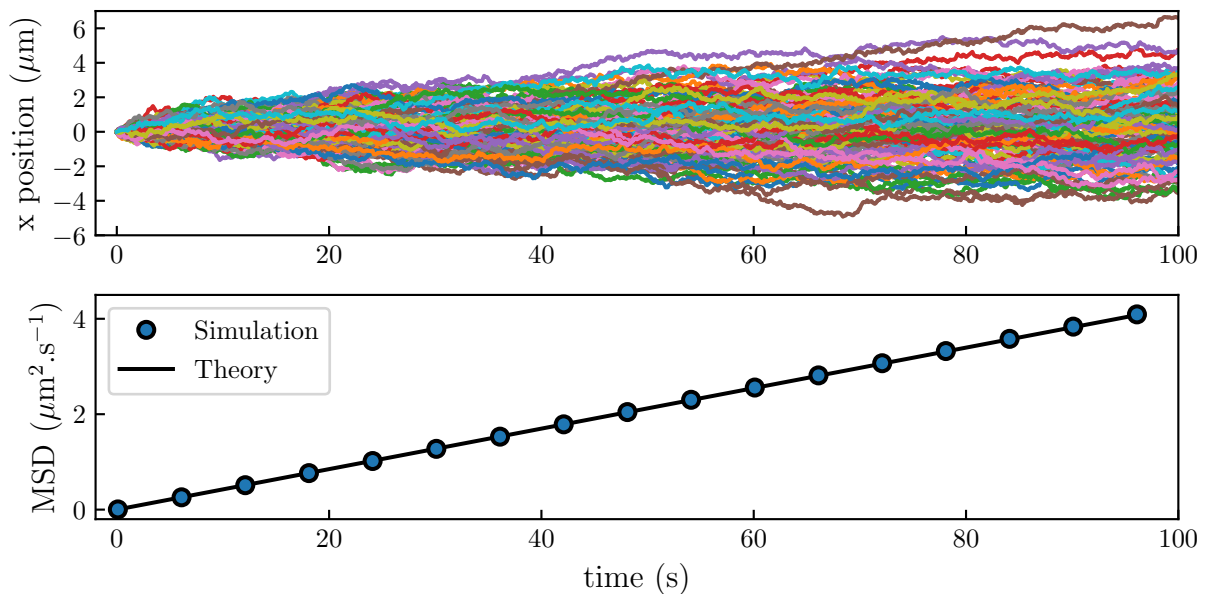


Figure 2: Simulation of bulk Brownian motion of 1 μm particles in water. On the top each line represents the trajectory of a Brownian particle over 100 seconds a total of 100 trajectories or shown. On the bottom, bullets represents the MSD computed from the simulated trajectories. The black plain line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

2.3 Stochastic Differential Equations

In physics we generally write Brownian motion with Stochastic Differential Equations (SDE). This model was introduced in 1908 by Langevin [6], since it benefits of a correct mathematical definition of the noise, this model is now used by the major part of physicists working on random processes. Note than it can also be found under the name of Langevin equation. This model is write as follows:

$$mdV_t = -\gamma V_t dt + \alpha dB_t \quad (2.3.1)$$

with m the mass and V_t the velocity of the particle. This SDE is finally the Newton's second law, relating the particle momentum changes on the left-hand side of the equation and an external force on the right-hand side. We see that the external force applied on the particle is given by two terms: a friction term, with a friction coefficient γ plus a random force with a a coefficient that we will detail for a spherical particle and dB_t is a random noise which has a Gaussian distribution of zero mean thus:

$$\langle dB_t \rangle = 0 \quad (2.3.2)$$

and we chose de variance to be equal to dt giving :

$$\langle dB_t^2 \rangle = dt \quad (2.3.3)$$

For a spherical particle the friction term is given by the Stoke's formula: $\gamma = 6\pi\eta a$ with η the fluid viscosity and a the particle radius. Thus, we can derive the mean value of the particle velocity as:

$$\langle dV_t \rangle = -\frac{\gamma}{m} \langle V_t \rangle + \frac{\alpha}{m} \langle dB_t \rangle \quad (2.3.4)$$

with the properties of dB_t given by Eq.2.3.2, it becomes:

$$\langle dV_t \rangle = -\frac{\gamma}{m} \langle V_t \rangle \quad (2.3.5)$$

which as a familiar solution:

$$\langle V_t(t) \rangle = V_0 e^{-\frac{\gamma}{m}t} \quad (2.3.6)$$

This result shows that the average of the velocity should decay to zero with a characteristic time $\tau_B = \frac{m}{\gamma}$ for the polystyrene particle used during my experiments which are micrometric we have $\tau_B \approx 10^{-7}$ s. This means that if we measure the displacement of a particle with a time interval $\Delta t \gg \tau_B$ the displacement can be taken as independent events as it was stated by Einstein. In physics terms, this means that we are in the over damped regime and $dV_t = 0$ thus leading to the over-damped Langevin equation :

$$-\gamma V_t + \alpha dB_t = 0 \quad (2.3.7)$$

The experiments done during my thesis used a video camera that can reach a maximum of hundreds frames per second (fps) reaching time steps of $\approx 10^{-2}$ s. Therefore, all my works falls into the over damped regime. Before dropping to full expression of the Langevin we can use it to compute how $\langle V_t^2 \rangle$ using Taylor expansion we have:

$$\begin{aligned} dV_t^2 &= \frac{\partial V_t^2}{\partial V_t} dV_t + \frac{1}{2} \frac{\partial^2 V_t^2}{\partial V_t^2} dV_t^2 \\ &= 2V_t dV_t + \frac{1}{2} 2dV_t^2 \\ &= 2V_t \left(-\frac{\gamma}{m} V_t dt + \frac{\alpha}{m} dB_t \right) + \frac{\alpha^2}{m^2} dB_t^2 + o(dt^2) \end{aligned} \quad (2.3.8)$$

Taking the average then gives:

$$\langle dV_t^2 \rangle = \left[2\frac{\gamma}{m} \langle V_t^2 \rangle + \frac{\alpha^2}{m^2} \right] dt \quad (2.3.9)$$

Since equilibrium average in thermodynamic must become time independent, we have:

$$\langle V_t^2 \rangle = \frac{\alpha^2}{2\gamma m}. \quad (2.3.10)$$

However, from the equipartition of energy we also know that:

$$\langle \frac{1}{2} m V_t^2 \rangle = \frac{1}{2} k_B T \quad (2.3.11)$$

This equation permits a direct determination of the amplitude of the noise α :

$$\alpha = \sqrt{2k_B T \gamma} \quad (2.3.12)$$

Using this model, the position of the particle is given by the integration of V_t such as the position at a time t is given by

$$X_t = \int_0^t V_{t'} dt'. \quad (2.3.13)$$

the MSD is then written as:

$$\langle X_t^2 \rangle = \int_0^t \int_0^t \langle V_{t'} V_{t''} \rangle dt' dt'' \quad (2.3.14)$$

We need to derive the correlation function of the velocity $\langle V_{t'} V_{t''} \rangle$ using Eq.2.3.6 we can write:

$$\langle V_t V_0 \rangle = \langle V_0^2 \rangle e^{-t/\tau_B} \quad (2.3.15)$$

As the equilibrium state is invariant with a time translation and assume that V_0 as an equilibrium steady state distribution such as $\langle V_0^2 \rangle = k_B T / m$ we have:

$$\langle V_t V_{t'} \rangle = \frac{k_B T}{m} e^{-|t-t'|/\tau_B} \quad (2.3.16)$$

By using the symmetry of the absolute function we can solve Eq.2.3.14 by splitting the integral where $t' > t''$ and where $t' < t''$:

$$\begin{aligned}
\langle X_t^2 \rangle &= 2 \frac{k_B T}{\gamma} = \int_0^t dt' \int_0^{t'} dt'' e^{-|t'-t''|/\tau_B} = 2 \frac{k_B T}{\gamma} \left(\int_0^t dt' [1 - e^{-t'/\tau_B}] \right) \\
&= 2 \frac{k_B T}{\gamma} (t - \tau_B [1 - e^{-t/\tau_B}])
\end{aligned} \tag{2.3.17}$$

We can extract two results from that equation, at short time $t \ll \tau_B$

$$\begin{aligned}
\langle X_t^2 \rangle &= 2 \frac{k_B T}{\gamma} \left(t - \tau_B \left[1 - 1 - \frac{t}{\tau_B} + \frac{t^2}{2\tau_B^2} \right] \right) \\
&= \frac{k_B T}{m} t^2
\end{aligned} \tag{2.3.18}$$

this is the ballistic regime, if one can experimentally explore time shorter than τ_B he will then measure the real velocity of the particle and observe that it has the Maxwell-Boltzmann distribution. At longer time, $t \gg \tau_B$ the MSD is given by:

$$\langle X_t^2 \rangle = 2 \frac{k_B T}{\gamma} t. \tag{2.3.19}$$

This is the Brownian regime where the MSD is linear with the time as depicted by Einstein, and we identify the diffusion coefficient of the particle $D = k_B T / \gamma$ which is commonly called the Stokes-Einstein relation. It is possible to simulate an over damped bulk Brownian trajectory by simply replacing in Eq.2.3.7 $\langle V_t \rangle$ by $(x_i - x_{i-1}) / \Delta t$ thus giving:

$$x_i = x_{i-1} + \sqrt{2D} w_i \tag{2.3.20}$$

with w_i a Gaussian distributed random number generated with a mean $\langle w_i \rangle = 0$ and a standard deviation $\langle w_i^2 \rangle = dt$, a trajectory of N points can simulated with a few lines of python as in the following snippet code which was used to create Fig.2.

```

import numpy as np
N = 1000 # trajectory length
D = 1 # diffusion coefficient
dt = 0.5 # time step
trajectory = np.cumsum(np.sqrt(2*D)*np.random.normal(0, np.sqrt(dt), N))

```

2.4 The confined Brownian motion

We have seen that the bulk Brownian motion is well known and documented for a long time. But, in the real world, the boundaries are not at infinity and could play a role in the process of diffusion. Indeed, it was theorized by H. Faxen [7] that the presence of a wall would change the Stokes-Einstein relation with a viscosity dependent to the position of the particle. As the particle get closer to a surface, the presence of the non-slip boundary condition make the fluid harder to push, thus increasing the local viscosity of the particle. This variation of the viscosity will be different for orthogonal and parallel displacement to the wall, thus we write respectively η_{\perp} and η_{\parallel} with η_0 being the fluid viscosity and z the height of the particle:

$$\eta_{\perp} = \frac{4}{3}\eta_0 \sinh\beta \sum_{n=1}^{\infty} \frac{n(n+1)}{2n-12n+3} \left[\frac{2\sinh(2n+1)\beta + (2n+1)\sinh 2\beta}{4\sinh^2(n+1/2)\beta - (2n+1)^2\sinh^2\beta} - 1 \right], \quad (2.4.1)$$

and

$$\eta_{\parallel} = \eta_0 \left[1 - \frac{9}{16}\xi + \frac{1}{8}\xi^3 - \frac{45}{256}\xi^4 - \frac{1}{16}\xi^5 \right]^{-1}, \quad (2.4.2)$$

where $\xi = \frac{a}{z}$ and $\beta = \cosh^{-1}(\xi)$. It is possible to simplify the form of η_{\perp} by using a Padé approximation, which is correct up to 1% of accuracy:

$$\eta_{\perp} = \eta_0 \frac{6z^2 + 9az + 2a^2}{6z^2 + 2az}. \quad (2.4.3)$$

Of course, this local viscosity is directly reflected on the diffusive properties of the particle, hence a local diffusion coefficient, which we write:

$$D_i(z) = \frac{k_B T}{6\pi\eta_i(z)a} \quad (2.4.4)$$

One of the first experimental measurement of the local diffusion coefficient was brought by Faucheux and Libchaber [8] where they measured the mean diffusion coefficient with various gaps and particle radius their results can be found in the Fig.3.

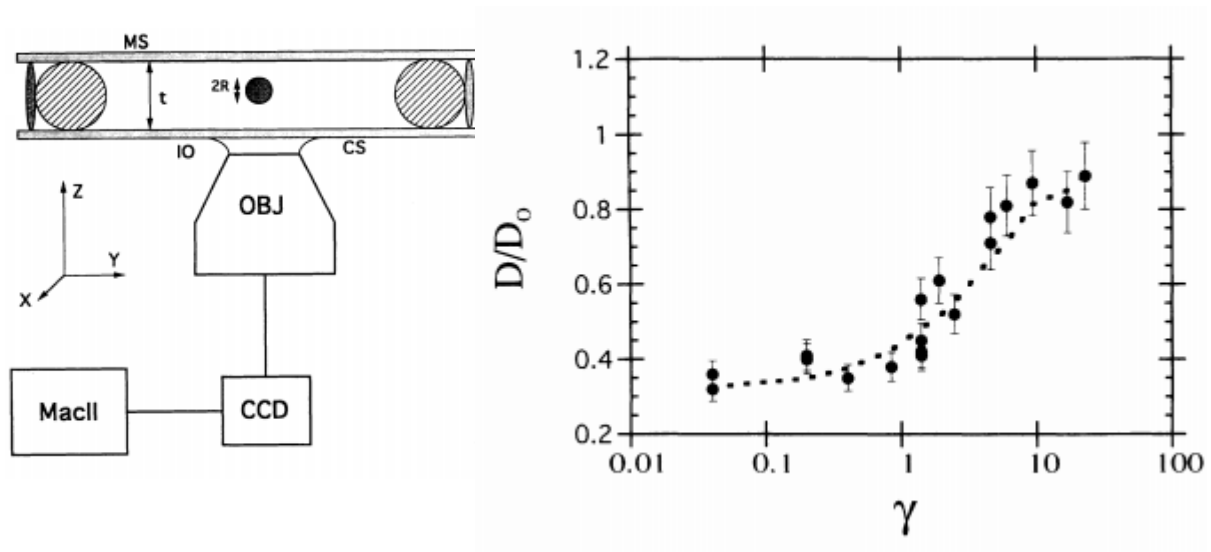


Figure 3: Figure extracted from [8], on the left is the experimental setup used. It is an inverted microscope used in order to track particle of size $2R$ inside a cell of thickness t . On the right is their final result, where they measure the diffusion parallel coefficient D_{\perp} given by Eq.2.4.2, here normalized by D_0 the bulk diffusion coefficient.

Another interesting physical aspect to take into account when looking at confined Brownian motion is the potential the particle is lying into. Let's first consider the weight of the particle. Indeed, if the particle density does not match the fluid's one, a spherical particle will lie in a gravity potential given by:

$$U_g(z) = \frac{4}{3}\pi a^3(\rho_P - \rho_F)gz \quad (2.4.5)$$

that we can rewrite for simplicity

$$\frac{U_g(z)}{k_B T} = \frac{z}{\ell_B} \quad (2.4.6)$$

with ℓ_B the Boltzmann length which represents the balance between the kinetic energy and the weight of the particle:

$$\ell_B = \frac{k_B T}{\frac{4}{3}\pi a^3 \Delta \rho g}. \quad (2.4.7)$$

Let's now consider the interactions with the substrate, glass side when immersed in water

do charged negatively as well as polystyrene particles that we use. We will then have repulsive interactions between the wall and the particles, the electrostatic potential can be written as [9]:

$$\frac{U_{\text{elec}}(z)}{k_{\text{B}}T} = B e^{-z/\ell_{\text{D}}} \quad (2.4.8)$$

Where B is the amplitude of electrostatic interactions, representing the surface charges and ℓ_{B} being the Debye length, which is the characteristic length of the electrostatic interactions. The particle is thus lying in a total potential given by:

$$\frac{U(z)}{k_{\text{B}}T} = B e^{-z/\ell_{\text{D}}} + \frac{z}{\ell_{\text{B}}} \quad (2.4.9)$$

From this total potential one can construct the Gibbs-Boltzmann distribution in position:

$$P_{\text{eq}}(z) = A e^{\frac{U}{k_{\text{B}}T}} \quad (2.4.10)$$

Where A is a normalization constant so that $\int P_{\text{eq}} = 1$. This probability distribution gives us the probability to find the particle at a height z . The exponential decay due to the gravity was first measured by Perrin [10] by methodically counting through a microscope the number of colloids in suspension as a function on the height.

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