

THÈSE PRÉSENTÉE
POUR OBTENIR LE GRADE DE
DOCTEUR
DE L'UNIVERSITÉ DE BORDEAUX
ECOLE DOCTORALE SCIENCES PHYSIQUES ET DE
L'INGÉNIEUR
LASERS, MATIÈRE, NANOSCIENCES

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Confined Brownian Motion

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Soutenue le 25 décembre 2019

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Abstract

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Nomenclature

α	Noise amplitude
ℓ_B	Boltzmann length
ℓ_D	Debye length
η	Fluid viscosity
η_{\perp}	Viscosity orthogonal to a wall, see Eq.4.1.40
η_{\parallel}	Viscosity parallel to a wall, see Eq.4.1.41
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	Avogadro constant
R	Gas constant
T	Temperature
V_t	Velocity of a particle
X_t	Particle position, see Eq.2.3.19

List of Abbreviations

fps	Frames per second
MRSE	Mean Relative Squared Error
MSD	Mean Squared Displacement
PDF	Probability Density Function
RICM	Reflection Interference Contrast Microscopy
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 knew technologies like the Deep Learning [1] 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 [2] or lab-on-a-chip technology [3]. 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 [4, 5]. 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 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 [6–8]. Besides, the particle can be subjected to electrostatic or Van der Waals forces [9] exerted by the interface, and might experience slippage too [10, 11]. Considering the two-body problem, the nearby boundary can also induce some effective interaction [12]. Previous studies have designed novel methods to measure the diffusion coefficient of confined colloids [13–18], or to infer surface forces [19–24].

In the first part of the manuscript I will present the history of the Brownian motion and its 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 an article [25] on his observation on the pollen of *Clarkia pulchella* with a lot of details on his thought 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 the goal of this movement was to test the presence of a male organ. In order to test this theory, he extended his observations to Mosses and *Equiseta*, which were drying for a hundred years. However, the fact that this peculiar movement was still observable made him invalidate his theory. 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 the same type of motion, although, he never understood its particle's movement.

The difficulty at this time to observe and capture such a movement made the study of what we call today Brownian motion quite difficult and the first theoretical work was actually done by Louis Bachelier in his PhD thesis “The theory of speculation”, where he described a stochastic analysis of the stock and option market. Nowadays, the mathematical description of random movement is still used in the modern financial industry.

It is finally in 1905 that Albert Einstein theoretically state 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” [4]. A 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” [26].

It is in 1908 that Jean Perrin published his experimental work on Brownian motion. that way he was able to measure the Avogadro number and prove the kinetic theory that Einstein developed. I would also cite Chaudesaigues and Dabrowski, who helped 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*” [27]. This is partly due the results this work that Perrin received the Nobel award in 1926.

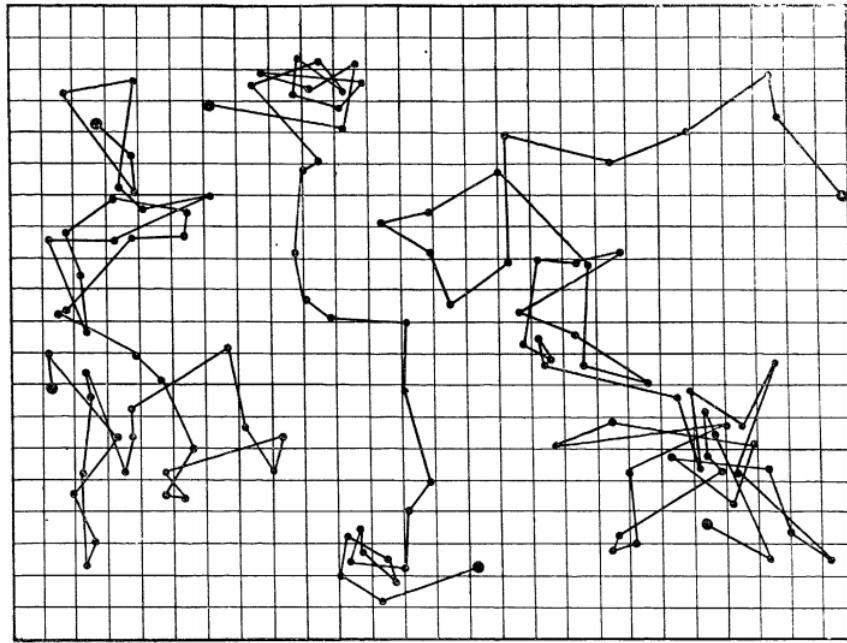


Figure 1: Brownian motion of $1 \mu\text{m}$ particles in water tracked by hand by Jean Perrin and his colleagues. The points are spaced in time by 30 seconds and 16 divisions represents $50 \mu\text{m}$.

2.2 Einstein's Brownian theory

In this section we will derive the main characteristics of bulk Brownian motion in the manner of Einstein in 1905 by summarizing the section 4 of [4]. We will then examine the random motion of particles suspended in a liquid and its relation to diffusion, caused by thermal molecular motion. We assume that each particle motion is independent of other particles; also the motions of one particle at different times are assumed to be independent of one another provided that the time interval is not too small. Furthermore, we now introduce a time interval τ which is small compared to the observation time but large enough so that the displacements in two consecutive time intervals τ may be taken as independent events.

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. The number of particles 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 the probability distribution of displacement. We assume for now, that φ is a Gaussian distribution, with a variance scaling linearly with τ . Additionally, since such a distribution is even, it 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 , through:

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

Since we suppose that τ is very small with respect to t , we have at first order in time:

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

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

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

Combining Eqs.2.2.4, 2.2.5 and 2.2.3 we obtain:

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

On the right-hand side, since $\varphi(x)$ is an even function, the second term vanishes. Taking into account Eq.2.2.2 and invoking the definition:

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

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 partial equation of diffusion with D the diffusion coefficient. We will now initiate the same position $x = 0$ for all the particles at $t = 0$ as in Fig.2. $f(x, t)dx$ denotes the number of particles whose positions have increased between the times 0 and 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 Eq.2.2.8 is then the Green's function of the heat equation in the bulk:

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

From this solution we can see that the mean value of the displacement 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 the Root Mean Square Displacement (RMSD)) is given by:

$$\lambda_x = \sqrt{\langle \Delta^2 \rangle} = \sqrt{2Dt}. \quad (2.2.11)$$

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 Brownian motion. In 3D, the square root of the MSD will be given by $\lambda_x\sqrt{3}$.

Previously in his article [4], Einstein had found by writing the thermodynamic equilibrium of a suspension of particles that the diffusion coefficient of a particle should read:

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

with R the gas constant, T the temperature, N_A the Avogadro number, η the fluid viscosity and k_B the Boltzmann constant. Thus, an experimental measurement of D could lead to a measurement of the Avogadro number since:

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

Furthermore, measuring N_A also gives us the mass of atoms and molecules since the mass of a mole is known; as an example the mass of an oxygen atom will be given by $\frac{16}{N_A}$ and the mass a water molecule by $\frac{18}{N_A}$. Finally, Einstein ends up in article [4] by writing “*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 would like here to emphasize the importance of solving this problem at the very beginning of the 20th century. At this time two theories about the fundamental matter components existed, one involving energy and a continuum description in terms of field, and the other one, discrete atoms, especially supported by Boltzmann and his kinetic theory of gases, used by Einstein. Due to a lot of theoretical misunderstandings and experimental error scientist such as Svedberg or Henri thought that Einstein’s theory was false [28] by even suggesting that the statistical properties of Brownian motion were changing with the pH of the solution. It is finally in 1908 that Chaudesaigues and Perrin published all the evidence to prove Einstein’s theory mainly by their ability to create particle emulsions of well controlled radii.

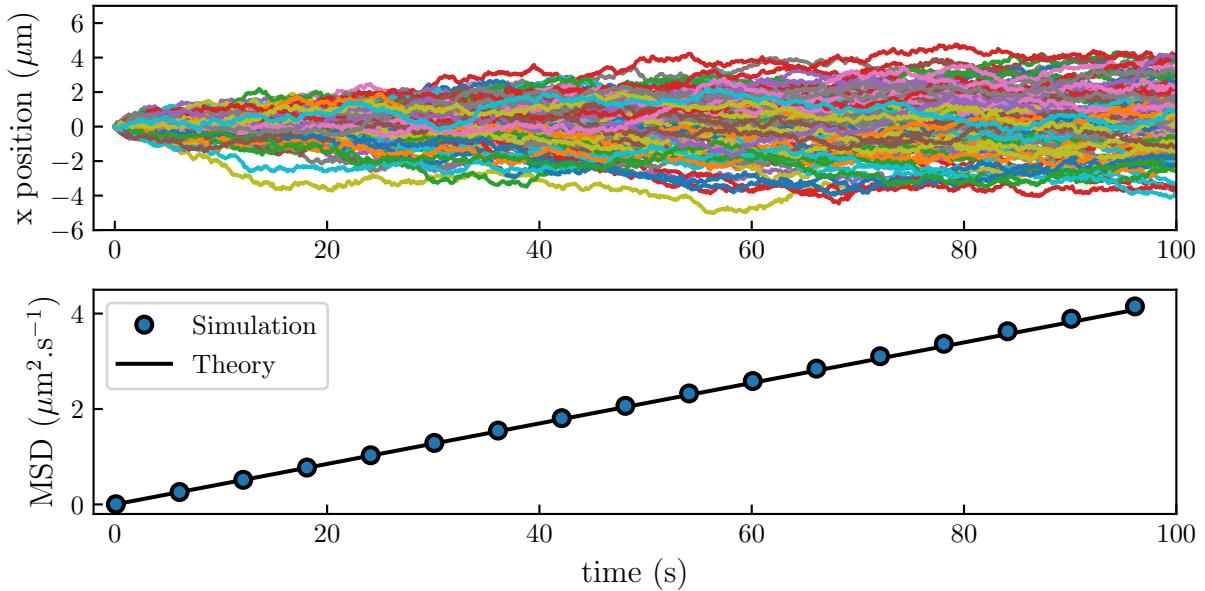


Figure 2: Simulation of the bulk Brownian motion of $1 \mu\text{m}$ particles in water. On the top each line represents the trajectory of a Brownian particle over 100 seconds. A total of 100 trajectories are shown. On the bottom, bullets represent the Mean Square Displacement (MSD) computed from the simulated trajectories. The black plain line represents Einstein’s theory, which is computed from the square of Eq.2.2.11.

2.3 The Langevin Equation

In physics we generally describe Brownian motion through a particular Stochastic Differential Equations (SDE). This model was introduced in 1908 by Langevin [29], this model is now used by the major part of physicists working on random processes. The Langevin equation for a free colloid reads:

$$m dV_t = -\gamma V_t dt + \alpha dB_t , \quad (2.3.1)$$

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

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

and variance equal to:

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

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:

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

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

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

Moreover, without a loss of generality, the average of a variable x , $\langle x \rangle$, is done over a set

of N observations $\{x_i\}$ such as:

$$\langle x \rangle = \frac{1}{N} \sum_{i=1}^N x_i , \quad (2.3.6)$$

one can then show that:

$$\frac{d}{dt} \langle x \rangle = \frac{d}{dt} \left[\frac{1}{N} \sum_{i=1}^N x_i \right] = \frac{1}{N} \sum_{i=1}^N \frac{d}{dt} x_i = \langle \frac{d}{dt} x \rangle . \quad (2.3.7)$$

The latter thus shows that it is possible to invert average value $\langle \cdot \rangle$ and a derivative. Therefor, Eq.2.3.5 becomes:

$$\frac{d}{dt} \langle V_t \rangle = -\frac{\gamma}{m} \langle V_t \rangle , \quad (2.3.8)$$

which has a familiar solution:

$$\langle V_t(t) \rangle = V_0 e^{-\frac{\gamma}{m} t} , \quad (2.3.9)$$

with V_0 an initial velocity. This result shows that the average of the velocity should decay to zero with a characteristic time $\tau_B = \frac{m}{\gamma}$. For instance, the polystyrene particles used during my experiments which are micro-metric we have $\tau_B \approx 10^{-7}$ s. This means that if we measure the displacements of a particle with a time interval $\tau \gg \tau_B$ the displacement can be taken as independent events as it was stated by Einstein. In physical terms, this means that we are in the over-damped regime, in this case the Langevin equation reads:

$$-\gamma V_t dt + \alpha dB_t = 0 . \quad (2.3.10)$$

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 work falls into the over damped regime. Before focusing definitely on Eq.2.3.10, we can use Eq.2.3.4 to characterize further the unknown coefficient α . In order to do so we compute the mean square value of Eq.2.3.4, starting by taking the second order Taylor expansion:

$$\begin{aligned} d(V_t^2) &\simeq \frac{\partial V_t^2}{\partial V_t} dV_t + \frac{1}{2} \frac{\partial^2 V_t^2}{\partial V_t^2} (dV_t)^2 \\ &= 2V_t dV_t + (dV_t)^2 \end{aligned} \quad (2.3.11)$$

combining Eqs.2.3.1 and 2.3.11, we obtain by only keeping the terms of order dt :

$$d(V_t^2) = 2V_t \left(-\frac{\gamma}{m} V_t dt + \frac{\alpha}{m} dB_t \right) + \frac{\alpha^2}{m^2} dB_t^2 . \quad (2.3.12)$$

Thus, the average value of $d(V_t^2)$ reads:

$$\langle d(V_t^2) \rangle = -2\frac{\gamma}{m} \langle V_t^2 \rangle dt + 2\frac{\alpha}{m} \langle V_t dB_t \rangle + \frac{\alpha^2}{m^2} \langle dB_t^2 \rangle . \quad (2.3.13)$$

Moreover, since dB_t is chosen independently of the velocity V_t , one can write $\langle V_t dB_t \rangle = \langle V_t \rangle \langle dB_t \rangle = 0$. Taking the latter remark into account and the fact that $\langle dB_t^2 \rangle = dt$, Eq.2.3.13 becomes:

$$\langle d(V_t^2) \rangle = \left[-2\frac{\gamma}{m} \langle V_t^2 \rangle + \frac{\alpha^2}{m^2} \right] dt . \quad (2.3.14)$$

Since equilibrium averages in thermodynamics must become time independent, we have $\langle d(V_t^2) \rangle = 0$, thus:

$$\langle V_t^2 \rangle = \frac{\alpha^2}{2\gamma m} . \quad (2.3.15)$$

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

$$\langle \frac{1}{2} m V_t^2 \rangle = \frac{1}{2} k_B T . \quad (2.3.16)$$

The latter equation permits a direct determination of the amplitude of the noise α :

$$\alpha = \sqrt{2k_B T \gamma} . \quad (2.3.17)$$

The latter result permits to compute the amplitude of the random force in the Langevin equation. Taking the over-damped Langevin equation, it reads:

$$V_t dt = \sqrt{2 \frac{k_B T}{\gamma}} dB_t \quad (2.3.18)$$

Furthermore, one can write the position of the particule X_t at a time t , such as:

$$X_t = \int_0^t V_{t'} dt' , \quad (2.3.19)$$

where we can suppose at the initial time $t = 0$ that $X_0 = 0$. Computing $\langle X_t^2 \rangle$ using Eqs.2.3.18,2.3.19 and 2.3.3 thus gives:

$$\langle X_t^2 \rangle = 2 \frac{k_B T}{\gamma} t = 2 D t \quad (2.3.20)$$

By relating $\langle X_t^2 \rangle$ to the Mean Square Displacement (MSD) to the initial position such as:

$$\text{MSD} = \langle (X_0 - X_t)^2 \rangle = \langle X_t^2 \rangle , \quad (2.3.21)$$

we obtain that the MSD should be linear with the time. This result confirms that using the over-damped Langevin equation, leads to the Einstein's result Eq.2.2.11. Where one can identify the diffusion coefficient of the particle to be $D = k_B T / \gamma$. Additionally, the latter identity is called the Stokes-Einstein relation.

Additionally, the Langevin equation is great to compute correlator such as the velocity correlator $\langle V_t V_{t''} \rangle$ which the simplest to compute and the one that we will detail below. Indeed, if we use the full Langevin equation, $\langle X_t^2 \rangle$ can't be that easily computed since $m dV_t$ does not vanish. We would thus need to rewrite Eq.2.3.20 using the velocity correletor such as:

$$\langle X_t^2 \rangle = \int_0^t \int_0^t \langle V_{t'} V_{t''} \rangle dt' dt'' . \quad (2.3.22)$$

Let us now study how the two-point correlator function $\langle V_t V_{t''} \rangle$, using the full Langevin

equation multiplied by V_0 and following the same steps as for Eq.2.3.9, one has:

$$\langle V_t V_0 \rangle = \langle V_0^2 \rangle e^{-t/\tau_B} . \quad (2.3.23)$$

As the equilibrium state is invariant under temporal translation and assuming that V_0 has an equilibrium steady-state distribution with $\langle V_0^2 \rangle = k_B T / m$ we have:

$$\langle V_t V'_t \rangle = \frac{k_B T}{m} e^{-|t-t'|/\tau_B} . \quad (2.3.24)$$

One can solve Eq.2.3.22 by splitting the integral in two parts, where $t' > t''$ and $t' < t''$:

$$\begin{aligned} \langle X_t^2 \rangle &= \frac{k_B T}{m} \int_0^t dt' \int_0^{t'} dt'' e^{-|t'-t''|/\tau_B} = 2 \frac{k_B T}{\gamma} \left(\int_0^t dt' \left[1 - e^{-t'/\tau_B} \right] \right) \\ &= 2 \frac{k_B T}{\gamma} \left(t - \tau_B \left[1 - e^{-t/\tau_B} \right] \right) . \end{aligned} \quad (2.3.25)$$

We can extract two results from that equation. At short time $t \ll \tau_B$, one has:

$$\begin{aligned} \langle X_t^2 \rangle &\simeq 2 \frac{k_B T}{\gamma} \left(t - \tau_B \left[1 - 1 + \frac{t}{\tau_B} - \frac{t^2}{2\tau_B^2} \right] \right) \\ &= \frac{k_B T}{m} t^2 . \end{aligned} \quad (2.3.26)$$

This is the ballistic regime. If one can experimentally explore times shorter than τ_B one will then measure the real velocity of the particle. At longer times, $t \gg \tau_B$, the MSD is given by:

$$\langle X_t^2 \rangle \simeq 2 \frac{k_B T}{\gamma} t = 2 D t . \quad (2.3.27)$$

This is the diffusive regime where the MSD, as found earlier, Eq.2.3.20 with the over-damped Langevin equation. To study this different results, it can be interesting to simulate the Brownian motion.

2.4 Numerical simulation of bulk Brownian motion

2.4.1 The numerical Langevin Equation

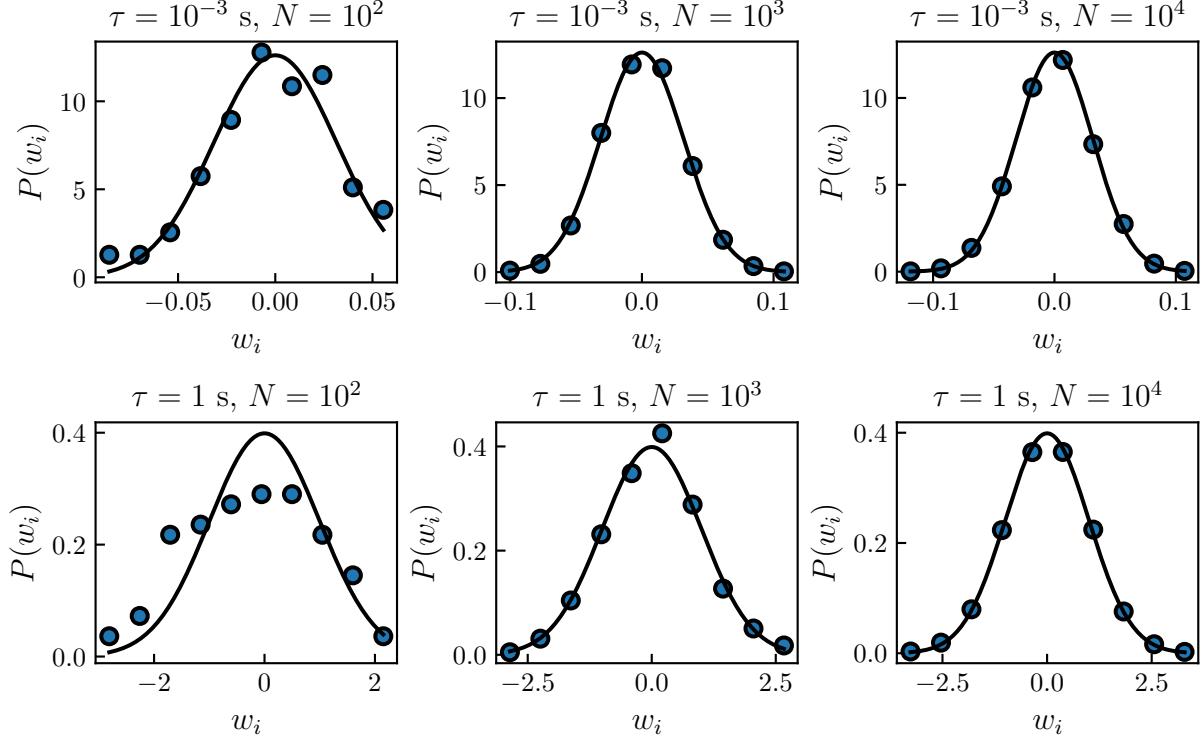


Figure 3: Bullets represents the probability density function of w_i , a Gaussian distributed number with a mean value $\langle w_i \rangle$ and a variance $\langle w_i^2 \rangle = \tau$. The plain black line represents a gaussian of zero mean and a τ variance, Eq.2.4.3. On the first line simulation is done with $\tau = 10^{-3}$ s and $\tau = 1$ s on the second one. Each column correspond to a number of draw N , from the left to the right $N = 10^2$, 10^3 and 10^4 .

The Langevin equation is an ordinary differential equation that can easily be numerically simulated in the bulk case. If one approximate the continuous position of a particle X_t at a time t by a discrete-time sequence x_i which is the solution of the equation at a time $t_i = i\tau$ with τ being the time step of the simulation. One can then use the Euler method to numerically write V_t as

$$V_t \simeq \frac{x_i - x_{i-1}}{\tau} , \quad (2.4.1)$$

and dV_t as

$$\begin{aligned}\frac{dV_t}{dt} &\simeq \frac{\frac{x_i - x_{i-1}}{\tau} - \frac{x_{i-1} - x_{i-2}}{\tau}}{\tau} \\ &= \frac{x_i - 2x_{i-1} + x_{i-2}}{\tau^2}.\end{aligned}\quad (2.4.2)$$

The only term remaining to be computed numerically is the random term dB_t . One can thus replace dB_t/dt by w_i ¹ a Gaussian distributed random number generated with a mean $\langle w_i \rangle = 0$ and a variance $\langle w_i^2 \rangle = \tau$. The Probability Density function (PDF) of the Gaussian distribution is thus given by:

$$P(w_i) = \frac{1}{\sqrt{2\pi\tau}} e^{-\frac{w_i^2}{2\tau}}. \quad (2.4.3)$$

Such a number can be simply generated with the following Python snippet.

```

1 import numpy as np
2
3 tau = 0.5 # time step in seconds
4 wi = np.random.normal(0, np.sqrt(tau))

```

In the latter, `random.normal()` is a built-in Numpy module that permits the generation of Gaussian distributed random numbers. Finally, by combining Eqs.2.4.1, 2.4.2 and w_i , the full Langevin equation becomes:

$$m \frac{x_i - 2x_{i-1} + x_{i-2}}{\tau^2} = -\gamma \frac{x_i - x_{i-1}}{\tau} + \sqrt{2k_B T \gamma} w_i. \quad (2.4.4)$$

From the latter, one can write x_i as:

$$x_i = \frac{2 + \tau/\tau_B}{1 + \tau/\tau_B} x_{i-1} - \frac{1}{1 + \tau/\tau_B} x_{i-2} + \frac{\sqrt{2k_B T \gamma}}{m(1 + \tau/\tau_B)} \tau w_i, \quad (2.4.5)$$

where we can observe that we need two initial condition are needed, the two first positions of the particle. Numerically, those positions could be randomly generated or simply set to 0, if enough statics are generated it will not play much into the results.

¹ The notation w was choose since in mathematical term, a real valued continuous-time stochastic process such as dB_t is called a Wiener process in honor of Norbert Wiener [30].

2.4.2 Simulating Brownian motion using Python

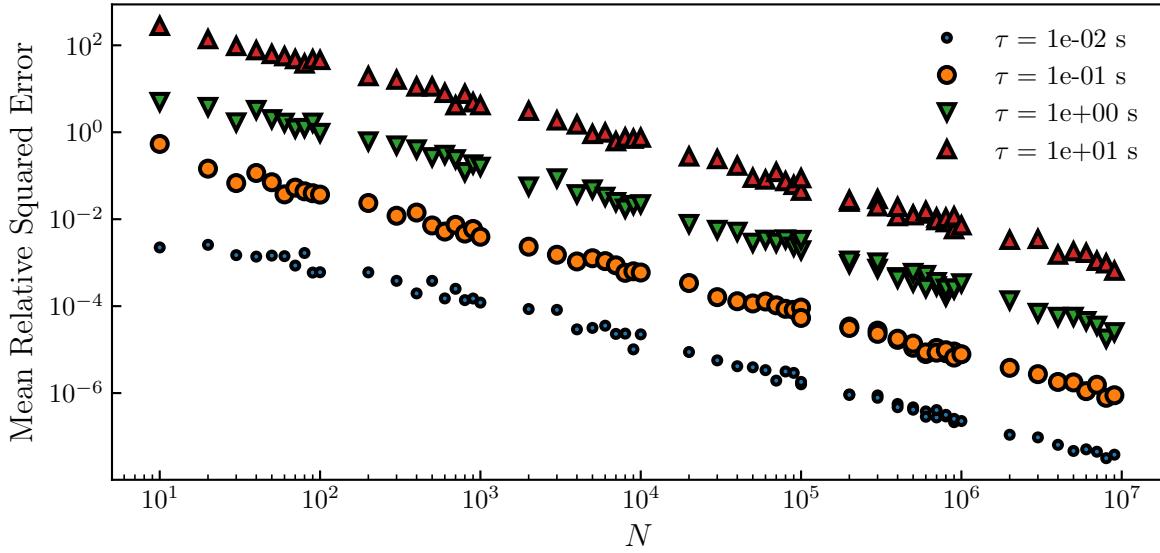


Figure 4: Mean Relative Squared Error (MRSE) of the PDF measured from a generation of N Gaussian random number w_i , and, the actual Gaussian over which the generation is done, Eq.2.4.3. The generation is done over a Gaussian which has a mean value $\langle w_i \rangle = 0$ and the variance $\langle w_i^2 \rangle = \tau$. We explore generation ranging from $N = 10$ to 10^7 and $\tau = 10^{-2}$ to 10 s

Before, deeping into the actual simulation, it could be interresting to ask ourselfe about how long the simulation should be. Indeed, for the different observables' mean value to remain constant we should wait a suffisient amount of time. It is possible to have qualitative approach by generating N number w_i and measuring the resulting PDF $P_c(w_i)$ and looking how much we need to increase N to have $P_c(w_i) \simeq P(w_i)$. As we can see on the Fig.3, for simulation made with $\tau = 10^{-3}$ s and $\tau = 1$ s, we obervre that as we increase the number of generated numbers N , the measured PDF, get closer to the real one given by Eq.2.4.3.

To have a more quantitative approach, one can compute the Mean Relative Squared Error (MRSE)) between the measured PDF $P_c(w_i)$ and $P(w_i)$ as a function of the number of generated numbers N , such as:

$$\text{MRSE} = \left\langle \frac{(P_c(w_i) - P(w_i))^2}{P(w_i)^2} \right\rangle_N \quad (2.4.6)$$

where the notation $|_N$ denotes that N numbers are generated. Additionaly, since we measure the $P_c(w_i)$ by doing an histogram, the question of how many bins is used should

be answered. It is possible to use the Freedan-Diaconis rule [31] to compute the width of the bins to be used in a histogram, this rule reads:

$$\text{Bin width} = 2 \frac{\text{IQR}(\{w_i\})}{\sqrt[3]{N}}, \quad (2.4.7)$$

where IQR is the interquartile range, and $\{w_i\}$ a sample of N random numbers. Moreover, one should only take 2 bins as a minimum. The actual number of bins can be computed using the following Python snippet.

```

1 import numpy as np
2
3 def _iqr(wi):
4     """Function to compute interquartile range."""
5     return np.subtract(*np.percentile(x, [75, 25]))
6
7 def optimal_bins(wi):
8     """
9         Function to compute the optimal number of bins using Freedan-diaconis rule.
10        Input: list of random numbers / Output: optimal bins number
11    """
12
13    n = int(diff(wi) / (2 * _iqr(wi) * np.power(len(wi), -1 / 3)))
14
15    if n <= 2:
16        return 2
17    else:
18        return n

```

As we can see on the Fig.4, for τ varying between 10^{-2} and 10 seconds, and, N between 10 and 10^6 , the MRSE decreases as N increases. More over, it is interesting to observe that the MRSE is greater as τ increases for a fix N value. Indeed, as an example we would need to only generate $N = 10^{-3}$ numbers to obtain a MRSE of 10^{-4} for $\tau = 0.1$ s, while we would need to $N = 10^6$ for $\tau = 1$ s.

Now that the Langevin equation is known numerically, one could use it to simulate some Brownian trajectories. A simple way to do the simulation is shown using Python in the Jupyter notebook framework in the appendix.???. A set of trajectory simulated for a fictive particle of radius $a = 1 \mu\text{m}$ and mass $m = 10 \mu\text{g}$ in water is shown in Fig.5-a). For such a particle the diffusive characteristic time is $\tau_B = 0.53\text{s}$. Moreover, as one can see on the Fig.5-b), the MSD is correctly modeled by the Eq.2.3.26 for $\tau \ll \tau_B$ and by the

Eq.2.3.27 for $\tau \gg \tau_B$. Please note that for non-continuous data such as the simulation or experimental trajectories, and for a given time increment Δt , the MSD, is generally defined by:

$$\langle \Delta x^2 \rangle|_t = \langle (x(t + \Delta t) - x(t))^2 \rangle|_t , \quad (2.4.8)$$

where the average $\langle \rangle|_t$ is performed over a time t . Additionally, it can be numerically using the following Python function.

```

1 def msd(x, Dt):
2     """Function that return the MSD for a list of time index Dt for a trajectory x"""
3     _msd = lambda x, t: np.mean((x[:-Dt] - x[Dt:]) ** 2)
4     return [_msd(x, i) for i in t]

```

Additionally, as we have seen earlier, the Langevin Equation can be simplified to it's over-damped version Eq.2.3.10. In this case, the time step of the simulation τ should be greater than the diffusion time τ_B . Thus, one who is interested at the long time statistical properties of the Brownian motion can use the over-damped Langevin equation. In this case by putting $m = 0$ into Eq.2.4.5, one can write x_i as:

$$x_i = x_{i-1} + \sqrt{2D}w_i . \quad (2.4.9)$$

The statistical properties at long time could be retrieved by simulating Brownian motion using the full Langevin equation. But, since the integration scheme used for Eq.2.4.5 requires $\tau \ll \tau_B$ long simulation are necessary to retrieve the over-damped properties. As an example, for the Fig.2 I directly used Eq.2.4.9 for the simulation using the Python Snippet below.

```

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

```

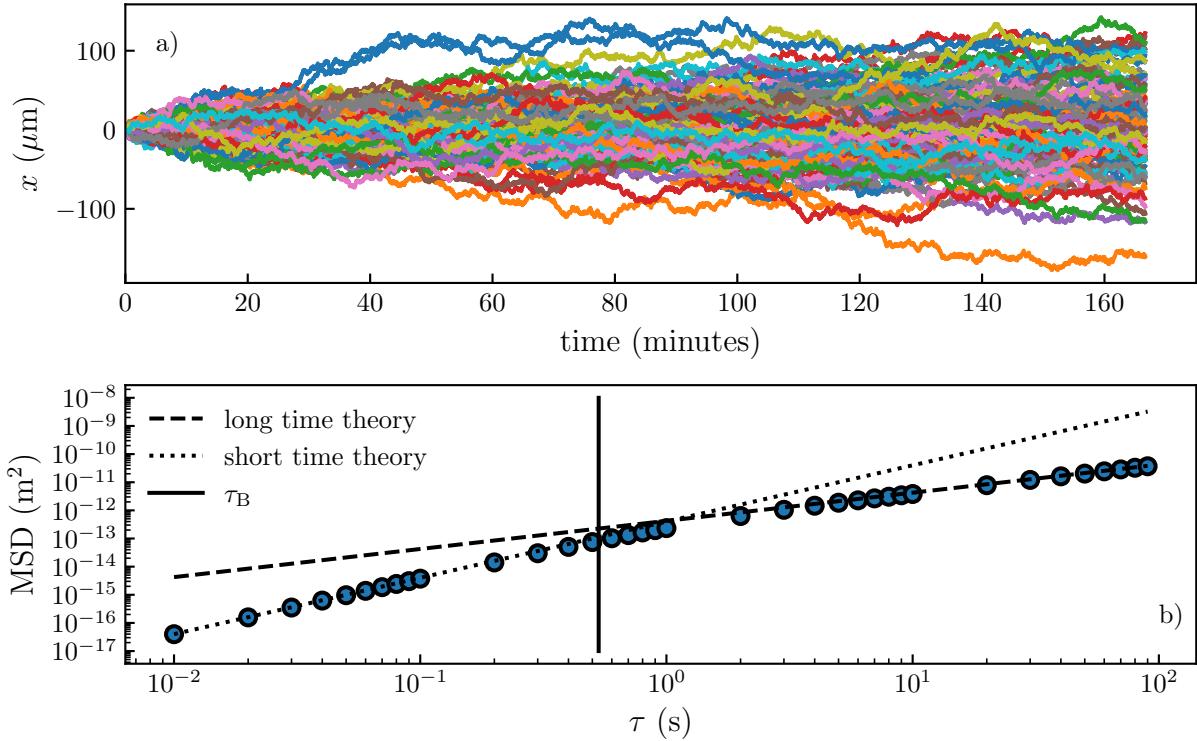


Figure 5: a) Set of 100 trajectories simulated using the full Langevin equation for particle of a radius $a = 1 \mu\text{m}$ and a mass $m = 10 \mu\text{g}$ in water, $\eta = 0.001 \text{ Pa.s}$. The simulations are done with a time step $\tau = 0.01 \text{ s}$. b) Bullets represents the measured Mean Squared Displacement (MSD) of the simulated trajectories. The plain black line represents the characteristic time of the diffusion, here $\tau_B = m/\gamma = 0.53 \text{ s}$. The dotted line represents the MSD theory when $t \ll \tau_B$, $\text{MSD} = \tau^2 k_B T/m$. The dashed line when $t \gg \tau_B$, $\text{MSD} = 2D\tau$. A detailed explanation of the simulation process can be found in the appendix.??.

2.4.3 Speedup using Cython

I would like to point out, that the optimization of a simple simulation of Brownian trajectory can be interesting. Indeed, using a pure Python code as presented in the first part of the appendix.??, the simulation of one trajectory of 10^6 steps, needs 6 s to be computed. Thus, more than 10 minutes should be required to compute the 100 trajectories showed in the Fig.5. This is long due to how Python always verify that what we do is allowed, it thus needs to verify at each step of the `for` loop the object type of each variable. This is in general the main drawback of the interpreted language, one solution is then to compile the part of the code where the `for` loops are computed. One can use the Cython package in order to specify the type of every single variable, once that done, it will convert the lengthy part in C and compile it. As presented in the appendix.??, doing that on full Langevin simulation reduces the time to generate a 10^6 steps trajectory from 6 s to 30 ms thus achieving a speedup of $\simeq 200\times$. Moreover, in the compiled version, we are here speed bound by the random number generation, indeed it takes $24.0 \pm 0.8 \text{ ms}$ using `numpy`.

Additionally, as shown at the end of the appendix.?? even pure C implementation of the random generation can be slower than the `numpy` one, thanks to impressive optimization. Thus, using those tools, this simulation is probably as optimize as it can get.

2.5 Conclusion

In this chapter, we have covered the history of the Brownian motion from the first observation of Robert Brown in the middle of 19th century to it's mathematical and experimental proofs in the early 20s. We have then described mathematically the bulk Brownian motion, and its important stastical properties. Finaly, we have used the later description in order to simulate Brownian motion using the both the full Langevin equation and it's over-damped version. In the following chapter, I will describe experimental methods using light interference properties in order to track colloidal particle.

3 Particle characterization and particle tracking using interference properties

3.1 Introduction

Properties of coherent light to produce interference is widely use in metrology for a long time with, for example, the famous Fabry-Pérot [32, 33] and Michelson interferometers [34]. The latter was initially used to measure earth's rotation and is still used today, in particular, for the recent measurement of gravitational waves [35]. Since the beginning of the century, interest on tracking and characterizing colloidal particles risen thanks to the democratization of micro fluidics and lab-on-a-chip technologies. In the following I will provide some insights on the three most used :

- Reflection Interference Contrast Microscopy (RICM)
- Lorenz-Mie fit
- Rayleigh-Sommerfeld back-propagation

The first one, RICM, uses the principle of optical difference path as a Michelson interferometer. The other two, uses the interference between the light scattered by the colloid and the incident light. Generally, both of the sources are colinear, thus, we speak of in-line holography.

3.2 Reflection Interference Contrast Microscopy

Reflection Interference Contrast Microscopy was first introduced in cell biology by Curtis to study embryonic chick heart fibroblast [36] in 1964. RICM gained in popularity 40 years after both in biology and physics [37–42]. It was also used recently in soft matter physics to study elastohydrodynamic lift at a soft wall [43].

When we illuminate a colloid with a plane wave from the bottom, a part of the light is reflected at the surface of the glass substrate and at the colloid's surface. The difference of optical path between two reflection create interference patterns. Let's take an interest at the mathematical description of this phenomenon. In the far field, we can describe two different one-dimensional electric field vectors of the same pulsation ω [44] as:

$$\vec{E}_1(\vec{r}, t) = \vec{E}_{01} \cos(\vec{k}_1 \cdot \vec{r} - \omega t + \epsilon_1), \quad (3.2.1)$$

and

$$\vec{E}_2(\vec{r}, t) = \vec{E}_{02} \cos(\vec{k}_2 \cdot \vec{r} - \omega t + \epsilon_2). \quad (3.2.2)$$

Where the k is the wave number $k = 2\pi n_m / \lambda$, λ being the illumination wavelength, n_m the optical index of the medium, $\epsilon_{1,2}$ the initial phase of each wave and \vec{r} the position from the source. Here, the origin ($\vec{r} = \vec{0}$) is taken at the position of the first reflection (on the glass slide). Thus at the particle, \vec{r} is given by the particle's height such that $|r| = z$, the particle-substrate distance.

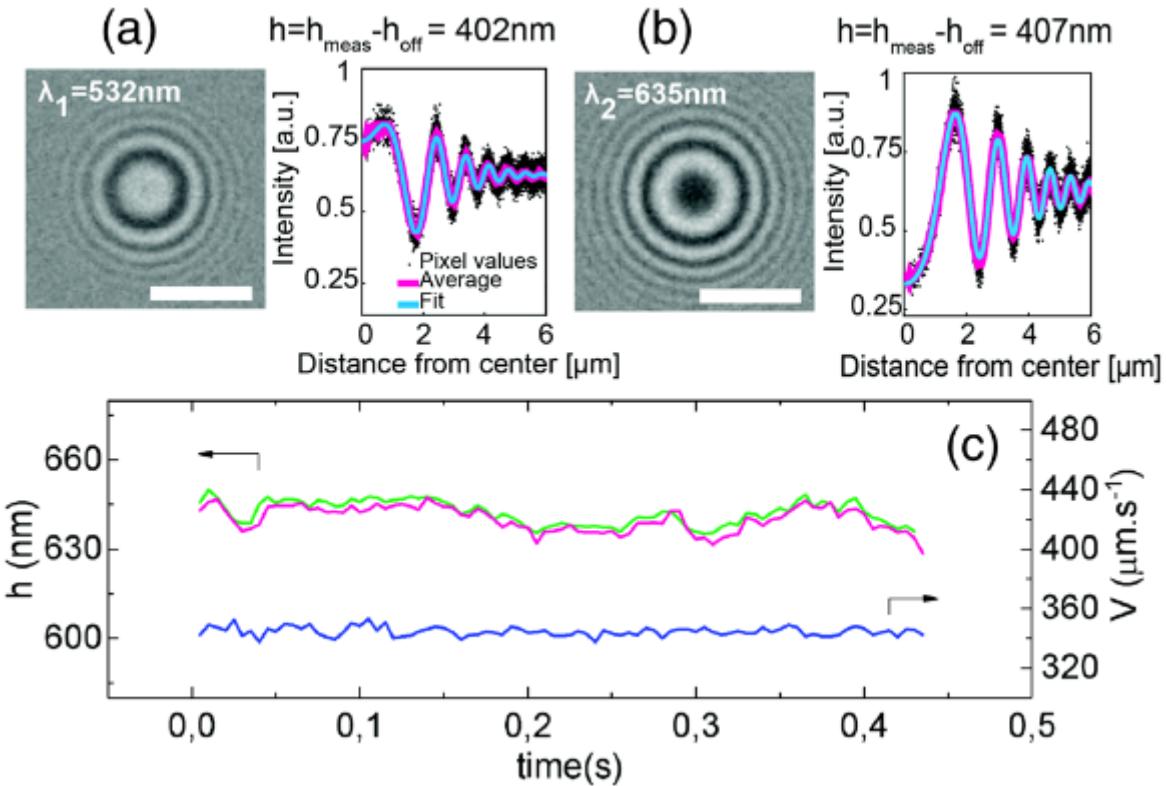


Figure 6: Figure from [43] representing RICM with two wavelengths. (a) Left: interference patterns created with a wavelength $\lambda_1 = 532\text{ nm}$ (scale bar $5\text{ }\mu\text{m}$). Right: radial intensity profile (black dots) extracted from the image, azimuthally averaged (magenta line) and fitted with Eq.3.2.8 to measure the height of the particle (here h). (b) Same as (a) with a wavelength $\lambda_2 = 635\text{ nm}$. (c) Time series of the height of a particle h (green: λ_1 , magenta: λ_2) and the particle velocity measured along the flow in blue.

Experimentally, one measures the intensity of the interference patterns, those can be computed from the time averaged squared sum of the electric field $\vec{E} = \vec{E}_1 + \vec{E}_2$. The measured intensity is thus given by:

$$I = \langle \vec{E}^2 \rangle = \langle \vec{E}_1^2 + \vec{E}_2^2 + 2\vec{E}_1 \cdot \vec{E}_2 \rangle = \langle \vec{E}_1^2 \rangle + \langle \vec{E}_2^2 \rangle + 2\langle \vec{E}_1 \cdot \vec{E}_2 \rangle \quad (3.2.3)$$

where $\langle \vec{E}_1^2 \rangle$ and $\langle \vec{E}_2^2 \rangle$ are respectively given by I_1 and I_2 , the incident light intensities. Using the trigonometric formula $2\cos(a)\cos(b) = \cos(a+b) + \cos(a-b)$ we have:

$$\langle \vec{E}_1 \cdot \vec{E}_2 \rangle = \left\langle \frac{1}{2} \vec{E}_{01} \vec{E}_{02} \left[\cos(\vec{k}_1 \cdot \vec{r} - \vec{k}_1 \cdot \vec{r} + \phi) + \cos(2\omega t + \phi') \right] \right\rangle. \quad (3.2.4)$$

As we average over the time, the second cos will vanish since in general $\langle \cos(at+b) \rangle_t = 0$ thus:

$$\langle \vec{E}_1 \cdot \vec{E}_2 \rangle = \frac{1}{2} \langle \vec{E}_{01} \vec{E}_{02} \rangle \cos(\vec{k}_1 \cdot \vec{r} - \vec{k}_2 \cdot \vec{r} + \phi) \quad (3.2.5)$$

with ϕ the phase difference between the two fields, which is generally equal to π due to the reflection properties on a higher optical index. Indeed, a colloid has generally a greater optical index than the dilution medium. Finally, the total intensity can be read as:

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos(\vec{k}_1 \cdot \vec{r} - \vec{k}_2 \cdot \vec{r} + \phi) \quad (3.2.6)$$

By taking $k_1 = -k_2$ due to the reflection properties, we have:

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos\left(\frac{4\pi n_m}{\lambda} z + \phi\right) \quad (3.2.7)$$

If we now suppose that we have a spherical particle at a height z we can develop the radial interference intensity $I(x)$ as [42]:

$$I(x) = A_0 + A_1 e^{-b_1 x^2} + A_2^{-b_2 x^2} \cos\left[\frac{4\pi n_m}{\lambda} (g(x) + z) + \phi\right] \quad (3.2.8)$$

Where A_i and b_i are fit parameters and $g(x)$ denotes the contour of the sphere. Finally, this method benefits of equations that are computationally light and permits to have a quick tracking of particles. However, as we can see on Eq.3.2.8, due to the periodicity of the cosinus, the interference pattern will be the same for all heights z separated by a distance $\lambda/2n_m \approx 200$ nm (for $\lambda = 532$ nm and $n_m = 1.33$).

It is possible to extend this limitation by using 2 different wavelength to $\simeq 1.2 \mu\text{m}$ as used in [43]. Despite the precision of this method which can reach the 10 nm spatial resolution; the measurement ambiguity is not compatible with the study of micro-particle Brownian motion due to its spacial extent, hence, RICM is not usable for our context. As a matter of fact, we experimentally reach height span of a few microns.

3.3 Lorenz-Mie Fit

When a colloid is illuminated with a plane wave, a part of the light is scattered. In consequence, the superimposition of the incident field \vec{E}_0 and scattered field \vec{E}_s interferes. The interference patterns thus obtained are called holograms. If the particle is not smaller than the illumination wavelength, it is not possible to use Rayleigh approximations [45] to describe the scattering of the particles. Indeed, one would need to use what we call the Lorenz-Mie theory which describes the scattering of dielectric spheres; this theory was found by Lorenz and independently by Mie in 1880 and 1908 [46, 47].

It is in the early 2000 that the Lorenz-Mie theory was first used in order to track and characterize particles [48, 49]. Since then, a lot of studies has been realized with this method [50]. In the following I will describe the Lorenz-Mie Fit method. In this part, the height of the particle z is the distance between the particle's center and the focal plane of the objective lens.

Let the incident field be a plane wave uniformly polarized along an axis \hat{e} , with an amplitude E_0 and propagating along the \hat{z} direction :

$$\vec{E}_0(\vec{r}, z) = E_0(\vec{r}) e^{ikz} \hat{e} \quad (3.3.1)$$

Let's consider a particle of radius a at a position \vec{r}_p , the scattered field can be written using the Lorenz-Mie theory [44] as:

$$\vec{E}_s(\vec{r}, z) = \vec{f}_s(k(\vec{r} - \vec{r}_p)) E_0(\vec{r}) \exp(-ikz) \quad (3.3.2)$$

With \vec{f}_s , the Lorenz-Mie scattering function [44]. The intensity I that we measure at \vec{r} is given by the superimposition of incident and scattered waves. Since the measurements are done at the focal plane, i.e. $z = 0$, I is given by:

$$\begin{aligned} I(\vec{r}) &= |\vec{E}_s(\vec{r}, 0) + \vec{E}_0(\vec{r}, 0)|^2 \\ &= E_0^2(\vec{r}) + 2E_0^2 \operatorname{Re} \left(\vec{f}_s(k(\vec{r} - \vec{r}_p))\hat{e} \right) + |\vec{f}_s(k(\vec{r} - \vec{r}_p))|^2 \end{aligned} \quad (3.3.3)$$

The most of the experimental defects on the images are due to spacial illumination variation caused by dust particle and such. It can be corrected by normalizing the image by the background. In another word, we normalize $I(\vec{r})$ by the intensity of the incident field $I_0 = E_0(\vec{r})^2$ which is the experimental background.

Experimentally, the background can be measured by different methods, one is to have an empty field of view and the other one, which is more convenient, is to take the median of a stack of images. Additionally, for having the latter to work, the movie should be long enough to have the particle diffuse enough, if not a ghost of the particle will appear on the background. Moreover, This process also permits getting rid of the immobile particle that could generate any additional noise. An example of hologram before and after the normalization is shown in Fig.7 a-c).

Finally, we write the normalized intensity I/I_0 :

$$\frac{I(\vec{r})}{I_0(\vec{r})} = 1 + 2 \operatorname{Re} \left(\vec{f}_s(k(\vec{r} - \vec{r}_p))\hat{e} \right) + |\vec{f}_s(k(\vec{r} - \vec{r}_p))|^2 \quad (3.3.4)$$

Now that we have the analytical form of the holograms' intensity, it is possible to fit an experimental one to Eq.3.3.4 as shown in Fig.7 d-e). For the sake of completeness, I will detail the Lorenz-Mie scattering function, $\vec{f}_s(k\vec{r})$ which is given by the series:

$$\vec{f}_s(k\vec{r}) = \sum_{n=1}^{n_c} \frac{i^n(2n+1)}{n(n+1)} \left(i a_n \vec{N}_{eln}^{(3)}(k\vec{r}) - b_n \vec{M}_{oln}^{(3)}(k\vec{r}) \right) \quad (3.3.5)$$

where $\vec{N}_{eln}^{(3)}(k\vec{r})$ and $\vec{M}_{oln}^{(3)}(k\vec{r})$ are the vector spherical harmonics. a_n and b_n are some coefficients that depend on the particle and illumination properties. For a spherical and isotropic particle of radius a and refractive index n_p , which is illuminated by a linearly polarized plane wave, the a_n and b_n coefficients are expressed in terms of spherical Bessel j_n and Hankel h_n functions as [44]:

$$a_n = \frac{\zeta^2 j_n(\zeta ka) k a j'_n(ka) - j_n(ka)[\zeta k a j_n(\zeta ka)]'}{\zeta^2 j_n(\zeta ka) k a h_n^{(1)'}(ka) - h_n^{(1)}(ka)\zeta k a j'_n(\zeta ka)}, \quad (3.3.6)$$

and

$$b_n = \frac{j_n(\zeta ka)kaj'_n(ka) - j_n(ka)\zeta kaj'_n(mka)}{j_n(\zeta ka)kah_n^{(1)'}(ka) - h_n^{(1)}(ka)\zeta kaj'_n(mka)}, \quad (3.3.7)$$

where $\zeta = n_p/n_m$ and the prime notation denotes differentiation with respect to the argument.

Finally, an hologram is mainly given by the Lorenz-Mie scattering function Eq.3.3.5. Moreover, as we can observe with the Eqs.3.3.6 and 3.3.7, an hologram will vary with a lot of parameters (λ , n_m , n_p , a and \vec{r}_p) which can all be fitted. In general, the illumination wavelength λ and medium index n_m are known and do not need to be fitted. From only one hologram, one can measure precisely the position of the particle \vec{r}_p and in the same time characterize the radius and optical index of the colloid. As a side note, it is even possible to characterize a particle without a priori knowledge of its characteristics using Bayesian approach [51, 52].

Computing Eq.3.3.5 numerically brings another interesting question, as it is analytically written as a sum over n ; one could ask after which number of terms n_c the series will converge. It has actually been found that the series converge after a number of terms [53]

$$n_c = ka + 4.05(ka)^{1/3} + 2. \quad (3.3.8)$$

Consequently, larger particles' holograms will need more terms to converge and, hence, are longer to fit. As an example, the largest particles used during my thesis have a radius $a = 2.5 \mu\text{m}$ leading to a number of terms $n_c = 55$ in water and illumination wavelength $\lambda = 532 \text{ nm}$. For the smallest ones, where $a = 0.5 \mu\text{m}$ we find $n_c = 18$ which makes a huge difference in practice. Indeed, if each of the terms of the sum take the same time to be computed; an image of a $2.5 \mu\text{m}$ particle's hologram will need $55/18 \simeq 3$ times more time to be fitted compared to the hologram of a $0.5 \mu\text{m}$ particle.

If a reader wants to evaluate an hologram given by the Lorenz-Mie theory for a peculiar particle and position, it can be done in a few lines with the `holopy` module using the following Python snippet which was used to make Fig.14 and 13:

```

1 import holopy as hp
2 from holopy.scattering import calc_holo, Sphere
3
4 sphere = Sphere(n=1.59, r=1.5, center=(4/0.1, 4/0.1, 10))

```

```

5 # n is the optical index of the particle, r it's radius in microns
6 # center is its center position in microns.
7
8 medium_index = 1.33
9 illum_wavelen = 0.532
10 illum_polarization = (1, 0)
11 detector = hp.detector_grid(shape=100, spacing=0.1)
12 # shape is the size in pixel of the camera and the spacing is the pixel's size in microns.
13
14 holo = calc_holo(
15     detector, sphere, medium_index, illum_wavelen, illum_polarization, theory="auto"
16 )
17 #the hologram can be directly be plotted using:
18 hp.show(holo)

```

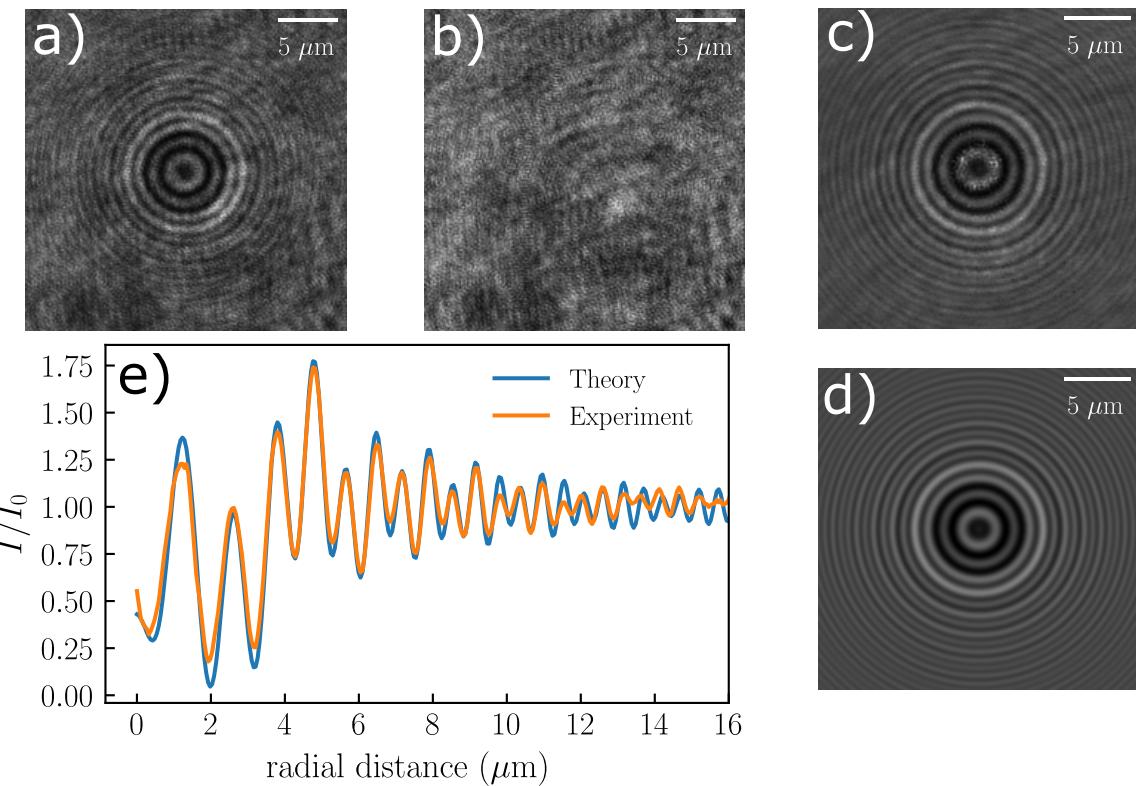


Figure 7: a) Raw hologram of a $2.5 \mu\text{m}$ polystyrene particle measured experimentally with the setup detailed in the chapter 3.5. b) Background obtained by taking the median value of the time series of images of the diffusing particle. c) Normalized hologram given by dividing a) by b). d) Result of the fit of c) using Eq.3.3.4 the particle is found to be at a height $z = 14.77 \mu\text{m}$. e) Comparison of the normalized radial intensity, obtained experimentally from c) and theoretically from d).

3.3.1 Hologram dependance on the particule characteristics

As we can see with the Eq.3.3.5, the in-line holograms vary with the position, radius and optical index of the particle. For in-line holograms, since the incident and scattered field, the x and y position of the particle will simply be given by the center of the hologram. Thus, it is possible to track only movement of the particle only in 2 dimensions by using algorithm such as the Hough transform to find the center. As a side note, in that case, it would be optimal to place the particle just above the focal plane to have an Airy disk like hologram, as shown in Fig.14 for $a = 2.5 \mu\text{m}$ and $z = 5 \mu\text{m}$.

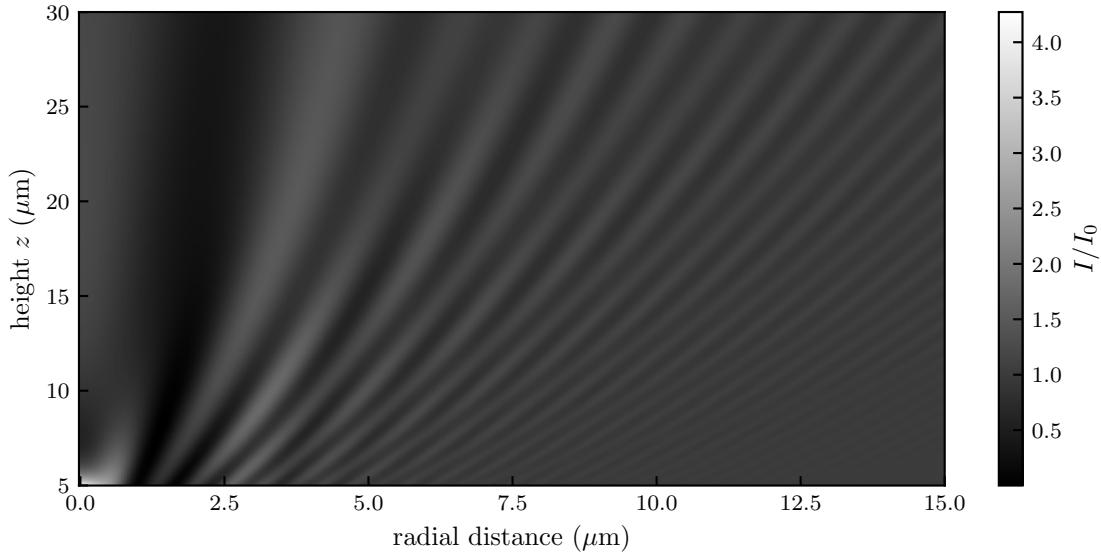


Figure 8: Radial intensity profile stack as a function of the distance between the particle center and the focal place of the objective lens, generated for a particle of radius $a = 1.5 \mu\text{m}$ and optical index $n = 1.59$.

In order to gain some insights on how the holograms vary with the different parameters, one can compute holograms for particles of different size and height. We will start by looking at the a particle of a radius $a = 1.5 \mu\text{m}$ and $n_p = 1.59$ as shown in the Fig.8. In this case, one can observe that as the distance between the particle and the focal plane z increases, the hologram's rings gets larger. Unlike a Michelson interferometer or RICM we do not observe the rings scrolling.

Additionally, this thickening of the rings can also be observed on the Fig.12, where hologram's intensity profile are plot as a function of the height z both theoretically and experimentally for a polystyrene colloidal particle of radius $a = 1.5 \mu\text{m}$, and, for different couples of parameters on the Fig.14.

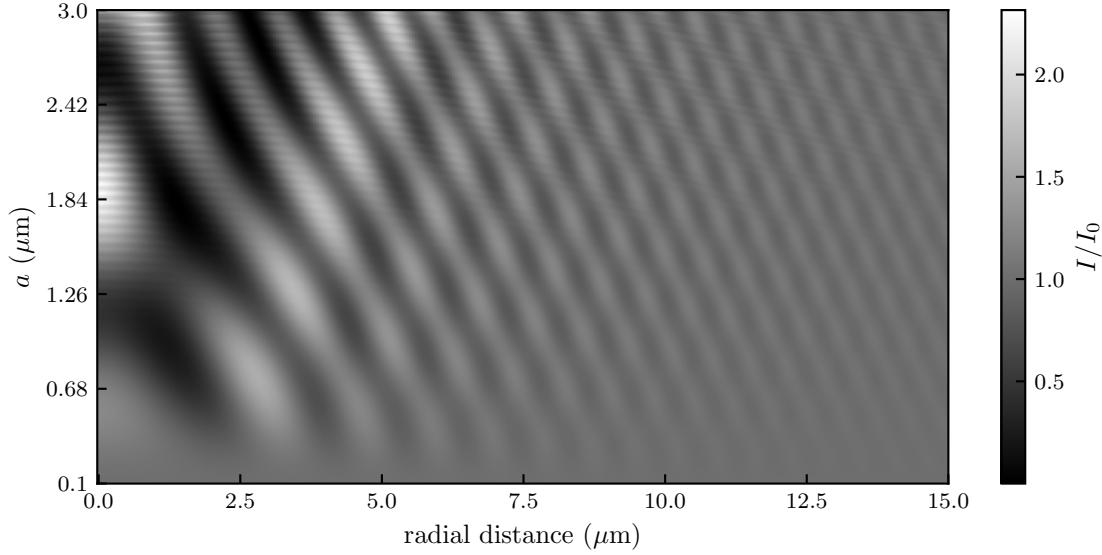


Figure 10: Radial intensity profile stack as a function of the particle radius, generated for a particle of optical index $n = 1.59$ with a distance between the particle center and the focal place of the objective lens $z = 15 \mu\text{m}$.

Also, we can note that if z is not large enough compared to the radius of the particle, the center of an hologram can be so bright that if the camera does not have a large enough dynamic range, the rings could not be seen. Thus, for having an optimal condition for the fits, one should take care to defocus the enough the objective lens to have $z \gg a$.

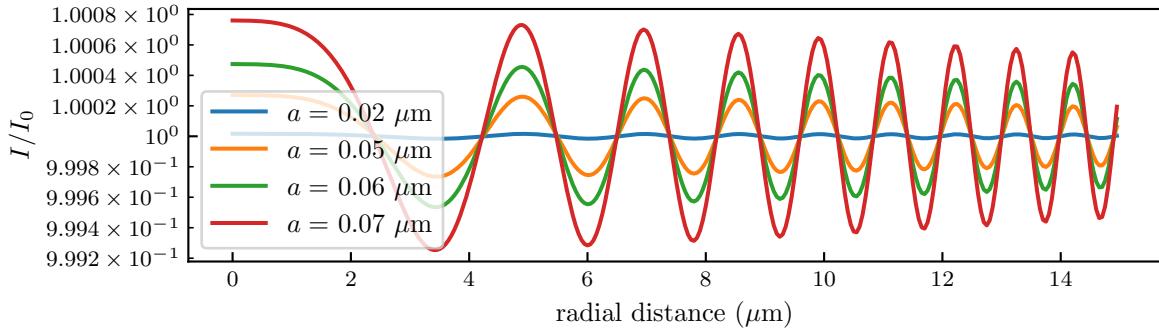


Figure 9: Radial intensity profile for of the particle radius $a \ll \lambda$, generated for a particles of optical index $n = 1.59$ with a distance between the particle center and the focal place of the objective lens $z = 15 \mu\text{m}$ and $\lambda = 532 \text{ nm}$.

We can now take a look at the variation with respect to the radius of the particle as shown on the Fig.10 for a particle of optical index $n = 1.59$ and at a distance $z = 15 \mu\text{m}$. One can observe that for small particles compared to the wavelength $a \ll \lambda$ we do not observe the rings this is due to the fact that for the small particles, the scattering can be approximated using the Rayleigh theory which tells us that the scattering is isotropic.

Thus, the variation of intensity around I_0 will be smaller for small particle.

Also, in this small particle regime, the particle size will not affect the general shape of the hologram but just the intensity of the hologram as it can be seen on the Fig.9, for particle of radius $a = 0.02 \mu\text{m}$ to $a = 0.07 \mu\text{m}$ for a wavelength $\lambda = 0.532 \mu\text{m}$.

Additionally, since the noise to signal ratio will be lower than for bigger particles, it will be less precise to characterize small colloids compared to the wavelength.

As the particle gets bigger, the scattering become anisotropic and it mostly towards the incident plane wave direction. This effects leads to an increase of the amplitude of the rings I/I_0 , as one can see on the Fig.10. Thus, the noise to signal ratio is high enough to easily discern the hologram on top of the noise as one can see on the experimental picture fig.7-a). One who wants to use this method should thus take care to use large enough particle for the holograms' intensity to be greater than the camera noise level.

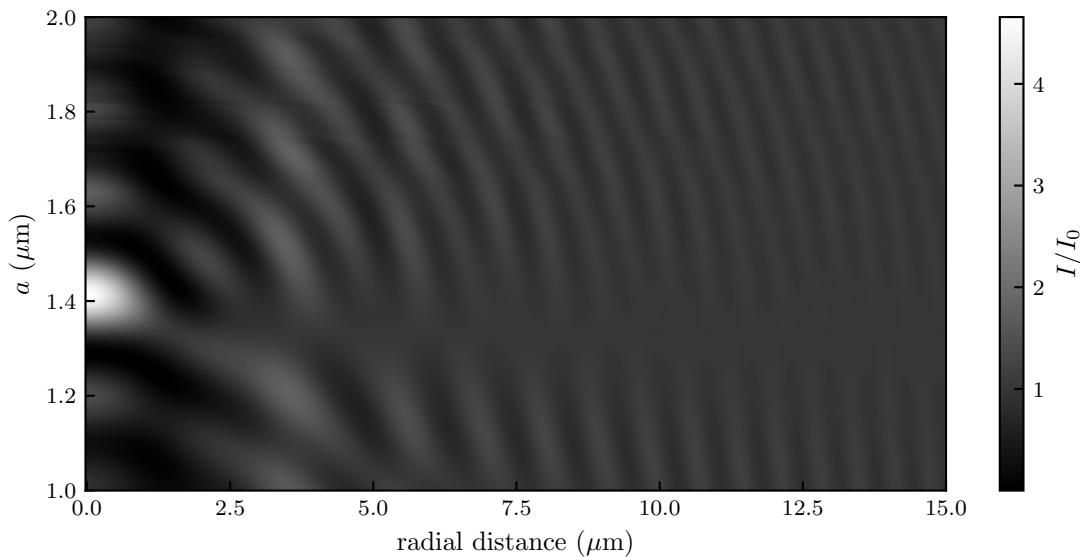


Figure 11: Radial intensity profile stack as a function of the particle optical index, generated for a particle of radius $a = 1.5 \mu\text{m}$ with a distance between the particle center and the focal place of the objective lens $z = 15 \mu\text{m}$.

Finally, one can also check how the holograms are varying with the optical index a particle. In this case it is not the particle's optical index n_p which will matter the most but the ratio $\zeta = n_p/n_m$ which can be found in the a_n and b_n formulas, Eq.3.3.6 and 3.3.7. Indeed, for the scatter to happen, the optical index n_p of the colloid needs to be different from the optical index of the surrounding medium n_m . Additionally, the numerical solution of the Lorenz-Mie scattering is not stable for $n_p \simeq n_m$. In the Fig.11, we can observe holograms of a particle of radius $a = 1.5 \mu\text{m}$ at fix distance between the particle and

the focal plane of the objective lens $z = 15 \mu\text{m}$ with a varying colloid's optical index, in water $n_m = 1.33$. On the Fig.11, one can thus observe that for $n_p \simeq n_m$ we do not observe any holograms. Additionally, one can observe that the noise to signal ratio gradually increases as n_p became different from n_m . One who wants to use this method should thus take care to the particle material or the solvent to have n_m different enough to n_p for the holograms' intensity to be greater than the camera noise level.

3.3.2 Lorenz-Mie conclusion

The combination of the height, optical index and radius of colloid thus gives unique holograms. This uniqueness of the holograms permits extracting precisely the position, optical index and radius of a colloid. In order to see how holograms are for different couples of parameters on the Figs.13 and 14, one can see possible holograms for different size and height. Additionally, one can use the Jupyter Notebook on my github repository in order to plot any hologram [Q](#).

Finally, Lorenz-Mie is the most versatile in-line holographic method, indeed, it permits tracking and characterize unique particles even without a priori knowledge. Besides, it is possible to write the Lorenz-Mie function \vec{f}_s for particular cases such as anisotropic [54], non-spherical particles [55] or particle clusters [54, 56] to name a few; such possibilities open the door to a lot of experimental studies. Additionally, it can reach really high precision as the tenth of nanometer on the position and radius as well as 10^{-3} on the optical index [49].

Unfortunately, the Lorenz-Mie fitting suffer from a major drawback which is the time needed to fit one image. For example, a 200 by 200 pixels image, of a $2.5 \mu\text{m}$ particle's hologram, can take up to two minutes to be fitted using a pure and straightforward python algorithm. A lot of work has been done to have faster tracking, such as random-subset fitting [57], GPU (graphical processing unit) acceleration, machine-learning [58, 59] and deep neural networks [60].

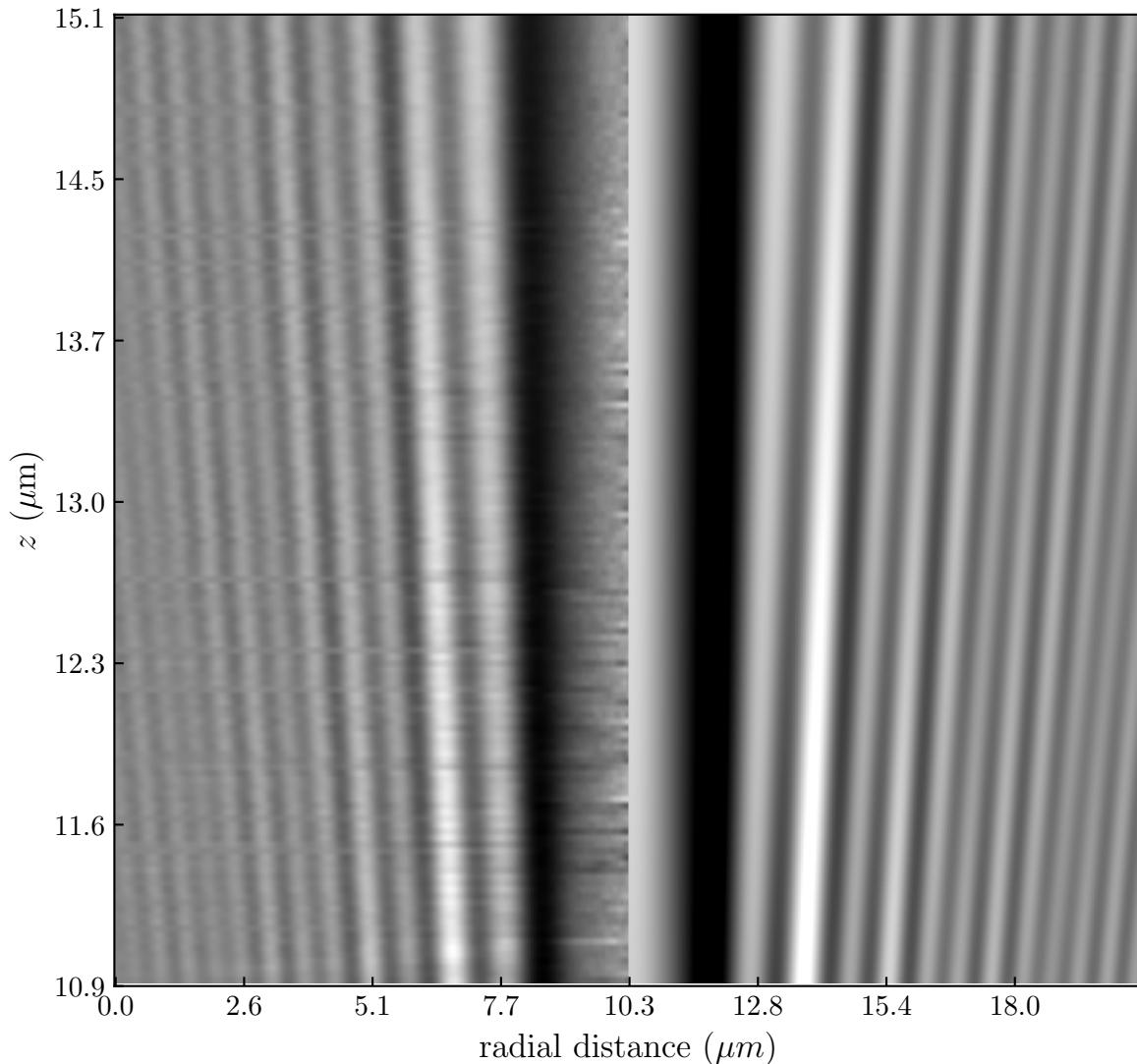


Figure 12: On the left, experimentally measured holograms' radial intensity profile stack, generated from a polystyrene bead of nominal radius $a = 1.5 \pm 0.035 \mu\text{m}$ using the experimental setup explained in chapter 3.5. The calibration of this particle radius and optical index is shown in Fig.18. On the right, the corresponding theoretical stack using the result of each individual hologram's fit.

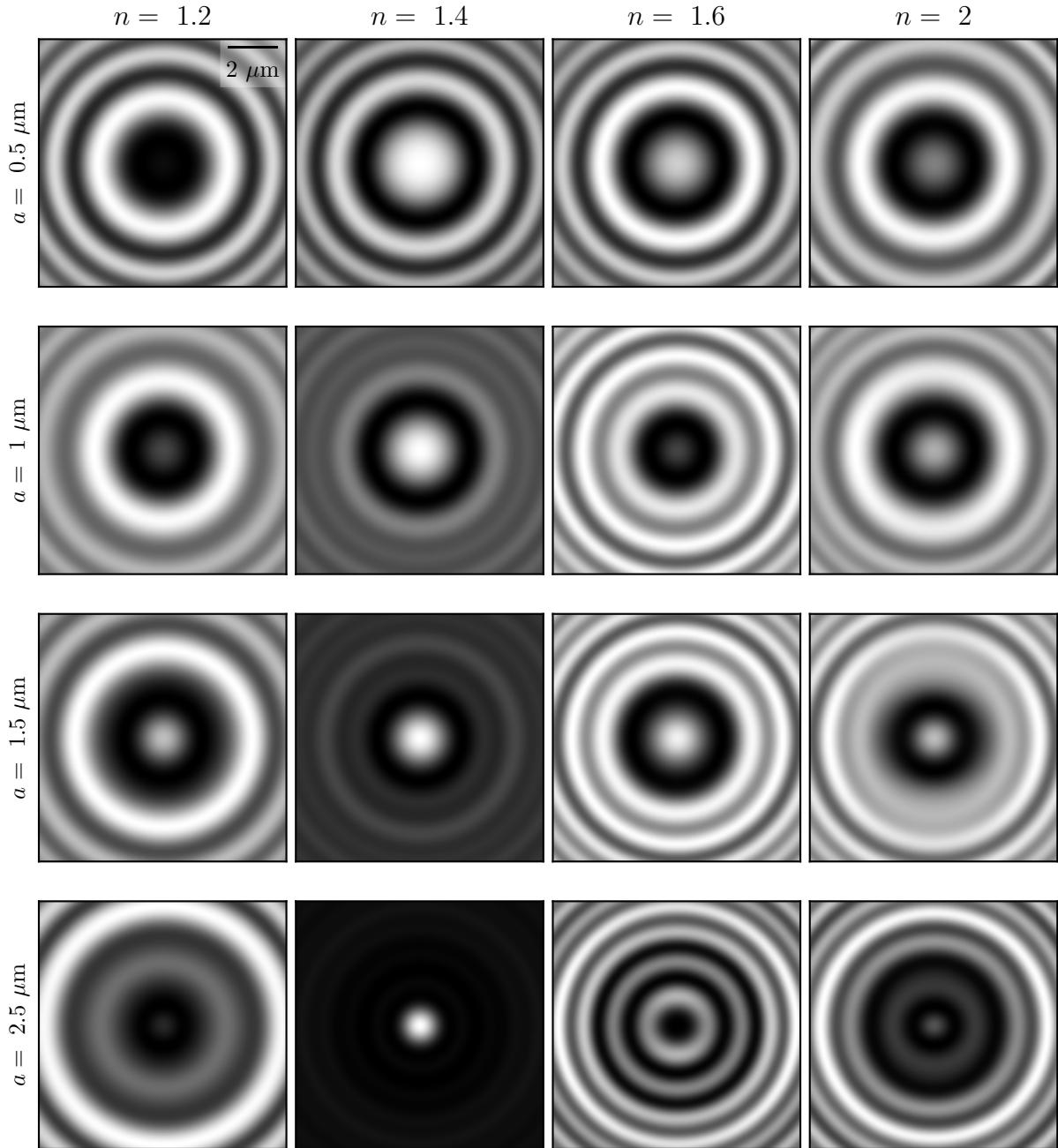


Figure 13: On the left, experimentally measured holograms' radial intensity profile stack, generated from a polystyrene bead of nominal radius $a = 1.5 \pm 0.035 \mu\text{m}$ using the experimental setup explained in chapter 3.5. The calibration of this particle radius and optical index is shown in Fig.18. On the right, the corresponding theoretical stack using the result of each individual hologram's fit.

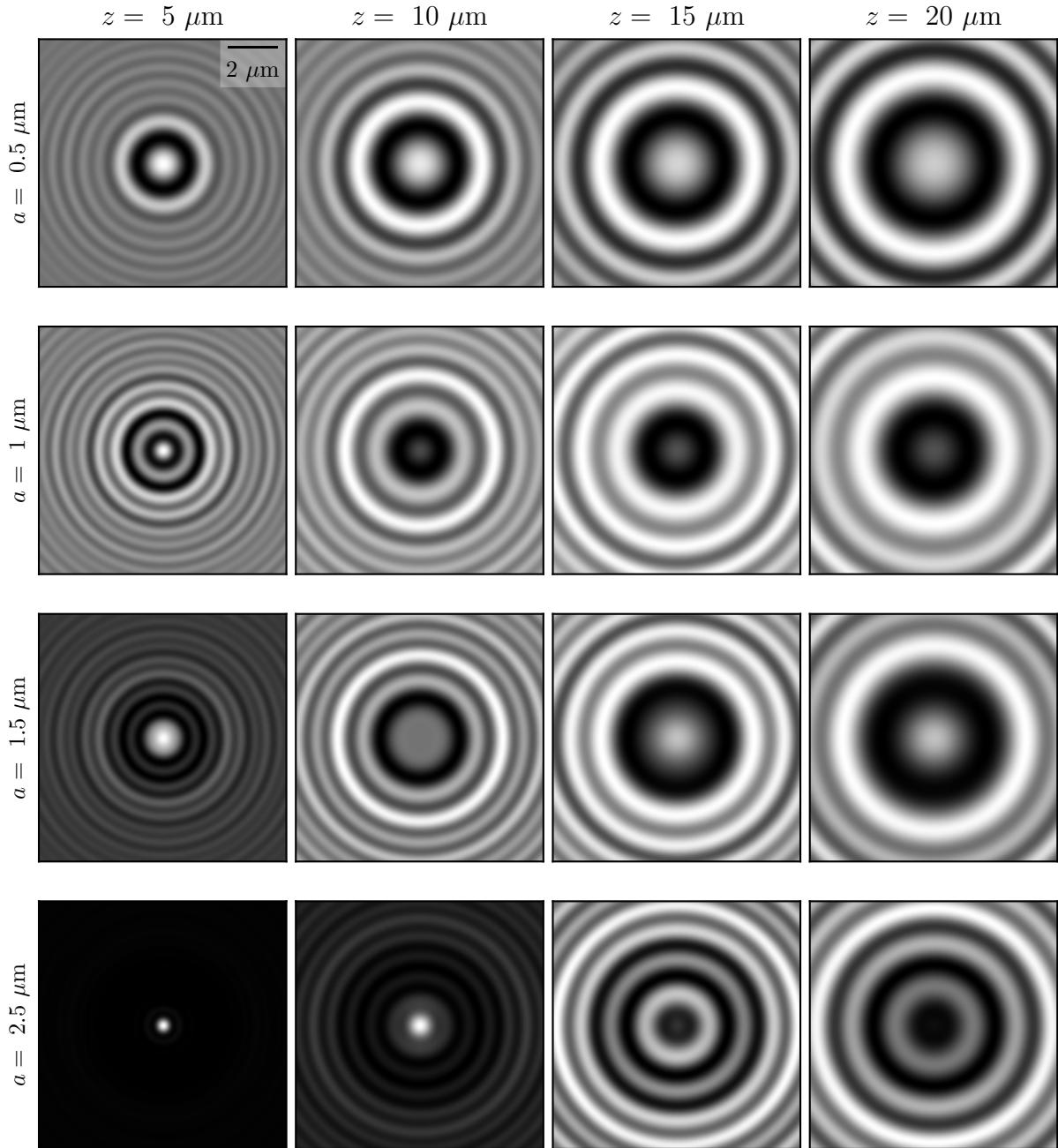


Figure 14: On the left, experimentally measured holograms' radial intensity profile stack, generated from a polystyrene bead of nominal radius $a = 1.5 \pm 0.035 \mu\text{m}$ using the experimental setup explained in chapter 3.5. The calibration of this particle radius and optical index is shown in Fig.18. On the right, the corresponding theoretical stack using the result of each individual hologram's fit.

3.4 Rayleigh-Sommerfeld back-propagation

Rayleigh-Sommerfeld back-propagation [61] works on the same principle as the Lorenz-Mie fitting but assumes that we have small scatterers, or, a low difference of optical index., such as :

$$|\zeta - 1| \ll 1 \text{ and } ka|\zeta - 1| \ll 1 . \quad (3.4.1)$$

In this case, at the focal plane, the intensity of the scattered field is smaller than the incident field, hence, the term $|\vec{E}_s|^2$ can be ignored. Thus, the normalized intensity, Eq.3.3.4 can be rewritten as:

$$\frac{I(\vec{r})}{I_0(\vec{r})} = 1 + 2 \operatorname{Re} \left(\frac{E_s(\vec{r}, 0)}{E_0(\vec{r})} \right) . \quad (3.4.2)$$

If one can retrieve completely the scattered field from an image, it is possible to reconstruct it above the focal plane by convolution using the Rayleigh-Sommerfeld propagator [62]:

$$h_{-z}(\vec{r}) = \frac{1}{2\pi} \frac{\partial}{\partial z} \frac{e^{ikR}}{R} , \quad (3.4.3)$$

where $R^2 = r^2 + z^2$ and the sign convention on the propagator indicates if the particle is below or above the focal plane. Using this propagator we have:

$$E_s(\vec{r}, z) = E_z(\vec{r}, 0) \otimes h_{-z}(\vec{r}) \quad (3.4.4)$$

By using the convolution theorem [62–65] and supposing a uniform illumination, one can write the reconstructed scattered field at a height z as:

$$E_s(\vec{r}, z) \approx \frac{e^{ikz}}{4\pi^2} \int_{-\infty}^{\infty} B(\vec{q}) H(\vec{q}, -z) e^{i\vec{q} \cdot \vec{r}} d^2 q , \quad (3.4.5)$$

where $B(\vec{q})$ is the Fourier transform of I/I_0 and $H(\vec{q}, -z)$ is given by

$$H(\vec{q}, -z) = e^{iz\sqrt{k^2 - q^2}} . \quad (3.4.6)$$

Finally, using Eq.3.4.5 one can reconstruct the scattered field and intensity since $I(\vec{r}) = |E_s(\vec{r})|^2$ as shown in Fig.15. Moreover, by finding the position where we have an inversion of the center from bright to dark Fig.15, we measure the position of the particle. Those equations are way less computational intensive than the Lorenz-Mie function Eq.3.3.5. Thus tracking can be way faster, moreover, Fourier transforms can be largely accelerated using GPU.

Additionally, as the propagator Eq.3.4.3 take only into account the intensity of the image, this method does not require any information on the particle and number of particles. As a matter of fact, to write Eq.3.4.5, one just need to assume that we have spherical colloids. Thus, this method is great to reconstruct the 3D position of a lot of particles or clusters formations.

However, the major drawback is that it is the less precise of the presented measurements and that we can't use it to characterize the particles generating the holograms.

3.4.1 Numerical Rayleigh-Sommerfeld back-propagation

The `holopy` Python module also provide a set of method that permits to user the Rayleigh-Sommerfeld back-propagation. Given the `hologram` variable containing all the needed metadata about the hologram such as the pixel size, medium index n_n illumination wavelength λ and the actual image. Then, one can use the `propagate` method to back-propagate an hologram over a set of height `zstack` using the following Python snippet.

```

1 import holopy as hp
2 import numpy as np
3
4 zstack = np.linspace(0, 20, 11)
5 rec_vol = hp.propagate(holo, zstack)
```

Please note that using the `propagate` each propagation will be done by performing a convolution of the reference hologram over the distance to be propagated. However, better reconstruction can be obtained iteratively propagating holograms over short distance. The latter method is called Cascaded Free Space Propagation, and is particularly useful when the reconstructions have fine features or when propagating over large distances [66]. It can be done by specifying the argument `cfsp` to the `propagate` method. For example, to propagate three steps over each distance, we can use `hp.propagate(holo, zstack, cfsp=3)`.

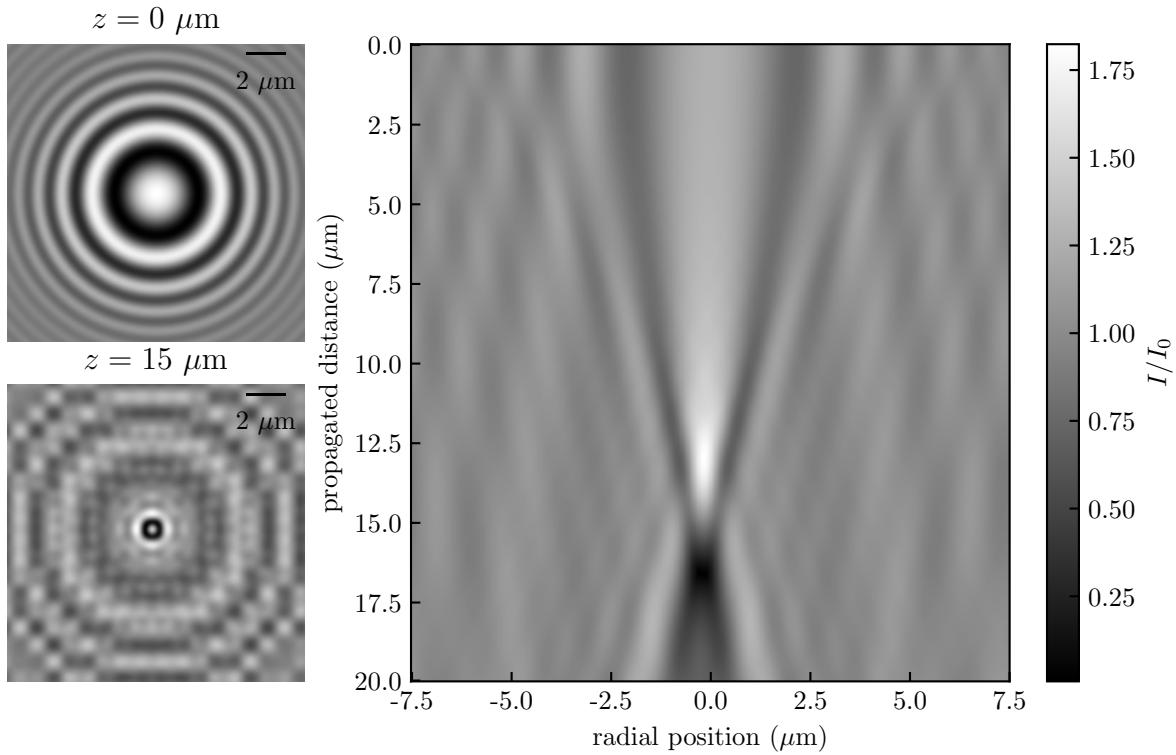


Figure 15: On the left: the original hologram on the top and propagated along $15 \mu\text{m}$ on the bottom. On the right: Reconstruction using Eq.3.4.5 of the scattered intensity of single colloidal sphere of a radius $a = 0.1 \mu\text{m}$ polystyrene spheres, $n_p = 1.59$ in water at a original $n_m = 1.59$, height of $15 \mu\text{m}$.

3.5 Experimental setup

The experimental setup I used during my PhD could be employed in order to use both Lorenz-Mie and Rayleigh-Sommerfeld Back propagation methods. In order to observe the holograms we use an homemade inverted microscope as shown on the Fig.16 and schematized in Fig.17. This microscope is built using Thor Labs cage system, as it permits doing vertical construction easily. Using this microscope, we observe the holograms coming form the interactions between a laser sourced and the beads present in a sample.

A sample consists of a parallelepipedic chamber ($1.5 \text{ cm} \times 1.5 \text{ cm} \times 150 \mu\text{m}$), made from two glass covers, a parafilm spacer, and sealed with vacuum grease, containing a dilute suspension of spherical polystyrene beads. Sealing the sample with vacuum grease permits to drastically decrease the evaporation, this permits to reduce the possible evaporation driven flow in the sample.

We used 3 different colloidal sizes, of nominal radii $0.56 \mu\text{m}$, $1.5 \mu\text{m}$ and $2.5 \mu\text{m}$, at room temperature T , in distilled water (type 1, MilliQ device) of viscosity $\eta = 1 \text{ mPa.s}$. The particles are made of polystyrene of density $\rho = 1050 \text{ kg.m}^{-3}$ and optical index $n_p = 1.598$

for a wavelength of 532 nm.

The sample is illuminated by a collimated laser beam with a 532 nm wavelength. The used laser delivers a power of 4 W and has a centimetric waist. Since the laser is collimated, it has a near zero exentricity such as it can be seen as a plane wave. With this characteristics, we can assume that there is no optical force exerted on the particles [NEED TO CHECK HOW TO EVALUATE THAT]. As depicted in the chapter 3.3, the light scattered, by one colloidal particle at a given time t , interferes with the incident beam.

An oil-immersion objective lens (x60 magnification, 1.30 numerical aperture) collects the resulting instantaneous interference pattern, and relays it to a camera (Basler acA1920-155um) with a 51.6 nm/pixel resolution (see Fig.7a)).

The exposure time of the camera is set to $\tau_{\text{expo}} = 3$ ms to avoid motion-induced blurring of the image. As a general rule, the particle should not diffuse more than the pixel size during that time, such that here $2D\tau_{\text{expo}} < 51.6$ nm.

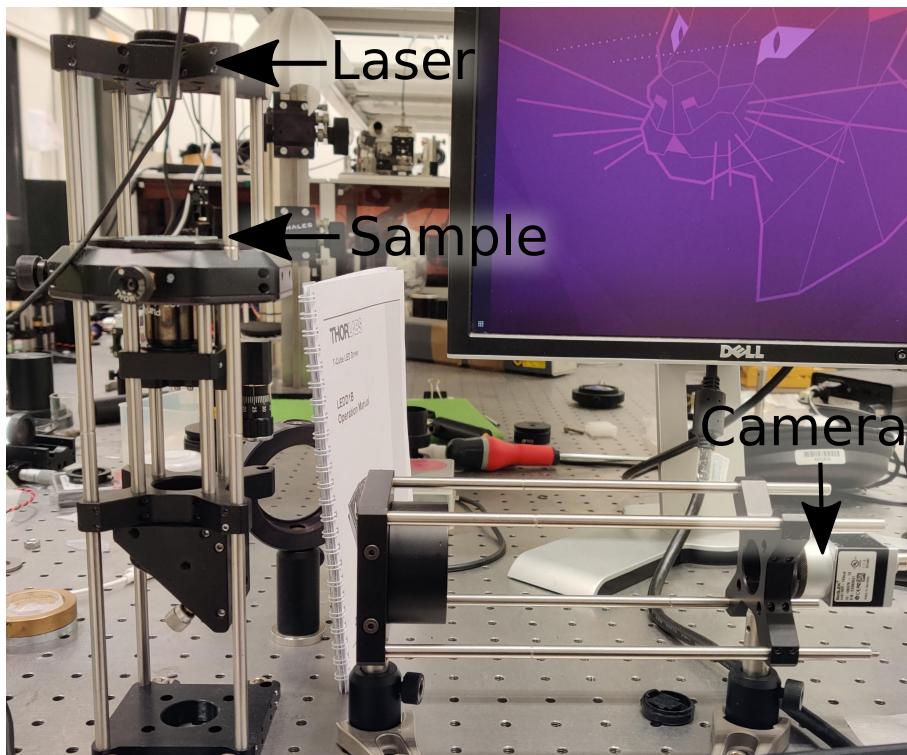


Figure 16: Photo of the custom build microscope used along my thesis. It is mainly composed of Thorlabs cage system. The camera used is a Basler acA1920-155um, we use a x60 magnification and 1.30 numerical aperture oil-immersion objective lens. The light source is a collimated 521 μm wavelength laser.

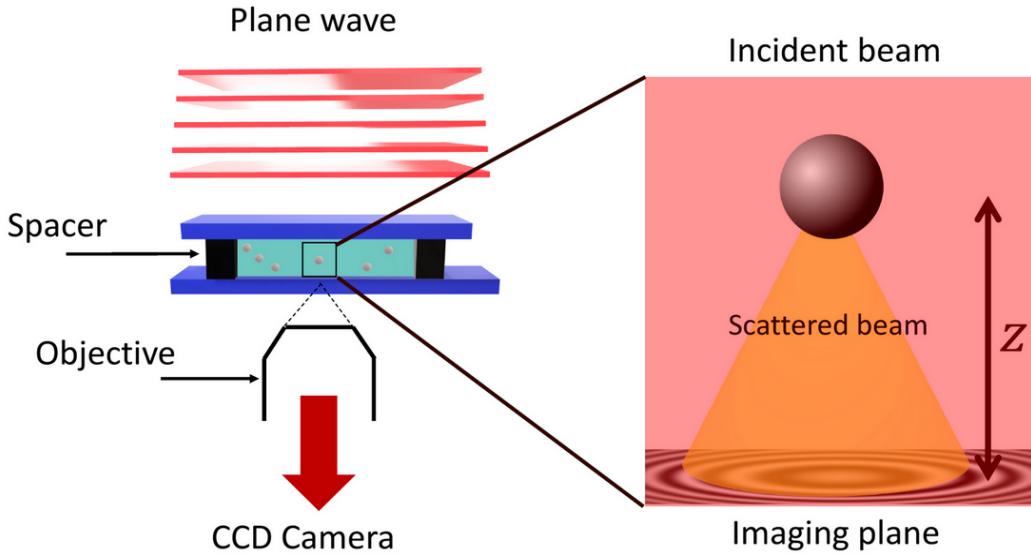


Figure 17: Schematic of the experimental setup. A laser plane wave of intensity I_0 illuminates the chamber containing a dilute suspension of micro-spheres in water. The light scattered by a particle interferes with the incident beam onto the focal plane of an objective lens, that magnifies the interference pattern and relays it to a camera.

3.6 Experimental pipeline

The method we choose is the Lorenz-Mie fitting method, since this permits the characterization of single particles. Indeed, since we are interested in fine effects near the surface, we need to know perfectly the radius of the particle we have recorded. This feature also makes our process calibration free, as we don't need to assume any physical properties. An example of the pipeline that permits to track a single particle trajectory is shown in the appendix ???. In the following, the different steps of the pipeline are going to be described.

3.6.1 Recording the holograms

Since we use a Basler camera, we use the provided Pylon software in order to record the holograms. The latter permits to adjust the parameters of the camera, such as the region of interest (ROI), frames per second (fps) or the exposure time to name a few. Also, movies can be recorded as a time series of images, AVI or MP4 files. AVI files or time series are a great way to save the movies since they are lossless. However, in general we use an ROI of 1000×1000 pixels to record the particle for a long time enough.

Additionally, since the recording is done using 8 bits per pixel (or 256 gray levels), an image of 1000×1000 pixels needs a disk space of 1 MB². One can thus see that image sequences and AVI files are not suitable for our case because of several points: i) at 100 fps one would need 108 GB to store a 30 minutes film, it could lead to TB of data per experiment which was not manageable. ii) it would require a sequential writing speed of 60 MB/s, which is just below the limit of the better HDD. iii) AVI files are bound to 2 GB maximum thus dramatically reducing the length of the experiments.

To conclude, for all of these reasons, we choosed to use the MP4 files format (MPEG-4 encoding) for the video recording. Using the lowest compression, we did not observe any impact on the fitting process due to quality loss. Finally, a video of 30 minutes will size $\simeq 3$ GB.

3.6.2 Fitting the holograms

Once the holograms are recorded, we fit all of the images to retrieve the trajectory of the particle. To do so, we choosed to use the Pylorenzmie module developed by the Grier's lab at the New York University. Although this module present a lot of capabilities, it is quite cumbersome to use, thus, I developed a wrapper around the module that I called wraplorenzmie which can be found on my github repository [Q](#).

This wrapper permits to directly load the MP4 files, compute the background and choose if what parameters should be fitted. While fitting a series of images, it uses the results of the previous image as the initial fit parameters.

However, as presented in the section 3.3 about the Lorenz-Mie fitting, the main drawback is the time to fit an image. Indeed, using a Python algorithm, one needs 30 seconds to fit images of 100×100 pixels and a few minutes for a 500×500 pixels hologram. We can directly see a bottleneck, indeed, if one want to track one trajectory made of 100 000 images one would need to wait a minimum of $\simeq 70$ days; for a series of images that need only a few minutes to be shot experimentally.

When I started my PhD, two groups, the Grier's lab and the Manoharan's lab, had already introduced python packages, respectively, Pylorenzmie and Holopy in order to inverse holograms. They had introduced ways to only fit a set of randomly chosen pixels,

² An uppercase B denotes Byte which is equivalent to 8 bits, such as $1\ B = 8\ b$. For storage indications, Bytes are generally used, since historically a set of 8 bits encodes a single text character, and, are for this reason the smallest addressable memory unit in most of the computer architectures. As an example, in binary "LOMA" would be encoded by "01001100 01001111 01001101 01000001"

and, demonstrated that taking only 1 % of the image pixels, could lead to similar precision and improve considerably the fit's execution time [57].

Unfortunately, even if fitting a random subset of pixels is faster, it leads to a few images per second, and, is still too long for the amount of data we wanted to have. Ironically, this part of my project is certainly the one where I spent the most my time, and I certainly learned a lot about code optimization and computer cluster usage.

It is around the half of my thesis, that Pylorenzmie got a new commit on their github repository which was telling that they succeeded on using GPU acceleration using CUDA³. This was not an easy task since they needed to reconstruct the Bessel functions in an understandable way for the GPU, fortunately it is possible to do so by using continued fractions [53]. This humongous update permits fitting whole images at a whooping speed improvement of 20 fps. At this speed, we fit the tridimension position of the particle, the radius and optical index.

As a remark, the fits are done by soliving a least square problem using the Levenberg-Marquardt algorithm [67]. This algorithm, is largely used in any curve-fitting applications due to its capabilities to find a minimum even by starting far from it. As mentioned, it is also possible to use various models of Machine Learning or Deep Learning to do the fits [60]. However since we can write analytically the holograms, the deep learnings models can't be more precise than a standard least-square fitting process. Deep Learning however, could be a great option if one wants to prioritize the computation time over the fit's precision.

Finally, to have a more reliable and fast tracking, we begin by fitting the first 10 000 with \vec{r}_p , a and n_p as free parameters. Using the results of this fit we can characterize the physical properties of the observed colloid with high precision. Then, using the later result we can fit all the images with only the particle position \vec{r}_p as a free parameter.

3.6.3 Radius and optical index characterization

Once the data of the radius and optical index retrieved, the quantity we can look at is the distribution of measurements. Using 10 000 measurements one can do a 2D histogram of the a and n_p as presented in the fig.18 here smoothed using a Gaussian KDE (Kernel

³ CUDA is the acronym of Compute Unified Device Architecture. It is a parallel computing platform and programming model made to permit an easier use the GPU for general purpose. CUDA is developed by NVIDIA since 2012, thus all recent NVIDIA's GPUs are CUDA enable. It is possible to use it with every language as long as a library has been developed, such as cupy for Python .

Density Estimator). Using the later using the top 10% measurements couple possibility, we measure that the radius of the observed particle is $a = 1.514 \pm 0.003 \mu\text{m}$ and its optical index $n_p = 1.585 \pm 0.002$.

Finally, using this measurement of radius and optical index, we fit the whole movie by removing them from the free parameters. Doing so, we have measured the trajectory of the particle as shown in Fig.19 in tridimension for the particle previously characterized.

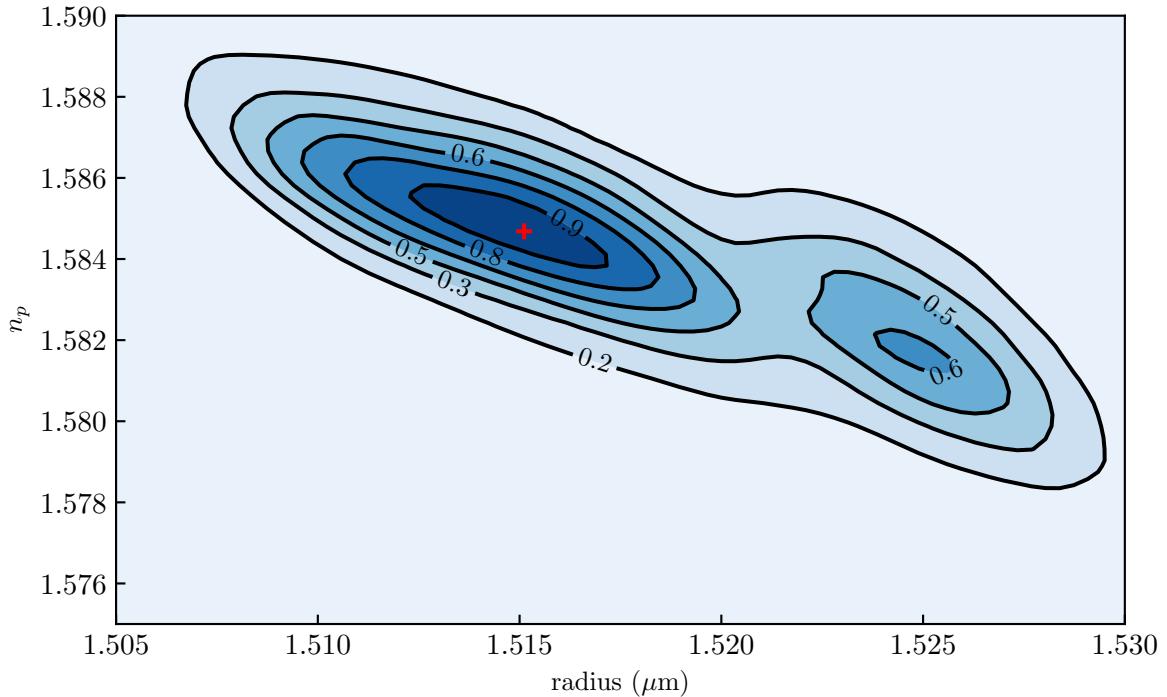


Figure 18: 2D Probability density function of the measurements of the optical index n_p and radius a . Black lines indicate iso-probability. Taking the 10% top probability, we measure $n_p = 1.585 \pm 0.002$ and $a = 1.514 \pm 0.003 \mu\text{m}$.

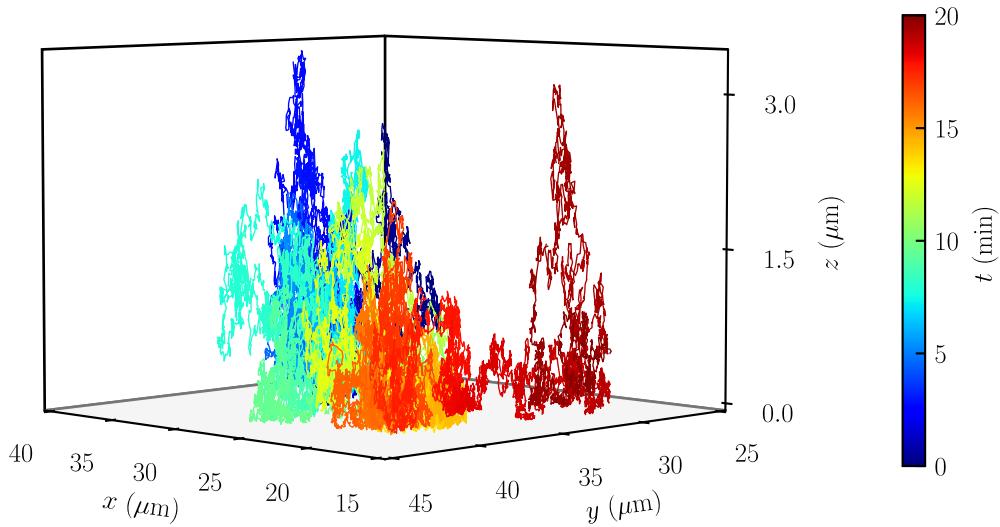


Figure 19: 3D plot of an experimental trajectory measured in water for a particle of optical index $n_p = 1.585$ and radius $a = 1.514 \mu\text{m}$.

3.6.4 Conclusion

In this chapter, we have covered different method that enable the tracking of individual particles. All the different method each come with pros and cons. We decided to use Lorenz-Mie since it is requires no calibration. Then we have shown how we use it in practice, from the experimental setup to the numerical treatment. Also, an exemple of the Jupyter notebooks used for the traking can be found in the appendix ???. We have discussed on how to have fast and accurate fits to retrieve the particle trajectory. To do so, we first characterize fully the particle, namely, its radius and optical index; before tracking a whole movie.

Now that we have an understanding on the tracking of single colloids, we can use the later measured trajectory in order to understand how the Brownian motion is affected in various configurations. In the following, use confined Brownian motion in order to do a stochastic inference of surface-induced effects.

4 Stochastic inference of surface-induced effects using Brownian motion

4.1 Confined Brownian motion theory

By observing the trajectory along the z axis of a particle of $1.5 \mu\text{m}$ as shown on the fig.20, one can see that the particle height does not get higher than $\simeq 4 \mu\text{m}$. Indeed due to gravity, the particle is confined near the surface. Brownian motion in confinement and at interfaces is a canonical situation, encountered from fundamental biophysics to nanoscale engineering. This confinement induces near-wall effects, such as hindered mobility and electrostatic interactions.

In the first part of this chapter, I will detail the theory background of the confined Brownian motion and how to numerically simulate it. In a second part, I will present how to analyse experimental data. In particular, I will detail a multi-fitting procedure that allows a thermal-noise-limited inference of diffusion coefficients spatially resolved at the nanoscale, equilibrium potentials, and forces at the femtometre resolution.

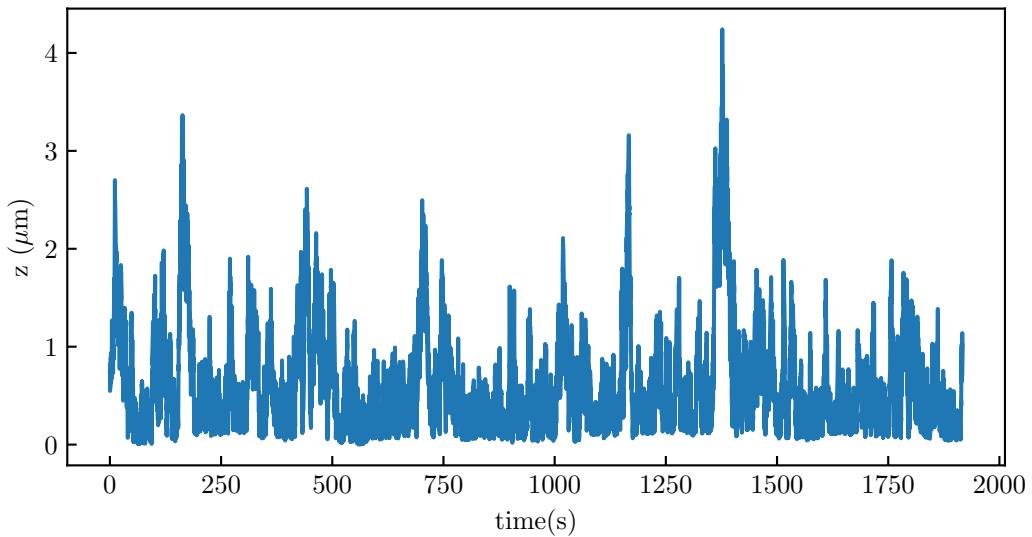


Figure 20: Experimental trajectory of a particle of polystyrene of radius $a = 1.5 \mu\text{m}$ near a wall ($z = 0$) along the z axis — perpendicular to the wall.

4.1.1 Gravitational interactions

In our experiment, we observe confined Brownian motion since the colloids are subject to gravity. Indeed, the density of the observed colloid ρ_p is different of the medium ρ_m — in our experiment water, $\rho_m = 1000 \text{ kg.m}^{-3}$. Thus, the particle lies into a gravitational potential given by:

$$U_g(z) = \Delta m g z = \frac{4}{3} \pi a^3 g \Delta \rho z , \quad (4.1.1)$$

where Δm is the mass difference of the particle and a fluid sphere of the same size, $\Delta \rho$ the corresponding density difference such as $\Delta \rho = \rho_m - \rho_p$ and g the gravitational acceleration. By invoking the definition of a distance that we call the Boltzmann length,

$$\ell_B = \frac{k_B T}{4/3 \pi a^3 \Delta \rho g} , \quad (4.1.2)$$

one can rewrite the gravitational potential Eq.4.1.1 as:

$$U_g = \frac{k_B T}{\ell_B} . \quad (4.1.3)$$

The Boltzmann length ℓ_B is the typcal gravitational decay length and represents the balance between the gravitational potential and thermal energy. This distance was first measured by Perrin [5], by enumerating the number of particles as a function of height to reconstruct the concentration of the colloidal suspension that exponentially decays as e^{-z/ℓ_B} . As an exemple, in water, for a particle polystyrene, $\rho_p = 1050 \text{ kg.m}^{-3}$ and of radius $a = 1.5 \mu\text{m}$ we have $\ell_B = 0.58 \mu\text{m}$.

For particle with $\ell_B \gg a$, one can consider that the particle does not feel the gravity. This is particulary the case when the density of the colloids and fluid matches, in this particular case $\ell_B = 0$. Thus density matching can be a way to do gravitation free experiments. In the case of our experiment, we want to measure confinement induced effects, therefore, we need this gravitational interaction to have the particles near the surface. Indeed, as a particle gets larger, or, denser ℓ_B decreases and the particle will be, in average, closer to the surface.

4.1.2 Sphere-wall interactions

As we have seen, external forces acts on the particle such as the gravity, however it is not the only one. As the Brownian particle is close to a wall we can expect some interactions between the surfaces. In our case, we suppose that the Brownian particles do not interact between each other, which is the case for the dilute solution used. Indeed, the particles studied are at a minimum $50 \mu\text{m}$ apart which correspond to 10 times their size for the larger beads.

To describes the interaction between, the Brownian particle and the wall, we use the DLVO⁴ theory. This theory was first developed to describe the interactions between colloids to explain the stability of colloidal suspension. It describes the interactions using two forces components; the Van Der Waals force which arise form the interactions between surface's molecules and electrostatic interactions due the a double-layer formed with the ions present in the solution.

Double-Layer interactions

When a surface is immersed in water are usually charged [68] due to a high dielectric constant $\epsilon \simeq 80$ that permit the build up of charges for low energetic price. Commonly, surface charging is done through ionization of dissociation of surface groups⁵, from the binding of ions from the solution — for example, adsorption of $-\text{OH}^-$ onto the water-air interface that charge it negatively. In the bulk, a fluid should be electrically neutral, thus the fluid contains as many ions of opposite charge. However, when a surface is charged negatively, negative ions are repelled from the surface, while positive ions are attracted towards the surface. Therefore, a double-layer charge distribution is formed near the surface, as shown Fig.28-a). Experimentally, we use glass slides and polystyrene beads, that are both negatively charged in water, thus leading to repulsive double-layer. This repulsive force prevent the colloids to stick together or to the surface of the substrate.

If the solution contains an electrolyte (ions of positive and negative charges), for example a salty solution, containing Na^+ and Cl^- ions. In the DLVO theory, the electrostatic field $\Psi(\vec{r})$ generated by the double layer satisfies the mean field Poisson's equation [68]:

⁴ The DLVO theory is named after Derjaguin, Landau, Verwey, and Overbeek [68].

⁵ For example, the dissociation of protons from surface carboxylic groups [68] ($-\text{COOH} \rightarrow -\text{COO}^- + \text{H}^+$) which charge negatively the surface.

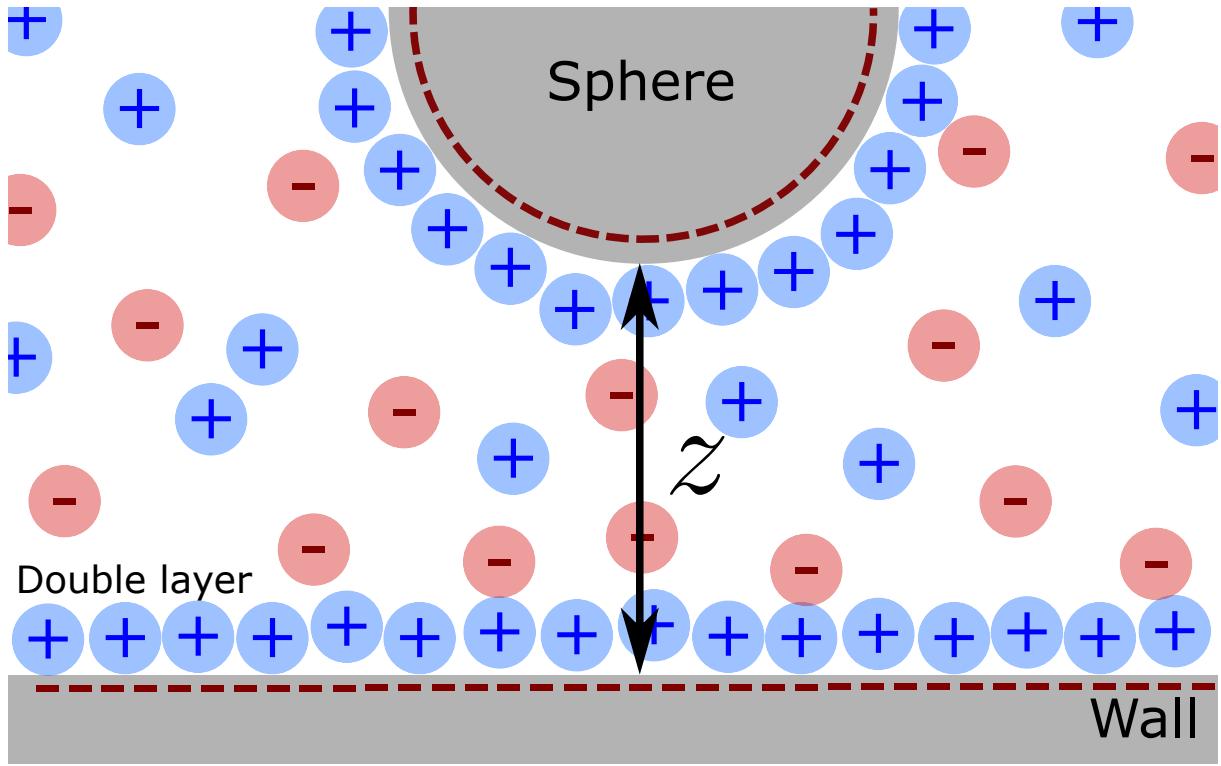


Figure 21: A Brownian colloid diffusing near a wall. Both wall and colloid's surface charge negatively, in consequence, a layer of positively charge ions are towards the surfaces, forming a double-layer charge distribution.

$$\nabla^2 \Psi(\vec{r}) = -\frac{1}{\epsilon_r \epsilon_0} \rho_e(\vec{r}) , \quad (4.1.4)$$

where ϵ_0 the vacuum permittivity, ϵ_r the relative permitivity of the fluid, $\rho_e(\vec{r})$ the local charge density. The latter can be written as:

$$\rho_e(\vec{r}) = e \sum_i z_i c_i(\vec{r}) , \quad (4.1.5)$$

where e is the elementary charge, i denotes an ionic species of valence z_i and local ionic concentration $c_i(\vec{r})$ (number density). If the solution is at the thermodynamic equilibrium, the Boltzmann equation is used to calculate the local ion density such that:

$$c_i(\vec{r}) = c_i^0 \exp \left(\frac{z_i e \Psi(\vec{r})}{k_B T} \right) , \quad (4.1.6)$$

where c_i^0 is the bulk concentration (number density) of the ionic species i . By combining Eqs.4.1.4, 4.1.5 and 4.1.6, one can obtain the Poisson-Boltzmann equation:

$$\nabla^2 \Psi(\vec{r}) = \sum_i \frac{z_i e c_i^0}{\epsilon_0 \epsilon_r} \exp\left(-\frac{z_i e \Psi(\vec{r})}{k_B T}\right) . \quad (4.1.7)$$

Since the Poisson-Boltzmann is non-linear, it is most likely to be solve numerically. However, for simple geometry such as uniformly charged plane or sphere it can be solve analytically. Let consider, to simplify, that we have a monovalent electrolyte, meaning that the electrolyte is composed of two ions of valence equal to one — Na^+ Cl^- for example — and c_i^0 is equal to the electrolyte solution concentration c_s^0 . In that case Eq.4.1.7 simplifies to:

$$\begin{aligned} \nabla^2 \Psi(\vec{r}) &= \frac{e c_s^0}{\epsilon_0 \epsilon_r} \left[\exp\left(\frac{-e \Psi(\vec{r})}{k_B T}\right) - \exp\left(\frac{+e \Psi(\vec{r})}{k_B T}\right) \right] \\ &= 2 \frac{e c_s^0}{\epsilon_0 \epsilon_r} \sinh\left(\frac{e \Psi(\vec{r})}{k_B T}\right) . \end{aligned} \quad (4.1.8)$$

In the case, where the Ψ is small enough everywhere to have the electrostatic potential energy $e\Psi \ll k_B T$, which generally the case when using salty solution. In that case, it is possible, using the a Taylor approximation at the second order to write:

$$\exp\left(-\frac{z_i e \Psi(\vec{r})}{k_B T}\right) \simeq 1 + \frac{z_i e \Psi(\vec{r})}{k_B T} . \quad (4.1.9)$$

Thus, the Poisson-Boltzmann equation (Eq.4.1.7) becomes:

$$\nabla^2 \Psi(\vec{r}) = \sum_i \frac{z_i e c_i^0}{\epsilon_0 \epsilon_r} \left(1 + \frac{z_i e \Psi(\vec{r})}{k_B T} \right) . \quad (4.1.10)$$

Since the fluid in the bulk, is electrically neutral, the first term vanishes as $\sum_i z_i c_i^0 = 0$. One thus have a linearized version of Eq.4.1.7, which is known as the Debye-Hückel equation:

$$\nabla^2 \Psi(\vec{r}) = \left[\sum_i \frac{z_i^2 e^2 c_i^0}{\epsilon_0 \epsilon_r k_B T} \right] \Psi(\vec{r}) . \quad (4.1.11)$$

From this approximation, one can identify that the term between brackets is the inverse of a distance squared. We can thus define a distance ℓ_D , the Debye length such as:

$$\ell_D = \sqrt{\sum_i \frac{\epsilon_0 \epsilon_r k_B T}{z_i^2 e^2 c_i^0}} . \quad (4.1.12)$$

The Debye length is the characteristic length of the double-layer, and, the electrostatic interactions. For a monovalent electrolyte, at 25 °C (298 K), the Debye length of aqueous solution is:

$$\begin{aligned} \ell_D &= \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{2c_s^0 e^2}} = \sqrt{\frac{8.854 \times 10^{-12} \times 78.4 \times 1.381 \times 10^{-23} \times 298}{2 \times (1.602 \times 10^{-19})^2 \times 6.022 \times 10^{26} M}} \\ &= 0.304 \times 10^{-9} / \sqrt{M} \text{ m ,} \end{aligned} \quad (4.1.13)$$

with M the molar concentration ($1 \text{ M} = 1 \text{ mol.L}^{-1}$ corresponding to a number density of $c_s^0 = 6.022 \times 10^{26} \text{ m}^{-3}$). Thus, for a salty concentration we have $\ell_D = 0.304 / \sqrt{[\text{NaCl}]} \text{ nm}$. For example, for NaCl solution, one can have $\ell_D = 100 \text{ nm}$ for a concentration $[\text{NaCl}] = 9.2 \mu\text{M}$ and $\ell_D = 10 \text{ nm}$ for a concentration $[\text{NaCl}] = 9.2 \text{ mM}$.

Finally, the Debye-Hückel approximation finally writes:

$$\nabla^2 \Psi(\vec{r}) = \kappa^2 \Psi(\vec{r}) , \quad (4.1.14)$$

with $\kappa = 1/\ell_D$. Using the latter approximation one can compute the electrostatic potential around a sphere. Let us consider a perfect sphere of radius a and charge Qe of charge density $\sigma = Qe/4\pi a^2$. With Q being the number of charge on the surface. Since the system has a spherical symmetry, one has $\Psi(\vec{r}) = \Psi(r)$ with $r = |\vec{r}|$. Using the Laplacian operator ∇^2 in the spherical coordinates, Eq.4.1.14 writes:

$$\frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial \Psi(r)}{\partial r} \right) \right] = \kappa^2 \Psi(r) , \quad (4.1.15)$$

which has a general solution:

$$\Psi(r) = C_1 \frac{\exp(\kappa r)}{r} + C_2 \frac{-\exp(\kappa r)}{r} \quad (4.1.16)$$

For one sphere, the electrostatic field vanishes at infinity such as $C_1 = 0$, such it has the form of a Yukawa potential:

$$\Psi(r) = C_2 \frac{-\exp(\kappa r)}{r} . \quad (4.1.17)$$

Additionally, at the surface of a charged sphere, the electrostatic potential satisfies:

$$\left. \frac{\partial \Psi(r)}{\partial r} \right|_{r=a} = \frac{Qe}{4\pi\epsilon_0\epsilon_r a^2} = \frac{\sigma}{\epsilon_0\epsilon_r} . \quad (4.1.18)$$

By applying the latter boundary condition to Eq.4.1.17 we find:

$$\Psi(r) = \frac{\sigma a^2}{\epsilon_0\epsilon_r} \frac{\exp(\kappa a)}{1 + \kappa a} \frac{\exp(-\kappa r)}{r} \quad (4.1.19)$$

This solution can be used to determine the electrostatic field between two spheres. Indeed, if we suppose that the presence of a second sphere, do not interfere with the distribution of ions in the double layer of the other. We can thus use the superposition approximation to write the potential $\Psi_2(z)$ between two spheres surfaces. Where z is the distance between the 2 colloids. For two spheres of charge σ_1 and σ_2 and radius a_1 and a_2 , $\Psi_2(z)$ writes [69]:

$$\Psi(z) = \frac{4\pi}{\epsilon_0\epsilon_r} \left(\frac{\sigma_1 a_1^2}{1 + \kappa a_1} \right) \left(\frac{\sigma_2 a_2^2}{1 + \kappa a_2} \right) \frac{\exp(-\kappa z)}{a_1 + a_2 + z} . \quad (4.1.20)$$

From the latter equation, it is possible to write the electrostatic field between a wall and a spherical colloid, by setting one of the radius to infinity. Doing so and multiplying by e , one can have the electrostatic potential $E_{elec}(z)$ between a Brownian particle and the wall:

$$E_{elec}(z) = B e^{-\frac{z}{\ell_D}} . \quad (4.1.21)$$

Where B is the constant that represent the surface charges, for sphere of radius a and charge σ_1 and a wall of charge σ_2 , one has:

$$B = \frac{4\pi}{\epsilon_0\epsilon_r} \left(\frac{\sigma_1 a^2}{1 + \kappa a} \right) \frac{\sigma_2}{\kappa} . \quad (4.1.22)$$

Additionally, B is often written as a function of the surfaces potential as [CITE PRIEVES]:

$$B = 16\epsilon_r\epsilon_0 \left(\frac{k_B T}{e} \right) \tanh \left(\frac{e\phi_1}{4k_B T} \right) \tanh \left(\frac{e\phi_2}{4k_B T} \right), \quad (4.1.23)$$

where ϕ_1 and ϕ_2 are the Stern potentials of the sphere and the wall surfaces. Typical values for B ranges from $1 k_B T$ to $50 k_B T$. In our study we will keep B to describe the electrostatic energy potential as it complicated to decouple the σ_1 and σ_2 when the colloid and wall's surface materials are different [70]. However, this is not impossible and is the idea of future work.

Van der Waals interactions

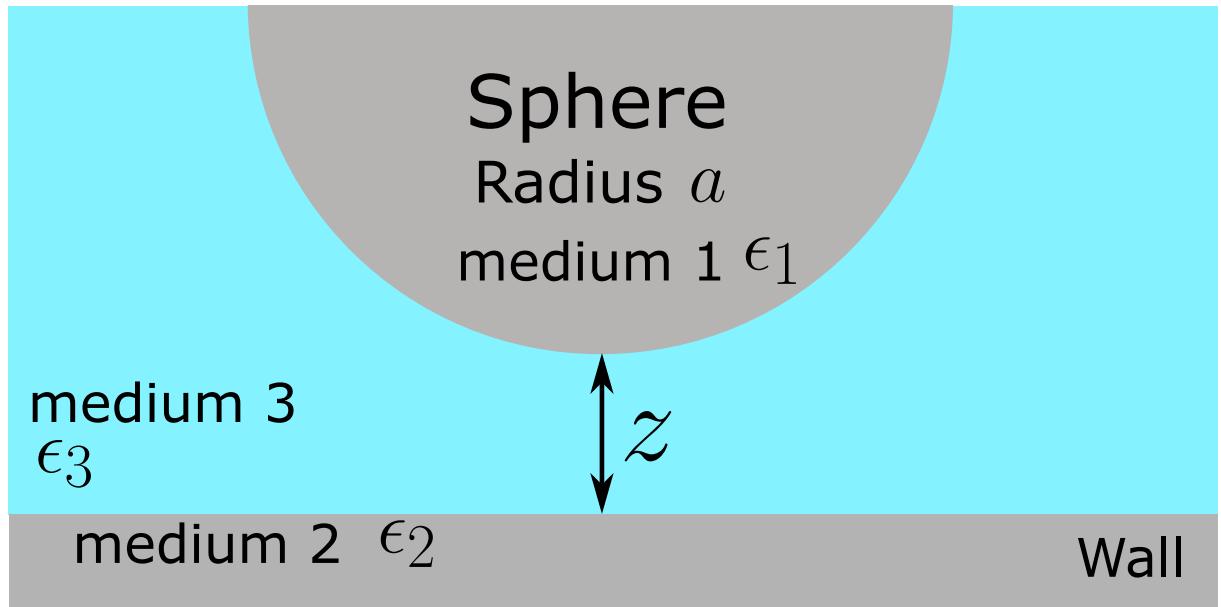


Figure 22: A colloid of radius a separated from a wall from a distance z . The colloid material has a static dielectric constant ϵ_1 , the wall ϵ_2 and the solution ϵ_3 .

In the DLVO theory, the Van der Waals forces describes the interaction between colloids at very short range. This forces are mainly attractive and in our case having Van der Waals interactions would lead to the particles stick to the wall. The Van der Waals potential energy E_{VdW} for a spherical colloid of radius a , at a height z at a few nanometers (< 5 nm) to the surface [68]:

$$E_{VdW} = -\frac{Aa}{6z} \quad (4.1.24)$$

where A is the retarded Hamaker constant. For our system, where the particle, medium and wall are different medium as schematize in Fig.22. In that case the Hamaker constant

writes [68]:

$$A = \frac{3}{4}k_B T \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right) \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right) + \frac{3h}{4\pi} \int_{\nu_1}^{\infty} \left(\frac{\epsilon_1(i\nu) - \epsilon_3(i\nu)}{\epsilon_1(i\nu) + \epsilon_3(i\nu)} \right) \left(\frac{\epsilon_2(i\nu) - \epsilon_3(i\nu)}{\epsilon_2(i\nu) + \epsilon_3(i\nu)} \right) d\nu , \quad (4.1.25)$$

where ϵ_1 , ϵ_2 and ϵ_3 are the static dielectric constants of the three media, $\epsilon(i\nu)$ are the imaginary dielectric constant at a frequency ν and $\nu_n = (2\pi k_B T n / h) = 4 \times 10^{13} \text{ ns}^{-1}$ at 300 K; and; h is the Plank's constant. The first term fives the zero-frequency energy of the van der Waals interaction and the second term the dispersion energy. However, since the static dielectric of water is large compared to the other terms [68], one can approximate the Hamaker constant of our system to only the zero-frequency term:

$$A = \frac{3}{4} 1.381 \times 10^{-23} \times 298 \left(\frac{2.5 - 80}{2.5 + 80} \right) \left(\frac{5 - 80}{5 + 80} \right) \simeq 2.48 \times 10^{-21} \text{ J} = 0.62 k_B T . \quad (4.1.26)$$

Since A is positive we correctly have an attractive Van der Waals force, this case will always be the case due to the high dielectric constant of water. More over, the zero-frequency Van der Waals force is mainly due to electrostatic interaction and is thus screened by electrolytes, we thus need to add a factor $\approx e^{-z/\ell_D}$ to the Van der Waals forces. Also, it has been proposed [71] that to compute the force at higher distances, one should add a second factor, to account for the retarded Van der Waals force of $\simeq (1 + 11z/100\text{nm})^{-1}$.

All the effects added together we can see that the Van der Waals forces will play a role only a few nanometer (< 10 nm) as it is commonly observed [M,P]. In our experiments, the Debye length ℓ_D (> 20 nm) is large enough for the particle to avoid this region, in the following of this work the Van der Waals interactions will be neglected. To study the Van der Waals interactions with Brownian motion, it is possible, if one add enough salt to have $\ell_D \simeq 1$ nm. However, with such a short Debye length, all the colloids would stick to the surface and between each other. However, we have experimentally observed some dynamics on the sucked particles, further work on this movement could lead to interesting determination of the near-wall potential.

Total potential and equilibrium distribution

If we combine the gravitational and electrostatic interactions the particules lies into a total energy potential $U(z)$:

$$U(z) = U_g + U_{\text{elec}} \quad (4.1.27)$$

By combining Eqs.4.1.3, 4.1.21 and 4.1.27, and also adding the condition that the particle can't go inside the wall $U(z)$ finally writes:

$$\frac{U(z)}{k_B T} = \begin{cases} B e^{-\frac{z}{\ell_D}} + \frac{z}{\ell_B}, & \text{for } z > 0 \\ +\infty, & \text{for } z \leq 0 \end{cases}, \quad (4.1.28)$$

From this total potential energy, one can then construct the Gibbs-Boltzmann distribution to write the equilibrium PDF of position $P_{\text{eq}}(z)$:

$$P_{\text{eq}}(z) = A \exp\left(-\frac{U(z)}{k_B T}\right), \quad (4.1.29)$$

where A is a normalization constant such that $\int_0^\infty P_{\text{eq}}(z) dz = 1$. Given an array of heights z_i one can use compute P_{eq} using the following Python snippet, where the A is computed using the `np.trapz` function. An example of a theoretical energy potential and PDF of position can be seen Fig.23 for $\ell_B = 500$ nm, $B = 4 k_B T$ and $\ell_D = 50$ nm.

```

1 import numpy as np
2
3 def _Peq(z):
4     if z <= 0:
5         return 0
6     else:
7         return np.exp(-(B * np.exp(-z / 1d) + z / 1b))
8
9
10 def Peq(z):
11     P = np.array([_Peq(zi) for zi in z])
12     return P / np.trapz(P, z)

```

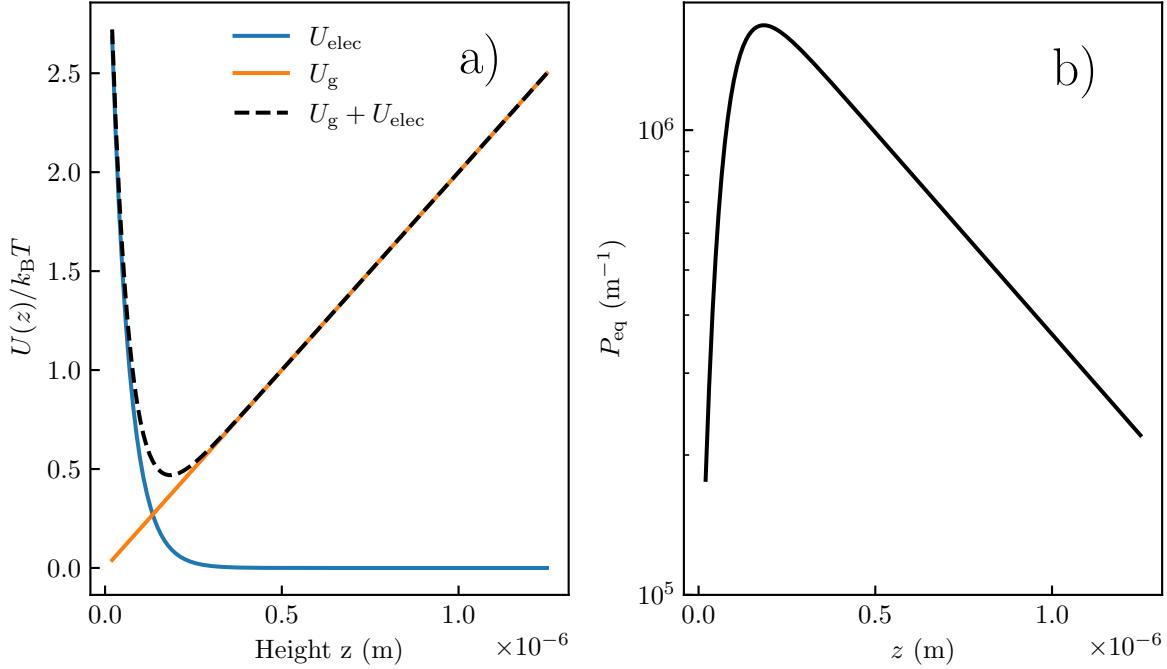


Figure 23: a) Potential energy of a colloid of Boltzmann length $\ell_B = 500$ nm. The electrostatic potential U_{elec} is here characterized by a surface charge constant $B = 4 k_B T$ and a Debye length $\ell_D = 50$ nm. b) Corresponding Gibbs-Boltzmann equilibrium distribution of position.

4.1.3 Local diffusion coefficient

As we have seen in the Chapter 2, for a freely diffusing colloid in bulk the diffusion coefficient is given by Eq.2.2.12 and is a constant. However, when a particle is confined, the diffusion is hindered, this means that the diffusion coefficient vary with the height of the particle and becomes anisotropic. One of the first measurement that has been done by Faucheux and Libchaber [13]. As we can see on the Fig.24, using a microscope, they tracked Brownian colloids in two dimensions, and, measured the average coefficient diffusion for different confinement constant $\gamma = (\langle z \rangle_t - a)/a$. Finally, on the Fig.24, one can observe that the diffusion coefficient parallel to the surface decreases as the particle get closer to the wall, and, seems to saturate around $0.3D_0$ for high confinement.

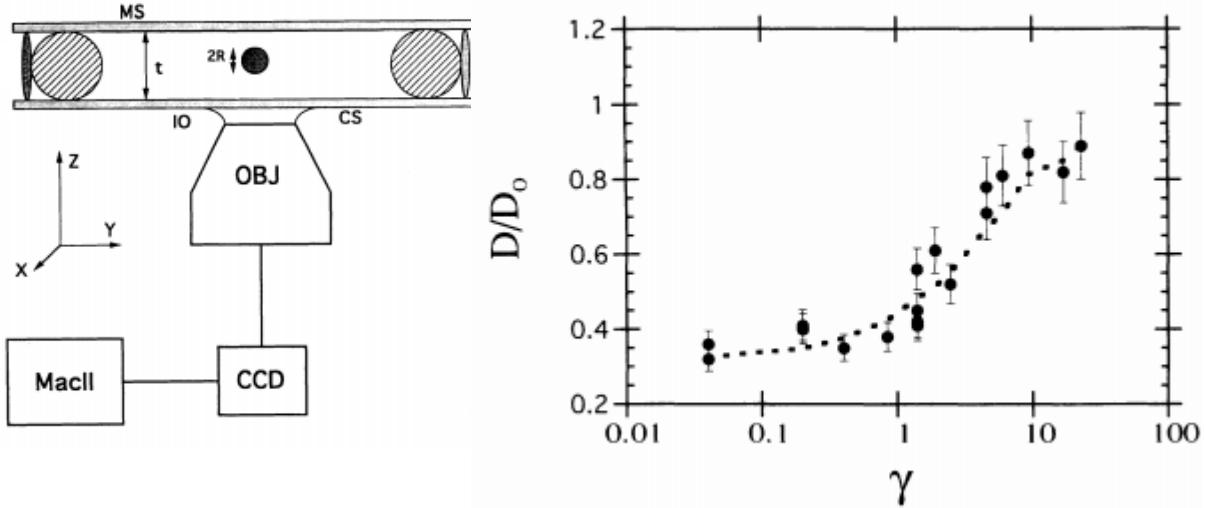


Figure 24: Figure extracted from [13], on the left is the experimental setup used. It is an inverted microscope used in order to track particle of size $2R$ inside a cell of thickness t . On the right is their final result, where they measure the diffusion parallel coefficient D_{\perp} given by Eq.4.1.41, here normalized by D_0 the bulk diffusion coefficient as a function of γ a confinement constant $\gamma = (\langle z \rangle - a)/a$.

To understand the reason of this hindered diffusion coefficient, let us start by writing the diffusion coefficient D using the fluctuation dissipation theorem:

$$D = \mu k_B T , \quad (4.1.30)$$

with:

$$\mu = \frac{v_{\text{sphere}}}{F_{\text{drag}}} , \quad (4.1.31)$$

where v_{sphere} is the terminal velocity to an applied force F_{drag} . For a spherical colloid of radius R moving at a velocity v_{sphere} the drag force in bulk $F_{\text{drag}}^{\text{B}}$ is given by the Stockes' law:

$$F_{\text{drag}}^{\text{B}} = c\pi\eta av_{\text{sphere}} , \quad (4.1.32)$$

where c is a constant that depends on the boundary conditions imposed at the surface of

the colloid, typically $c = 6$ for no-slip and $c = 4$ (such as air bubbles for example) for slip boundary conditions. Combining Eqs.4.1.30, 4.1.31 and 4.1.32 for a freely diffusing hard sphere in bulk we retrieve Eq.2.2.12:

$$D_0 = \frac{k_B T}{6\pi\eta a} . \quad (4.1.33)$$

The Stocke's drag force can be computed by solving the Navier-Stokes equation:

$$\rho \left[\frac{\partial \vec{v}}{\partial} + (\vec{v} \cdot \nabla \vec{v}) \right] + \nabla p = \eta \nabla^2 \vec{v} , \quad (4.1.34)$$

and the continuity equation for incrompressible fluids:

$$\nabla \cdot \vec{v} = 0 \quad (4.1.35)$$

where \vec{v} and p is the velocity and pressure fields ρ is the density of the fluid. When the Reynolds number $Re = \rho a v_{\text{sphere}} / \eta \ll 1$, the first two terms are inertial and are negligibly small compared to the viscous term $\eta \nabla^2 \vec{v}$. In that case, the Navier-Stokes Eq.4.1.34, is simplified to the Stockes flow formula:

$$\nabla p = \eta \nabla^2 \vec{v} \quad (4.1.36)$$

The diffusion coefficient for a freely diffusing spherical colloid in bulk can thus be found by solving Eqs.4.1.36 and 4.1.35 by having a no-slip boundary condition on the particle surface and the velocity vanishing at infinity. However, in the case of a confined particle, there is an additional no-slip condition at the wall surface. Indeed, as shown on the Fig.25, the fluid velocity drop to zero at the wall surface, with a shear rate:

$$\dot{\gamma} = \frac{\partial v_{\text{sphere}}}{\partial z} \quad (4.1.37)$$

This shear rate, due to the presence of the wall introduce a shear force $F(z) = \simeq \eta \dot{\gamma}(z)$ acting on the particle. Hence, the drag force acting on the particle will increase inversely with the distance to the wall, due to additional hydrodynamic pressure arising from velocity gradients. At the macro scale, this effect can be seen with a frisbee, indeed, as it

gets closer to the grounds, hydrodynamic pressure increases due to air velocity gradient and one can observe that the frisbee seems to stop falling and continue to glide really near the ground's surface.

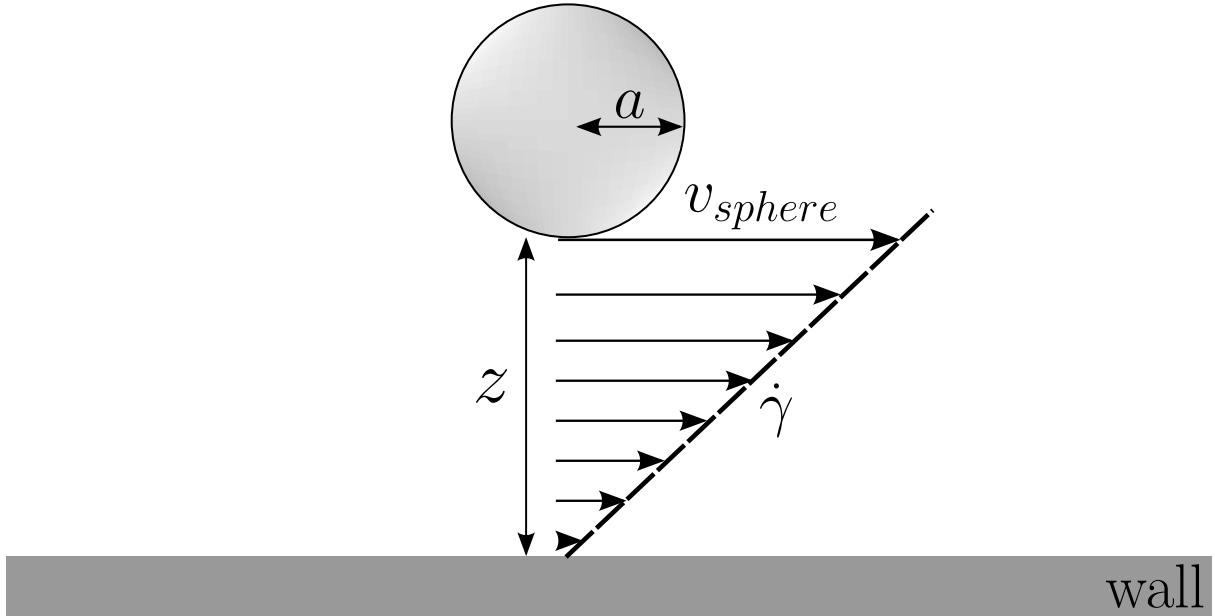


Figure 25: Schematic representation of a spherical colloid moving near a wall and the induced shear rate $\dot{\gamma}$.

A colloid diffusing near a wall thus experience a local drag force that depends on both it's distance to the wall z and the movement direction. Thanks to the linearity of the Stokes equation, one can separate this local drag force for motion parrallel and perpendicular to the wall. As the presence of the wall correct the drag force from a multiplicative coefficient, the confinement effect often expressed as an effective viscosity:

$$\eta_{\perp}(z) = \eta \lambda_{\perp}(z) , \text{ and, } \eta_{\parallel}(z) = \eta \lambda_{\parallel}(z) , \quad (4.1.38)$$

where λ_{\perp} and λ_{\parallel} are respectively perpendicular and parallel correction factor to the drag force due to the presence of the wall. Due to this correction, the diffusion coefficients for parallel and perpendicular motion relative to the wall writes:

$$D_{\perp}(z) = \frac{D_0}{\lambda_{\perp}(z)} , \text{ and, } D_{\parallel}(z) = \frac{D_0}{\lambda_{\parallel}(z)} . \quad (4.1.39)$$

For a no-slip boundary conditions imposed at the wall and the surface of the colloid, Brenner [72] obtained for perpendicular motion:

$$\lambda_{\perp}(z) = \frac{4}{3} \sinh \beta \sum_{n=1}^{\infty} \frac{n(n+1)}{(2n-1)(2n+3)} \left[\frac{2 \sinh(2n+1)\beta + (2n+1)\sinh 2\beta}{4 \sinh^2(n+1/2)\beta - (2n+1)^2 \sinh^2 \beta} - 1 \right], \quad (4.1.40)$$

where $\beta = \cosh^{-1}((z+a)/a)$. The solution for the diffusion parallel to the wall, Faxén found [73]:

$$\lambda_{\parallel}(z) = \left[1 - \frac{9}{16}\xi + \frac{1}{8}\xi^3 - \frac{45}{256}\xi^4 - \frac{1}{16}\xi^5 \right]^{-1}, \quad (4.1.41)$$

where $\xi = a/(z+a)$. Eqs.4.1.40 and 4.1.41 are precise for all z . However, the solution for the perpendicular motion can be quite complex to compute as it is an infinite series, to be computed numerically it requires a software that enable arbitrary-precision floating-point arithmetic⁶ — such as Mathematica or the `mpmath` Python's module for example. D_{\perp} can be evaluated using the following Python snippet, where `nsum` function is used to compute the infinite sum:

```

1 from mpmath import nsum
2
3 def Dz(eta, z, a):
4     a = (z + a) / a
5     beta = float(acosh(a))
6     summ = nsum(
7         lambda n: (n * (n + 1) / ((2 * n - 1) * (2 * n + 3)))
8         *
9         (
10            (2 * sinh((2 * n + 1) * xi) + (2 * n + 1) * sinh(2 * beta))
11            /
12            (4 * (sinh((n + 1 / 2) * beta) ** 2)
13             - ((2 * n + 1) ** 2) * (sinh(beta) ** 2)
14            )
15        )
16        -
17    ),
18    [0, inf],
19    )
20     summ = float(summ)
21 return kT / (6 * pi * eta * 4 / 3 * float(sinh(beta)) * summ * a)

```

⁶ Arbitrary-precision floating-point arithmetic enables to evaluate mathematical expression with any precision, in other words, any number of digits.

To simplify the computation of λ_{\perp} , Goldman *et al.* [74] showed that Eq.4.1.40 can be Padé approximated, giving:

$$\lambda_{\perp} = \frac{6z^2 + 9az + 2a^2}{6z^2 + 2az} . \quad (4.1.42)$$

In the near-wall regime, such that $z \ll a$, it is also possible to further approximate λ_{\perp} to:

$$\lambda_{\perp} = \frac{a}{z} . \quad (4.1.43)$$

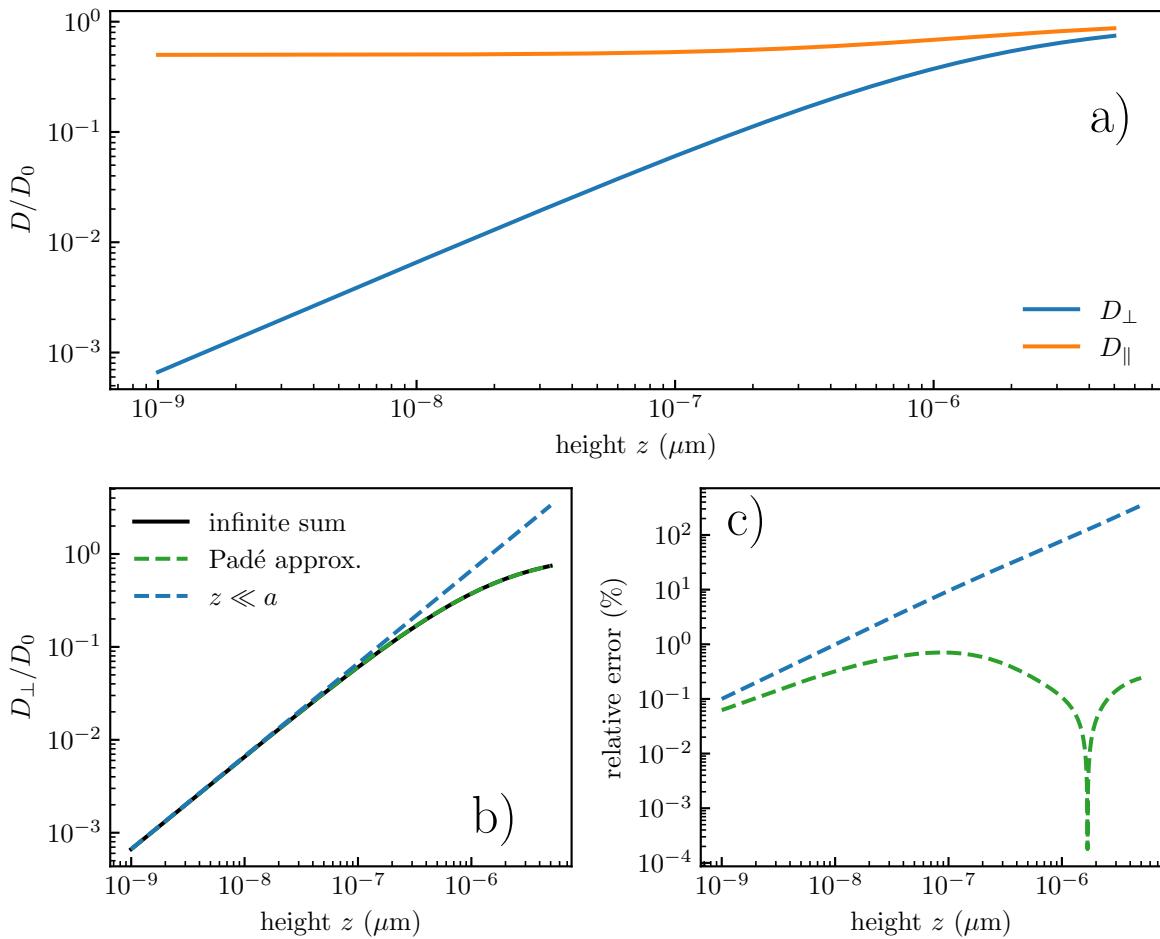


Figure 26: a) Parallel and perpendicular hindered relative diffusion coefficient for a colloidal particle of radius $a = 1.5 \mu\text{m}$. b) Perpendicular hindered relative diffusion coefficient for a colloid particle of radius $a = 1.5 \mu\text{m}$. In black the exact solution given by the infinite sum Eq.4.1.40. In green the Padé approximation, Eq.4.1.42 and in blue the near wall regime Eq.4.1.43. c) Relative error of the perpendicular hindered coefficient.

The Padé approximation and the near-wall approximation for the hindered diffusion are

plotted on Fig.26-b). The Padé approximation fits really well with the exact solution given by the infinite sum Eq.4.1.40, the near-wall approximation fits well when $z < a/10$. To check how precise the approximation are, it is possible to plot the relative error as in the Fig.26-c). The Padé approximation shows a precision up to 1%, thus, in the following of this work, when we refer to any evaluation of the hindered perpendicular diffusion, the Padé approximation will be used.

4.1.4 Langevin equation for the confined Brownian motion

Now that the external forces acting on the particle and hindered diffusion coefficient is known, we rewrite the overdamped Langevin Eq.2.3.10 equation as:

$$V_t^i dt = -\frac{1}{\gamma(z)} \frac{\partial U(z)}{\partial x_i} dt + \sqrt{2D_i(z)} dB_t . \quad (4.1.44)$$

where $\gamma(z) = 6\pi\eta_i(z)a$ and i denotes three spatial directions, x , y and z ⁷, and, dB_t still is a Gaussian distribution satisfying $\langle dB_t \rangle = 0$ and $\langle dB_t^2 \rangle = dt$. As we have discussed previously, the potential U only varies along the z axis, thus, the external forces only acts on the particle on the z axis while the particle diffuses freely along the x and y axis.

4.1.5 Spurious drift

It is interesting to observe that due to the hindered diffusion the magnitude of the Langevin force, $\sqrt{2D_i(z)}$, is not anymore a constant, but varies with the height of the particle. This effect is called multiplicative noise and will have some interesting effects on the dynamics properties of the Brownian motion. To show the effects of the multiplicative noise, one can integrate over a time τ the Eq.4.1.44, in the absence of the external force one has:

$$\Delta x_i = \int_{t_0}^{t_0+\tau} \sqrt{2D_i(z)} dB_t \quad (4.1.45)$$

where Δx_i is a space increment. However, the noise term is not well-defined and the time at which the magnitude of the force $\sqrt{2D_i(z)}$ in the integration Eq.4.1.45 needs to

⁷ Where the previously determined $\eta_{||}$ and $D_{||}$ correspond to the x and y axis and η_{\perp} and D_{\perp} correspond to the z axis.

be specified. It is thus necessary to determine where the Diffusion coefficient $D(z)$ in Eq.4.1.45 is evaluated in the time interval $[t_0, t_0 + \tau]$. In general, $D(z)$ is represented by $D(z + \alpha\Delta z)$, or in the same way $D(z(t_0 + \alpha\tau))$, with $\alpha \in [0, 1]$. The value of α determines at which time in the interval $[t_0, t_0 + \tau]$ the local diffusion is evaluated, hence, the magnitude of the random force. The physics will thus change on how the noise is calculated, however, the requirement is that the long-time thermal equilibrium must be consistent with the Boltzmann distribution and, hence, constrain the choice of α . Taking into account α , the langevin equation without external 4.1.45 forces along the z axis becomes:

$$\Delta z = \sqrt{2D_{\parallel}(z + \alpha\Delta z)}dB_t . \quad (4.1.46)$$

By Taylor expendig D_{\parallel} to the first order one has:

$$D_{\parallel}(z + \alpha\Delta z) \simeq D_{\parallel}(z) + \alpha \frac{dD_{\parallel}(z)}{dz} \Delta z . \quad (4.1.47)$$

Substituting the later in Eq.4.1.46 leads to:

$$\begin{aligned} \Delta z &\simeq \sqrt{2D_{\parallel}(z) + \alpha \frac{dD_{\parallel}(z)}{dz} \Delta z dB_t} \\ &= \sqrt{2D_{\parallel}(z)} \left[1 + \alpha \frac{dD_{\parallel}(z)}{dz} \frac{\Delta z}{D_{\parallel}(z)} \right]^{-1/2} dB_t . \end{aligned} \quad (4.1.48)$$

Additionally, since the last term satisfies:

$$\alpha \frac{dD_{\parallel}(z)}{dz} \frac{\Delta z}{D_{\parallel}(z)} \ll 1 , \quad (4.1.49)$$

one can thus Taylor expend at the first order the last term of Eq.4.1.48 as:

$$\left[1 + \alpha \frac{dD_{\parallel}(z)}{dz} \frac{\Delta z}{D_{\parallel}(z)} \right]^{-1/2} \simeq 1 + \frac{\alpha}{2} \frac{dD_{\parallel}(z)}{dz} \frac{\Delta z}{D_{\parallel}(z)} . \quad (4.1.50)$$

By finally substituting the first-order expansion of $\Delta z \simeq \sqrt{2D(z)}dB_t$, we obtain:

$$\begin{aligned}
\Delta z &\simeq \sqrt{2D_{\parallel}(z)} \left[1 + \frac{\alpha}{2} \frac{dD_{\parallel}(z)}{dz} \frac{\Delta z}{D_{\parallel}(z)} \right] dB_t \\
&\simeq \sqrt{2D_{\parallel}(z)} \left[1 + \frac{\alpha}{2} \frac{dD_{\parallel}(z)}{dz} \frac{\sqrt{2D(z)}dB_t}{D_{\parallel}(z)} \right] dB_t \\
&= \sqrt{2D_{\parallel}(z)}dB_t + \alpha \frac{dD_{\parallel}(z)}{dz} dB_t^2
\end{aligned} \tag{4.1.51}$$

Since for short time $dB_t \rightarrow 0$ it is possible to replace dB_t^2 by its average value $\langle dB_t^2 \rangle_t = \tau$, the latter thus become [75]:

$$\begin{aligned}
\Delta z &= \alpha \frac{dD_{\parallel}(z)}{dz} \tau - \frac{1}{\gamma(z)} \frac{\partial U(z)}{\partial z} \tau + \sqrt{2D_{\parallel}(z)}dB_t \\
&= \left(-\frac{1}{\gamma(z)} \frac{\partial U(z)}{\partial z} + \alpha \frac{dD_{\parallel}(z)}{dz} \right) \tau + \sqrt{2D_{\parallel}(z)}dB_t \\
&= \bar{v}_d \tau + \sqrt{2D_{\parallel}(z)}dB_t ,
\end{aligned} \tag{4.1.52}$$

where:

$$\bar{v}_d = -\frac{1}{\gamma(z)} \frac{\partial U(z)}{\partial z} + \alpha \frac{dD_{\parallel}(z)}{dz} = v_d + v_{\text{noise}} , \tag{4.1.53}$$

are the total drifts acting on the particle. The first term v_d is the drift due to “real” deterministic forces due to the electrostatic double-layer and gravity interactions, while the second term v_{noise} represents a noise induced drift. This spurious drift does disappear when the coefficient diffusion is homogeneous as for the x and y axis as the coefficient diffusion only depends on the colloid’s height. Theoretically, α can take any value between 0 and 1. However, α generally takes 3 different values [76]: $\alpha = 0$, the Itô integral, corresponding to the use of the initial value of $D(z)$; $\alpha = 1/2$, the Stratonovich integral, corresponding to the mid-point value; and $\alpha = 1$ the anti-Itô or isothermal integral, corresponding to the use of the final value.

In particular, the Itô integral $\alpha = 0$ is commonly used in economics and biology as integrals are approximated by a sum, the first point of the integral is chosen. The Stratonovich integral $\alpha = 1/2$ arises in Physical systems where noise correlation time $\tau_c > 0$, and, where the velocities are often computed at mid-points using three measurements. Finally, the isothermal integral $\alpha = 1$ is used in physical systems at equilibrium with a heat bath [22] such as our case with Brownian motion. Using the Padé approximation Eq.4.1.42, the spurious drift v_{noise} writes:

$$v_{\text{noise}}(z) = 2\alpha D_0 a \frac{2a^2 + 12az + 21z^2}{(2a^2 + 9az + z^2)^2}, \quad (4.1.54)$$

and the deterministic part of the drift writes:

$$v_d = -\frac{k_B T}{\gamma(z)} \left[-\frac{1}{\ell_D} B \exp\left(-\frac{z}{\ell_D}\right) + \frac{1}{\ell_B} \right]. \quad (4.1.55)$$

A typical example of drift velocity for a colloidal particle of radius $a = 1.5 \mu\text{m}$ in water, confined in interaction potential with a Debye length $\ell_D = 50 \text{ nm}$, $B = 4 k_B T$ and a Boltzmann length $\ell_B = 500 \text{ nm}$, is plotted in Fig.27. As one can observe, the spurious drift is not negligible, and, even the presence of this additional drift doubles the total drift \bar{v}_d near the surface.

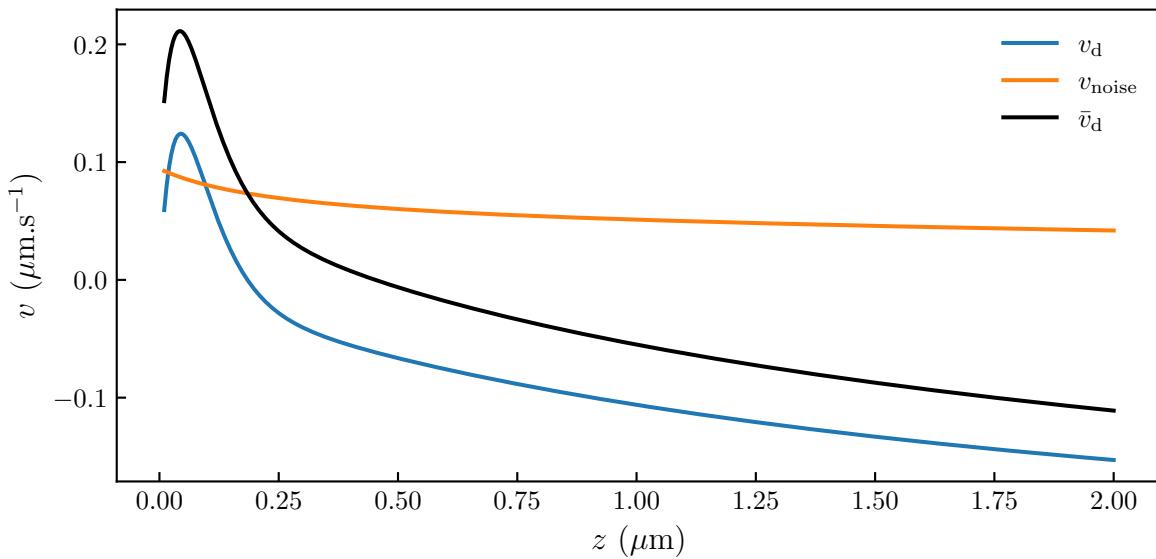


Figure 27: Typical drift velocity for a confined colloidal particle of radius $a = 1.5 \mu\text{m}$ in water. The physical properties of the interaction are $\ell_D = 50 \text{ nm}$, $B = 4 k_B T$ and $\ell_B = 500 \text{ nm}$.

4.1.6 Fokker-Plank equation

The Fokker-Plank equation is an alternative way to describe Brownian motion. Instead of explicitly calculating a Brownian trajectory by solving the Langevin equation, Fokker-Plank equation describes the particle distribution function $P(x, x_0; t)$ where x denotes the particle position and x_0 its initial position. To derive the Fokker-Plank plank equation,

let us start by taking generic Langevin equation:

$$dX_t = u(X_t)dt + a(X_t)dB_t , \quad (4.1.56)$$

where X_t is the particle position, u is the drift due to external forces and a the magnitude of the random force. Let consider the average value of an arbitrary function $f(X_t)$ for a stochastic process obeying Eq.4.1.56, that started at position x_0 at time $t = 0$, by definition [77]:

$$\langle f(X_t) \rangle = \int dx p(x, x_0; t) f(x) , \quad (4.1.57)$$

with the initial conditions that can be written as:

$$p(x, x_0; 0) = \delta(x - x_0) . \quad (4.1.58)$$

We now take the time derivative of Eq.4.1.57, we start by expending f at the dt as:

$$\begin{aligned} \left\langle \frac{df(X_t)}{dt} \right\rangle &= \frac{d}{dt} \left\langle \frac{\partial f(X_t)}{\partial x} u(X_t) dt + \frac{1}{2} \frac{\partial^2 f(X_t)}{\partial x^2} a^2(X_t) dB_t^2 \right\rangle \\ &= \frac{d}{dt} \left(\frac{\partial f(X_t)}{\partial x} u(X_t) dt + \frac{1}{2} \frac{\partial^2 f(X_t)}{\partial x^2} a^2(X_t) dt \right) \\ &= \frac{\partial f(X_t)}{\partial x} u(X_t) + \frac{1}{2} \frac{\partial^2 f(X_t)}{\partial x^2} a^2(X_t) . \end{aligned} \quad (4.1.59)$$

By combining Eqs.4.1.57 and 4.1.59, we get:

$$\begin{aligned} \left\langle \frac{df(X_t)}{dt} \right\rangle &= \int dx \frac{\partial p(x, x_0; t)}{\partial t} f(x) \\ &= \frac{\partial f(X_t)}{\partial x} u(X_t) + \frac{1}{2} \frac{\partial^2 f(X_t)}{\partial x^2} a^2(X_t) \\ &= \int dx p(x, x_0; t) Gf(x) , \end{aligned} \quad (4.1.60)$$

where G in an operator called the generator and is define by its action on a function f by:

$$Gf = \frac{1}{2}a^2(x)\frac{\partial^2 f(x)}{\partial x^2} + u(x)\frac{\partial f(x)}{\partial x} . \quad (4.1.61)$$

Using the definition of the adjoint of G , denoted by G^\dagger , one has:

$$\begin{aligned} \int dx \frac{\partial p(x, x_0; t)}{\partial t} f(x) &= \int dx p(x, x_0; t) Gf(x) \\ &= \int dx G^\dagger p(x, x_0; t) f(x) . \end{aligned} \quad (4.1.62)$$

From the latter, we thus have:

$$\frac{\partial p(x, x_0; t)}{\partial t} = G^\dagger p(x, x_0; t) . \quad (4.1.63)$$

Which leads to the Forward-Fokker-Planck equation:

$$\frac{\partial p(x, x_0; t)}{\partial t} = \frac{\partial^2}{\partial x^2} \left[\frac{a^2(x)}{2} p(x, x_0; t) \right] - \frac{\partial}{\partial x} [u(x)p(x, x_0; t)] \quad (4.1.64)$$

The latter is called Forward because the partial differential equation is in terms of the variable x , the position of the particle at which the stochastic process ends up, at time t . For a confined Brownian motion near a wall, using the previously determined drifts \bar{v}_d Eq.4.1.53, the Fokker-Plank equation for the movement along the z axis, perpendicular to the wall writes:

$$\frac{\partial p(z, z_0; t)}{\partial t} = \frac{\partial^2}{\partial z^2} [D(z)p(z, z_0; t)] - \frac{\partial}{\partial z} [\bar{v}_d p(z, z_0; t)] . \quad (4.1.65)$$

As an example, the stationary solution of the latter, $\partial p / \partial t = 0$, is given by the Gibbs-Boltzmann distribution $P_{eq}(z)$ (Eq.4.1.29). The solution for the Eq.4.1.63 with the particle starting at position z_0 , at time $t_0 = 0$ writes:

$$\begin{aligned} P(z, z_0; t) &= \exp(G^\dagger t)p(z, z_0, 0) \\ &= \exp \left(\frac{\partial^2}{\partial z^2} D(z)t - \frac{\partial}{\partial z} \bar{v}_d t \right) \delta(z - z_0) \end{aligned} \quad (4.1.66)$$

4.1.7 Numerical simulation of confined Brownian motion

We had previously determined with that the simulation of a bulk Brownian motion, without external forces can by the simple formula (Eq.2.4.9):

$$x_i = x_{i-1} + \sqrt{2D}w_i . \quad (4.1.67)$$

However, with the confined Brownian motion one needs to take into account the hindered diffusion, external forces due to gravity and double-layer interactions and the noise-induced drift. Putting all that together, leads to a new equation for x_i which writes for the movement parallel to wall:

$$x_i = x_{i-1} + \sqrt{2D_{\parallel}}w_i , \quad (4.1.68)$$

where i represents x and y axis. For the particle movement perpendicularly to the wall (z axis), one needs to add the total drift \bar{v}_d Eq.4.1.53, such that:

$$z_i = z_{i-1} + \bar{v}_d(z_{i-1})\tau + \sqrt{2D_{\perp}}w_i , \quad (4.1.69)$$

where τ is the simulation time step and w_i being a Gaussian distribution of mean value $\langle w_i \rangle = 0$ and variance $\langle w_i^2 \rangle = \tau$. Unlike the bulk Brownian motion where the time step τ can be chosen for the desired precision as shown previously on Fig.4; for an accurate simulation, the time-step should here be short enough for the drifts \bar{v}_d and local diffusion coefficient to be relatively constant in the time periods $t_{i+1}-t_i = \tau$ and in the displacement range $\Delta z = z_{i+1} - z_i$, such that:

$$\bar{v}_d(z \in [z_i, z_{i+1}]) \simeq \bar{v}_d(z_i) , \quad (4.1.70)$$

and,

$$D_{\perp,\parallel}(z \in [z_i, z_{i+1}]) \simeq D_{\perp,\parallel}(z_i) . \quad (4.1.71)$$

Since that the diffusion coefficient vary less for the movement parallel one can only consider

the perpendicular motion to determine the simulation time step. Also, as it can be seen on the Fig.XX where the drift v_d and diffusivity gradient are plotted, the diffusion gradient are negligible compared to the drift gradient, we thus focus on the drifts condition Eq.4.1.70. Moreover, the drifts vary more when the colloid is near the surface where one can approximate the diffusion coefficient D_{\perp} by the approximation Eq.4.1.43 such that:

$$D_{\perp}^{z \ll a}(z) = D_0 \frac{z}{a}. \quad (4.1.72)$$

As near the surface, the gravitational interaction can be neglected as it is smaller than the electrostatic interactions has it has been shown on the potential plot Fig.23. In that case, by taking $\alpha = 1$, the total drifts Eq.4.1.53 near the surface simplifies to:

$$\begin{aligned} \bar{v}_d &= \frac{k_B T}{\gamma_0} \frac{z}{a} \left[\frac{B}{\ell_D} \exp\left(-\frac{z}{\ell_D}\right) \right] + \frac{\partial}{\partial z} D_0 \frac{z}{a} \\ &= D_0 \frac{z}{a} \left[\frac{B}{\ell_D} \exp\left(-\frac{z}{\ell_D}\right) \right] + \frac{D_0}{a} \\ &= \frac{D_0}{a} \left[1 + \frac{Bz}{\ell_D} \exp\left(-\frac{z}{\ell_D}\right) \right] \end{aligned} \quad (4.1.73)$$

By expending the exponential term to the order z/ℓ_D order, we get:

$$\begin{aligned} \bar{v}_d &= \frac{D_0}{a} \left[1 + \frac{Bz}{\ell_D} \exp\left(-\frac{z}{\ell_D}\right) \right] = \frac{D_0}{a} \left[1 + \frac{Bz}{\ell_D} \left(1 - \frac{z}{\ell_D}\right) \right] \\ &= \frac{D_0}{a} \left(1 + \frac{Bz}{\ell_D} \right) \end{aligned} \quad (4.1.74)$$

To satisfy Eq.4.1.70, we need to have small relative change of drifts in an interval $[z, z+\Delta z]$ which can be written as:

$$\frac{\bar{v}_d(z + \Delta z) - \bar{v}_d(z)}{\bar{v}_d(z)} \ll 1 \quad (4.1.75)$$

Combining Eqs.4.1.74 and 4.1.75, we get:

$$\Delta z \ll \frac{\ell_D}{B} + z. \quad (4.1.76)$$

Using the MSD, it is possible to link the latter to the simulation time step τ by using the average value of Δz^2 , such that:

$$\langle \Delta z^2 \rangle(z) = 2D_{\perp}(z)\tau = 2D_0 \frac{z}{a} \tau \quad (4.1.77)$$

Combining Eqs.4.1.76 and 4.1.77 thus leads to:

$$\tau = \frac{a \langle \Delta z^2 \rangle}{2D_0 z} < \frac{a}{2D_0} \frac{\left(\frac{\ell_D}{B} + z\right)^2}{z} = \tau_{\max}(z) , \quad (4.1.78)$$

where τ_{\max} is thus the maximal time step that satisfies Eq.4.1.76. At this point, there is two different way to do the simulation: the first one is to do an adaptive time step where τ_{\max} for each step of the simulation ; the second one is to find the smallest $\tau_{\max}(z)$ and use for all the simulation a time step τ satisfying $\tau < \min(\tau_{\max})$. The latter can be evaluated by finding the height z_{\min} , at which the derivative of τ_{\max} nullifies, such that:

$$\left. \frac{\partial \tau_{\max}}{\partial z} \right|_{z_{\min}} = 0 . \quad (4.1.79)$$

Solving the latter gives:

$$z_{\min} = \frac{\ell_D}{B} . \quad (4.1.80)$$

which finally gives a maximal simulation time step, $\min(\tau_{\max})$:

$$\min(\tau_{\max}) = \frac{2a}{D_0} \frac{\ell_D}{B} , \quad (4.1.81)$$

this time should be the maximal time step τ used for a confined Brownian simulation near a wall to ensure an accurate simulation of the near-wall effects. In the Fig.28-b) some typical τ_{\max} are plotted for a colloid of radius $a = 1.5 \mu\text{m}$, $B = 4$ and ℓ_D varying between 20 and 100 nm. We can observe that for this range of values that well represents the experiments that I have done during my thesis, taking a simulation time step $\tau < 0.01 \text{ s}$ can be used for all set of parameters.

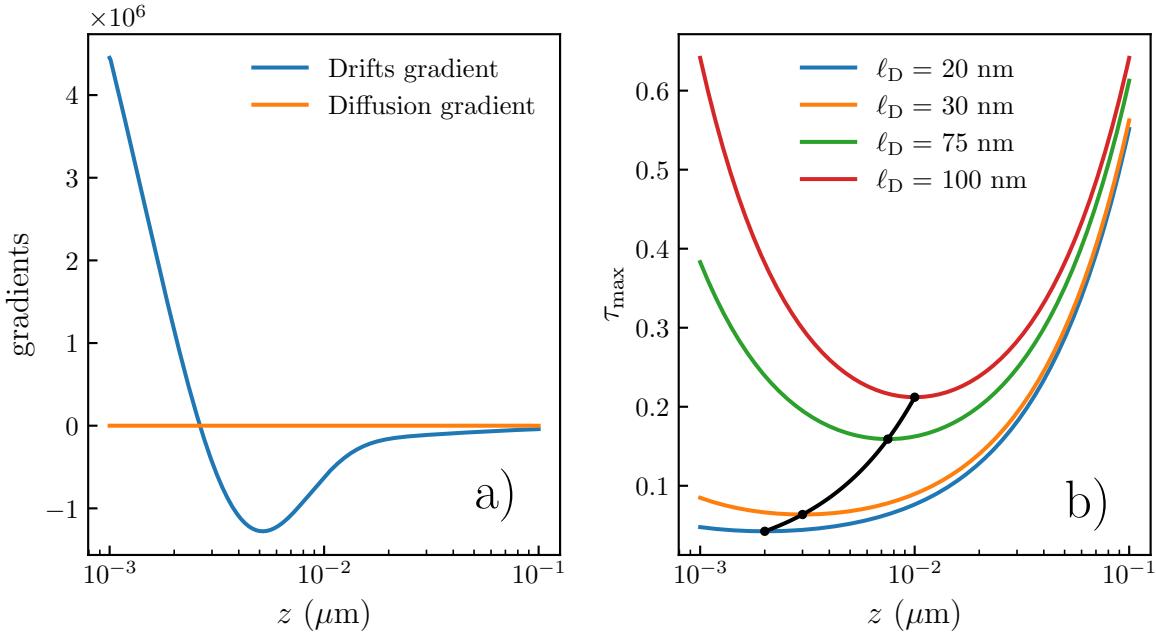


Figure 28: a) Drift and diffusive gradients for a confined colloidal particle of radius $a = 1.5 \mu\text{m}$ in water. The physical properties of the interaction are $\ell_D = 50 \text{ nm}$, $B = 4 k_B T$ and $\ell_B = 500 \text{ nm}$. b) τ_{\max} for a particle of radius $a = 1.5 \mu\text{m}$ and $B = 4$ for different Debye length. The black line represent the minimum value τ_{\max} for ℓ_D varying between 20 and 100 nm, this minimal time represent the maximal simulation time step that should be use for an accurate simulation.

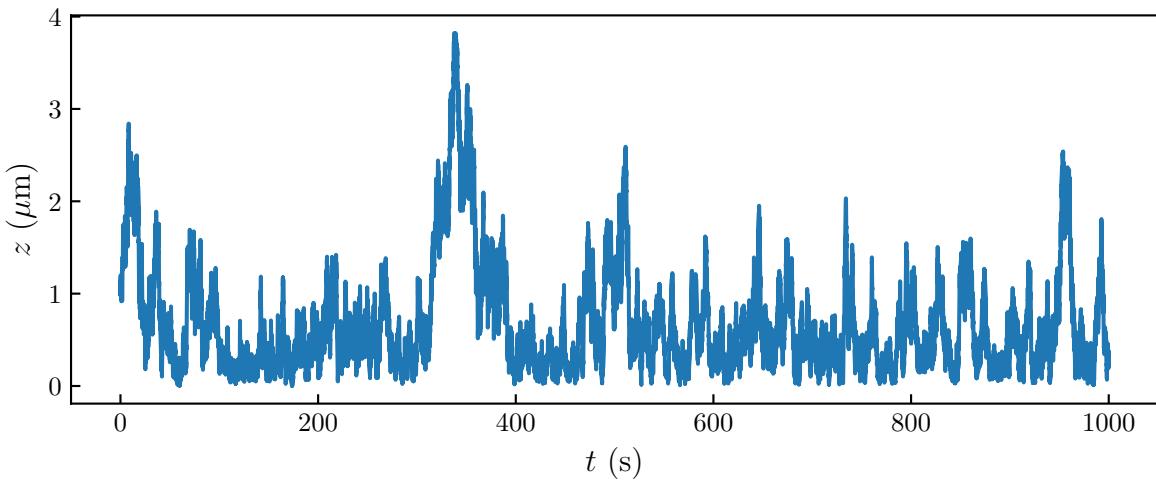


Figure 29: Simulated confined Brownian motion height trajectory of a colloidal particle of radius $a = 1.5 \mu\text{m}$ of density $\rho_p = 1050 \text{ kg.m}^{-3}$, $\alpha = 1$ and the potential is characterized by $\ell_D = 50 \text{ nm}$ and $B = 4$.

We have developed the simulation of the Confined Brownian motion using Python, as part of the Master's internship of Élodie Millan, the interested reader will find more information on confined Brownian motion in more complex systems in her forthcoming

thesis. A trajectory of a colloidal particle of radius $a = 1.5 \mu\text{m}$ of density $\rho_p = 1050 \text{ kg.m}^{-3}$ and the potential characterized by $\ell_D = 50 \text{ nm}$ and $B = 4$, is plotted in the Fig.29 which do look like the experimental trajectory that was shown in Fig.20 as an introduction to the chapter. In this trajectory, the noise induced lift is taken in account by using the isothermal approach $\alpha = 1$. However, to check if it is the correct way to take into account the spurious drift, the constraint we have is that the long time statistics should satisfy the Gibbs-Boltzmann equation Eq.4.1.29. To compute an experimental probability density function from a set of points, one can use the following Python snippet.

```

1 def pdf(data, bins=10, density=True):
2
3     pdf, bins_edge = np.histogram(data, bins=bins, density=density)
4     bins_center = (bins_edge[0:-1] + bins_edge[1:]) / 2
5
6     return pdf, bins_center

```

The Gibbs-Boltzmann distribution for $\alpha = 0, 0.5$ and 1 is shown in Fig.30. We see that the Isothermal integral of the noise gives the correct distribution, in the other two cases, we observe that the particle is more likely to be found nearer the surface, this is corrected by the additional spurious drift Eq.4.1.54.

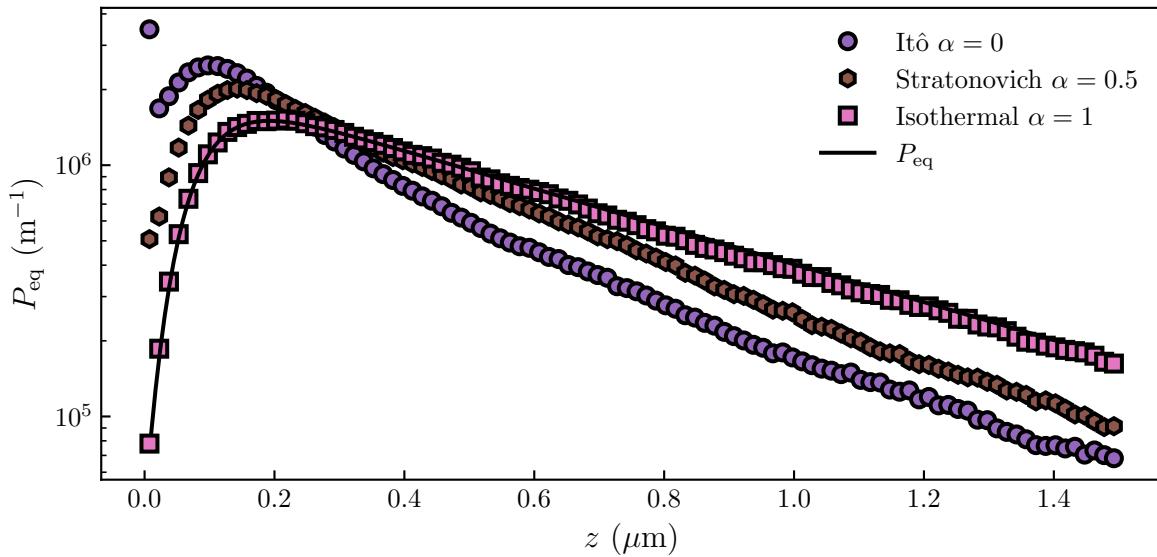


Figure 30: Probability Density Function of the height of the particle for different computation of the spurious drift, Itô $\alpha = 0$, Stratonovich $\alpha = 0.5$ and Isothermal $\alpha = 1$. The plain black line represents the expected Gibbs-Boltzmann distribution. The simulation parameters : $a = 1.5 \mu\text{m}$, $\rho_p = 1050 \text{ kg.m}^{-3}$, $\ell_D = 50 \text{ nm}$, $B = 4$ and $\ell_B = 577 \text{ nm}$.

4.2 Experimental study

4.2.1 MSD

4.2.2 Non-gaussian dynamics - Displacement distribution

4.2.3 Local diffusion coefficient inference

4.2.4 Precise potential inference using multi-fitting technique

4.2.5 Measuring external forces using the local drifts

4.3 conclusion

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