

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

$\alpha$	Noise amplitude
$\ell_B$	Boltzmann length
$\ell_B$	Debye length
$\eta$	Fluid viscosity
$\eta_\perp$	Viscosity orthogonal to a wall, see Eq.2.4.1
$\eta_\parallel$	Viscosity parrallel to a wall, see Eq.2.4.2
$\gamma$	Friction coefficient
$\rho_F$	Fluid density
$\rho_P$	Particle density
$B$	Amplitude of the electrostatic interactions
$D$	Diffusion coefficient, see Eq.2.2.12
$g$	Gravity constant
$k_B$	Boltzmann Constant
$m$	Mass of a particle
$N_A$	Avogrado constant
$R$	Gas constant
$T$	Temperature
$V_t$	Velocity of a particle
$X_t$	Particle position, see Eq.2.3.13

## List of Abbreviations

<b>fps</b>	Frames per second
<b>MSD</b>	Mean Squared Displacement
<b>SDE</b>	Stochastic Differential Equations

# 1 Introduction

Since the observations of Gordon Moore in the 60's we know that the technological progress is bound to our ability to miniaturize. It's indeed due to the miniaturization that we are able to have more computational power leading to the rise of new technologies like the Deep Learning [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 now starting to be extensively used in physics with in 2020 the first focus session on machine learning at the *March Meeting* that continued this year with presentations at every sessions. The success of Deep learning is not due to the fact that it's new and fancy algorithm since it known for several decade but only the fact that the miniaturization permitted to do the stunning amount of computation needed to have a smart AI. Our ability to use this technologies is finally bound to our ability to understand the surface physics at the nanometer scale.

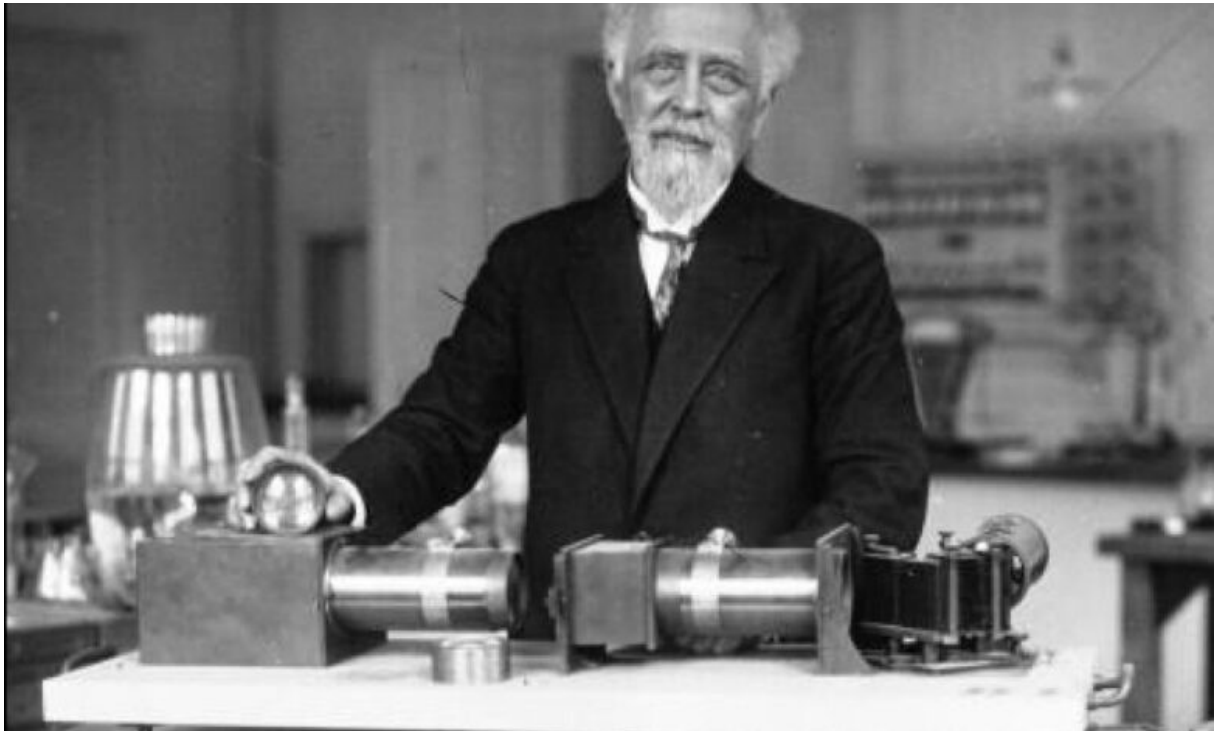
On another side we have microfluidic since the 80s which is an incredible multidisciplinary field involving chemistry, engineering, soft matter physics and also biotechnology. Microfluidic permitted the development of daily life technologies like the ink-jet printers or more advanced tools such as DNA chips [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 is characterized by a typical spatial extent evolving as the square root of time, as well as Gaussian displacements. At a time of miniaturization and interfacial science, and moving beyond the idealized bulk picture, it is relevant to consider the added roles of boundaries to the above context. Indeed, Brownian motion at interfaces and in confinement is a widespread practical situation in microbiology and nanofluidics. In such case, surface effects become dominant and alter drastically the Brownian statistics, with key



implications towards: i) the understanding and smart control of the interfacial dynamics of microscale entities; and ii) high-resolution measurements of surface forces at equilibrium. Interestingly, a confined colloid will exhibit non-Gaussian statistics in displacements, due to the presence of multiplicative noises induced by the hindered mobility near the wall [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 the first part of the manuscript I will present the history of the Brownian motion and it's basic theory. In a second part I will present particle tracking using Mie holography and our experimental setup. Then the third part will focus on one trajectory analysis in order to infer the surface induced effects on the Brownian motion. In a last chapter I will present more complex inference.



## 2 Brownian motion

### 2.1 The Brownian motion discovery

In 1827 the Scottish botanist Robert Brown published a paper [25] on his observation on the pollen of *Clarkia pulchella* with a lot of details on his taught processes. His experiments were made to understand the flower reproduction, but, as he was looking through the microscope he observed some minute particles ejected from the pollen grains. At first, he thought this movement was a test to find the male organ, then looking at grains Mosses and *Equiseta* which had been dried up for one hundred years, he was surprised to see this "peculiar" movement and since he was able to increase the number of particle by bruising ovule or seeds of *Equisetum* he abandoned his supposition. Interestingly each time that he encountered a material that he was able to reduce to a fine enough powder to be suspended in water, he observed a constant motion, although, he never guessed the origin of the particle's movement.

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

It's finally in 1905 that Albert Einstein describe that "bodies of microscopically visible size suspended in a liquid will perform movements of such a magnitude that they can be easily observed in a microscope" [4]. A nice remark to make here is that in 1948 Einstein wrote a letter to one of his friend where he stated having deduced the Brownian motion "from mechanics, without knowing that anyone had already observed anything of the kind" [26].

It's in 1908 that Jean Perrin published his experimental work on the Brownian motion, that way he was able to measure the Avogadro number and prove the kinetic theory that Einstein developed. I would also cite M. Chaudesaigues and M. Dabrowski, who helped J. Perrin to track the particles by hand, half-minutes by half-minutes, for more than 3000 displacements (25 hours) and several particles. This impressive and daunting work is highly detailed in "*Mouvement brownien et molécules*" [27]. This is partly due to this work than J. Perrin received the Nobel award in 1926.

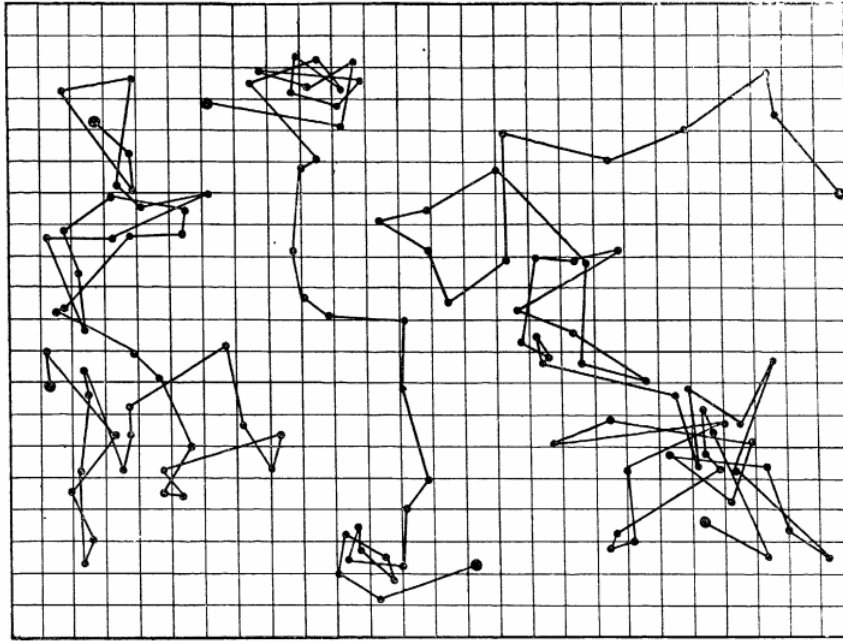


Figure 1: Brownian motion of  $1 \mu\text{m}$  particle in water tracked by hand by Jean Perrin and his colleagues, each point are timely space by 30 seconds and 16 divisions represents  $50 \mu\text{m}$

## 2.2 The Einstein Brownian theory

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

For simplicity, we will here look only at the Brownian motion of  $n$  particles in 1D along the  $x$  axis. In a time interval  $\tau$  the position of each individual particle will increase by a displacement  $\Delta$ , positive or negative and different for all the particles. The number of particle  $dn$  experiencing a displacement lying between  $\Delta$  and  $\Delta + d\Delta$  in a time interval  $\tau$  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  $\varphi$  is nonzero only for very small displacement  $\Delta$  and satisfies  $\varphi(\Delta) = \varphi(-\Delta)$ .

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

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

Since  $\tau$  is very small, we have:

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

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

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

Putting all together, in Eq.2.2.3 we obtain:

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

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

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

the Eq.2.2.6 finally becomes:

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

We can here recognize a differential equation for the diffusion with  $D$  the diffusion coefficient. We will now initiate the same position  $x = 0$  for all the particle at  $t = 0$  as in the Fig.2 and  $f(x, t)dx$  now denoting the number of particles whose position as increased between the times  $t = 0$  and  $t = t$  by a quantity lying between  $x$  and  $x + dx$  such that we must have:

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

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

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

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

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

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

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

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

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

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

Finally, he ends up in paper [4] by saying *"Let us hope that a researcher will soon succeed in solving the problem posed here, which is of such importance in the theory of heat!"*. I'd like here to emphasize on the importance of solving this problem in very beginning of the 19's. At this time two theory about the fundamental matter components existed, one's seeing only energy and a second one, atoms, especially supported by Boltzmann and his kinetic theory of gases, here used by Einstein. Thus, an experimental proof of Eq.2.2.12 would prove the existence of atoms and molecules. Due to a lot of theoretical misunderstanding of the theory and experimental error scientist such as Svedberg or Henri thought that Einstein's theory was false [28] by even proving that the statistical properties of the Brownian motion was changing with the pH of the solution. It's finally in 1908 that Chaudesaigues and Perrin published all the evidence to prove Einstein's theory mainly by their ability to create particle emulsion of well controlled radius.

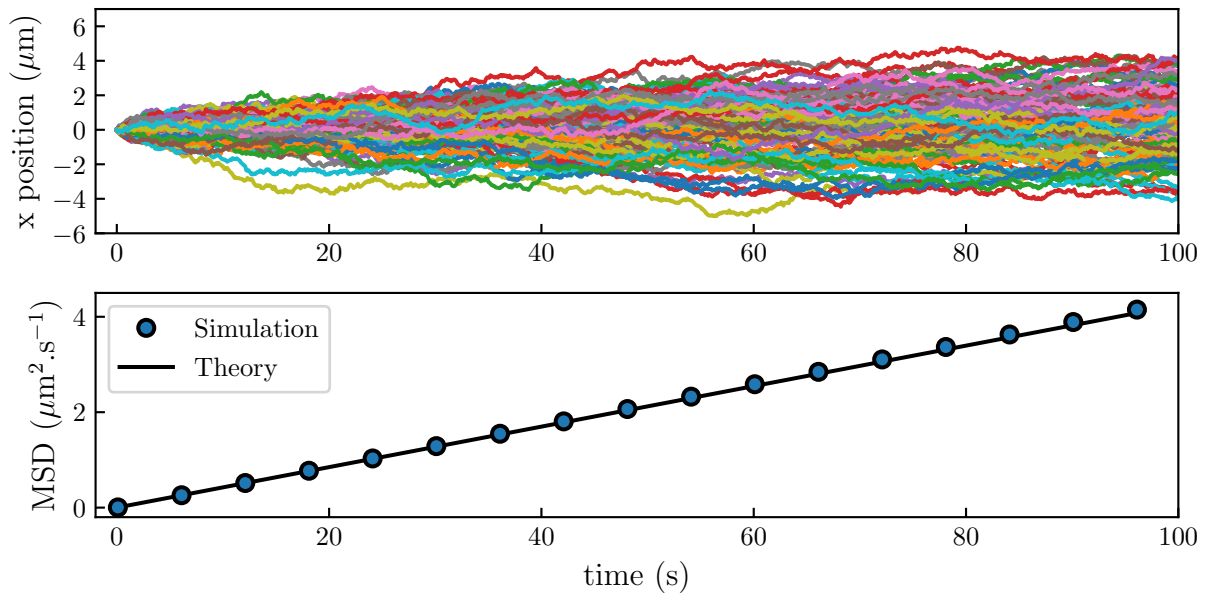


Figure 2: Simulation of bulk Brownian motion of  $1 \mu\text{m}$  particles in water. On the top each line represents the trajectory of a Brownian particle over 100 seconds a total of 100 trajectories or shown. On the bottom, bullets represents the MSD computed from the simulated trajectories. The black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

## 2.3 Stochastic Differential Equations

In physics we generally write Brownian motion with Stochastic Differential Equations (SDE). This model was introduced in 1908 by Langevin [29], since it benefits of a correct mathematical definition of the noise, this model is now used by the major part of physicists working on random processes. Note than it can also be found under the name of Langevin equation. This model is write as follows:

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

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

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

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

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

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

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

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

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

which as a familiar solution:

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

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

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

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

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

Taking the average then gives:

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

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

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

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



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

this equation permits a direct determination of the amplitude of the noise  $\alpha$  :

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

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

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

the MSD is then written as:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

```

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

```

## 2.4 The confined Brownian motion

We have seen that the bulk Brownian motion is well known and documented for a long time. But, in the real world, the boundaries are not at infinity and could play a role in the process of diffusion. Indeed, it was theorized by H. Faxen [30] that the presence of a wall would change the Stokes-Einstein relation with a viscosity dependent to the position of the particle. As the particle get closer to a surface, the presence of the non-slip boundary condition make the fluid harder to push, thus increasing the local viscosity of the particle. This variation of the viscosity will be different for orthogonal and parallel displacement to the wall, thus we write respectively  $\eta_{\perp}$  and  $\eta_{\parallel}$  with  $\eta_0$  being the fluid viscosity and  $z$  the height of the particle:

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

and

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

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

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

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

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

One of the first experimental measurement of the local diffusion coefficient was brought by Faucheux and Libchaber [13] where they measured the mean diffusion coefficient with various gaps and particle radius their results can be found in the Fig.3.

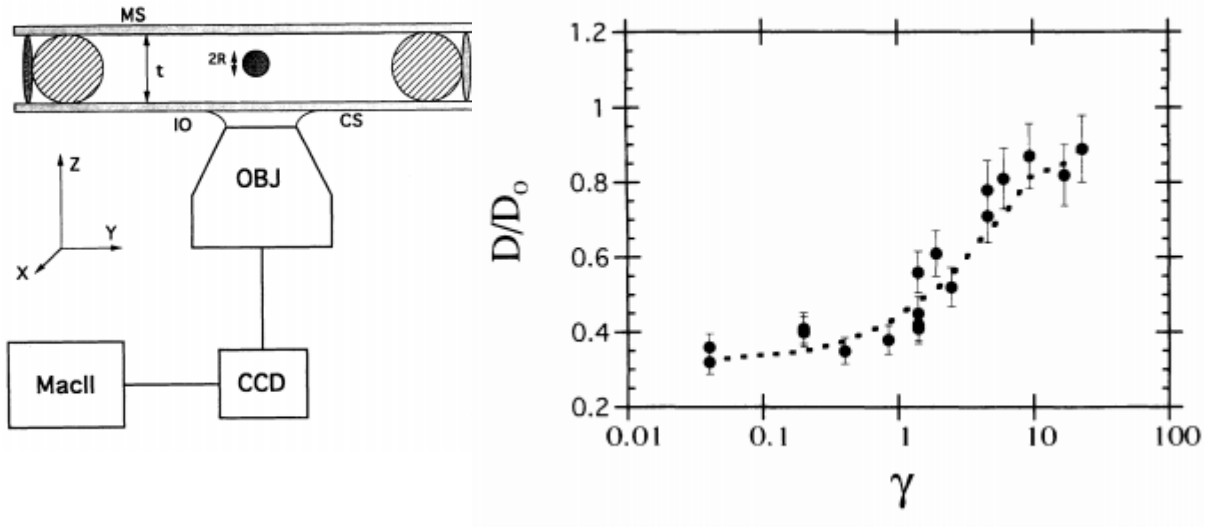


Figure 3: Figure extracted from [13], on the left is the experimental setup used. It is an inverted microscope used in order to track particle of size  $2R$  inside a cell of thickness  $t$ . On the right is their final result, where they measure the diffusion parallel coefficient  $D_{\perp}$  given by Eq.2.4.2, here normalized by  $D_0$  the bulk diffusion coefficient as a function of  $\gamma$  a confinement constant  $\gamma = (\langle z \rangle - a)/a$ .

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

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

that we can rewrite for simplicity

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

with  $\ell_B$  the Boltzmann length which represents the balance between the kinetic energy and the weight of the particle:

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

Let's now consider the interactions with the substrate, glass slides when immersed in water do charge negatively as well as polystyrene particles that we use. We will then have repulsive electrostatic interactions between the wall and the particles, the corresponding potential can be written as [31]:

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

where  $B$  is the amplitude of electrostatic interactions, representing the surface charges and  $\ell_{\text{D}}$  being the Debye length, which is the characteristic length of the electrostatic interactions. The particle is thus lying in a total potential given by:

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

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

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

where  $A$  is a normalization constant so that  $\int P_{\text{eq}} = 1$ . This distribution gives us the probability to find the particle at a height  $z$ . The exponential decay due to the gravity was first measured by Perrin [5] by methodically counting through a microscope the number of colloids in suspension as a function on the height.

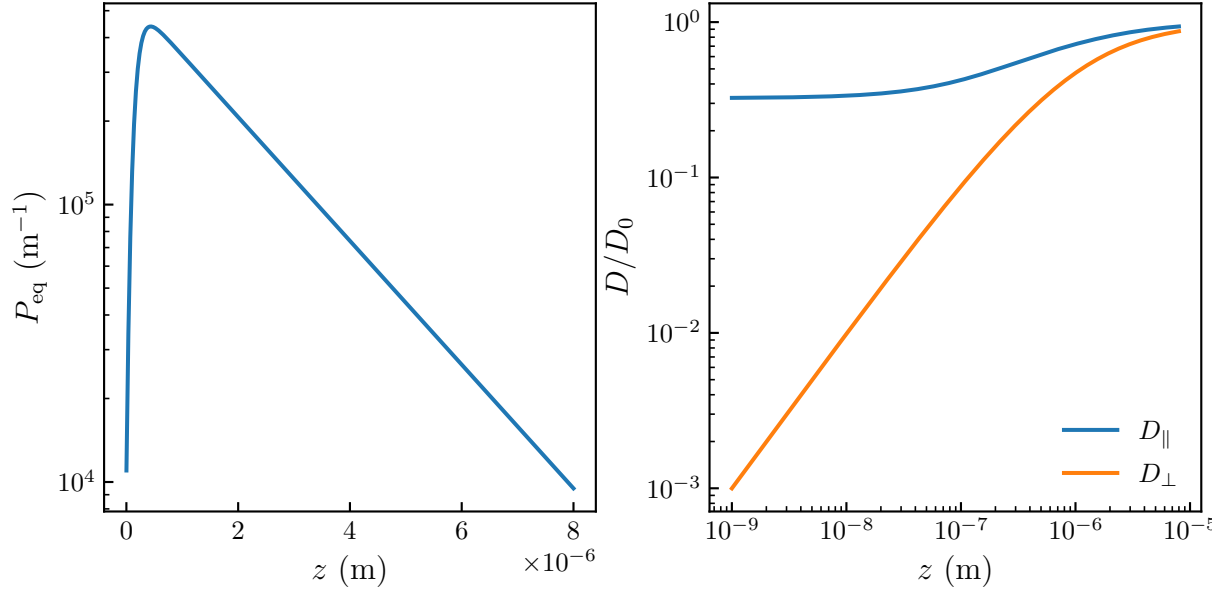


Figure 4: On the left, plot of the Gibbs-Boltzmann distribution Eq.2.4.10 for  $a = 1 \mu\text{m}$ ,  $B = 4$ ,  $\ell_D = 100 \text{ nm}$  and  $\Delta\rho = 50 \text{ kg.m}^{-3}$ . On the right, local diffusion coefficient normalized by bulk diffusion coefficient  $D_0 = k_B T / \gamma$ , given by Eq.2.4.2 and Eq.2.4.1

## 3 Particle characterization and particle tracking using interference properties

### 3.1 Introduction

Properties of coherent light to produce interference is widely used 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, speak of in-line holography.

### 3.2 In-line holographic video microscopy theory

#### 3.2.1 Reflection Interference Contrast Microscopy

Reflection Interference Contrast Microscopy was first introduced in cell biology by Curtis to study embryonic chick heart fibroblast [37] in 1964. RICM gained in popularity 40 years after both in biology and physics [38–43]. It was also used recently in soft matter physics to study elastohydrodynamic lift at a soft wall [36].

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

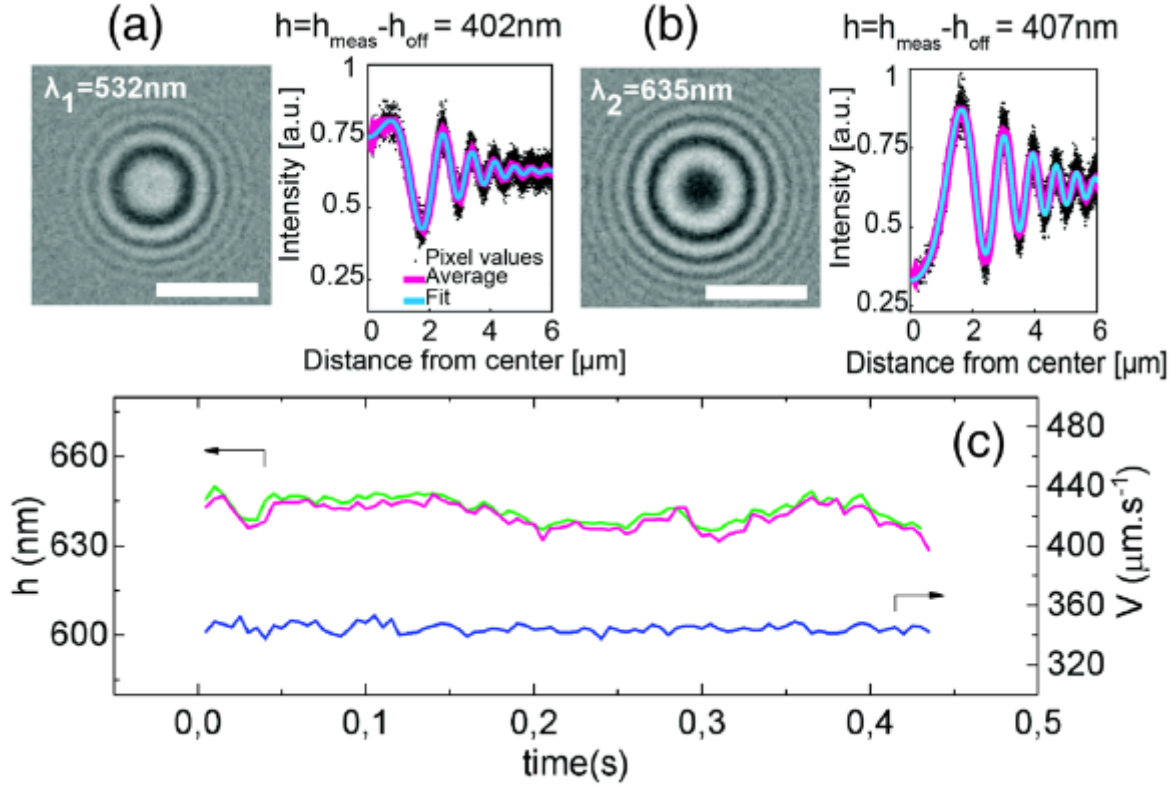


Figure 5: Figure from [36] representing RISM with two wavelengths. (a) Left: interference patterns created with a wavelength  $\lambda_1 = 532 \text{ nm}$  (scale bar  $5 \mu\text{m}$ ). Right: radial intensity profile (black dots) extracted from the image, azimuthally averaged (magenta line) and fitted 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:  $\lambda_1$ , magenta:  $\lambda_2$ ) and the particle velocity measured along the flow in blue.

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  $\omega$  [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  $k = 2\pi n_m / \lambda$ ,  $\lambda$  denoting 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 ( $\vec{r} = \vec{0}$ ) could be taken at the position of the first reflection (on the glass slide) thus at the particle,  $\vec{r}$  would be given by the particle's height such that  $|\vec{r}| = z$  the particle-substrate distance. Experimentally, we measure 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:

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

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  $\phi$  the phase difference between the two fields, which is generally equal to  $\pi$  due to the reflection properties on a higher 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 [43]:

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

Where  $A_i$  and  $b_i$  are fit parameters and  $g(x)$  denotes the contour of the sphere. Finally, this method is great because the equation is 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  $\approx 1.2 \mu\text{m}$  as used in [36]. 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, hence, RICH is not usable for our context. As a matter of fact, we experimentally reach height span of a few microns.

### 3.2.2 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 size is at the same order of magnitude or greater than the illumination wavelength, it is not possible to use Rayleigh approximations [45]. Indeed, we 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 background 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.

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

$$\vec{E}_0(\vec{r}, z) = E_0(\vec{r})e^{ikz}\hat{e} \quad (3.2.9)$$

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:

$$\vec{E}_s(\vec{r}, z) = \vec{f}_s(k(\vec{r} - \vec{r}_p))E_0(\vec{r})\exp(-ikz) \quad (3.2.10)$$

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,  $I$  is given by:

$$\begin{aligned} I(\vec{r}) &= |\vec{E}_s(\vec{r}, 0) + \vec{E}_0(\vec{r}, 0)|^2 \\ &= E_0^2(\vec{r}) + 2E_0^2 \operatorname{Re} \left( \vec{f}_s(k(\vec{r} - \vec{r}_p))\hat{e} \right) + |\vec{f}_s(k(\vec{r} - \vec{r}_p))|^2 \end{aligned} \quad (3.2.11)$$

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. It 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. Naturally, 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. 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.6 a-c). We write the normalized intensity  $I/I_0$ :

$$\frac{I(\vec{r})}{I_0(\vec{r})} = 1 + 2 \operatorname{Re} \left( \vec{f}_s(k(\vec{r} - \vec{r}_p)) \hat{e} \right) + |\vec{f}_s(k(\vec{r} - \vec{r}_p))|^2 \quad (3.2.12)$$

Now that we have the analytical form of the holograms' intensity, it is possible to fit an experimental one to Eq.3.2.12 as shown in Fig.6 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:

$$\vec{f}_s(k\vec{r}) = \sum_{n=1}^{n_c} \frac{i^n (2n+1)}{n(n+1)} \left( ia_n \vec{N}_{eln}^{(3)}(k\vec{r}) - b_n \vec{M}_{oln}^{(3)}(k\vec{r}) \right) \quad (3.2.13)$$

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]:

$$a_n = \frac{\zeta^2 j_n(\zeta ka) ka j'_n(ka) - j_n(ka) [\zeta ka j_n(\zeta ka)]'}{\zeta^2 j_n(\zeta ka) ka h_n^{(1)'}(ka) - h_n^{(1)}(ka) \zeta ka j'_n(\zeta ka)} \quad (3.2.14)$$

and

$$b_n = \frac{j_n(\zeta ka) ka j'_n(ka) - j_n(ka) \zeta ka j'_n(mka)}{j_n(\zeta ka) ka h_n^{(1)'}(ka) - h_n^{(1)}(ka) \zeta ka j'_n(mka)}, \quad (3.2.15)$$

where  $\zeta = n_p/n_m$  and the prime notation denotes differentiation with respect to the argument. As we can see, the holograms given by Eq.3.2.13 will vary with a lot of

parameters ( $\lambda$ ,  $n_m$ ,  $n_p$ ,  $a$  and  $\vec{r}_p$ ) which can all be fitted. In general, the illumination wavelength  $\lambda$  and medium index  $n_m$  are known and do not need to be fitted. From only one hologram it is thus possible to 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.3.2.13 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]

$$n_c = ka + 4.05(ka)^{1/3} + 2 . \quad (3.2.16)$$

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  $\lambda = 532 \text{ nm}$ , for the smallest ones, where  $a = 0.5 \mu\text{m}$  we find  $n_c = 18$  which makes a huge difference in practice.

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].

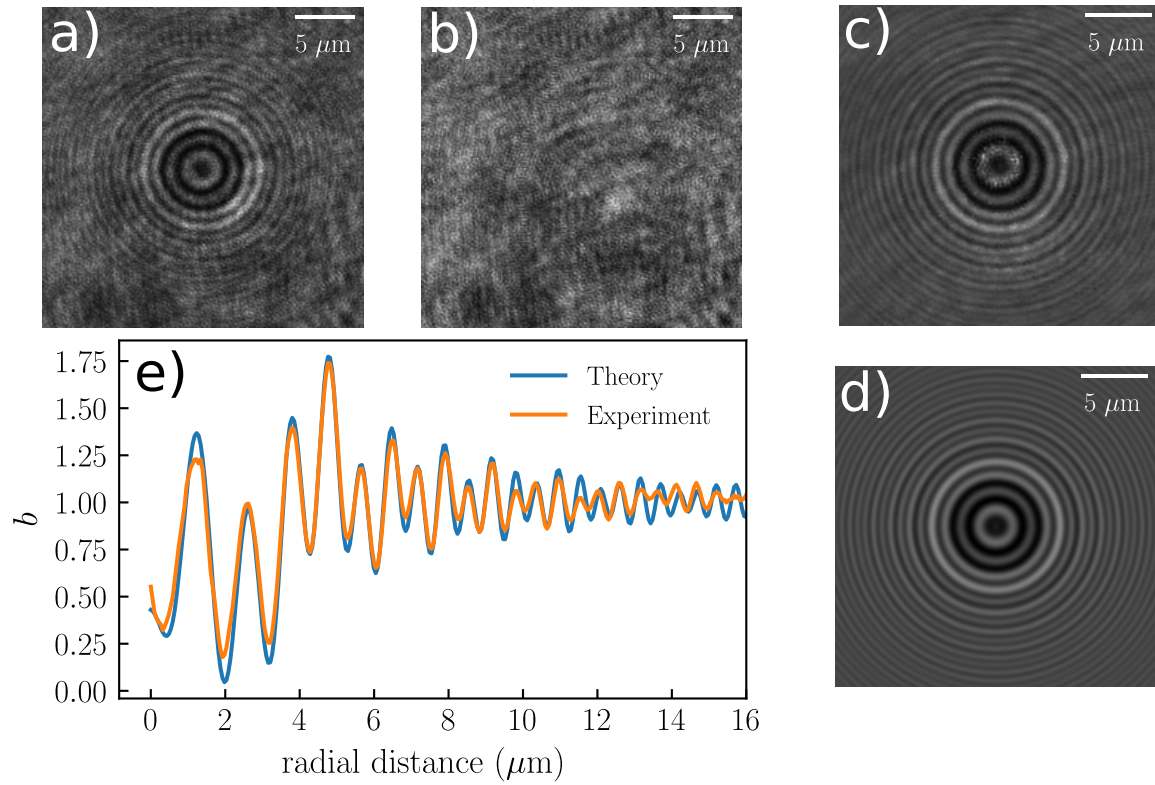


Figure 6: a) Raw hologram of a 2.5  $\mu\text{m}$  polystyrene particle measured experimentally with the setup detailed in the chapter 3.3. b) Background obtained by taking the median value of the time series of images of the diffusing particle. c) Normalized hologram given by dividing a) by b). d) Result of the fit of c) using Eq.3.2.12 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).

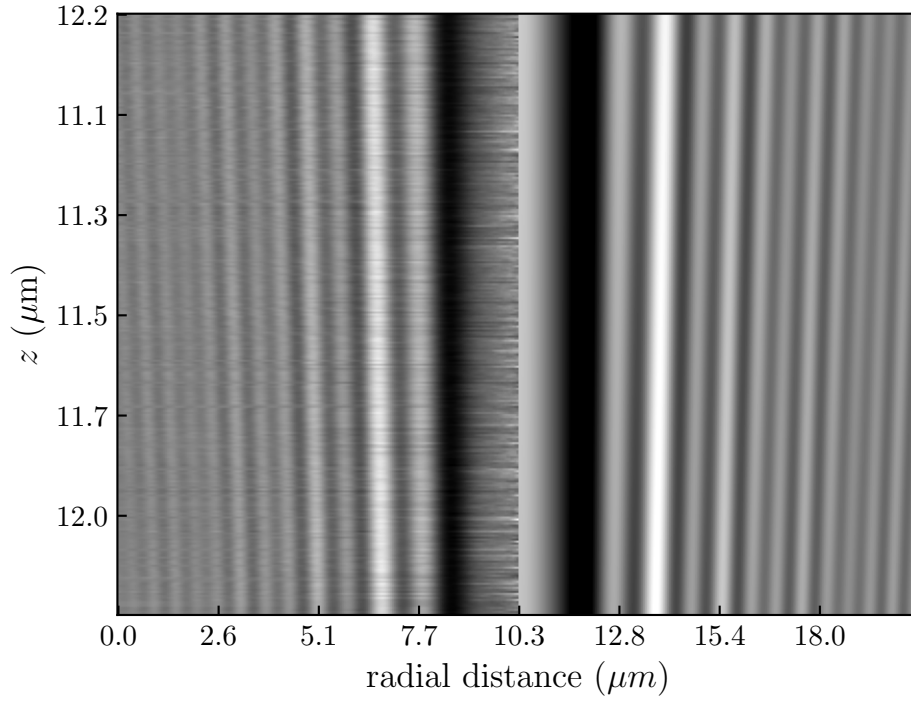


Figure 7: On the left, experimentally measured holograms' radial intensity profile stack, generated from a polystyrene bead of nominal radius  $a = 1.5 \pm 0.035 \mu\text{m}$  using the experimental setup explained in chapter 3.3. The calibration of this particle radius and optical index is shown in Fig.11. On the right, the corresponding theoretical stack using the result of each individual hologram's fit.

### 3.2.3 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., such as :

$$|\zeta - 1| \ll 1 \text{ and } ka|\zeta - 1| \ll 1 . \quad (3.2.17)$$

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.3.2.12 can be rewritten as:

$$\frac{I(\vec{r})}{I_0(\vec{r})} = 1 + 2 \operatorname{Re} \left( \frac{E_s(\vec{r}, 0)}{E_0(\vec{r})} \right) . \quad (3.2.18)$$

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]:

$$h_{-z}(\vec{r}) = \frac{1}{2\pi} \frac{\partial}{\partial z} \frac{e^{ikR}}{R} , \quad (3.2.19)$$

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:

$$E_s(\vec{r}, z) = E_z(\vec{r}, 0) \otimes h_{-z}(\vec{r}) \quad (3.2.20)$$

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

$$E_s(\vec{r}, z) \approx \frac{e^{ikz}}{4\pi^2} \int_{-\infty}^{\infty} B(\vec{q}) H(\vec{q}, -z) e^{i\vec{q} \cdot \vec{r}} d^2q , \quad (3.2.21)$$

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

$$H(\vec{q}, -z) = e^{iz\sqrt{k^2 - q^2}} . \quad (3.2.22)$$

Finally, using Eq.3.2.21 we can reconstruct the scattered field and intensity since  $I(\vec{r}) = |E_s(\vec{r})|^2$  as shown in Fig.8. Those equations are way less computational intensive than the Lorenz-Mie function Eq.3.2.13. Thus tracking can be way faster, moreover, Fourier transforms can be largely accelerated using GPU. Additionally, as the propagator Eq.3.2.19 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.3.2.21 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.

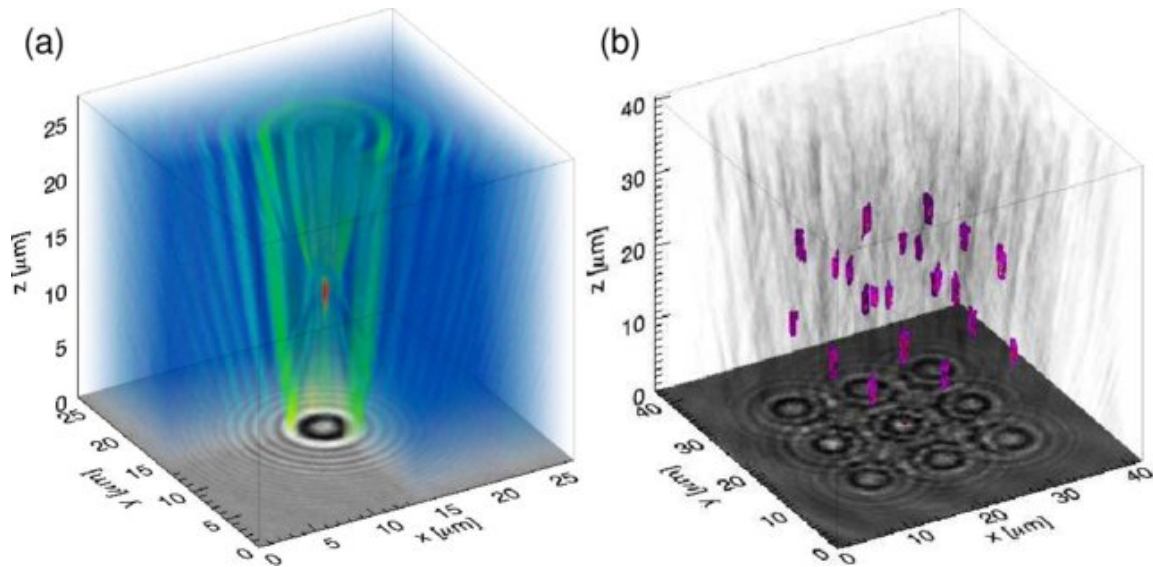


Figure 8: Figure from [63] a) Volumetric reconstruction using Eq.3.2.21 of the scattered intensity of single colloidal sphere, colored by intensity. b) Volumetric reconstructions of 22 individual  $1.58 \mu\text{m}$  diameter silica spheres organized in bcc lattice using holographic optical tweezers in distilled water. Colored regions indicate the isosurface of the brightest 1 percent of reconstructed voxels.

### 3.2.4 Conclusion

Finally, the method we choose is the Lorenz-Mie fitting method, since this it permits the characterization of single particles. Indeed, since we are interested to fine effects near the surface, we need to know perfectly the radius of the particle we have recorded. This feature also make our all process calibration free, as we don't need to assume any physical properties. In the following, the experimental setup is going to be detailed.



### 3.3 Experimental setup

In order to observe the holograms we use an homemade inverted microscope as shown on the Fig.9 and schematized in Fig.10. A sample consists of a parallelepipedic chamber ( $1.5 \text{ cm} \times 1.5 \text{ cm} \times 150 \text{ }\mu\text{m}$ ), made from two glass covers, a parafilm spacer, and sealed with vacuum grease, containing a dilute suspension of spherical polystyrene beads. We used 3 different sizes, of nominal radii  $0.56 \text{ }\mu\text{m}$ ,  $1.5 \text{ }\mu\text{m}$  and  $2.5 \text{ }\mu\text{m}$ , at room temperature  $T$ , in distilled water (type 1, MilliQ device) of viscosity  $\eta = 1 \text{ mPa.s}$ . The sample is illuminated by a collimated laser beam with a  $521 \text{ }\mu\text{m}$  wavelength. As depicted in the chapter 3.2.2, 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  $51.6 \text{ nm/pixel}$  resolution (see Fig.6a)). The exposure time of the camera is set to 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.

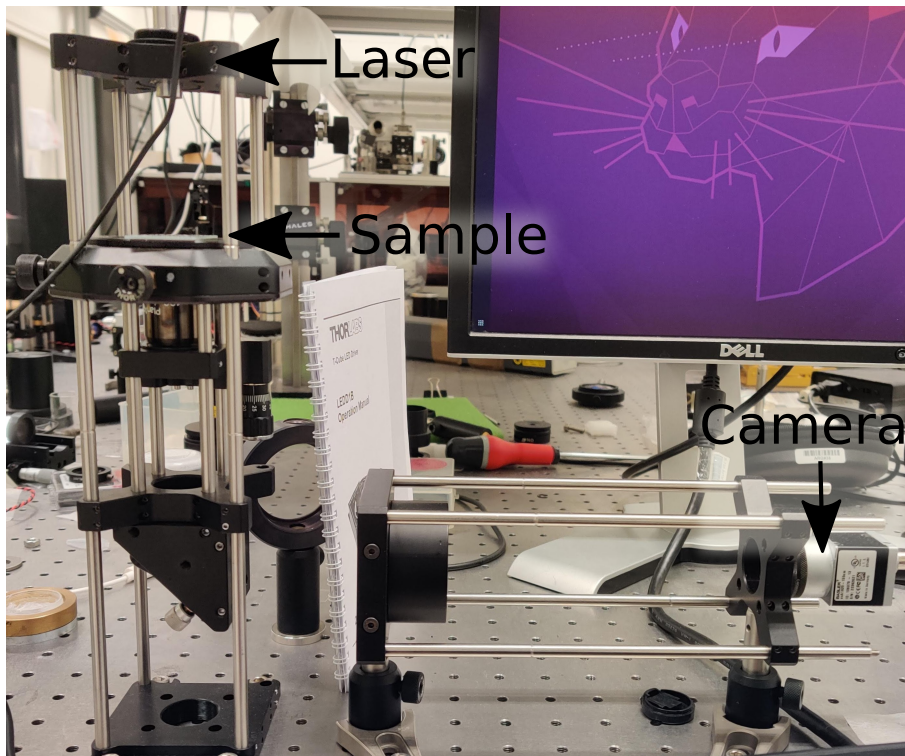


Figure 9: Photo of the custom build microscope used along my thesis. It is mainly composed of Thorlabs cage system. The camera used is a Basler acA1920-155um, we use a x60 magnification and 1.30 numerical aperture oil-immersion objective lens. The light source is a colimated  $521 \text{ }\mu\text{m}$  wavelength laser.

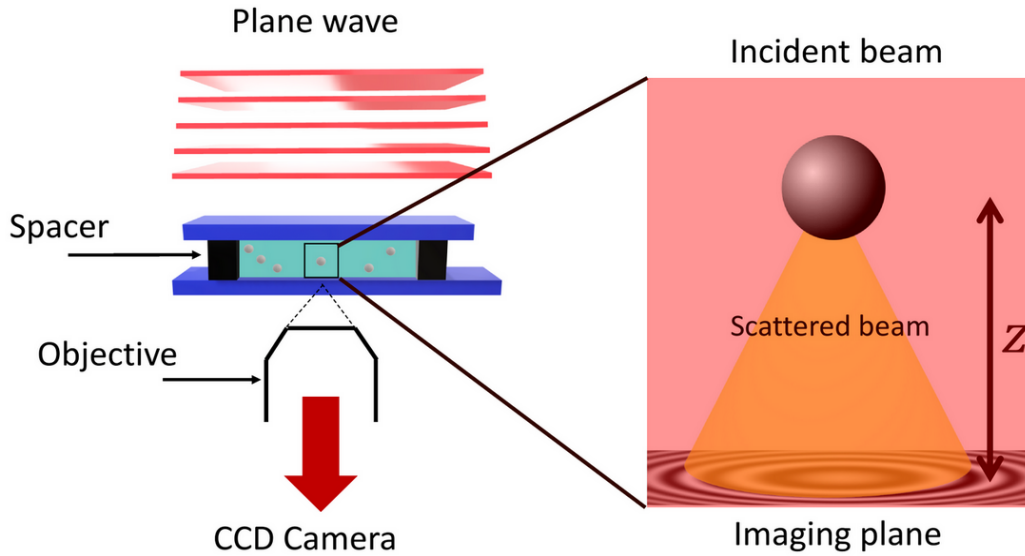


Figure 10: Schematic of the experimental setup. A laser plane wave of intensity  $I_0$  illuminates the chamber containing a dilute suspension of micro-spheres in water. The light scattered by a particle interferes with the incident beam onto the focal plane of an objective lens, that magnifies the interference pattern and relays it to a camera.

### 3.4 Hologram fitting strategy

#### 3.4.1 How to fasten the process ?

As presented in the section 3.2.2 about the Lorenz-Mie fitting, the main drawback is the time to fit an image, from 30 seconds for the images of  $100 \times 100$  pixels to a few minutes for the  $500 \times 500$  pixels. We can directly see a bottleneck, indeed, if we want to track one trajectory made of 100 000 images we would need to wait a minimum of  $\approx 70$  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, *Pylorenz* and *Holopy* in order to inverse holograms. They had introduced ways to only fit a set of randomly chosen pixels, 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 this is faster, it leads to a few images per second and still is 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 actually learned a lot of things on code optimization and computer cluster usage. It's around the half of my thesis, that *Pylorenz* got a new commit on their github repository which was telling that they succeeded on using GPU acceleration using

CUDA. 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. To have a more reliable and fast tracking, what we do is that we fit with all free parameters the first 10 000 images of a movie. We then determine the physical properties of the colloidal particle and then fit the whole movie with only the position as a free parameter.

### 3.4.2 Radius and optical index characterization

Once the data of the radius and optical index retrieved, the quantity we can look at is the the distribution of measurements. Using 10 000 measurements we can plot the histograms of the measured  $a$  and  $n_p$ .

This simple histogram could suffice to measure the physical properties of the colloidal particle. However, we can go a bit further and look at the 2D histogram of the  $a$  and  $n_p$  as presented in the fig.11 here smoothed using a Gaussian kernel density estimator. As we can see it is not isotropic, and it seems that the measurement of  $n_p$  and  $a$  are correlated.

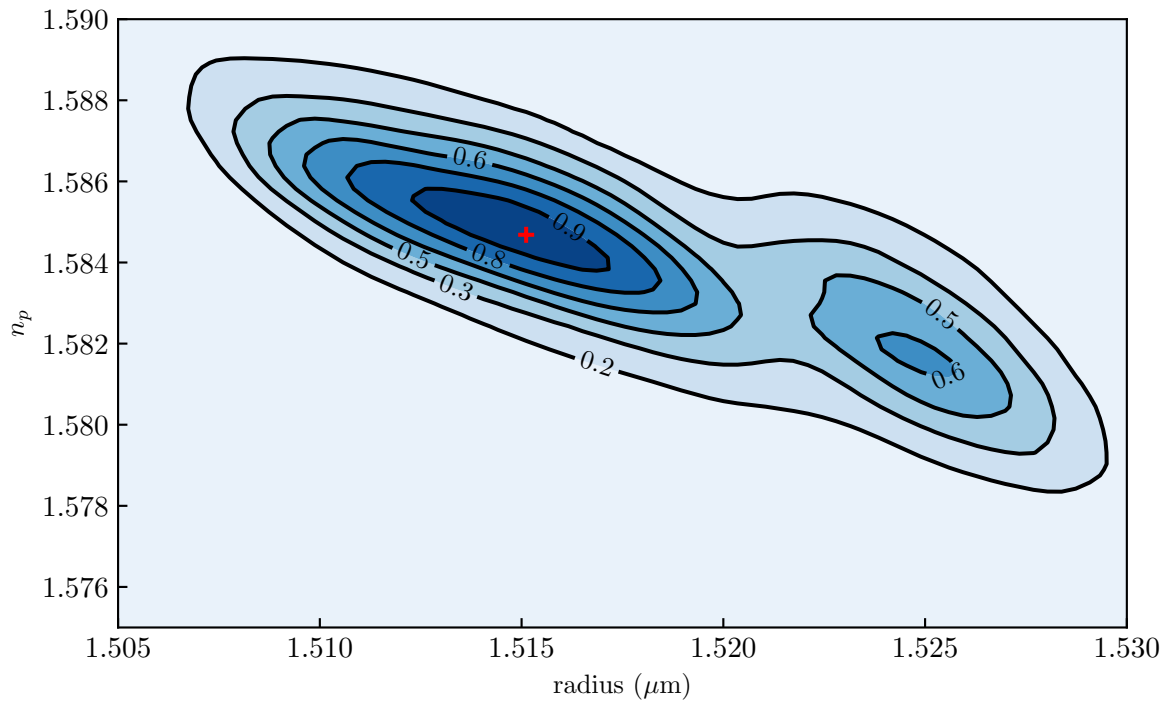


Figure 11: 2D Probability density function of the measurements of the optical index  $n_p$  and radius  $a$ . Black lines indicate iso-probability. Taking the 10% top probability, we measure  $n_p = 1.585 \pm 0.002$  and  $a = 1.514 \pm 0.003$   $\mu\text{m}$ .

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