Abstract

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0.1 Introduction

This experiments serves to examine the position fluctuations of polystyrene particles with a diameter of

$$a = 4{,}28\,\mu\text{m}$$

in an aqueous dispersion that is highly dilute. The observed motion is called the *Brownian motion* (compare Abschnitt 0.2). To this end, the form of the potential surrounding the single particles is to be determined. Moreover, the determination of the dependency of the diffusion coefficient on the distance between particle and the walls of the cuvette containing the dispersion along with the total distance for a given particle are main goals of the experiment. Regarding the used optical tweezers, the light force on the particles is measured. Last, through measurements of silica particles' movement in aqueous dispersions with different concentrations of salt, the variation of the screening length is examined.

0.2 Brownian motion

The motion of particles suspended in a fluid resulting from their collision with fast moving molecules (or atoms) of the fluid is called the *Brownian motion*.

Within a fluid at thermal equilibrium at a given temperature, no preferential direction of flow exists. Therefore, the movement the fluid's molecules is random yielding no linear or angular momenta over time. Suffieciently small particles suspended in this fluid move in random patterns, too, changing its velocity $\vec{v}$ upon colliding with one of the fluid's molecules. As a matter of fact, the observation has been used as evidence for the existence of individual water (fluid) molecules.

Because of the sheer number of involved fluid molecules, the many-body interactions resulting in the *Brownian motion* cannot be solved relying only on classical mechanics. To put a number to it, the number of collisions of a single particle suspended in the fluid (a so called *Brownian particels*) with the fluid molecules is roughly of the order 10^{14}. Therefore, among other, Albert Einstein produced a probabilistic model using statistical mechanics. Einstein started by formulating a diffusion equation for the *Brownian particels*. To this end, he regarded a one dimensional x-space with the origin at the initial position of the modelled *Brownian particles*. Assuming the conservation of the number of fluid molecules and introducing the density function $\varphi(\Delta)$, with the random variable Δ, he expanded the *Brownian particle* density ρ at a time $t + \tau$ in a Taylor series

$$\begin{aligned}
\rho(x,t) + \tau\frac{\partial\rho(x)}{\partial t} + \cdots = \rho(x,t+\tau) &= \rho(x,t)\cdot\int_{-\infty}^{\infty}\varphi(\Delta)\mathrm{d}\Delta \\
&= \rho(x,t)\cdot\int_{-\infty}^{\infty}\varphi(\Delta)\mathrm{d}\Delta - \frac{\partial\rho}{\partial x}\cdot\int_{-\infty}^{\infty}\Delta\varphi(\Delta)\mathrm{d}\Delta \\
&\quad + \frac{\partial^2\rho}{\partial x^2}\cdot\int_{-\infty}^{\infty}\frac{\Delta^2}{2}\varphi(\Delta)\mathrm{d}\Delta + \cdots \\
&= \rho(x,t)\cdot 1 + 0 + \frac{\partial^2\rho}{\partial x^2}\cdot\int_{-\infty}^{\infty}\frac{\Delta^2}{2}\varphi(\Delta)\mathrm{d}\Delta + \cdots .
\end{aligned}$$

While the integral in the second line equals one by definition of the probability, terms with even partials vanish due to symmetry of the 1D space. The above equation is equivalent to

$$\begin{aligned}
\frac{\partial\rho}{\partial t} &\approx \frac{\partial^2\rho}{\partial x^2}\cdot\int_{-\infty}^{\infty}\frac{\Delta^2}{2\tau}\varphi(\Delta)\mathrm{d}\Delta \\
&= D\cdot\frac{\partial^2\rho}{\partial x^2}
\end{aligned} \tag{0.1}$$

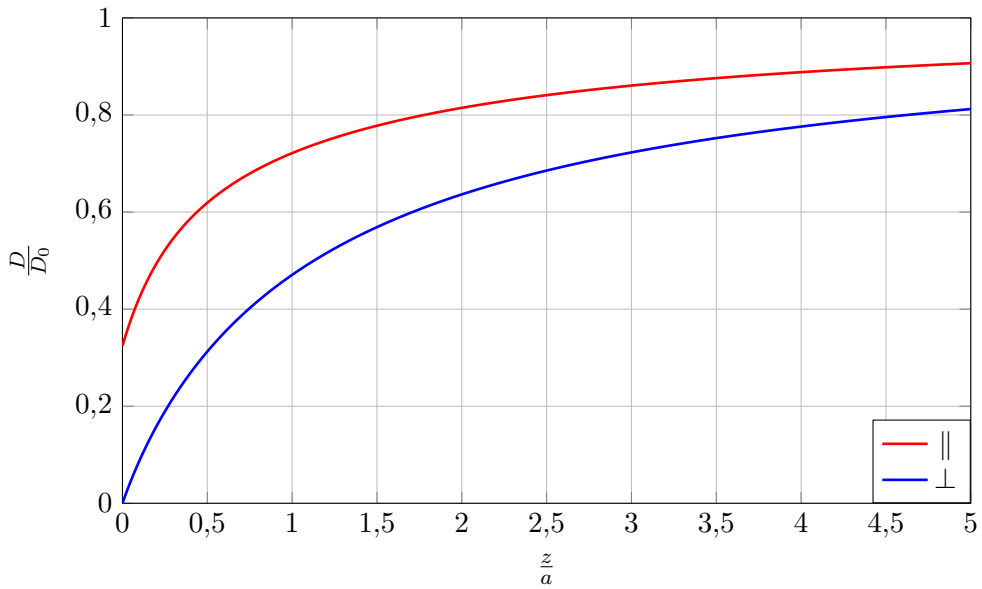

Figure 0.1 Distance dependent diffusion coefficients for a particle of diameter a at a distance z from the walls for parallel and perpendicular components of motion (compare Abschnitt 0.2.1).

if only terms with orders smaller than 2 of Δ are regarded and using the *mass diffusivity* or *diffusion coefficient*

$$D = \int_{-\infty}^{\infty} \frac{\Delta^2}{2\tau} \varphi(\Delta) \mathrm{d}\Delta. \tag{0.2}$$

0.2.1 Brownian motion in proximity of the cavity walls

In Abschnitt 0.2, only the fluid's molecules surrounding the *Brownian particles* have been taken into account for the diffusion equation Gleichung (0.1). When the fluid is confined in a cavity though, the cavity's walls affects the flow of the fluid. This statement can be proven by simply regarding a fluid molecule or *Brownian particle* next the cavity wall. It's motion'S component orthogonal to the wall is limited to one direction which is away from the wall. The interaction between the confining walls andthe particles is called *hydrodynamic interaction*.

The mathematical description of this phenomenon makes use of distance z dependent diffusion coefficients

$$D_{\parallel}(z) = D_0 \left[1 - \frac{9}{16} \left(\frac{a}{z+a} \right) + \frac{1}{8} \left(\frac{a}{z+a} \right)^3 - \frac{45}{256} \left(\frac{a}{z+a} \right)^4 - \frac{1}{16} \left(\frac{a}{z+a} \right)^5 + \cdots \right] \tag{0.3}$$

$$\begin{aligned} D_{\perp}(z) &= D_0 \left[\frac{4}{3} \sinh(\alpha) \sum_{n=0}^{\infty} \frac{n(n+1)}{(2n-1)(2n+3)} \left(\frac{2\sinh((2n+1)\alpha) + (2n+1)\sinh(2\alpha)}{4\sinh^2((n+\frac{1}{2})\alpha) - (2n+1)^2 \sinh^2(\alpha)} - 1 \right) \right]^{-1} \\ &\approx D_0 \cdot \frac{6\left(\frac{z}{a}\right)^2 + 2\frac{z}{a}}{6\left(\frac{z}{a}\right)^2 + 9\frac{z}{a} + 2} \end{aligned} \tag{0.4}$$

for the motion orthogonal ($\perp$) and parallel ($\parallel$) to the walls, where z is the distance between particle and wall and $\alpha = \arccos\left(\frac{z+a}{a}\right)$. For the approximation of Gleichung (0.4) please refer to [2]. The diffusion coefficients are plotted in Abb. 0.1. As expected from the thought experiment this section has been introduced with, $D_{\perp}(z=0) = 0$, whereas $D_{\parallel}(z=0) \neq 0$. [3]

0.3 Forces on the Particles

There are several forces affecting particles suspended in a solution. Most relevant for this experiment are the gravitational, the electrostatic double layer, the Van der Waals and the light force (the latter when using the optical tweezers).

Gravitational force:
The particles interact with the gravitational field of the earth. If their density is higher then the density of the solution that they are suspended in, the particles sink. In front of a wall were it is affected by a repulsive force a potential well forms ???. The gravitational potential V_{G} can be described as:

$$V_{\mathrm{G}} = \frac{4\pi R^3}{3} g(\rho_{\mathrm{p}} - \rho_{\mathrm{m}})z = F_{\mathrm{G}} z \tag{0.5}$$

with the density of the particle ρ_{p} and of the medium ρ_{m}, the earth acceleration g, the particles radius R and the distance from the wall z.

Eletrostatic double layer force:
The eletrostatic double layer force accounts for the repulsion between particles with the same charge and attraction between those particles of opposite charge. In this eperiment, it describes the interaction between particles and the wall. If the particles are suspended in an electrolyte solution, as is the case here, the Poisson equation describes the relation between the electrostatic potential $\Phi(\vec{r})$ and the elementary charge e, $\vec{r}$ being the distance between the two interacting particles. The equation is given by

$$\Delta\Phi(\vec{r}) = -\frac{e^2}{\epsilon k_{\mathrm{B}} T} \underbrace{\rho_+(\vec{r} + \rho_-(\vec{r}}_{\rho}(\vec{r}),$$

where $\rho_+(\vec{r})$ ist the cation and $\rho_-(\vec{r})$ the anion concentration, ϵ the permittivity, k_{B} the Boltzmann constant and T the temperature.

If the two concentrations are symmetrical, as is the case for monovalent electrolytes like KBr, the Poisson-Boltzmann equation takes the form

$$\Delta\Phi = \frac{\beta e^2}{\epsilon} 2\rho_+ \cdot \sinh\Phi = \underbrace{\frac{e^2}{\epsilon k_{\mathrm{B}} T} \sum_i \rho_i q_i^2}_{=\kappa^2} \cdot \sinh\Phi$$

using the inverse Debye length κ, with q_i as the ion charge and $r \in G$, G being the area which is not particle or surface ???. Introducing the surface charge density of the particles particles σ_{p} and of the wall σ_{w} and z as the distance between particle surface and wall yields

$$\beta V_{dl}(z) = \frac{64\pi\epsilon a}{\beta e^2} \gamma_p \gamma_w e^{-\kappa(z)},$$

$$\gamma_{\mathrm{w/p}} = \tanh\left[\frac{1}{2}\sinh^{-1}\left(\frac{\beta e \sigma_{\mathrm{w/p}}}{2\epsilon\kappa}\right)\right].$$

β ???

Van der Waals force:
In comparison to the previously described electrostatic force, the Van der Waals force is much weaker. Moreover, it occurs mostly as an attractive force in nature. Microscopically, it is derived from the interactions between the fluctuating dipolmoments of the particles. Integration of the particle-particle and the particle-wall Van der Waals force over the sphere wall symmetry of this experiment provides

$$\beta V_{disp}(z) = \frac{A(z)}{6k_B T}\left(\frac{2R}{z}\frac{z+R}{z+2R} - \log\frac{z+2R}{z}\right), \tag{0.6}$$

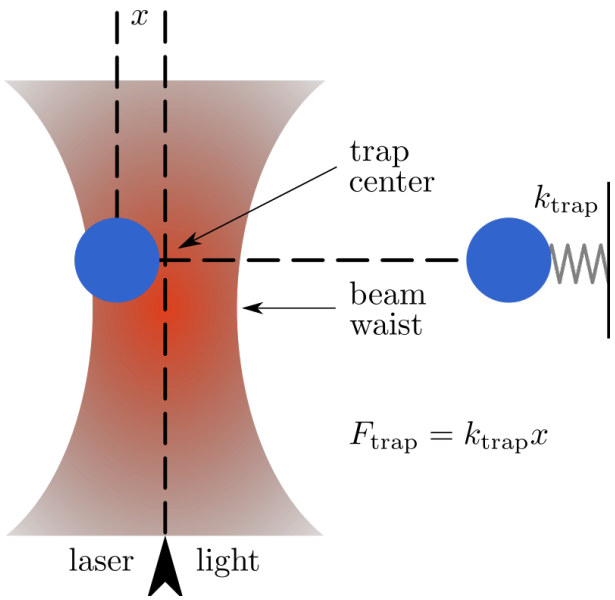

Figure 0.2 Particle trapped by an optical tweezer. The dielectric particle gravitates towards the beam center slightly above the beam waist. [5]

log oder ln ???? with the distance between particle surface and wall z, R the particle radius and $A(z)$ the Hamaker constant.

Light force with optical tweezers:
Counteracting some of the previously mentioned forces, optical tweezers can be used to hold particles in place by utilizing the light force. The light force accounts for the impulses of the icident photons being transferred to the particle when absorbing or reflecting the photons.

To keep it simple, a one dimensional system is regarded. The graviational force acting in negative x-direction $vec F_{\text{G}}^{x}$ can be counteracted by light force in positive x-direction $\vec{F}_{\text{L}}^{x}$ to keep a particle floating at $x = x_0 = const.$ yielding

$$\vec{F}_{\text{G}}^{x} = -\vec{F}_{\text{L}}^{x}.$$

But optical tweezers can also hold dielectric particles in place against forces perpendicular to the light beam. To this end, a slightly focalised laser beam is utilized which holds the particle in the focus point as illustrated in 0.2.

The force which moves the particle towards the beam's center is called the gradient force. It only moves the particle towards the center if the refractive index of the particle is larger then the one of the solution in which the particle is suspended, though. If this is the case and there is an intensity gradient, the gradient force moves the particle towards the point of the highest intensity. The procces is similar to a dielectric being sucked into a capacitor. With a strong focus point it is also possible for the gradient force to override the light force ???. For optical tweezers in x- and y-direction the potentials are

$$V_{\nabla,x}(x) = C_x P x^2 \tag{0.7}$$
$$V_{\nabla,y}(y) = C_y P y^2 \tag{0.8}$$

with the laser power P and the parameter C depending on particle size, focus radius, refractive indexes and more.
Finally, for the z direction the light force and the gravitational force add up to

$$F_{\text{G,eff}}^{z} = F_{\text{L}}^{z} + F_{\text{G}}^{z}. \tag{0.9}$$

0.4 Evanescent Field

To analyze the position fluctuations of the particles in the aqueous dispersion, an evanescent field is utilized. An evanescent field is a field of any kind, were there is no net energy flow in any given direction. In this experiment, this is achieved by total reflection.
If a lightbeam hits a transition between two media with the refraction indices n_1 for medium 1 and n_2 for medium 2 at the angle Θ_1, part of it is refracted with the angle Θ_2 and part of it is reflected with the angle Θ_1. This relation is described by snells law

$$n_1 \sin(\Theta_1) = n_2 \sin(\Theta_2).$$

If $n_1 > n_2$, there is a critical angle Θ_c at which all the light is reflected and non of it transmits into medium 2 with

$$\Theta_c = \arcsin\left(\frac{n_2}{n_1}\right).$$

Still, an exponentially decaying field component of the incident wave enters the second medium. As it decays exponentially, there is no energy flow and it is therefore an evanescent wave. The resulting field distribution in Medium 2 is given by

$$E_r = E_0 \exp\left(-\frac{\beta}{2}z\right) \exp\left(i\frac{n_1}{n_2}\sin(\Theta_1)kx - i\omega t\right),$$

$2/\beta$ being the characteristic decay length. This means that the wave decays with β^{-1} in the medium and this decay is defined as

$$\beta^{-1} = \frac{\lambda_0}{4\pi\sqrt{n_1^2 \sin^2\Theta_1 - n_2^2}},$$

which shows that the penetration depth diverges at the critical angle ($\Theta_1 = \Theta_c$) and the minimum penetration depth is

$$\beta^{-1} = \frac{\lambda_0}{4\pi\sqrt{n_1^2 - n_2^2}}.$$

0.5 Determination of the potential form

The scattering intensity $I(z)$ depends, in the following manner, on the distance z between the particle and the wall:

$$\begin{aligned} I(z) = I_0 \exp(-\beta z) \leftrightarrow z &= -\beta^{-1} \ln\left(\frac{I_z}{I_0}\right) \\ &= -\beta^{-1} \ln I(z) + \underbrace{\beta^{-1} \ln I_0}_{=z_0} \end{aligned} \tag{0.10}$$

Where β^{-1} is the penetration depth of the evanescent field and I_0 is the scatter intensity that results when particles and wall are in direct contact. Without knowing this constant, only relative distances can be determined, since z_0 can not be computed. The absolute distance is determined hydrodynamically in the second section of the evaluation; here $I_0 = 10$ is assumed arbitraily. The Boltzmann equation combines the distance-dependent probability distribution $p(z)$ with the interaction potential $V(z)$ between particle and wall:

$$p(z) = p_0 \exp\left(-\frac{V(z)}{k_\mathrm{B}T}\right) \leftrightarrow \frac{V(z)}{k_\mathrm{B}T} = -\ln\left(\frac{p(z)}{p_0}\right)$$

The distance-dependant probability distribution is calculated using Gleichung (0.10), and can then be converted into en intensity probability distribiution $N(I)$:

$$p(z) = N(I)\frac{\mathrm{d}I}{\mathrm{d}z} = -\beta N(I)I(z),$$

where $N(I)$ is obtained directly from the measured data as a histogram. The resulting potential is then

$$\frac{V(z)}{k_\mathrm{B}T} = -\ln\left(\frac{-\beta N(I)I(z)}{p_0}\right) = -\ln\left[N(I)I(z)\right] + \ln\left(-\frac{p_0}{\beta}\right). \tag{0.11}$$

Before creating the histogram, the background must first be subtracted from the measured data. This corresponds to the scatter signal in the absence of the particle. For this purpose, the particle can be pulled out of the field of view with the optical tweezers and the background at the measuring position can be determined directly (approximately 10 s to 30 s measurement averaged). The number of bins in the histogram determines the number of potential values that are calculated. The error on the calculated potential value decreases with increasing number of counts per bin. Approximately 100 bins represent a good compromise between a small error of the individual potential values on the one hand and good local resolution on the other. Gleichung (0.11) potential already has the correct shape, but not yet the correct absolute distance from the surface.

0.6 Hydrodynamic evaluation

For the determination of the potential shape, only the probability distribution has so far been used. However, much more information is available in the measurement data. An analysis of the dynamics of the measured data provides information on the distance dependence of the diffusion coefficient and also allows the determination of the absolute distance. The 3D diffusion coefficient (far from the surface), D_0 is described by the Stokes-Einstein equation

$$D_0 = \frac{k_\mathrm{B}T}{6\pi\eta R},$$

where η is the vescosity of the liquid and R corresponds to the particule's radius. In the vincinity of a wall, where the liquid molecules can not move (stick boundary conditions), the diffusion coefficient becomes distance-dependent and anisotropic (compare Abschnitt 0.2.1). The distance-dependent diffusion coefficient for diffusion perpendicular to the wall $D_\perp$ was calculated analytically by Brenner as an infinite series [1]. This series can be approximated very well for small distances $z < R$ to

$$D_\perp = \frac{D_0}{\frac{R}{z} + 0,2\ln\left(\frac{R}{z}\right) + 0,9712}. \tag{0.12}$$

Considering the solution of the Langevin equation for a spherical particle near a wall, the distance-dependent diffusion coefficient can also be determined from the measured trajectory of the particle [4]. To do this, the following procedure is applied:

1. The measured intensity data are converted into distances, whereby an arbitrary value is initially assumed for the scatter intensity at the contact of particle and wall (I_0 in Gleichung (0.10)). The maximum input voltage of the A/D card of 10 V is for example a realistic starting value for I_0.
2. For the analysis of the dynamics, the measured trajectory is divided into about 20 intervals a_j . For each a_j , a histogram of the distance changes Δz_i is generated within a certain time interval Δt. That under the condition that the i-th distance value z_i measured in the trajectory is in the interval a_j, $z_i = z_{i+k} - z_i$ is calculated and entered into the histogram. The time interval $t = k\delta t_\mathrm{mess}$ is necessarily an integer multiple of the measurement interval δt_mess

and $k = 1, 2$, in order not to average over too long time intervals. Neglecting the effects of the interaction potential (curvature), a Gaussian distribution of p the distance changes is to be expected, whose width is $\sigma_{z_i,\Delta t} = \sqrt{2D_{z_i}\Delta t}$. In principle, $D_{(z_i)}$ can already be determined from the fit parameter $\sigma_{(z_i,t)}$ for a certain Δt. However, a smaller measurement error is obtained if $\sigma_{(z_i,t)}$ against Δt, and $D_{(z_i)}$ is determined from the slope [4].

3. The unknown parameter I_0 is now adapted such that the distance-dependent diffusion coefficient D_z coincide with the theoretical predictions from Gleichung (0.12) (η and a are known). From this follows the correct absolute particle wall distance for the potential.

In the practice of the experiment, the described evaluation is implemented by a predetermined MatLab routine, in which only I_0 has to be adapted as a parameter.

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