Determining the Relationship between Diffusion Coefficient and Particle Concentrations in Colloidal Suspensions

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(Dated: October 3, 2025)

In this report, we investigate the relationship between the diffusion coefficient D and particle concentration in colloidal suspensions of polystyrene particles in water. According to theory, the diffusion coefficient should be independent of particle concentration, provided that interactions between particles are negligible. Using optical microscopy and image analysis, we measured particle distributions at different heights for four concentrations. From the exponential decrease of the particle number density with height, we extracted the parameter z_0 and determined D via the relation $D = z_0 v_t$. The obtained values of D fluctuated between $(1.01 \pm 0.11) \cdot 10^{-12}\mathrm{m}^2/\mathrm{s}$ and $(1.18 \pm 0.12) \cdot 10^{-12}\mathrm{m}^2/\mathrm{s}$, with an average of $(1.09 \pm 0.08) \cdot 10^{-12}\mathrm{m}^2/\mathrm{s}$, showing no dependence on concentration. This supports the theoretical expectation of concentration independence. However, the absolute values deviate from the theoretical predictions, which we attribute to simplifying assumptions in the application of Fick's law and to systematic errors in the calibration of vertical displacement, particularly due to refractive index effects.

I. INTRODUCTION

Fluids containing microscopic particles are common in both natural and industrial systems. The motion of such particles is determined by a combination of thermal fluctuations, hydrodynamic interactions, and external forces. Understanding how these particles move and distribute is an important topic in physics and used for many practical applications.

Brownian motion, the phenomenon of random particle motion in liquids, was first explained by Einstein [2], who derived the relation between thermal fluctuations and diffusion. From theory it follows that the diffusion coefficient D does not depend on the concentration from the suspended particles.

In our experiment, we set out to validate this independence. This will be done by counting the amount of particles at different heights for different concentrations of particle suspensions. We expect the diffusion coefficient to be independent of the concentration, and expect to find $D = (8.64 \pm 0.27) \cdot 10^{-13}\mathrm{m}^2/\mathrm{s}$ (12).

II. THEORY

When a system is maintained at a fixed temperature T, the probability of finding the system in a state with energy E is given by the Boltzmann distribution:[1]

$$P(E) \propto e^{-\frac{E}{k_B T}}, \tag{1}$$

where k_B is Boltzmann's constant.

Particles suspended in a liquid experience two opposing forces. The first is the downward gravitational force, and the second is the upward force due to Archimedes' principle [3].

For a particle with mass m at height z, the potential energy is given by $(m - m_0)gz$. Here is m_0 the mass of the diplaced liquid, and g the gravitational acceleration. Hence, the particle number density $n(z)$ at height z is given by

$$\begin{aligned} n(z) &= n_0 e^{-\frac{E}{k_B T}} \\ &= n_0 e^{-\frac{(m-m_0)gz}{k_B T}} \\ &= n_0 e^{-\frac{\frac{1}{6}\pi d^3(\rho-\rho_0)gz}{k_B T}} \\ &= n_0 e^{-\frac{z}{z_o}}, \end{aligned} \tag{2}$$

where n_0 is the particle number density at $z = 0$, d is the particle diameter, ρ is the particle density, and ρ_0 is the density of the displaced liquid. The parameter

$$z_0 = \frac{6k_B T}{\pi d^3(\rho - \rho_0)g} \tag{3}$$

defines the distance over which the particle concentration n decreases by a factor of $\frac{1}{e}$.

Initially, the particles are evenly distributed throughout the liquid. Over time, the statistical equilibrium will be reached, at which point Equation (2) holds. The particle flux is affected by both gravity and diffusion. According to Fick's first law of diffusion, the flux due to the diffusion ϕ_{diff} across an area in one dimension is given by

$$\phi_{\text{diff}} = -D\frac{\delta n}{\delta z}, \tag{4}$$

where D is the diffusion coefficient in m^2/s, and ϕ is the number of particles passing through a given area and given time in m^2/s. Here we assume no interaction between the particles. Since the particle density depends only on the vertical coordinate (z), the problem can be treated as one-dimensional. The flux due to gravity is determined by the balance of forces acting on a particle moving with velocity v through a viscous medium. The net force is

$$F = (m - m_0)g - 3\pi\eta dv, \tag{5}$$

where $3\pi\eta dv$ is the viscous drag of the particle is according to Stokes' law [1].

At terminal velocity v_t, these forces balance, yielding

$$v_t = \frac{(m - m_0)g}{3\pi\eta d} = \frac{d^2(\rho - \rho_0)g}{18\eta}. \quad (6)$$

Thus, gravity induces a constant downward drift of particles with velocity v_t. The total particle flux ϕ_{total} is therefore the sum of the graviational and diffusive contributions:

$$\phi_{\text{total}} = -D\frac{\partial n}{\partial z} - nv_t. \quad (7)$$

It holds that

$$\frac{\partial}{\partial t}\int ndV = -\int \phi dS, \quad (8)$$

because $\int ndV$ is the total number of particles inside a control volume V and $\int \phi dS$ is the net rate at which particles cross the surface S bounding the volume V. So Equation (8) says that the rate of change of the number of particles inside a volume equals the negative of the net outward flux of particles through the surface of that volume. From the Equations (7) and (8) follows the differential equation

$$\frac{\partial n(z)}{\partial t} = D\frac{\partial^2 n(z)}{\partial z^2} + v_t\frac{\partial n(z)}{\partial z}. \quad (9)$$

Solving $\frac{\partial}{\partial t}n = 0$ yields $n(z) = n_0 e^{-\frac{v_t}{D}z}$. Comparing this with Equation (2) gives

$$D = z_0 v_t. \quad (10)$$

III. SETUP AND METHOD

The experimental setup is shown schematically in Figure 1. Measurements were performed using a dispersion of polystyrene particles in water with a specified diameter of $0.51 \pm 0.01\mu$m. We chose this particle size because test measurements indicated that it is optimally detectable with the image analysis software. All experiments were conducted at a constant temperature of (20 ± 0.5)°C, since the diffusion coefficient D is theoretically temperature-dependent.

For each particle concentration (1%, 0.5%, 0.1%, and 0.05%), images were recorded at 20 consecutive heights. We found that the 0.01% concentration was too low to be usable. The samples we used are fabricated by the glass workshop at Utrecht University [4]. These are schematically shown in Figure 2. The lowst visible height was chosen as the starting point, and each subsequent height was increased by 2/5 of a full turn. At each height, 50 images were recorded, resulting in a total of $4 \cdot 20 \cdot 50 = 4000$ images. These were analyzed using TrackPy [5] (settings: `pixelsize = 15`, `minmass = 275`) to determine the number of particles per image.

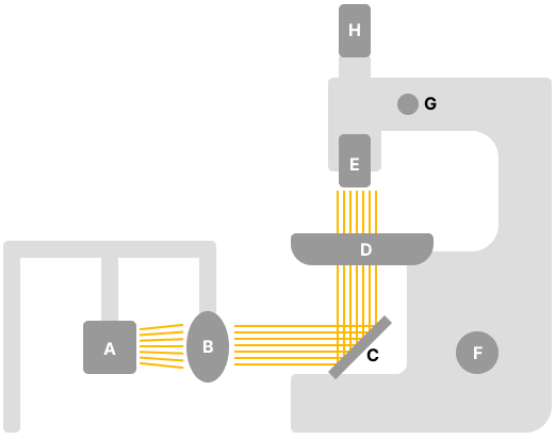

FIG. 1. The experimental setup. It consists of a microscope (Nedoptifa №12095) with external illumination and an optical filter, connected to a stable frame. The light source (A) is an Edmund Optics model M6x1 M4x0.7, connected to a wall socket. The light passes through an optical filter (B) and is directed via the microscope mirror (C) through the sample (D) to the objective lens (E). The vertical position of the sample can be adjusted using control dials (F, fine adjustment) and (G, coarse adjustment). The resulting image is recorded with a camera (H, DinoEye Eyepiece Camera), which transfers the data directly to a connected laptop.

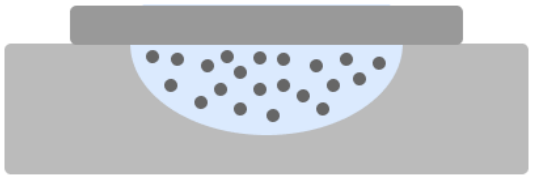

FIG. 2. Schematic representation of the sample: a layer of $(1000 \pm 10\%)\mu$m with a $(600 \pm 10\%)\mu$m well, covered by a $(150 \pm 10\%)\mu$m cover slip.

To calibrate the vertical displacement inside the sample, we applied a small reference mark (grease spot) to both the top and bottom of the sample. These marks were located and imaged with the microscope. The number of rotations of the height adjustment dial required to move between the two marks was recorded, allowing the conversion of dial rotations into a physical displacement.

A systematic error may arise from stains or defective pixels on the camera, which the TrackPy analysis software may falsely identify as particles. To correct for this effect, a reference image was recorded at a height without particles and analyzed with TrackPy. The resulting number of false positives was subtracted from all measurements.

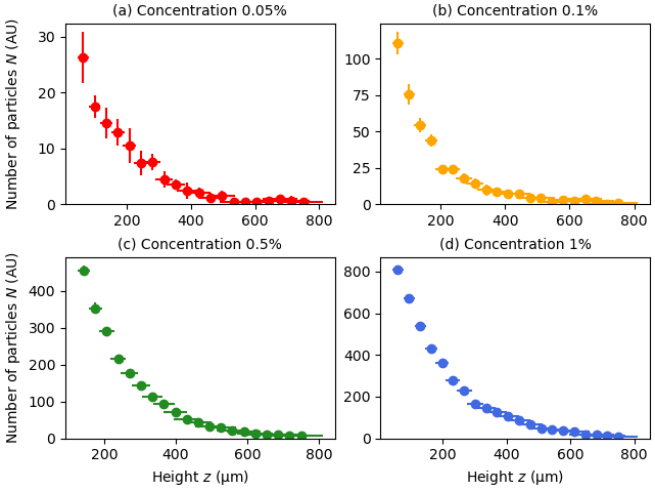

FIG. 3. The amount of particles N as a function of height z, for different particle concentrations.

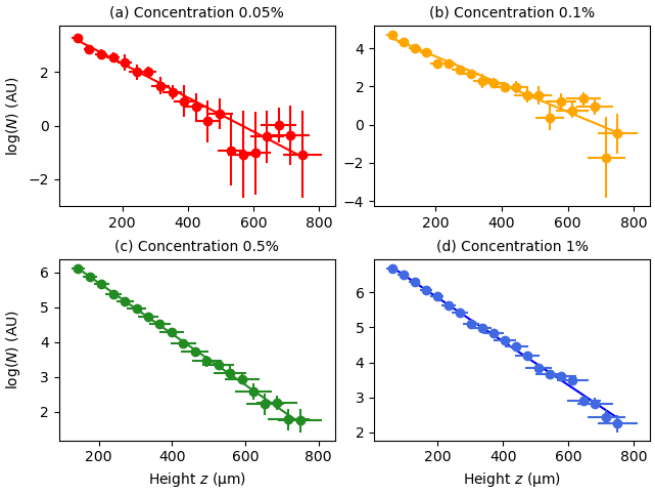

FIG. 4. The natural logarithm of the amount of particles N as a function of height z with a linear fit for different particle concentrations. The χ^2_{red}-values are 4.8, 15.2, 0.6 and 2.0 for concentrations 0.05%, 0.1%, 0.5% and 1% respectively.

IV. RESULTS & DISCUSSION

Figure 3 shows the number of particles plotted against height, for each concentration. We observe that this follows an exponential relationship, which corresponds to Equation (2). We also see that higher concentrations have, on average, more particles, as expected. For the concentrations of 0.05% and 0.1%, a small peak is observed at higher z-values. This effect arises because, under these dilute conditions, the measurement essentially reflects the difference between detecting zero or one particle. The randomness in the number of particles detected can therefore lead to an occasional peak.

Taking the natural logarithm of both sides in Equation (2) gives

$$\log(N) = \log(n_0 V) - \frac{1}{z_0} z, \tag{11}$$

where $N(z) = n(z)V$ denotes the amount of particles at height z. So there is a linear relationship between $\log(N)$ and z. Figure 4 shows the natural logarithm of the number of particles plotted against height, for each concentration. Since this relationship is linear, we can perform a linear fit. We can then determine the value of z_0 for each concentration. We observe that for lower concentrations, the χ^2_{red}-values are rather high. We attribute these to measurement uncertainties. These values are shown in Table I.

From Equation (3), it follows that this z_0 value should be independent of concentration. Yet, large fluctuations are observed among the different z_0 values. These variations do not follow a clear trend; both the lowest and highest concentrations yield relatively large z_0 values, whereas the intermediate concentrations produce smaller values. Since z_0 is expected to remain constant, we attribute these fluctuations to measurement uncertainties.

Using Equations (6) and (10), we calculate the D values. These are shown in Table I and visualised in Figure 5. The average of these values is $(1.09 \pm 0.08) \cdot 10^{-12} \text{m}^2/\text{s}$.

Here we again see large fluctuations in the values, which, because v_t is the same each time, are directly caused by the fluctuations in z_0. Again, we attribute

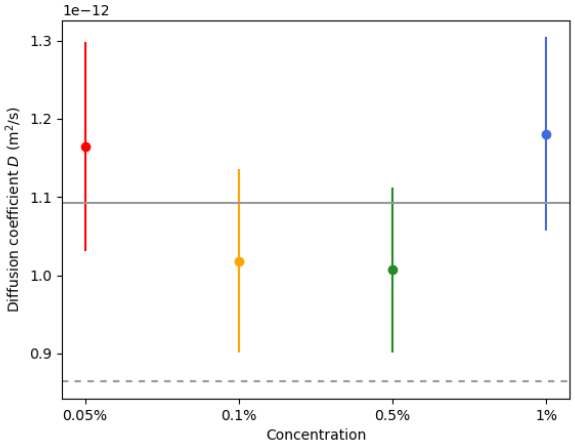

FIG. 5. The computed D-values for different concentrations. The solid line is the average of all D-values and the dashed line is the expected value from combining Equations (3), (6) and (10).

Concentration	z_0 (μm)	D ($10^{-12}\text{m}^2/\text{s}$)
0.05%	158 ±7	1.16 ±0.13
0.1%	138 ±7	1.02 ±0.12
0.5%	136.5 ±1.2	1.01 ±0.11
1.0%	160.0 ±1.9	1.18 ±0.12

TABLE I. Values of z_0 and D for different concentrations.

these to measurement uncertainties.

By calculating z_0 directly using Equation (3), we find $z_{0,\text{exp}} = (114 \pm 13)\,\mu\text{m}$, which leads to

$$D_{\text{exp}} = (8.64 \pm 0.27) \cdot 10^{-13}\text{m}^2/\text{s}. \tag{12}$$

This is shown in Figure 5 as a dashed line. This value deviates significantly from the value we obtained $(1.09 \pm 0.08) \cdot 10^{-12}\,\text{m}^2/\text{s}$. Possible reasons for this are unrealistic assumptions in Fick's law and not accounting for refractive index of the medium, as well as limitations of the TrackPy tracking algorithm, which is inherently subjective and not perfectly calibrated.

Fick's law, which we used in our derivation, assumes that no particles collide. Because particles do collide in reality, the value of the diffusion flux ϕ_{diff} in our experiment is lower. From Equation (4), it then follows that D in our experiment would be higher.

A systematic effect that was not accounted for in our calibration is the refractive index of the medium. When focusing on a sample with refractive index $n > 1$, the optical displacement along the z-axis differs from the mechanical displacement of the microscope stage. In our calibration procedure we assumed that one rotation of the adjustment knob corresponds directly to the same physical displacement inside the sample. In reality, the optical path length is shortened by a factor $\frac{1}{n}$, which implies that the true displacement in the suspension is larger by approximately a factor n compared to our calibration. This influences our measured value of z_0, and thus the value of D.

V. CONCLUSIONS

The goal of our experiment was to verify that the diffusion coefficient D is independent of concentration, as suggested by the relation $D = \frac{k_B T}{3\pi d\eta}$. Our results indicate that this is very likely the case. Additional measurements would help reduce random uncertainties and strengthen the reliability of the conclusion.

However, the absolute value of the measured diffusion coefficient D does not match the theoretically expected value. This discrepancy can be attributed to unrealistic assumptions in the application of Fick's law, as well as to inaccuracies related to the refractive index in the analysis.

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