Experimental Methods in Engineering Mechanics, Module 3: Brownian Motion close to singularities

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Brownian motion corresponds to the random displacement of small suspended particles in a fluid. In this paper, we analyze such motion for a colloid made of a water-glycerol viscous mixture. Several cases are studied to compare the resultant Brownian motion close to different singularities such as an edge, a bubble or both. We observe that the presence of a bubble has a significant impact on the diffusion of particles, causing it to decrease. However, a border or an edge have a negligible influence on the diffusion coefficient.

In physics and thermodynamics, diffusion is a well-known phenomenon that has been the subject of many researches since the 19th century. In particular, diffusion in a liquid medium could only be completely described from the 20th century thanks to George Stokes and Albert Einstein. One of the phenomena at the origin of this diffusion is the Brownian motion. It describes the random displacement of small particles suspended in a fluid. The study of the Brownian motion allowed new equations to be established, making it possible to considerably extend this field.

The Stokes-Einstein relation (2) highlights the influence of temperature, viscosity or particle size on diffusion and therefore the Brownian motion. However, this description is valid in the bulk solution, where the displacement of the particles is only influenced by the fluid and the other particles. What happens when the particles are close to a singularity in the solution? How does the presence of an air bubble or a nearby edge influences the Brownian motion? As an edge or a bubble constrains the movement of the fluid, it cannot enter the bubble or cross the edge, and the flow near these singularities is theoretically stagnant. We make the hypothesis that the presence of such singularities reduces the general flow of the fluid and consequently the Brownian motion of the particles. The present work will try to verify this experimentally.

In order to test the hypothesis, a colloid is placed onto a glass slide, and trapped in-between glass surfaces (on top and to the sides), as shown in Figure 1. A sealing agent is applied to the sides, in the form of a transparent nail polish. The colloid is prepared in order to obtain a viscosity of $1.5cSt = 1.5mm^2/s$, which we attain by mixing a 0.158 to 0.842 ratio of glycerol to water. This is based on calculations for a room temperature of $22.9^\circ C$. During our experiment however, the temperature was of $24.3^\circ C$, which means our experimental viscosity is of $1.45cSt$ instead. For $1mL$ of solution, $0.364\mu L$ of a suspension of latex beads is added. It has a negligible volume compared to the rest, and is governed by the following equation :

$$N = \frac{6 \times 10^{10} \cdot S \cdot P_L}{\pi \cdot P_S \cdot d^3} \tag{1}$$

With N the number of particles per mL, $S = 1$ the weight to weight ratio of solids in %, $d = 1.1$ the diameter of the beads in μm, $P_S = 1.05$ is the density of the bulk polymer in g/mL and $P_L = 1.005$ is the density of latex in g/mL. Inputting our data, we find a value of $N = 1.37 \times 10^{10}$, which, after dilution in the glycerol and water mix, becomes $N_f = 5.00 \times 10^6$.

A reasonable concentration is of approximately $N_e = 50$ particles per 1 mm x 1mm x 10 microns, which translates to $N_e = 5.0 \times 10^3$ particles per mm^3, or $N_e = 5.0 \times 10^6$ particles per mL. We therefore have $N_f = N_e$, which means our setup favors an easy processing of the experimental data.

The testing apparatus consists of a Nikon Eclipse Ti microscope, set at a 10 times zoom. The image has a 0.64 μm per pixel ratio.

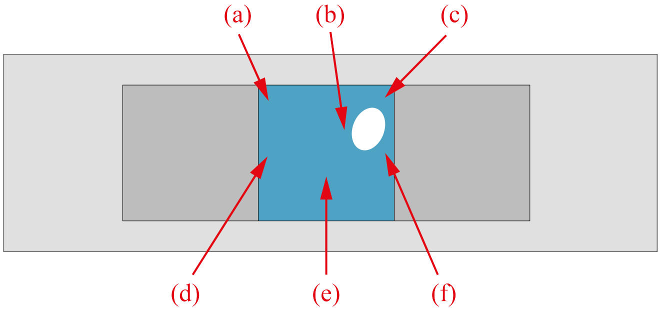
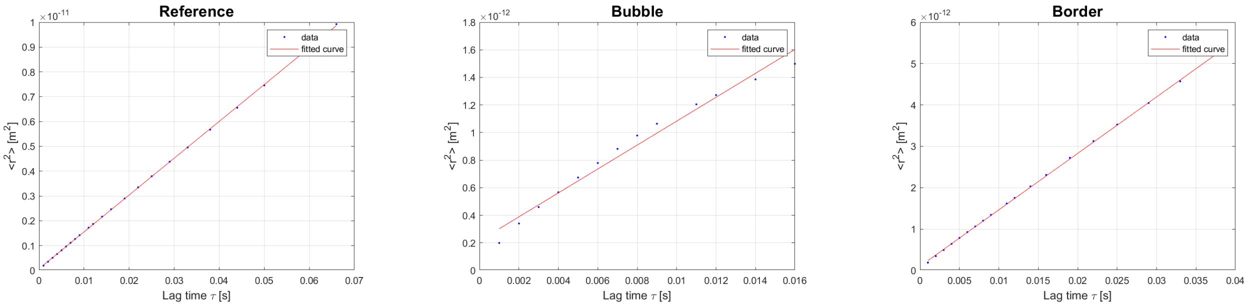


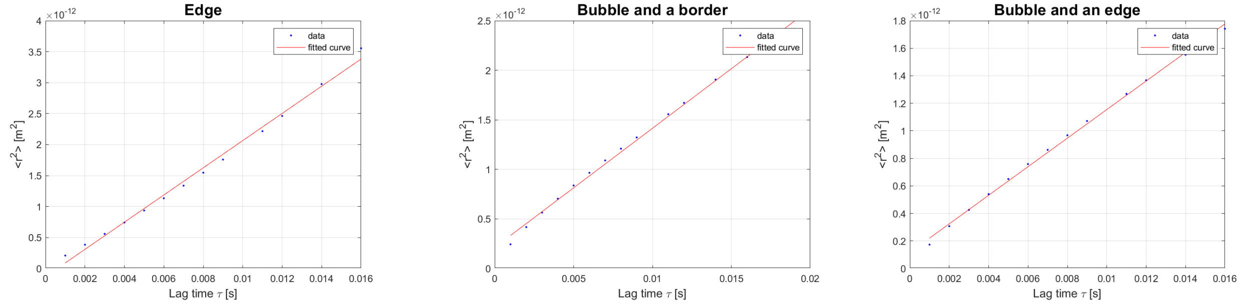
FIG. 1: Schematic representation of the sample used with the corresponding tests made : (a) Edge, (b) Bubble, (c) Bubble and an edge, (d) Border, (e) Reference test, (f) Bubble and a border.

From the Stokes-Einstein relation, it is possible to obtain the theoretical value of the diffusion coefficient D

$$D = \frac{k_B T}{6\pi\eta r} = 2.6394\text{e}{-10}\ m^2/s \tag{2}$$



(a) Reference (b) Bubble (c) Border



(d) Edge (e) Bubble + Border (f) Bubble + Edge

FIG. 2: Results of data analysis obtained after a couple of experiments : (a) Reference sample, (b) Fluid close to a bubble inside the sample, (c) Fluid close to a border of the glass plate, (d) Fluid close to an edge of the glass plate, (e) Fluid close to a bubble and a border of the glass plate, (f) Fluid close to a bubble and an edge of the glass plate. The x-axis is the lag-time τ in seconds and the y-axis is the mean displacement squared $\langle r^2(t)\rangle$ of the particles. The curves obtained experimentally are linear, as predicted by theory.

Where k_B is the Boltzmann's constant, $T = 294.3\ K$ is the temperature of the room, η is the viscosity of the fluid, fixed at $1.5\ cSt$ in the present case, and $r = 0.55e-6\ m$ is the radius of the particles [1]. To obtain an experimental value of the diffusion coefficient D, it is possible to relate D and the trajectories of the particles. The key is to analyze a 2D random walk. Each walker obeys some rules. First, each particle starts at $x = y = 0$ and $t = 0$ and can move along the x- or y-directions with a step size of δ. We can obtain the mean square displacement of all particles at a time $t = n\tau$:

$$\langle x^2(n)\rangle = \frac{\delta^2}{\tau}\cdot t \qquad \langle y^2(n)\rangle = \frac{\delta^2}{\tau}\cdot t \tag{3}$$

And since the diffusion coefficient can be expressed exactly by:

$$D = \frac{\delta^2}{2\tau}$$

The mean square trajectories can be related to D by:

$$\langle x^2(t)\rangle = 2Dt \qquad \langle y^2(t)\rangle = 2Dt \tag{4}$$

It is possible to modify the coordinates to obtain $r^2 = x^2 + y^2 \Rightarrow \langle r^2(t)\rangle = \langle x^2(t)\rangle + \langle y^2(t)\rangle = 4Dt$, which is now also related to the diffusion coefficient. When the mean square trajectory $\langle r^2(t)\rangle$ is plotted with respect to a lag time τ, which represents the interval for which the mean is calculated, the slope of the resulting line is equal to $4D$. We therefore found a way to express diffusivity in terms of particle motions. The graphs obtained after tracking and computing the particles trajectories for each sample are shown in Figure 2.

A couple of experiments were performed to explore the effect of a perturbation on the diffusion coefficient D predicted above. There are three different types of perturbations (Figure 1). The first one is a bubble placed inside of the sample, which could affect the motion of the particles (b). The second one is a border (d) of the glass plate, which could interact with the fluid placed near it. The last one is an edge of the glass plate (a), consisting of a spot near the meeting of two borders. Combinations of these perturbations were tested, like the impact of the presence of a bubble and a border, or a bubble and an edge (c). All of the tests carried out and their respective positions on the sample are shown in Figure 1. The samples and resulting diffusion coefficient are summarized in Table I.

It can be seen that, with reference to the sample without any perturbation, the impact of a border is not determinant : it only lead to an 8.0% decrease in

TABLE I: Numerical results obtained after analysis of data for each sample where D is the diffusion coefficient corresponding to the slope of the mean square of the trajectories $\langle r^2(t) \rangle$ divided by 4.

Sample	**Diffusion coefficient** D [m^2/s]
Reference	$3.71e-11$
Bubble	$2.1675e-11$
Border	$3.41e-11$
Edge	$5.485e-11$
Bubble + Border	$3.005e-11$
Bubble + Edge	$2.595e-11$

D. Strangely enough, an edge, which equates to the presence of two borders, increases diffusivity by 47.8% with regards to the reference. This value can hardly be explained, as it contradicts the findings at the border sample, which show the negligible impact having borders. Moreover, it goes against theoretical expectations as borders are meant to, if anything, decrease diffusivity. This may be explained by an improper sealing of the sample, or by the unexpected influence of the nail polish, which could cause an increase in D.
It is known that a bubble tends to reduce the diffusion coefficient D [2]. Our experiment indeed confirms it, and further states that when a bubble is combined to other elements (eg. a border or an edge), its influence, though decreased, remains. A bubble on its own brings a 41.6% decrease in diffusivity, combined with a border it creates a 19.00% decrease, and with an edge a 30.1% decrease. As the presence of an edge decreases the diffusivity more than the presence of a single border, the results show our inexplicably high edge value can be taken as an outlier.

Our reference value of diffusion is one order below the expected theoretical value, which is of $D = 2.6394e-10\ m^2/s$. This may be partly due to a difference in temperature between the moment when the sample was prepared and the one when the tests were performed (since temperature has an effect on the viscosity), or to a potential lack of precision in our measurement method — which could have been prevented by testing the reference value multiple times. This, however, only partly explains the difference in magnitude. We believe that, instead of showing inaccuracy in our results, this difference is due to the influence of the top and bottom glass plates, which are both in direct contact with the liquid. As a liquid-to-surface interaction creates a zone with less movement (boundary layers), it would not be surprising that it is here responsible for a slowing down of certain particles, which in turns decreases the overall diffusion. This is something to be proven in a later paper.

The aforementioned change, deemed explainable by the presence of top and bottom surfaces, does not invalidate the findings of our paper, as they rely on the comparison of multiple values, and not on a single absolute value. To improve our results, more data could have been collected, which would require a greater amount of time than what we were provided with. To ensure the accuracy of our results, we could have checked the colloid viscosity before the tests. Another factor whose influence was not accounted for is the passage of time ; we expect it to decrease progressively the Brownian motion and therefore the diffusivity.

This experimental study delves into the Brownian motion of colloids in a water-glycerol viscous mixture, particularly focusing on the influence of singularities such as edges and bubbles on particle diffusion. The Stokes-Einstein relation is utilized to establish theoretical values for the diffusion coefficient, and the experiments are conducted to validate these predictions.

The findings reveal that the presence of a bubble significantly reduces the diffusion coefficient, indicating a notable impact on particle motion. In contrast, the influence of an edge or border is comparatively less important, or even negligible. The experimental results, presented in Table I, highlight variations in diffusion coefficients for different perturbations. Notably, the presence of an edge appears as an outlier, and caution is advised in interpreting this result.

Further avenues for improvement and exploration are suggested, including conducting additional reference tests to confirm values, monitoring and accounting for temperature variations, checking viscosity before experiments, and investigating the time-dependent behavior of Brownian motion.

[1] *LB11 Product specification*.
[2] Y. Asakuma, R. Nakata, M. Asada, Y. Kanazawa, and C. Phan, Bubble formation and interface phenomena of aqueous solution under microwave irradiation, International Journal of Heat and Mass Transfer **103**, 411 (2016).