

Diffusion - Determination of Diffusion Constants using the Schlieren Method

Protocol for the PC 2 lab course by
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Abstract:

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1 Theory

Molecular diffusion describes the movement of particles from a region of high concentration to a region of low concentration, which leads to an even distribution of particles.^[1] It was first discovered by Robert Brown, who observed the random movement of tiny particles suspended in a liquid, which is called Brownian motion. Then German physicist Adolf Fick lay the theoretical foundation for diffusion by formulating two laws.

The first Fick's law describes how the particle flux density $j(z)$ is connected to the Diffusion coefficient D and the concentration gradient $\frac{\partial c(z)}{\partial z}$, which is shown in Equation 1.

$$j(z) = -D \cdot \frac{\partial c}{\partial z} \quad (1)$$

The physical meaning of the first Fick's law is that a concentration gradient leads to mutual diffusion of particles, leading to an even distribution. The diffusion coefficient can also be defined by the „Einstein relation“ in Equation 2.

$$D = \frac{1}{2} \nu \Delta z^2 \quad (2)$$

ν is the jump rate and Δz^2 the mean square jump distance of particles, assuming that they can only move along the z axis. Second Fick's law describes the temporal course of concentration as shown in Equation 3.

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial z^2} \quad (3)$$

Equation 3 states that the concentration equalization proceeds faster the stronger the concentration gradient. By integrating second Fick's law from Equation 3 under certain boundary conditions and using the substitution $\mu = \frac{z}{\sqrt{4Dt}}$, Equation 4 for the profile of concentration can be obtained.

$$c = \frac{c_2}{2} \cdot \left(1 - \frac{2}{\sqrt{\pi}} \int_0^\mu e^{-\mu^2} d\mu \right) \quad (4)$$

By deriving Equation 4, the function is simplified into Equation 5 which leads to the concentration gradient profile having the shape of a Gaussian bell curve, as is illustrated in Figure 1.

$$\frac{dc}{dz} = -\frac{c_2}{2\sqrt{\pi Dt}} \cdot e^{-\mu^2} \quad (5)$$

Assuming that the refractive index n is proportional to c and knowing that the gradient has an extreme value at $z = 0$, as can be seen in Figure 1, Equation 6 describes the refractive index gradient at $z = 0$ with the indices of water n_1 and of the salt solution n_2 .^[1]

$$\left(\frac{dn}{dz} \right)_{z=0} = -\frac{n_1 - n_2}{2\sqrt{\pi Dt}} \quad (6)$$

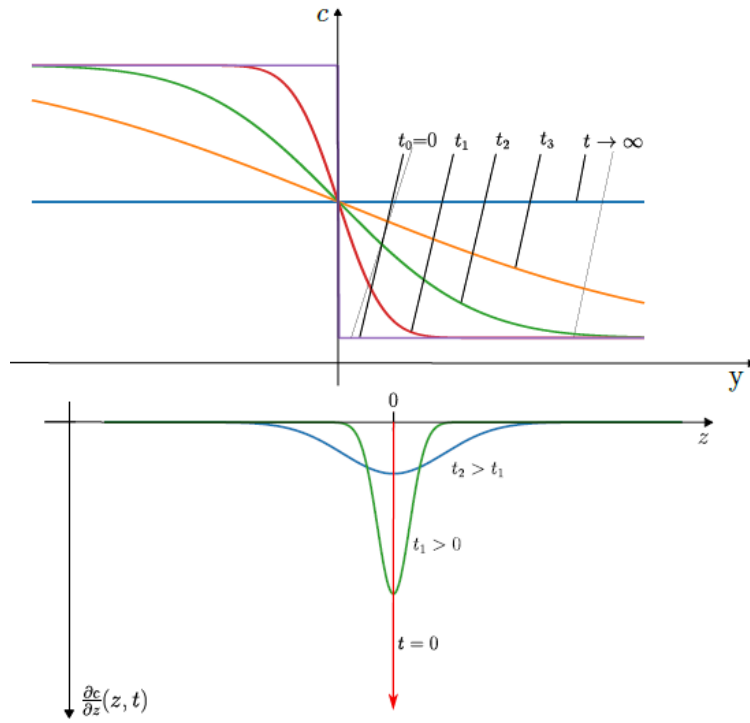


Figure 1: Profiles of the concentration and concentration gradient.^[1]

Following this argumentation, diffusion leads to a continuously changing refractive index profile which causes a light beam directed to a cuvette of a salt solution with a concentration gradient to be refracted toward the optically denser medium. That is called Snell's law of refraction and shown in Figure 2. The exit angle β and the degree of curvature can be described with Equation 7 and 8, where α is the angle of incidence and r the radius of the curvature of the light beam.^[1]

$$\beta = \frac{n}{n_0} \alpha \quad (7)$$

$$\frac{1}{r} = \frac{1}{n} \frac{dn}{dz} = \frac{d \ln(n)}{dz} \quad (8)$$

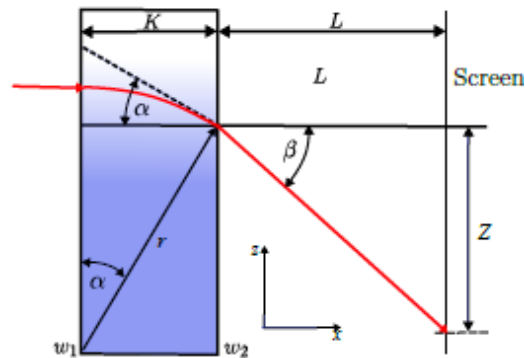


Figure 2: Scheme of the experimental setup geometry.^[1]

The Huygen's principle states that every point of a wavefront can be seen as the origin of a spherical elementary wave. That's why the path of the light beam is curved in a medium with a spatially dependent refractive index $n(z)$ due to a lateral phase shift within the wavefront. The strongest deflection is experienced by the part of the beam that passes through the steepest concentration gradient region. With the small-angle approximation and Equation 7 and 8, the refractive index gradient can be described by Equation 9.

$$\frac{dn}{dz} \approx \frac{Z}{L} \cdot \frac{n_0}{K} \quad (9)$$

L is the distance between the cuvette and the screen, K the thickness of the cuvette, n_0 the refractive index of air and Z the distance between the straight extension of the beam at the exit point and the impact point on the screen. By equating Equation 9 and Equation 6 and rearranging to the diffusion constant D , Equation 10 is derived to calculate D using the Schlieren Method.^[1]

$$D = \frac{(n_1 - n_2)^2 L^2 K^2}{4\pi n_0^2 Z^2 t} \quad (10)$$

2 Procedure

The experimental setup was already built prior to the start of the measurements as shown in Figure 2. The laser beam light path was tilted at about 45°.

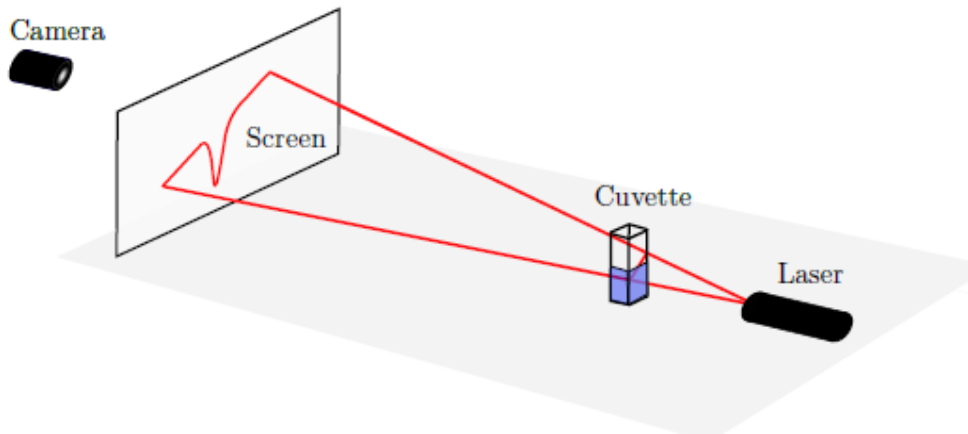


Figure 3: Scheme of the laser beam geometry.^[1]

The experiment began by doing a calibration measurement where the settings of the camera were adjusted, so that the only visible part was the laser beam. Afterwards the cuvette was half filled with deionized water and underlayered with a 2 molar solution of sodium chloride. As soon as the sodium chloride solution was underlayered the video recording was started. After 15 minutes the recording was stopped the resulting video was analyzed by taking snapshots at relevant timestamps. Those snapshots were uploaded into the python skript "convert-image.py" which converted

the snapshots into xy-value pairs. The resulting ".dat" file was then uploaded into the python skript "auswertung diffusion.py" where the amplitude was determined by adjusting slider. These steps were repeated for the 2 molar potassium chloride and zinc sulfate solutions. The potassium chloride solution was also recorded for 15 minutes and the zinc sulfate solution was recorded for 30 minutes. During the recording of the sodium chloride solution the refracting indices of deionized water, and the three solutions were measured using a refractometer.

3 Analysis

3.1 Refractive indices

The refractive indices of deionized water and the different salt solutions were measured with a refractometer and are listed in Table 1.

Table 1: Measured refractive indices of deionized water and different salt solutions.

| Solution | n |
|------------------------------|--------|
| H ₂ O (deionized) | 1.3375 |
| NaCl (2M) | 1.3541 |
| KCl (2M) | 1.3514 |
| ZnSO ₄ (2M) | 1.3725 |

The NaCl and KCl solutions have similar refractive indices of $n_{\text{NaCl}} = 1.3541$ and $n_{\text{KCl}} = 1.3514$, while the ZnSO₄ solution has a significantly higher refractive index of $n_{\text{ZnSO}_4} = 1.3725$ than the others. This is due to the much higher polarizability of the larger SO₄²⁻ ion with a higher ionic charge in comparison to the Cl⁻ ion. Additionally, the higher molar mass of ZnSO₄ results in a significantly higher mass density at the same molar concentration (2M). Na⁺ has a higher charge density than K⁺ due to its smaller size, which polarizes the surrounding water molecules more, leading to a slightly higher refractive index.

3.2 Diffusion coefficients

To evaluate ??, Equation 10 is rearranged to Z^{-2} to get Equation 12, which shows the connection between the slope m and the diffusion coefficient.

$$Z^{-2} = \frac{4\pi D n_0^2}{(n_1 - n_2)^2 L^2 K^2} \cdot t \quad (11)$$

$$= m \cdot t \quad (12)$$

4 Error Discussion

The refractive indices of the salt solutions deviate from literature values due to manual adjustment of the borderline in the refractometer, which was based on subjective visual inspection. Especially in the case of ZnSO_4 , the borderline was very blurred, which led to a measurement uncertainty in the refractive index. The measurements of the refractive indices were performed at room temperature without active thermal stabilization, which can lead to deviations as well, since refractive indices are temperature dependent.

It is assumed that at a concentration of 2M, the refractive index is still proportional to the concentration. However, at higher concentrations, deviations can occur due to strong Coulomb interactions between multivalent ions such as ZnSO_4 , which lead to the formation of ion pairs and an electrostriction effect. This results in a higher density of the solution and a higher molar refractivity than expected, contributing to a deviation of the linear relationship between refractive index and concentration. The influence of deviations in the refractive indices on the diffusion coefficients calculated with Equation 10 is significant, since the refractive indices appear squared in the denominator.

5 Conclusion

6 References

- [1] H. Dilger, *2025-pc2-script-en*, **2025**.