Liquid Diffusion

Elijan Mastnak

Winter Semester 2020-2021

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1 Tasks

- 1. Find the diffusion constant for a mixture of ethanol and water by observing the shape of the projected diffusion curve.
- 2. Measure the area S under the diffusion curve from your sketches on graph paper and compare it to the theoretically expected value. Discuss the similarity or discrepancy between the two values.

2 Equipment, Procedure and Data

2.1 Equipment

- Cuvette to hold a mixture of ethanol and water
- Laser as a source of monochromatic light incident on the cuvette
- Glass rod, used to disperse the laser from a beam into a diagonal line.

• Screen on which to observe the diffusion curve

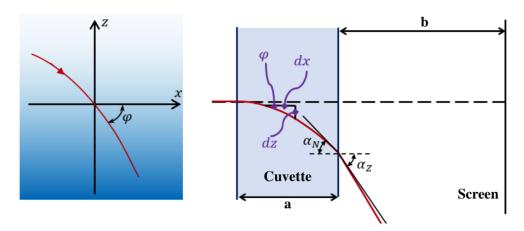


Figure 1: Left: Refraction of a light beam as it passes through a substance with a index of refraction that change linearly with z. Right: Schematic of the measurement setup: light comes in from the left, hits the cuvette, refracts as it passes through, and creates the diffusion curve on the far-right screen.

2.2 Procedure

Figure 1 shows a schematic of the experiment, which proceeds as follows:

- Place the laser roughly 180 cm from the screen. Place the cuvette halfway between the laser and the screen such that the laser beam passes through the center of the cuvette onto the portion of the screen marked with graph paper. Between the laser and cuvette, place a glass rod angled at 45° to the optical axis. The rod serves to disperse the laser beam into a plane wave and change the laser from a beam into a diagonal line with a varying z coordinate.
- Fill the cuvette halfway with ethanol, then use a capillary funnel to fill it the remainder of the way with water from the bottom up. Pour carefully and slowly so that the alcohol and water do not mix. A curve should form on the display screen.
- Sketch the diffusion curve (to scale, on graph paper) and measure the maximum displacement y_{max} first at shorter (e.g. a few minute) intervals, then at longer intervals as time increases and the concentration gradient grows more uniform.

2.3 Data

Independent Variable: Time t, measured on a minute scale.

Dependent Variable: Maximum displacement y_{max} of the diffusion curve on the graph paper display.

Parameters: Cuvette width $a=1.5\,\mathrm{cm}$, distance from cuvette to screen $b=72.0\,\mathrm{cm}$, distance between light source and cuvette $c=35.5\,\mathrm{cm}$. Note that c is the distance between the cuvette and the dispersing glass rod, not the distance between the cuvette and the laser.

3 Analysis

3.1 Diffusion Constant from a Linear Fit

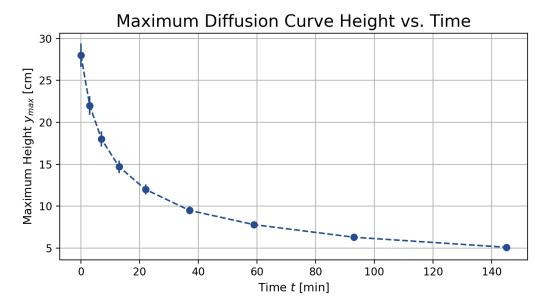


Figure 2: The diffusion curve's maximum height falls with time as $y_{\rm max} \sim t^{-1/2}$.

The diffusion curve's maximum height height depends on time as

$$y_{\text{max}}(t) = \frac{ab\Delta n}{\sqrt{4\pi Dt}} = \frac{S}{k\sqrt{4\pi Dt}}$$

The above relationship implies plotting the quantity Q, defined as

$$Q \equiv \frac{(ab\Delta n)^2}{4\pi y_{\rm max}^2} = \frac{1}{4\pi} \left(\frac{S}{ky_{\rm max}}\right)^2 = Dt,$$

on the ordinate axis as a function of time t should yield a straight line with slope D. The quantity $k=\frac{b+c}{c}$ is magnification and S is area under the diffusion curve, theoretically expected to be

$$S=abk\Delta n$$

where $\Delta n = 0.029$ is the difference in refractive index between water and ethanol. Figure 3 shows a graph of the relationship Q = Dt and the corresponding linear fit for the diffusion constant D, which takes the value

$$D = 2.02 \times 10^{-4} \,\mathrm{min}^{-1} = 3.37 \times 10^{-6} \,\mathrm{s}^{-1}$$

Finding Diffusion Constant with a Linear Fit 0.035 $D = 2.02e - 04 \text{ [min}^{-1}\text{]}$ Linearized Quantity $Q = \frac{(ab\Delta n)^2}{4\pi y^2}$ 0.030 $\sigma_D = 1.73e - 05 \text{ [min}^{-1}\text{]}$ Data (simulated) 0.025 0.020 0.015 0.010 0.005 0.000 20 40 60 80 100 120 140 Time t [min]

Figure 3: Finding the diffusion constant D with a linear fit of the quantity Q = Dt.

3.2 Comparing Values of Area

The theoretically predicted area under the diffusion curve (derivation is cussed in Appendix A.2) is

$$S = k \int y(z) dz = k \int \left(ab \frac{dn}{dz}\right) dz = kab(n_1 - n_0)$$

where $k = \frac{b+c}{c}$ is the magnification of the diffusion curve between the cuvette and the display screen; b and c are the distances between the cuvette and display screen and between the light source and the cuvette, respectively. Note that the area under the curve is theoretically independent of time, which, I believe, could be explained by the continuity equation or conservation of mass in the diffusing cuvette.

In any case, the theoretically predicted area under the curve is

$$S_{\text{theory}} = kab\Delta n = \frac{72.0 \text{ cm} + 35.5 \text{ cm}}{35.5 \text{ cm}} \cdot 1.5 \text{ cm} \cdot 72.0 \text{ cm} \cdot 0.029 = \boxed{9.48 \text{ cm}^2}$$

Figure 4 shows the areas under the simulated diffusion curves, found with numerical integration.

The simulated/measured areas, have an average value and sample standard deviation

$$\mu_S = 4.09 \, \mathrm{cm}^2$$
 and $\sigma_S^2 = 0.53 \, \mathrm{cm}^2$

The measured and theoretically expected values disagree by a factor of roughly two. I assume the discrepancy exists because the simulated diffusion curves were not calibrated to match the experiment's dimensional parameters a, b, c. As such, the theoretically predicted area, which relies directly on the values of a, b, and c, does not match the areas under the simulated curves.

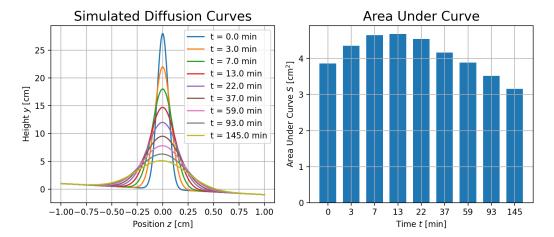


Figure 4: Simulated diffusion curves at various times throughout the experiment and the corresponding area under each curve, found with numerical integration.

4 Error Analysis

The linearized quantity Q from Subsection 3.1 is found with the formula

$$\mathcal{Q} \equiv \frac{(ab\Delta n)^2}{4\pi y_{\max}^2}$$

The input quantities are a, b, Δn and y_{max} . Since the data is simulated and given without measurement error, I assumed the following uncertainties:

$$a = (1.5 \pm 0.1) \,\mathrm{cm}$$
 $b = (72.0 \pm 0.5) \,\mathrm{cm}$ $\Delta n = 0.029 \pm 0.001$

and a five percent uncertainty $u_y = 0.05 \cdot y_{\text{max}}$ in the maximum height y_{max} . The sensitivity coefficients for each quantity are

$$c_{a} = \frac{\partial \mathcal{Q}}{\partial a} = \frac{2a(b\Delta n)^{2}}{4\pi y_{\text{max}}^{2}} \qquad c_{b} = \frac{\partial \mathcal{Q}}{\partial b} = \frac{2b(a\Delta n)^{2}}{4\pi y_{\text{max}}^{2}}$$

$$c_{n} = \frac{\partial \mathcal{Q}}{\partial \Delta n} = \frac{2\Delta n(ab)^{2}}{4\pi y_{\text{max}}^{2}} \qquad c_{y} = \frac{\partial \mathcal{Q}}{\partial y_{\text{max}}} = -\frac{(ab\Delta n)^{2}}{2\pi y_{\text{max}}^{3}}$$

The corresponding error in Q is

$$u_{\mathcal{Q}} = \sqrt{(c_a u_a)^2 + (c_b u_b)^2 + (c_n u_n)^2 + (c_y u_y)^2},$$

which is shown in the error bars in Figure 3. I estimated the uncertainty in the diffusion constant D using the uncertainty in the fitted slope parameter from the linear fit shown in Figure 3, where the dependent variable Q is weighted with the error u_Q .

5 Results

The diffusion constant for the ethanol-water mixture in the cuvette was

$$D = (2.02 \pm 0.17) \times 10^{-4} \,\mathrm{min}^{-1} = (3.37 \pm 0.03) \times 10^{-6} \,\mathrm{s}^{-1}$$

The theoretically predicted area S_{theory} under the diffusion curve, mean measured value μ_{S} and standard deviation σ_{S}^2 of the measured value were, respectively

$$S_{\text{theory}} = 9.48 \,\text{cm}^2, \qquad \mu_S = 4.09 \,\text{cm}^2, \qquad \sigma_S^2 = 0.53 \,\text{cm}^2$$

The results do not agree, likely because of complications when generating the simulated "measured" data.

A Background Theory

A.1 Light Ray Path in a Nonhomogeneous Substance

• We model our ethanol-water cuvette as a substance consisting of parallel liquid planes, such that the refraction index n is a function of the single coordinate z (see Figure 1). The familiar law of diffraction $\frac{\cos \phi_1}{\cos \phi_2} = \frac{n_2}{n_1}$ then generalizes to

$$\cos \phi = \frac{\text{constant}}{n(z)}$$

• Again referring to the geometry of Figure 1, we find how the angle of refraction ϕ changes with the coordinate x on a light beam's passage through the cuvette. Taking the logarithm of $\cos \phi = \frac{\text{constant}}{n(z)}$, differentiating to remove the constant, integrating, and dividing through by $\mathrm{d}x$ gives

$$\mathrm{d}[\ln\cos\phi] = -\,\mathrm{d}[\ln n] \implies \frac{\sin\phi}{\cos\phi}\,\mathrm{d}\phi = \frac{1}{n}\,\mathrm{d}n \implies \tan\phi\frac{\mathrm{d}\phi}{\mathrm{d}x} = \frac{1}{n}\frac{\mathrm{d}n}{\mathrm{d}x}$$

We then apply the chain rule $\frac{dn}{dx} = \frac{dn}{dz} \frac{dz}{dx}$ to get

$$\tan \phi \frac{\mathrm{d}\phi}{\mathrm{d}x} = \frac{1}{n} \frac{\mathrm{d}n}{\mathrm{d}x} = \frac{1}{n} \frac{\mathrm{d}n}{\mathrm{d}z} \frac{\mathrm{d}z}{\mathrm{d}x} \implies \frac{\mathrm{d}\phi}{\mathrm{d}x} = \frac{1}{n} \frac{\mathrm{d}n}{\mathrm{d}z}$$

The last line uses the equality $\frac{dz}{dx} = \tan \phi$ (see Figure 1). Separating the variables ϕ and x and integrating shows the light ray bends by an angle

$$\alpha_1 \equiv \int d\phi = \frac{1}{n} \frac{dn}{dz} \int_0^a dx = \frac{a}{n} \frac{dn}{dz}$$

on is path through the cuvette.

• As the ray exits the cuvette and passes between the cuvette-air interface, the refraction angle increases to

$$\alpha_2 = n\alpha_1 = a \frac{\mathrm{d}n}{\mathrm{d}z}$$

where n = n(z) is the refraction index at the z coordinate where the light exits the cuvette. For a screen a distance b away, the ray is thus displaced from the optical axis by a distance

$$y = b\alpha_Z = ab\frac{\mathrm{d}n}{\mathrm{d}z}$$

Of course, the above derivation holds only in the regime of the small angle approximation $\alpha \approx \sin \alpha$ and for $a \ll b$.

A.2 Diffusion and Geometry of the Diffusion Curve

• The concentration ρ of a diffusing substance is a function of both position and time and obeys the diffusion equation

$$D\nabla^2 \rho = \frac{\partial \rho}{\partial t}$$

For diffusion in only one dimension, this simplifies to

$$D\frac{\partial^2 f}{\partial z^2} = \frac{\partial \rho}{\partial t}$$

• The general solution is the Gaussian function

$$\rho(z,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{z^2}{4Dt}}$$

The solution represents a distribution for the initial condition in which at time t=0 the entire mass of the diffusing substance occurs at z=0 (think of a delta function density distribution).

• In the experiment, the substance is initially uniformly distributed as

$$\rho(z) \begin{cases} \rho_0 = 1 & z > 0 \\ 0 & z < 0 \end{cases}$$

and the solution is

$$\rho(z) = \frac{\rho_0}{2} \left[1 + \theta \left(\frac{z}{\sqrt{4Dt}} \right) \right] \quad \text{where} \quad \theta(\xi) = \frac{2}{\sqrt{\pi}} \int_0^{\xi} e^{-\eta^2} d\eta$$

• Assuming the index of refraction is a linear function of concentration, we have

$$n(z) = \frac{n_0 + n_1}{2} + \frac{n_1 - n_0}{2} \theta \left(\frac{z}{\sqrt{4Dt}}\right)$$

Using this expression for n(z), the height y of the diffusion curve is thus

$$y = ab \frac{\mathrm{d}n}{\mathrm{d}z} = ab(n_1 - n_0) \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{z^2}{4Dt}}$$

The maximum height, which occurs at z=0, evidently falls as $y_{\rm max} \sim t^{-1/2}$

$$y_{\text{max}} = ab \frac{n_1 - n_0}{\sqrt{4\pi Dt}} = \frac{S}{k\sqrt{4\pi Dt}}$$

• The area S under the curve is independent of time:

$$S = k \int y(z) dz = k \int \left(ab \frac{dn}{dz}\right) dz = kab(n_1 - n_0)$$

where $k = \frac{b+c}{c}$ is the magnification of the diffusion curve between the cuvette and the display screen; b and c are the distances between the cuvette and display screen and between the light source and the cuvette, respectively.