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Transient Diffraction Grating Measurements of Molecular Diffusion in the Undergraduate Laboratory

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Mass diffusion is a central process in many biological, chemical, and physical systems, and although the mathematics of diffusion has long been an important component of an undergraduate physics education, experimental measurements of diffusion are not very common in the undergraduate laboratory. We describe here an experiment that employs the interference of laser beams to allow measurement of molecular diffusion on micron length scales. The interference fringes of two intersecting “pump” beams within a dye solution create a sinusoidal distribution of long-lived molecular excited states. A third “probe” beam is incident at a wavelength at which the indices of refraction of the ground and excited states are different, so that the probe beam diffracts from the spatially periodic excited-state pattern. After the pump beams are switched off, the excited-state periodicity washes out as the system diffuses back to equilibrium, and the molecular diffusion constant is easily obtained from the rate constant of the exponential decay of the diffracted beam. It is also possible to measure the excited-state lifetime. The experiment provides hands-on insight into fluid dynamics, random walks, and coherent optics.

Introduction. Students learn about ballistic motion (e.g. constant acceleration) when they first begin physics, but one can argue random-walk diffusive motion is much more common and important in the microscopic world. Bacterial motility,¹ the motion of electrons and holes in the formation of a pn junction, the distribution of CO₂ in the ocean,² and thermal diffusion in everyday solids³ are important examples of diffusive kinetics. Undergraduate laboratory experiments on mass diffusion are not especially common, at least in part due to the long time scales often involved for macroscopic distances; for example, it would take small molecules on the order of a few years to diffuse 1 cm through a block of ice.⁴ We suggest here an undergraduate experiment for measurement of dye diffusion through a liquid on micron length scales, so that the time scales will be thousandths or hundredths of seconds. The students employ the interference fringes of two intersecting coherent “pump” laser beams, absorbed by a dye molecule in solution, to produce a spatially periodic molecular excited-state concentration profile. If a third “probe” laser beam is incident at a wavelength at which the indices of

refraction of the ground-state and excited-state solvated dye molecule are different, then the probe beam is subjected to a “laser-induced diffraction grating” (a phase grating), and a portion of the probe will diffract at an angle that depends on the pump-beam fringe spacing. If the pump beams are removed, the diffracted intensity will decay exponentially as the periodic excited-state profile diffuses away, with a rate constant that is proportional to the dye molecule’s diffusion coefficient. A typical length scale for the fringe spacing is on the order of microns, and a typical decay time due to diffusion is tens of milliseconds. Students can therefore study diffusion over a convenient time frame.

Two lasers are required for the experiment: one for the pump beams and the other for the probe beam. The sample is usually a photochromic dye in an organic solvent, held within a cuvette with a thickness of 1 or 2 mm. It is necessary that the dye has a long-lived excited-state lifetime, so that at least a portion of the decay of the laser-induced diffraction grating is due to diffusion rather than solely excited-state decay. The diffracted beam can be detected with an avalanche photodiode and recorded with a standard digital oscilloscope that permits signal averaging. Mirrors mounted on translation stages are required to precisely set the required angles of incidence for the pump and probe beams.

Figure 1 depicts a simple sketch of the interactions between the laser beams. All beams are polarized perpendicular to the page, so that the propagating electric fields can be treated as scalars. The equal-intensity pump beams, incident at wavevectors \mathbf{k}_1 and \mathbf{k}_2 , cross and form Mach-Zehnder interference fringes⁵ within the sample, as shown in Fig. 1a. The electric fields of the pump beams are $E_0 e^{i(\mathbf{k}_1 \cdot \mathbf{r} - \omega t)}$ and $E_0 e^{i(\mathbf{k}_2 \cdot \mathbf{r} - \omega t)}$, which yields a combined interference irradiance of

$$| E_0 e^{i(\mathbf{k}_1 \cdot \mathbf{r} - \omega t)} + E_0 e^{i(\mathbf{k}_2 \cdot \mathbf{r} - \omega t)} |^2 = 2|E_0|^2 (1 + \cos(qx)) \quad (1)$$

where $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$ as shown in Fig. 1b. The interference fringes, with a spatial period of $d = 2\pi/q$, generate a spatially periodic modulation at wavevector \mathbf{q} in the excited-state population, and the modulation will serve as a temporary diffraction grating for a probe laser beam incident at a wavelength λ' at which the index of refraction is different for solutions of excited-state and ground-state molecules.

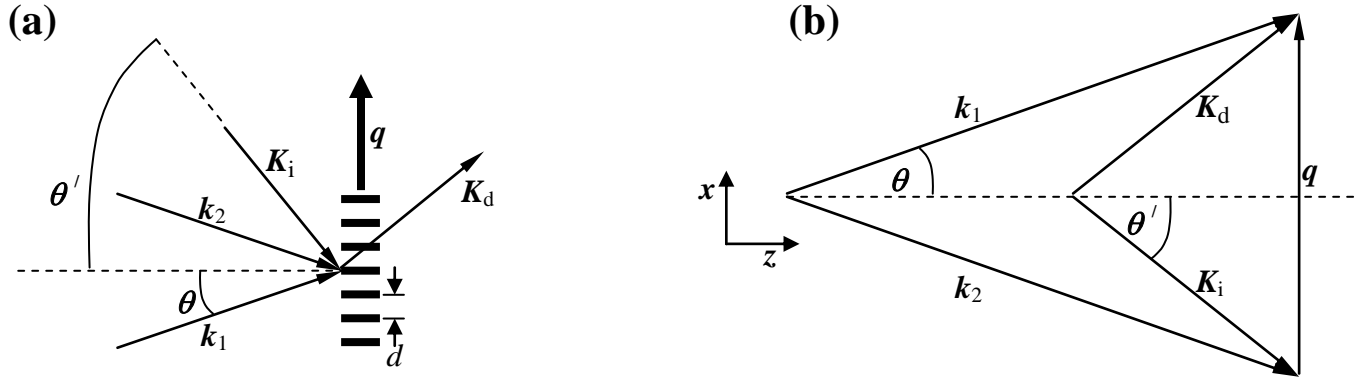


Fig. 1. Wavevector diagrams. (a) Coherent pump beams with wavevectors k_1 and k_2 , incident at angles $\pm\theta$, create a sinusoidal interference pattern within the sample with a wavevector $q = k_1 - k_2$ and fringe spacing $d = 2\pi/q$. The periodic modulation of the index of refraction caused by the absorbed pump beams results in a probe beam, incident at K_i and angle θ' , being diffracted at wavevector K_d and angle $-\theta'$. (b) The interference wavevector q serves as a momentum transfer between the incident and diffracted probe-beam wavevectors, so that $K_d = K_i + q$.

The value of the grating period d produced by the pump-beam interference, and the relation between the angles of incidence of the pump and probe beams (θ and θ' , respectively) can be easily inferred from momentum conservation. As indicated in Fig. 1b, the wavevector q of the pump-beam interference modulation is added to the incident probe-beam momentum K_i to produce a diffracted photon momentum K_d . From the triangles of Fig. 1b, it is clear that $q/2 = k_1 \sin\theta = K_i \sin\theta'$, so that (since $q = 2\pi/d$) the grating period generated for a pump incidence angle of θ is

$$d = \lambda / 2 \sin\theta \quad (2)$$

and the correct angle of probe incidence θ' for diffraction from the grating is related to the pump angle of incidence very simply by

$$\sin\theta' = (\lambda' / \lambda) \sin\theta. \quad (3)$$

This means that the probe incidence angle is related to the grating period via

$$2d \sin\theta' = \lambda' \quad (4)$$

which is familiar from elementary x-ray Bragg scattering. The deflection of the probe beam can therefore be interpreted as Bragg diffraction from planes of excited-state molecules (the yz

planes of Fig. 1a) separated by a spatial period d . The wavevector \mathbf{q} provides a momentum transfer only in the x -direction, and the scattering is elastic ($K_i = K_d$), so that the z -component of the probe-photon momentum is conserved, and the diffraction occurs at the symmetric angle $-\theta'$, as shown with the diffraction wavevector \mathbf{K}_d in Fig. 1. The wavelengths and angles in Equations 1-4 are to be taken inside the solution; however for the small angles recommended in this study, Equations 1-4 are valid if the angles and wavelengths are measured in air.⁶

If the molecules employed have very long-lived excited states, then after the pump beams are switched off (say at $t = 0$), the excited-state grating relaxes to a state of uniform excited-state concentration via molecular diffusion rather than excited-state decay. The rate at which the diffracted intensity decays provides a direct simple measurement of the molecular diffusion coefficient D . (We assume here, as is usually the case, that the diffusion coefficients of the excited and ground-state molecules are nearly the same.⁷) This rate can be derived by writing down the diffusion equation for excited-state molecules with diffusion coefficient D at concentration $c(x, t)$:

$$\partial c / \partial t = D \partial^2 c / \partial x^2 \quad (5)$$

subject to the initial condition $c(x, 0) = c_0(1 + \cos(qx))$. The solution is

$$c(x, t) = c_0(1 + \cos(qx) e^{-q^2 D t}). \quad (6)$$

The solution to the diffusion equation is particularly intuitive in this case since, as a linear equation, the diffusion equation cannot mix different Fourier components during the decay. Since the excited state concentration is initially harmonic with a single wavevector \mathbf{q} , it will remain harmonic with the same wavevector and a smaller amplitude as time advances. The harmonic decay of $c(x, t)$ due to diffusion is shown in Fig. 2.

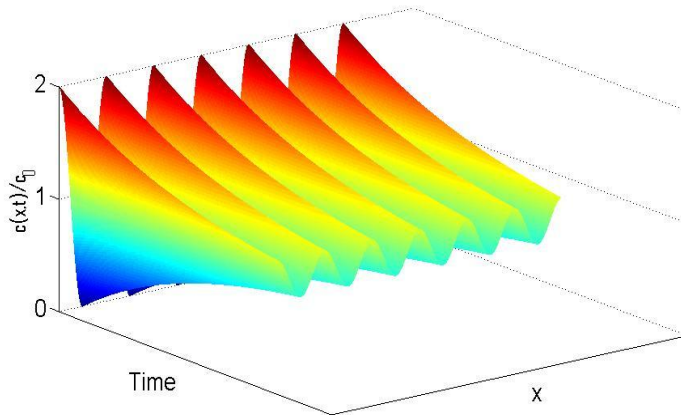


Fig. 2. A “transient diffraction grating.” The figure shows the concentration profile $c(x, t)$ of the diffusing excited-state molecules, normalized to its average c_0 , after the pump beams are turned off. In an actual experiment, there will be on the order of 100 grating periods for a 1 mm^2 pump-beam cross-section, rather than just six or seven.

The diffracted electric field is proportional to the refractive index increment $\Delta n(t) = (\partial n / \partial c) c_q(t)$, where n is the solution's refractive index, and $c_q(t) \sim e^{-q^2 D t}$ is the spatial Fourier component of the excited-state concentration at wavevector q generated by the interference fringes.⁶ Thus the diffracted intensity will decay with time according to

$$I = I_0 e^{-2q^2 D t} \quad (7)$$

and the diffusion coefficient D can be obtained from the slope of a graph of $\ln(I)$ vs. time. If the excited-state decay rate $1/\tau$ is actually comparable to, but not much larger than, the diffusion decay rate $q^2 D$, then the experiment can be repeated at different pump-beam incidence angles (hence different q), and both the diffusion constant and the excited-state decay rate can be extracted from the slope and intercept, respectively, of a plot of the total measured decay rate r vs. q^2 , where

$$r = 2(q^2 D + 1/\tau). \quad (8)$$

The use of transient gratings to measure diffusion was pioneered in 1973 by Pohl⁸ and Eichler.⁹ Because the diffraction is elastic and is “forced” to an angle determined by the pump-beam interference pattern, the method became known as “forced Rayleigh scattering” (FRS). Early FRS experiments employed dyes with long-lived excited states to measure molecular diffusion in simple solvents,¹⁰ liquid crystals,¹¹ polymer solutions,⁷ and magnetic fluids.¹² More recently FRS has been employed to measure the Soret effect (“thermodiffusion”) for small molecules and polymers,¹³ as originated by Kohler,¹⁴ in which sinusoidal molecular concentration gradients are driven by the inhomogeneous solvent heating caused by pump-beam absorption. In the current study we wish to keep things simple and employ an easily obtainable photochromic dye in a common solvent.

Experimental Apparatus. The apparatus employed for the experiments is shown in Fig. 2. The 9-mW Ar⁺ pump laser beam at $\lambda = 488$ nm is split 50/50 with a beam splitter, and prisms and mirrors are used to direct the two components so that they intersect at the sample. The pump beam is switched on and off using a chopper blade with only one of the six slots open. The incident probe beam is a 2 mW HeNe laser at $\lambda' = 633$ nm; the diffracted probe beam is detected with an avalanche photodiode wired to an oscilloscope. Long focal length (1 m) positive lenses are used to compensate for beam divergence for both the pump and probe beams, so that when they meet at the sample the three beams have areas on the order of 1 mm². The optics, optical mounts, and the detector were purchased from Thor labs; the chopper was purchased from Stanford Research, and the Ar⁺ laser was purchased from JDS/Uniphase. The sample employed, which absorbs blue light and transmits red light, was ethyl red dissolved at 0.3 g/L in isopropanol, both used as received from Sigma-Aldrich. The sample was contained in a 1-mm thick glass cuvette purchased from Spectrocell. Upon absorbing blue light, ethyl red undergoes

an isomerization from a ground-state *trans* form to a long-lived *cis* excited state; the refractive index difference between the *trans* and *cis* states generates the phase grating.

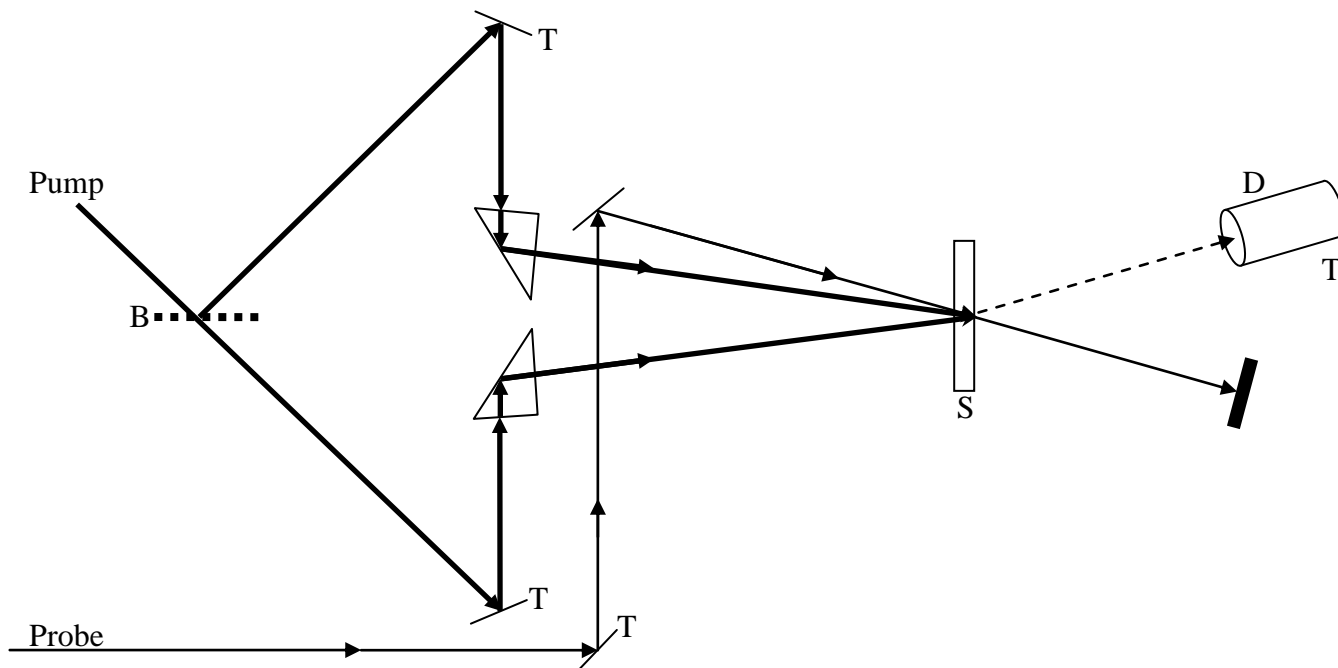


Fig. 3. Experimental forced Rayleigh scattering apparatus. The pump beams and probe beam are depicted with thicker and thinner lines, respectively, and the diffracted beam is dashed. B, S, and D label the beam splitter, the sample cell, and the avalanche photodiode detector. Components mounted on translation stages are labeled with T. The prisms are useful in allowing small incidence angles – the incidence angles in the figure are greatly exaggerated.

During the formation of the grating, while the pump beam is on, there is a competition between the photoproduction of excited states to produce the grating, and the diffusion of the newly formed excited states, which depletes the grating. The diffusion rate q^2D is proportional to $\sin^2\theta$ (Eq. (2) above). Therefore, the peak diffracted signal diminishes for larger pump angles of incidence, so that, at least in initial studies, it is beneficial to work at small angles of incidence. In the current study the pump incidence angle was kept at less than 2° .

The diffracted signal obtained at a pump incidence angle of $\theta = 1.50^\circ$, corresponding to a grating spacing of $d = 2\pi/q = 9.3 \mu\text{m}$, is shown in Fig. 4a, which displays the detected diffracted intensity as a function of time. In Fig. 4b we plot the logarithm of decaying portion of the signal, showing that the decay is nearly exponential over about four time constants.

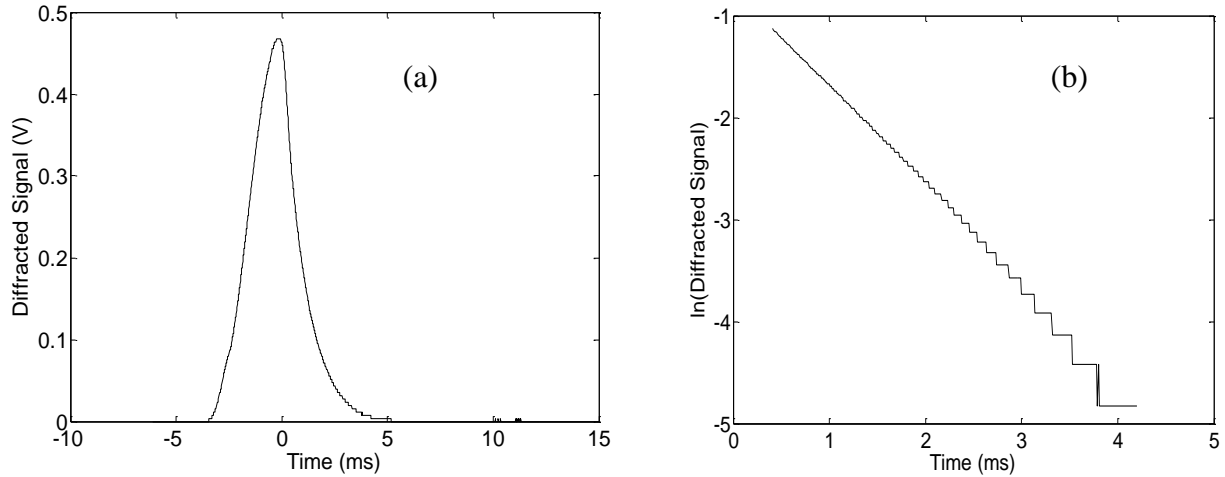


Fig. 4. The diffracted signal for a pump incidence angle of $\theta = 1.50^\circ$, corresponding to a grating spacing of $d = 9.3 \mu\text{m}$, in a sample of ethyl red in isopropanol.

To decouple the contributions of diffusive relaxation and the finite excited-state lifetime to the overall signal decay rate r , students should be encouraged to take data at several different pump incidence angles to see if the decay rate (obtained from the slope of graphs like Fig. 4b) increases linearly with q^2 . The result of such an experiment is shown in Fig. 5. Using the slope and intercept of a best-fit line and referring to Eq. (8), we obtain a diffusion coefficient of $D = 770 \pm 30 \mu\text{m}^2/\text{s}$ and an excited-state lifetime of $\tau = 6.2 \pm 0.2 \text{ ms}$.

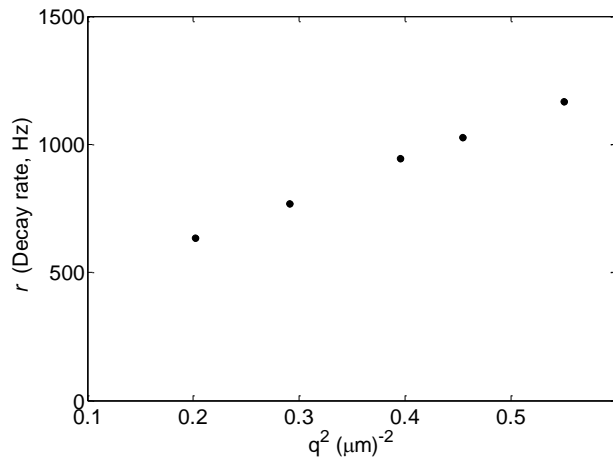


Fig. 5. The decay rate plotted as a function of $q^2 = 4\pi^2/d^2$, where d is the grating spacing. The diffusion coefficient and the excited-state lifetime are obtained from the slope and intercept, respectively, of a best-fit line.

The cost of the Ar^+ laser employed to pump the current gratings at 9 mW may be beyond the budget of many undergraduate laboratories. Much less expensive blue diode lasers with output powers on the order of 1 W are currently available,¹⁵ but most out-of-the-box diode lasers will only have coherence lengths on the order of a millimeter, making them impractical for interference experiments. However, the coherence length of a diode laser can be increased, with

the loss of some intensity, by spatially filtering the beam using a pinhole aperture placed between a pair of short-focal-length positive lenses.¹⁶ Spatial filtering should bring the coherence length up to several centimeters so that the beam can be employed in the experiments described above.

To conclude, we have described an undergraduate experiment that permits measurements of molecular diffusion in solution on sub-second time scales. The experiment should permit students to gain experience with coherent optics, and allows the student to explore the physics of random-walk motion. It is hoped that such an experience will serve as good complement both to the studies of ballistic motion that are usually strongly emphasized in introductory physics courses and laboratories, and to the mathematics of diffusion usually taught in later courses.

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