

LIGHT SCATTERING

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I. Introduction

Brownian motion is the irregular, random motion of microscopic particles observed first by Robert Brown in 1872. The motion is caused by the random impingement of molecules of the medium on the observed particle and represents the response of the particle to a random force. The first accurate value of Boltzmann's constant k_B was obtained by Perrin in 1909 by measuring the position of a particle observed under the microscope at equal time intervals. The figure shows one of his records of observation.



Figure 1 shows the position at 30 second intervals of a 0.53 micron particle in water as observed by Perrin under a microscope. (From Mandelbrot, **Fractals**, 1983)

In this experiment Brownian motion will be studied by observing the fluctuations in the intensity of light scattered from a mixture of water and small latex spheres. The spheres have a diameter comparable to the wavelength of the scattering light, which is provided by a Helium-Neon laser of wavelength $\lambda = 632.8$ nm in vacuum. The physical phenomena that you will encounter in this experiment are quite diverse: random walk and diffusion, viscosity and Stokes' law, the equipartition theorem, the Einstein relation, and the diffraction of light. Simple derivations of most of the results needed are given in this description, but you should be aware that numerical factors are chosen sometimes arbitrarily to give the correct numerical coefficients known from more elaborate discussions. In addition to the theory of the experiment, this write-up includes a detailed description of the experimental apparatus and procedure. The next section examines the connection between the intensity fluctuations of the scattered light and Brownian motion.

II. Light Scattering by a Statistical Medium

Imagine that the sample consists of a vial of water with just two latex spheres in it. An observer (the PMT) is located at a rather distant origin O at \mathbf{r}_1 and \mathbf{r}_2 respectively from the particles (See figure 2).

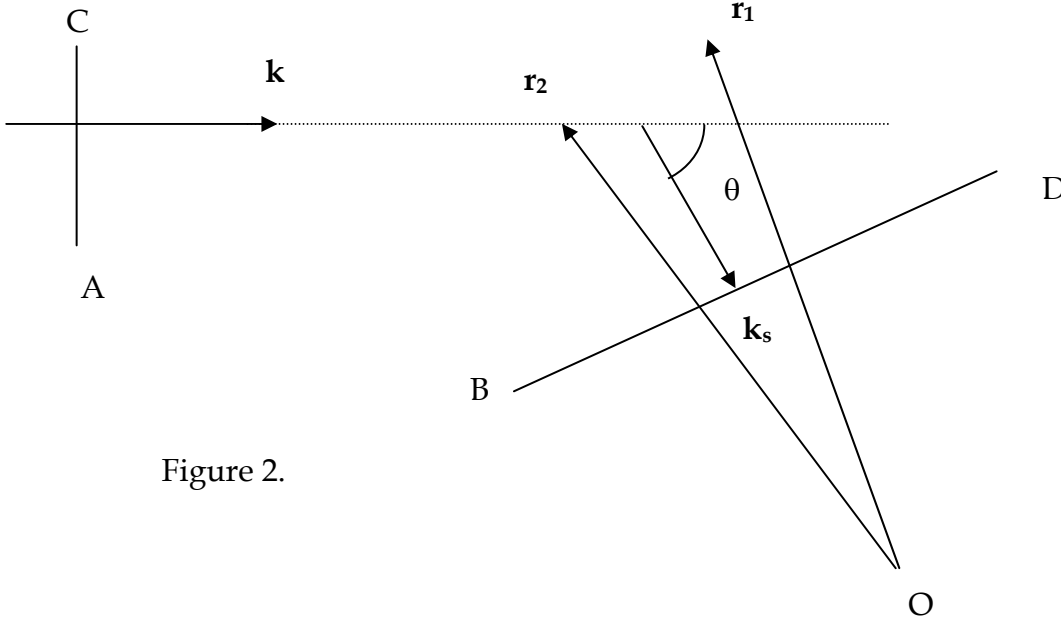


Figure 2.

The incident light with wavevector \mathbf{k} and plane wavefront AC is scattered by particles at \mathbf{r}_1 and \mathbf{r}_2 through angle θ . The plane wavefront BD is focused on the photocathode of an RCA 931 photomultiplier tube. The amplitude of the light that reaches the photomultiplier depends on the amplitude of the incident light E_0 , the amplitude of the light scattered in the θ direction by each sphere $f(\theta)$, and (the only important part) the relative phase of the light when incident on each sphere, plus the additional phase accumulated as the scattered light reaches O at time t . The wave incident on particle $i=1,2$ at t is

$$E = E_0 \cos(\omega t - \mathbf{k} \cdot \mathbf{r}_i) \quad (1)$$

Note that in order to keep signs straight in the following, the phase (the argument of the cosine in (1), that is) increases as t increases. The light striking the PMT at time t (same time) has accumulated the additional phase $\mathbf{k}_s \cdot \mathbf{r}_i$ in traveling the additional distance \mathbf{r}_i . So we can write the total amplitude of the light striking the detector

$$e(PMT) = f(\theta) E_0 \sum_{i=1}^2 \cos(\omega t - (\mathbf{k} - \mathbf{k}_s) \cdot \mathbf{r}_i) \quad (2)$$

The PMT is sensitive to incident average energy, so its output is proportional to the time average of the square of $e(PMT)$. The time average is taken over many optical periods $T = 2\pi/\omega$.

$$\langle e^2 \rangle = |f(\theta)|^2 E_0^2 \left\langle \left[\cos^2(\omega t - \Delta \mathbf{k} \cdot \mathbf{r}_1) + \cos^2(\omega t - \Delta \mathbf{k} \cdot \mathbf{r}_2) + 2 \cos(\omega t - \Delta \mathbf{k} \cdot \mathbf{r}_1) \cos(\omega t - \Delta \mathbf{k} \cdot \mathbf{r}_2) \right] \right\rangle \quad (3)$$

where the angular brackets $\langle \dots \rangle$ indicate time average and

$$\Delta \mathbf{k} = \mathbf{k} - \mathbf{k}_s \quad (4)$$

is the difference between the incident and scattered wave vectors. The first two terms in the brackets on the right-hand side of (3) are each $\frac{1}{2}$ since the average of $\cos^2 x$ is $\frac{1}{2}$ over any integral number of periods. The third term yields, after time averaging, $\cos(\Delta \mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2))$, as one may show by using the identity

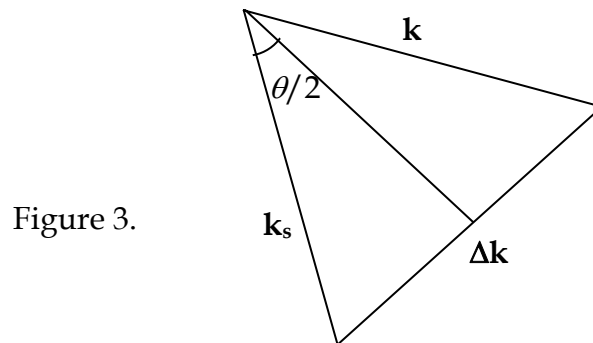
$$\cos(a + b) = \cos(a)\cos(b) - \sin(a)\sin(b)$$

before time averaging. Thus the PMT power output is proportional to

$$I_{out} \propto |f^2(\theta)| E_0^2 [1 + \cos(\Delta \mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2))] \quad (5)$$

Equation (5) depends on $\mathbf{r}_1 - \mathbf{r}_2$, so the output fluctuates as the second term fluctuates in response to changes in the relative distance between particles 1 and 2. Examine the reproduction of Perrin's data and imagine two particles undergoing such motion. The vector from one to the other also undergoes a "random walk." Also, the distance $|\mathbf{r}_1 - \mathbf{r}_2|$ that the particles must move relative to one another to produce any given signal change depends on θ , since the phase depends on $\Delta \mathbf{k}$ (see Figure 2 and Figure 3).

Imagine that for some fixed \mathbf{r}_1 and \mathbf{r}_2 , θ is chosen so that the scattered intensity is, say, a maximum. Figure 3 shows the vector relation between wavevectors and θ .



The wavelength of the light is not changed by the scattering process, so $|\mathbf{k}_s| = |\mathbf{k}| = k = 2\pi/\lambda$. From the geometry of Figure 3,

$$\sin(\theta/2) = \Delta k/2k \quad (6)$$

or

$$\Delta k = (4\pi/\lambda) \sin(\theta/2) \quad (7)$$

Equation (7) will be important in determining the angular dependence of the fluctuating output of the PMT. The correlation time τ_c for the PMT fluctuations mentioned above may be estimated by computing how long it will take the phase factor in Equation (5) to change by, say 1 radian. That calculation will be the subject of the next section. However, we first must acknowledge that our sample will not have just two spheres in it, but many millions of spheres. The extension of the discussion to many spheres is not easy or always entirely obvious, but the result for the angular dependence of Δk of the two particle scattering is preserved, as is the correlation time argument given next, as long as the density of scatterers is small enough not to seriously attenuate the beam intensity as it passes through the sample.

III. Brownian Motion and Diffusion

The spheres move in response to random forces, both in magnitude and direction, and random in time as well. We will replace reality, which is too complicated, with a simple model. We will assume that there is a very small time interval Δt during which the particle suffers a displacement \mathbf{L} which is constant in magnitude but random in direction. The interval Δt must be short compared to our time of observation (to be specified later) but long compared to the time of an individual collision of a molecule with the sphere. When the problem is formulated in these terms, it reduces to the famous problem of the random walk. The derivation here is from *The Feynman Lectures in Physics, Vol. I*.

We wish to calculate the mean square displacement of the particle, $\langle R_N^2 \rangle$ after N steps of length L . We want to find the average of the square because the average of many trials (the meaning of $\langle \dots \rangle$ in this) of \mathbf{R}_N is zero, since displacements in any direction are equally probable. The result is obtained by induction, as follows. The displacement after N steps is $\mathbf{R}_N = \mathbf{R}_{N-1} + \mathbf{L}$. Hence

$$\mathbf{R}_N \cdot \mathbf{R}_N = R_N^2 = R_{N-1}^2 + L^2 + 2\mathbf{R}_{N-1} \cdot \mathbf{L}$$

If we take the average of this expression over many separate trials of N steps each, we get

$$\langle R_N^2 \rangle = \langle R_{N-1}^2 \rangle + L^2$$

since

$$\langle \mathbf{R}_{N-1} \cdot \mathbf{L} \rangle = 0$$

Both equalities come from the independence of \mathbf{R}_{N-1} and \mathbf{L} . The rest of the derivation is by induction:

$$\begin{aligned}\langle R_1^2 \rangle &= L^2 \\ \langle R_2^2 \rangle &= L^2 + L^2 \\ \langle R_N^2 \rangle &= NL^2\end{aligned}$$

Thus the root mean square (rms) distance traveled in N steps is $\sqrt{N} \cdot L$.

If a step occurs every Δt , then in $t \gg \Delta t$, the distance traveled is $R(t) = \sqrt{t/\Delta t} \cdot L$ or $\langle R^2(t) \rangle = t/\Delta t \cdot L^2$. The parameters L and Δt are artifacts of our model. They describe something about both the latex spheres and the medium they move in. This information is conventionally absorbed into the diffusion constant D , which is defined such that the mean square displacement, *parallel to any given direction*, say x , is given by

$$\langle x^2 \rangle = 2 D t \quad (8)$$

Consequently, since $\langle R^2 \rangle = 3 \langle x^2 \rangle$, (why?) we see that $D = L^2/6 \Delta t$. But (8) is the important result that we will use.

We are not finished with the discussion because D is not directly available in the literature for a system of this type. However, we can pause to use (8) to obtain a formula for the characteristic decay (i.e., correlation) time for the fluctuations. For example, a maximum in the scattered intensity, produced by some particular configuration of spheres, will decay in the time necessary for the spheres to change their relative distance

$$|\mathbf{r}_1 - \mathbf{r}_2| \approx 1/\Delta k = \lambda/4\pi\sin(\theta/2)$$

from Equation (7).

The correlation time τ_c is, according to conventional definition, given by

$$\tau_c = 1/(2D\Delta k^2) = (\lambda/4\pi\sin(\theta/2))^2/2D = \lambda^2/(32\pi^2\sin^2(\theta/2)D) \quad (9)$$

At this point, go back to some definitions and verify that (9) is dimensionally correct. In particular, what are the dimensions of the diffusion constant D ?

Now we know the characteristic fluctuation time if we know D , the scattering angle θ , and the wavelength of the light in the liquid. It is perfectly reasonable to use the measurement of τ_c to find D , but we can do something more interesting if we use a well-known theory to write D in terms of some microscopic and other macroscopic physical constants. So we will now derive the Stokes-Einstein relation between D , the liquid's temperature, its viscosity, and Boltzmann's constant.

IV. The Microscopic-Macroscopic Connection

If an object moves through a fluid medium slowly enough, it will generate no turbulence, and the retarding force will be proportional to its velocity. The proportionality constant depends on the geometry of the body and the properties of the fluid. The latter is described by the coefficient of viscosity η , which is defined most simply as follows. Imagine a plane plate moving parallel to the plane of an identical stationary plate with constant speed v . The plates are separated by distance d , with the intervening space filled with liquid. The force needed to maintain constant velocity on the moving plate of area A is

$$F = \eta v A / d \quad (10)$$

This equation defines η , the viscosity, which has dimensions of gm/cm-sec, or dyne-sec/cm². A unit of viscosity is 1 poise, after Poiseuille. The viscosity of water is 0.01 poise, or one centipoise.

The force necessary to maintain a sphere with radius a moving through a viscous liquid at constant velocity was worked out by Stokes. He found

$$F = 6 \pi \eta a v \quad (11)$$

Equation (11) is often known as Stokes' law. The quantity $6\pi a$ is entirely geometrical, and would be different for a non-spherical object. Stokes' law is first encountered by most physicists in discussions of the Millikan Oil Drop experiment that first measured the charge on the electron.

Our purpose now is to replace the diffusion constant in (8) by factors such as those in (11) that depend separately on the geometry of the diffusing particle and the properties of the liquid. The connecting link is the equipartition theorem, which assigns $\frac{1}{2}k_B T$ of energy to each degree of freedom of the particle. In the case of the latex spheres

$$\frac{1}{2} k_B T = \frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} m \langle v_y^2 \rangle = \frac{1}{2} m \langle v_z^2 \rangle \quad (12)$$

We can make use of (12) if we manipulate the equation of motion of the particle to obtain the energy equation. The x -component of the equation of motion is

$$m \, d^2x / dt^2 = -6\pi\eta a \, dx / dt + F_x(t) \quad (13)$$

where $F_x(t)$ is the x -component of the random force exerted on the sphere by the molecules of the liquid. [Thoughtful students or a more knowledgeable physicist will recognize a problem with (13); namely, the force of interaction between the liquid and sphere appears twice, once as Stokes' law, which is from a continuum approximation to the fluid, and again from forces which acknowledge the molecular nature of the fluid. The problem is, has this been done consistently, or have forces not been accurately defined, or counted twice? Suffice it to say here, that the procedure gives the answer which has been obtained by a variety of more careful techniques. As you will see almost immediately, the presence or absence of $F_x(t)$ does not matter here in any event.]

We have also not included gravity. If we did, the sedimentation rate would be one of the consequences of our calculation. Indeed, the student should include gravity and be satisfied that the spheres will not accumulate at the bottom of the container by the end of the semester. In fact, the sample containers should not be shaken, because large impurities do fall to the bottom in relatively short times, and such particles, if numerous enough, can seriously interfere with the experiment.

Ignoring gravity, then, we must cast (13) into a form which will yield a kinetic energy. The trick is to multiply (13) by x and average:

$$m \langle x \, d^2x/dt^2 \rangle = -6\pi\eta a \langle x \, dx/dt \rangle + \langle x \, F_x(t) \rangle \quad (14)$$

Since $x(t)$ and $F_x(t)$ are uncorrelated, the last term of (14) is zero. The first term on the right side can be written

$$6\pi\eta a \langle x \, dx/dt \rangle = -3\pi\eta a \, d\langle x^2 \rangle / dt$$

The left side may be written

$$m \langle x \, d^2x/dt^2 \rangle = m \left(d\langle x \, dx/dt \rangle / dt - \langle (dx/dt)^2 \rangle \right)$$

The net x -displacement and the x -velocity are uncorrelated, so $\langle x \, dx/dt \rangle = 0$, and $m \langle (dx/dt)^2 \rangle = k_B T$ from the equipartition theorem. Putting all of these together gives the result

$$k_B T = 3\pi\eta a \, d\langle x^2 \rangle / dt \quad (15)$$

Integrating, we get

$$\langle x^2 \rangle = k_B T t / 3\pi\eta a \quad (16)$$

Comparison with (8) yields the Stokes-Einstein relation

$$D = k_B T / 6\pi\eta a = k_B T / 3\pi\eta d \quad (17)$$

Finally, comparison with (9) gives for the inverse of the correlation time

$$\tau_c^{-1} = 32\pi n^2 \sin^2(\theta/2) \, k_B T / (3\lambda^2 \eta d) \quad (18)$$

The wavelength λ is the wavelength in air, so the laser wavelength in air, 632.8 nm, must be corrected by the index of refraction, $n=1.333$, of water. For 200 nm diameter spheres in water, with 90° scattering angle, τ_c is about 0.7 ms.

V. What has been neglected?

The discussion above has attempted to give as simple a picture as possible of the origin of the fluctuations in the intensity of the scattered light. The final result for τ_c is in fact correct only because the answer was known in advance, and care was taken to choose factors in the derivation given above to get the right answer. In particular, the

dephasing of one radian in Equation (5) is arbitrary, and such arbitrary choices are not needed in a full-blown treatment.

There are other factors that have been neglected. One of them is the fact that single particle scattering, which, from the above discussion should give rise to no fluctuations in the photocurrent does produce, because of the nature of the PMT, a very wide bandwidth noise spectrum (called "shot noise") which is always present as a background noise on which the two-particle scattering fluctuations are superimposed. We also have not shown that the decay of intensity from the two-particle scattering is exponential, as it is, nor have we discussed the complication from having more than two particles contributing to the scattered intensity at once. The experiment may be done in the frequency domain rather than, as here, in the time domain. Then the experiment measures the noise spectrum. An exponential decay in time results in a Lorentz-shaped line in frequency space centered at zero frequency, and the "shot noise" signal always present from the photomultiplier adds a constant to the frequency spectrum. Thus the spectrum has the form

$$S(f) = \Gamma / (4\pi^2 f^2 + \Gamma^2) + \text{const}$$

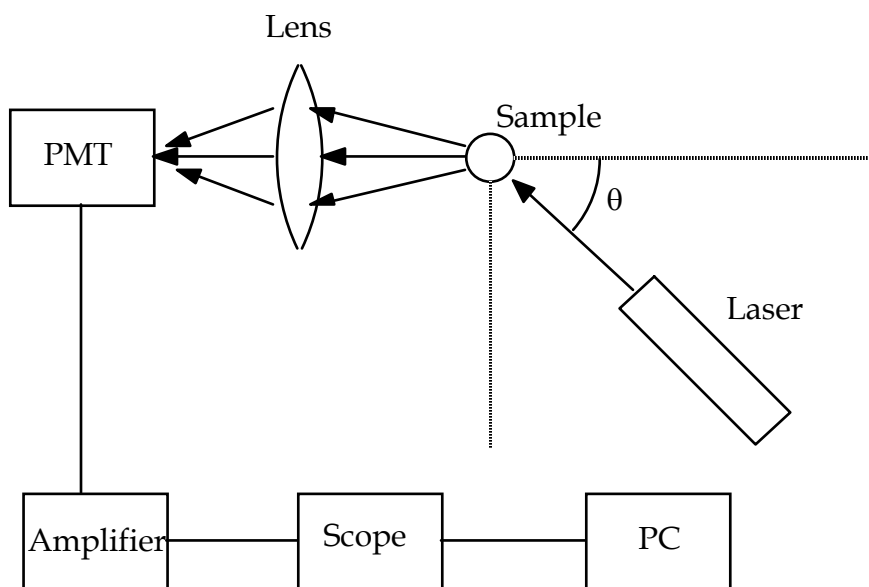
where $\Gamma = \tau_c^{-1}$, as given in Equation (18).

VI. Doing the Experiment

A. The Apparatus

The equipment is relatively simple, yet representative of apparatus used in research. Figure 4 provides a block diagram of the set-up.

Figure 4 Block diagram of apparatus.



The He-Ne laser provides a monochromatic and steady beam of red light (with minimal amplitude modulation at the power line frequency, for example). The laser is mounted on a rotating carriage which allows one to observe scattering for a range of angles from 90° to 35° . Note that the markings on the baseplate are the complement of the scattering angle, θ . The beam is focused by a lens (40 mm focal length) mounted at the end of the laser onto a cylindrical sample cell containing a suspension of latex (polymer) beads in water. Light is scattered away from the forward direction by the beads. This scattered light is collected by a lens (29mm focal length) and focused on the photocathode of a photomultiplier tube (PMT). The PMT is at the focal point of this lens so that plane waves scattered in the sample are, in principle, selected. The region seen by the PMT is limited by a small circular aperture, an iris, in the sample holder.

The PMT is a device that is very sensitive to light; and its output is a voltage proportional to the intensity, $I(t)$, of light on it. The argument t in $I(t)$ is explicitly written to call attention to the fluctuating nature of the signal. The fluctuations are not random, although they have a very large random component. The fluctuations change in response to the dynamics of the random motion of the latex spheres in the solution. The fluctuations of interest are characterized by an intrinsic time τ_c which depends on

the particle size, the scattering angle, and the wavelength of the laser light in the sample.

The PMT output is fed into an amplifier. To minimize leakage of 60Hz line voltage onto the signal, the amplifier is powered by a battery. A battery charger is attached to the amplifier. The amplifier output is fed into the first and fourth channels of a digitizing oscilloscope. Channel four is used to trigger the scope on the largest voltage fluctuations and channel one records and averages the signal. Analysis is performed on a PC after data transfer from the digital oscilloscope.

B. The Samples

The samples for this experiment consist of latex spheres suspended in water. The diameter of the latex spheres differs from sample to sample. The sample cell itself is a glass vial wrapped on top and bottom with Scotch tape which serves as a spacer between the glass of the sample cell and the aluminum of the sample cell holder to prevent scratching of the glass. Care should be taken when handling these samples. They should never be shaken since this will allow larger “dirt” particles which had settled to the bottom to mix with the spheres. Also, wear gloves whenever handling the cells since dirt or scratches will lead to erroneous results.

In fact, scratching the glass may lead to a phenomenon known as heterodyning (see the book by Berne and Pecora). In this case, incident light is deflected from the glass and can recombine with the light scattered from the spheres. This results in a value for the characteristic time for the intensity fluctuations which differs by a factor of 2 from that obtained by examining the scattered light alone (the homodyning case). For this apparatus, it is possible to observe the effects of heterodyning at the smaller scattering angles.

C. The Experiment

The experiment is done by processing the fluctuating PMT signal in a particular manner. As shown in the appendix, if you observe the average of the signal formed when the fluctuating voltage crosses some threshold, you will observe an exponential decay

$$\langle V(t) \rangle = V_0 e^{-t/\tau_c} + B. \quad (19)$$

If the threshold is too low, V_0 will be small compared to B and you will not be able to observe the exponential decay. The experiment consists of setting a scattering angle, finding an appropriate threshold, collecting a time averaged signal, and using data analysis to extract τ_c .

You will first take several sets at a single scattering angle to determine the reproducibility of your value of τ_c . 30° is a good angle to start with. Then take data at a

variety of scattering angles. You are to verify the form of Equation 18 and to determine the sphere diameter. What follows must be repeated at every angular setting for each sample. Use the thermometer to measure the temperature for each run and properly account for any variations using Equation 18.

First put the sample in place, making sure not to shake it. Check that the black cloth is properly draped over the PMT housing and is not blocking the iris. Select a scattering angle, keeping in mind that the angle that is to be entered into the equations presented in section 1 is the complement of the angle marked on the base plate. The laser should already have been turned on, since it requires a rather long warm-up time. Check to make sure that the beam block on the laser is in the open position. Make sure the Bertran 214 power supply for the PMT is on and set to approximately -800 Volts. Never set this power supply above -1150 Volts, as this will damage the PMT. (Don't turn the laser or the high voltage supply off during the entire period you are working on the experiment.) Turn on the PMT amplifier with the switch on top of the PMT housing. (Turn the amplifier off and turn the recharger to AC when the apparatus is not in use.) Turn on the scope and observe the input to channel 1 while triggering on channel 4 with a 0.V triggering level. The scope should be AC coupled. The output should look noisy, and any coherent modulation at the frequency of the power line should not be visible.

While taking data, the objective is to set the scope so that it will trigger on only the highest of the noise fluctuations, but not to set the trigger level so high that it does not trigger at all. A rate of about one trigger per second is fine. Finally, the scope must display the average of the incoming data. In general, you will have to experiment with each new sample and at each new scattering angle to determine the appropriate triggering and display parameters. Take some time and observe how the average signal evolves from noise to a recognizable time dependence as the trigger level is increased in steps, finally triggering on only larger signal fluctuations.

When you wish to begin taking data, clear the screen of the scope, so that the averaging will not be affected by signals occurring during the setting up of the experiment. If all is as it should be, the scope should immediately begin collecting and averaging incoming signals to produce a trace on the screen which should with the passage of time, begin to look more and more like a decaying exponential. When the trace looks like it is not changing much with each subsequent trigger, stop the accumulation of data on the scope. Keep in mind that the scope will only average the first 256 events; this number divided by the approximate trigger rate will tell you the longest time over which you may reliably collect data. Be sure the time scale of scope is long enough to see the averaged signal decay into a flat background. Also, put a small delay time on the trace so you can see some of the pretrigger data. When you have satisfactory data, transfer the data to the computer for analysis. On the computer, open the file marked "Benchlink" on the Windows screen. In Benchlink under the Waveform

menu, select new; and the data will appear on the screen. Under the same menu, you can select save and store your data as a time, amplitude file (filename.csv). Please place your data in a folder with your name on it and back-up your data on a disk.

After you have collected an averaged signal, estimate the parameters describing the exponential. Using the cursors on the oscilloscope, estimate V_0 , τ_c , and B on the trace and record these values in your notebook. Also estimate the scatter of the voltage points (the width of the line of points on the scope trace). This will give an estimate of the error bar to assign to each voltage reading. Are the error bars constant for all times across the trace? Collect data over the full range of angles available. At a few angles, collect multiple data sets. This will help you find the error in τ_c .

If you observe a spike at short times, investigate the nature of this signal. Without shaking the sample, remove it from its holder and put a small piece of paper into the holder so some static light enters the detector. Collect an averaged signal and roughly characterize the time over which it falls. This will give you an estimate of the number of points to eliminate from the data from the latex suspension.

Data analysis is performed using least squares methods described in recitation. Discuss with the instructor whether automated or “hand” search of the χ^2 hypersurface should be performed. Be sure you use your estimates of V_0 , B , τ_c to guide your search.

References

- 1) Berne and Pecora, Dynamic Light Scattering, call number 535.84 b52d
- 2) Schumacher, R. T., “Brownian motion by light scattering revisited”, Am. J. Phys. **54**, 137.

APPENDIX I. MORE SCATTERING THEORY

In this appendix I will show that the signal decay following triggering at an arbitrary threshold h is a decaying exponential with time constant $(2D\Delta k^2)^{-1}$, independent of h and of the number of scattering spheres in the beam, as long as the beam is not so strongly scattered as to substantially attenuate it across the length of the scattering cell.

We begin with eq.(2), extended to M particles:

$$I \propto \left[\sum_{i=1}^M \cos(\omega t - \Delta k \cdot r_i) \right]^2 \quad (A1)$$

Just as in the transition to eq. (5) we expand using the $\cos(a+b)$ identity, average over an optical period $T=2\pi/\omega$, and throw away the d.c. term, as the apparatus does with a blocking capacitor, to obtain in some normalized units:

$$I \propto \left[\sum_{i \neq j} \cos \Delta k \cdot (r_i - r_j) \right] \quad (A2)$$

The difference between the incident and the scattered wave vector, Δk can be taken to be in the x -direction, so the argument of the cosine in (A2) becomes $\Delta k(x_i - x_j)$. At $t=0$ the particles are at x_i^0 , $1 \leq i \leq M$. If we set the proportionality constant in (A2) equal to 1, the threshold intensity h is given by

$$h = \sum \cos[\Delta k(x_i^0 - x_j^0)] \quad (A3)$$

From here on we will represent the position of each particle by $x_i^0 - x_i$, so that in the random walk evolution of a particle's position the mean value of the variable x_i is zero, as is its initial value: $x_i(0)=0$. The experiment takes, in effect, an *ensemble* average of eq. (A2) because the experiment is repeated N times and the result is averaged. In the derivation that follows, we will denote the average of I as

$$\langle I \rangle = \lim_{N \rightarrow \infty} \sum_{i=1}^N I/N$$

with our theoretical results valid strictly only in the limit as $N \rightarrow \infty$.

Of course, $\langle h \rangle = h$ follows, but note there are an infinite number of different configurations of

pairs of initial positions that satisfy eq. (A3). We will assume that $t=0$ whenever particles align themselves to satisfy the threshold condition (A3), unless, of course, that situation has already happened within the past few time constants. That is also the way the apparatus works.

Ensemble averages of powers of x_i are computed with the distribution function $P(x,t|0,0)$, which gives the probability that a particle is at (x,t) given that it was at $x=0$ at $t=0$. Einstein showed that such a function satisfies the diffusion equation

$$\partial P / \partial t = D \partial^2 P / \partial x^2 \quad (\text{A4})$$

The solution of (A4) is the function

$$P(x,t|0,0) = (1/4\pi Dt)^{1/2} \exp(-x^2/4Dt) \quad (\text{A5})$$

Thus the n^{th} moment of a statistical variable x is

$$\langle x^n \rangle = \int_{-\infty}^{\infty} x^n P(x,t|0,0) dx \quad (\text{A6})$$

Note that the odd moments of x vanish, as do the ensemble averages of odd functions of x : $\langle \sin kx \rangle = 0$. With the aid of integral tables you can also verify the useful identity

$$\langle x^{2n} \rangle = (2n-1)!! \langle x^2 \rangle^n \quad (\text{A7})$$

where $(2n-1)!! = 1.3.5\dots(2n-3)(2n-1)$.

It should be remarked that eq. (A4) reduces to a non-physical delta-function at $t=0$ when used in integrals such as (A6). The behavior of the dynamics of Brownian motion at small times was investigated by Ornstein and Uhlenbeck (Physical Review, **36**, 823 (1930)). They found that modification of the dynamics was necessary for times on the order of $m/3\pi\eta d$, where m is the particle mass, d its diameter and η the viscosity of the medium. The student should verify that the short time scale is on the order of 10^{-9} seconds for the latex spheres used in this experiment. They also verified that the identity eq. (A7) was valid for the position distribution that is correct for all times, including the very short. The shortest time scale of our experiment, the inverse of the digitizing rate, is four to five orders of magnitude larger than $m/3\pi\eta d$.

Now we can complete the derivation. Write the cosine terms in eq. (A2) as

$$\begin{aligned} & \cos[\Delta k(x_i - x_i^0 - x_j + x_j^0)] = \\ & \cos\Delta k(x_i - x_j) \cos\Delta k(x_i^0 - x_j^0) + \sin\Delta k(x_i - x_j) \sin \Delta k(x_i^0 - x_j^0) \end{aligned} \quad (A8)$$

The ensemble average of the two terms on the right of (A8) is the product of the terms that make up each, since the subsequent development of $(x_i - x_j)$ is independent of the original positions. Since the sine function is odd, only the first term survives, giving

$$\langle I \rangle = \sum_{i \neq j} \langle \cos\Delta k(x_i - x_j) \rangle \langle \cos\Delta k(x_i^0 - x_j^0) \rangle \quad (A9)$$

We now expand $\cos\Delta k(x_i - x_j)$ in a power series:

$$\begin{aligned} \cos\Delta k(x_i - x_j) &= \sum_{n=0}^{\infty} (-1)^n \Delta k^{2n} (x_i - x_j)^{2n} / (2n)! \\ &= \sum_{n=0}^{\infty} (-1)^n \Delta k^{2n} / (2n)! \sum_{p=0}^{2n} \binom{2n}{p} x_i^p x_j^{2n-p} \end{aligned} \quad (A10)$$

For convenience in taking the ensemble average of (A10) define $p=2q$, so the sum over p from 0 to $2n$ becomes a sum over q from 0 to n , and the ensemble average of the sum over q is

$$\sum_{q=0}^n \binom{2n}{2q} \langle x_i^{2q} \rangle \langle x_j^{2n-2q} \rangle \quad (A11)$$

where again the ensemble average of the product is the product of the ensemble averages since the motions of the particles i and j are uncorrelated. We now use the identity (A7), and use $\langle x_i^{2q} \rangle \langle x_j^{2n-2q} \rangle = \langle x^2 \rangle^n = (2Dt)^n$ since the separate ensemble averages give the same result. We have now

$$\langle \cos\Delta k(x_i - x_j) \rangle = \sum_{n=0}^{\infty} (-1)^n (2\Delta k^2 Dt)^n \sum_{q=0}^n \binom{2n}{2q} (2q-1)!! (2n-2q-1)!! / (2n)! \quad (A12)$$

The term to the right of the sum over q in (A12) may be reduced using

$$\binom{2n}{2q} = (2n)! / (2n-2q)!(2q)!$$

and

$$\sum_{q=0}^n \binom{n}{q} = 2^n$$

which, combined with the numerator, becomes

$$\langle \cos \Delta k(x_i - x_j) \rangle = \sum_{n=0}^{\infty} (-1)^n (\Delta k^2 2Dt)^n (-1)^n / n! = \exp[-2\Delta k^2 Dt] \quad (\text{A13})$$

Thus (A9) becomes

$$\langle I \rangle = \sum_{i \neq j} \langle \cos \Delta k(x_i^0 - x_j^0) \rangle \exp(-2D\Delta k^2 t) = h \exp[-2\Delta k^2 Dt] \quad (\text{A14})$$

where h is substituted, using (A3).

Equation (A14) is the advertised result. It says that the experiment depends only on the sum of interference terms in the scattering of light off all *pairs* of particles, and that the decay time constant of an unusually large fluctuation is in fact independent of the extent of that fluctuation; i.e., $2D\Delta k^2$ is independent of h . Of course, the result (A14) assumes an infinite number of trials, so you can expect any finite number of passes to deviate from (A14) both in shape and decay rate. Nor does (A14) give any obvious guidance about a good strategy for data taking: small h and many passes per second, or large h and fewer passes, but each pass more likely to decrease (decay) rather than increase, since (A3) has a maximum value and *any* subsequent particle motion away from the configuration that makes $h > 0$ necessarily makes $d\langle I \rangle/dt < 0$. -----