Quasi-elastic Rayleigh Light Scattering

Please read this entire document before doing anything else with this experiment.

Introduction:

In concept, this experiment is very simple: a beam of light passes through a very slightly cloudy sample, and some of it is “scattered” meaning that it leaves the sample in different directions than the incident light beam. By measuring properties of the scattered light, we can learn about what it was in the sample that caused the scattering. Now we add the important fact that the beam of light is a laser beam, which is “coherent” throughout the volume of the sample that is illuminated, meaning that this is an ideal plane wave of light. We can now use what we have learned about waves to understand the details of the scattering process, and find quantitative relations between the source of the scattering and the observable properties of the scattered light.

What scatters light? In general, if light passes through a medium in which the index of refraction is not a constant, a plane wave will not continue to propagate straight ahead as a plane wave. If the index of refraction varies, the plane wave develops “wiggles” on an otherwise plane wave-front, and the light in these wiggles propagates off in other directions. Just what directions, and how intense the scattered light is, depend on the details of the wiggles, like their size and amplitude.

Examples:

* Sound waves make ripples in the index of refraction, and light scattered by them is called Brillouin scattering, after a famous French scientist.

* Random fluctuations in the density of atoms in a gas, that appear and disappear by diffusion, change the index of refraction locally, proportional to the density changes. The light they scatter is called “Rayleigh scattering” after a famous English scientist. This form of light scattering is why the sky is blue; short wavelength (blue) sunlight is scattered more strongly than red light by these random density fluctuations.

* The name Rayleigh Scattering is now generalized to scattering by any small fluctuations in index of refraction that diffuse in the sample, rather than propagating like sound waves. This includes little particles that diffuse by Brownian motion, and fluctuations in concentration in a mixture of two liquids, for instance.

* If one considers the time dependence of the Rayleigh scattering, the time dependence this introduces to the scattered light slightly changes its frequency, so the scattering is not completely “elastic”. Thus it is called “quasi-elastic Rayleigh scattering,” which is what we study in this laboratory. We start by studying a variety of little particles, and measure their diffusion constant, which can be related to their size. This is an important measurement in the study of small objects like protein molecules, for instance.

* We then look at diffusing concentration fluctuations in a two-liquid mixture, as it approaches a critical point at which the two liquids unmix. This is one of the classic experiments in “critical phenomena,” a fundamental topic in statistic physics that led to an important Nobel Prize not too long ago.
I. Things to learn in this experiment:

**Experimental design and coherent light optics:**

The fundamental set-up is based on four elements. First is a diode laser of wavelength 652 nm, and about 30 mW intensity, which can be cut to less that 1 mW, by a filter, for set-up and testing purposes. A mirror and lens system focuses the laser into the center of the sample. Second is a sample oven for precise temperature control, along with its temperature controller. Third is a light collection arm with optics to image the laser beam on a pinhole and optical fiber tip, configured to measure scattered light from a precise volume in the sample. Fourth is the detection electronics system, consisting of a photomultiplier tube and associated electronics, along with a dedicated autocorrelation computer. The autocorrelator and the oven control electronics are connected to a computer that controls the system and takes data. One can learn how each of these elements works.

The optics of this experiment is pretty simple. A lens focuses the laser beam to its smallest diameter in the sample. In the light collection arm, a lens makes a one-to-one image of the beam in the sample on a 100 micron diameter pinhole. The “piece” of that image that passes through the pinhole is the effective sample volume. A few mm behind the pinhole is the tip of a 50 micron diameter optical fiber, which carries scattered light to the photomultiplier. The choices of optical elements and their location is not completely arbitrary, and one can understand them with a few calculations.

**Coherent wave scattering:**

In the effective sample volume, defined by the image of the laser beam on the pinhole in the light collection arm, there are many randomly located particles which scatter light. At any instant the intensity of light scattered at one angle is determined by the coherent sum of the scattered waves from those particles. First, one can understand the scattering of light by one particle, in varying degrees of approximation. Second, one can understand the coherent sum of scattered waves, analyzing the probability distribution of the scattered light intensity, and how it changes in space (laser speckle) and in time, due to diffusion of the particles.

**Fluid dynamics and Brownian motion:**

Small particles immersed in a liquid move ceaselessly due to bombardment by the molecules of the liquid, making the particles move randomly; this motion is characterized by a diffusion constant. The same collisions with molecules are responsible for the drag force slowing down a moving particle, that is, they are the source of the viscosity of the liquid. Einstein saw the connection between these phenomena, one clearly an effect of individual collisions, and the other a property characteristic of macroscopic fluid flow. In his most-referred to paper, he gave us the formula relating the viscous drag force to the diffusion constant. He found that drag and diffusion both depend only on particle dimensions, not mass. You should understand this fundamental physics, an example of the “fluctuation dissipation theorem.”

**Measuring light intensity; data analysis:**

Light intensity is measured by the photoelectric effect, ejection of electrons from the surface of a conductor by incident photons. Each electron is amplified into a short current pulse. We “count photons” in this experiment to measure light intensity. This purely digital quantum measurement allows for the most detailed data analysis of the scattered light intensity possible. It is limited by
the properties of the photomultiplier tube. The diffusive motion of the scattering centers slightly changes the frequency of the scattered light, but we do not make measurements in the frequency domain, but in the time domain, which is completely equivalent, and a good lesson in basic Fourier analysis. The autocorrelation function of the scattered light intensity is our tool for analyzing the dynamics of our samples.

II. Preparation and Initial Problem Set:

Laser Safety:

Start by reading the Brandeis manual on laser safety, and the memo for use of low power visible lasers. You MUST do this before starting the experiment. NEVER look into a laser beam, or allow a beam to be reflected into your eyes or the eyes of someone else in the lab. Before working with any optics in the laser beam, THINK about what you are doing and where the beam might be aimed by what you are doing.

Basics of Handling Optics:

NEVER touch the optical surface of any optical component, lens, mirror, etc. Only handle things by their outer edges or by their mountings. NEVER lay lenses or mirrors on the bench with the optical surface touching the bench. DO NOT leave optical components lying horizontally and uncovered for a long time; they gather dust which can be hard to remove. If you see dirt or a finger print on an optical component, DO NOT try to rub it off with a tissue. Ask for help from the instructor on how to clean things. DO NOT wash optical components with solvents like alcohol or acetone; you may severely damage them.

Experimental set-up:

Learn how to set up the optics and the mechanical adjustments, especially the manipulation of the light collection arm, using the video camera and the optical fiber head. This element of the experiment is somewhat delicate and must be handled with care. Getting good data requires careful adjustments.

Reading:

Read the introductory papers by Clark et al. and by ... Pay special attention to the scattering geometry and the derivation of the autocorrelation function for the scattered light electric field amplitude and intensity.

Some Initial Problems: These problems address coherent light optics.

1) Assume the laser beam of wavelength 652 nm is 1 mm in diameter. It is focused by a 10 cm focal length lens into the center of the sample. What is the diffraction limited narrowest diameter of the beam in the sample?

2) The lens in the light collection arm images the laser beam on the video camera’s CCD detector or on the pinhole, with a magnification of one. The lens, limited by a diaphragm, has an effective diameter of about 3 mm and a focal length of about 4 cm. Does its diameter limit its resolution significantly for this purpose? Assuming the height of the CCD detector is 3 mm, how wide should the focused beam look on the monitor, that is what fraction of the screen height should it be? What diameter pinhole is needed to include the whole focused beam width in the
image plane of the lens?

3) Laser speckle: For an effective sample diameter of 100 microns, the pinhole diameter, we want to collect scattered light from about one laser speckle, or coherence area, in the scattered light pattern. At what distance from the pinhole should we place the 50 micron diameter optical fiber tip to cover about one speckle?

4) Scattered light intensity at one instant: The scattering volume of about 100 microns cubed has dimensions much larger than a wavelength of light. Therefore randomly placed identical particles in that volume produce scattered waves with equal amplitudes and random phases of their scattered wave electric fields. The total scattered wave electric field in a given direction is the coherent sum of those electric fields. Represent this sum with a phasor diagram of randomly oriented unit vectors in the complex plane, which is identical to a two dimensional random walk, with a number of steps equal to the number of scattering particles in the effective sample volume. Using properties of random walks, what is the mean intensity of the scattered light; how does it depend on the number of particles, and does this make sense? What is the distribution function of the scattered light intensity, that is, the distribution of intensities expected to be observed at any one point in a speckle pattern. As the particles move, this is the distribution of intensities we expect to see if we collect light from much less than one speckle area.

5) Scattered light time dependence: For the scattered light electric field amplitude to change and lose all “memory” of its value at one instant, each particle has to move to change the phase of its scattered wave by the order of 2\pi radians, to a new random value. Consider the scattering geometry, characterized by the scattering vector \( \vec{q} \), defined as the vector difference of the incoming (\( \vec{k}_i \)) and scattered (\( \vec{k}_s \)) wave vectors, \( \vec{q} = \vec{k}_s - \vec{k}_i \). The change of phase for the scattered wave, \( \delta \phi \), for change of particle position \( \Delta \vec{r} \) is \( \delta \phi = \vec{q} \cdot \Delta \vec{r} \). For our laser, accounting for the index of refraction of the water, then how far does the particle have to move for right angle scattering? How does this distance vary with magnitude of the scattering wave vector, and therefore with the scattering angle, for a laser of fixed wavelength?

6) How long does it take the particle to move diffusively a distance \( \Delta r \), given its diffusion constant \( D \). Use this to justify the formula for the correlation time for the scattered electric field amplitude, \( \tau_E = 1/Dq^2 \).

III. Experiments to Perform:

- After learning the operation of the software, and adjusting the optics to optimize the signal, study a suspension of monodisperse polystyrene particles in water. Record the autocorrelation function and using Mathematica, extract to intensity correlation time. From it, deduce the particle diameter. Vary the scattering angle and the temperature to test the theory, being sure to account for the temperature dependence of the viscosity of water.

- Make a very dilute sample of skim milk, and study it by 90\(^\circ\) scattering at room temperature. The intensity autocorrelation function will not be a single exponential, due to a distribution of particle sizes. From cumulant analysis, determine the mean particle size and the width of the distribution.

- Study critical opalescence from the sample of nitroethane and 3-methylpentane, using the computerized automated experimental system. Fit the temperature dependent scattered light
intensity and correlation time to the theoretical forms, for temperatures above the critical
temperature.

To make a new critical point sample, the correct composition is:
Nitroethane: 1.128 grams
3-methylpentane: 1.291 grams.

This gives a good total volume in the cell.

• Study some other samples of possible interest.

Books;

J. W. Goodman.
Statistical properties of laser speckle patterns.
In J.C. Dainty, editor, Laser Speckle and Related Phenomena, pages 9-75.
Call Number: TA1677 .L37 1984

Author: Goodman, Joseph W.
Call Number: Science Library - Stacks QC355 .G65

Call Number: Science Library - Stacks QC175 .S68
Author: Stanley, H. Eugene (Harry Eugene), 1941-
Title: Introduction to phase transitions and critical phenomena, by H. Eugene Stanley.

Author: Hecht, Eugene
Title: Optics / Eugene Hecht.
Edition: 3rd ed.

Call Number: Science Library - Stacks QC173.4.C74 A44 2005
Author: Amit, D. J., 1938-
Title: Field theory, the renormalization group, and critical phenomena : graphs to computers / 
Edition: 3rd ed.

Author: Sethna, James P.
Title: Statistical mechanics : entropy, order parameters, and complexity