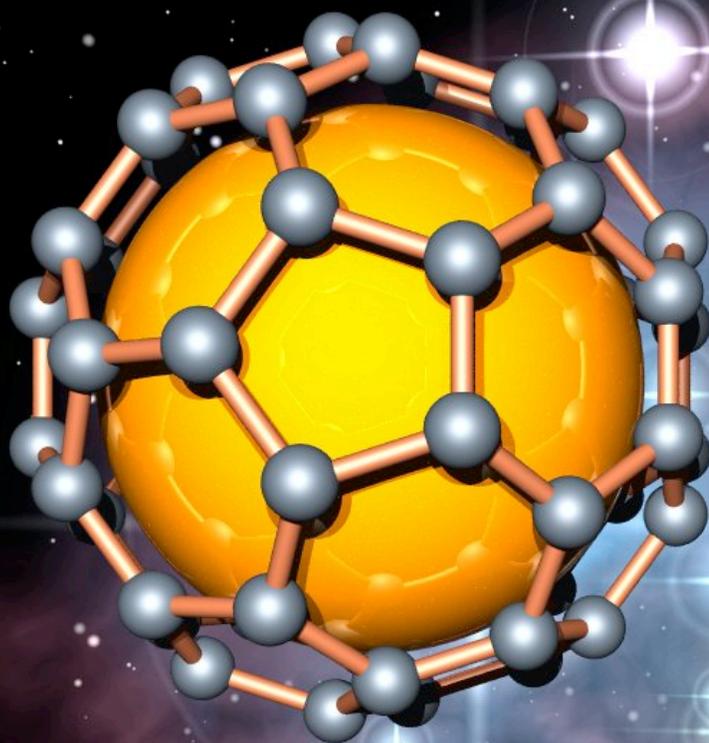


Chemistry at the Space-Time Limit



COSMOS UCI, summer 2007

Lab schedule COSMOS 2007

Lab Groups

Group I

Ahmed Afifi
Andrew Glidden
Yusuke Harada
Jiten Mehta
Gil Tabak

Group II

Magali Barba
Julie Han
Jasmine Harris
Brian Moon
Brian Toms

Group III

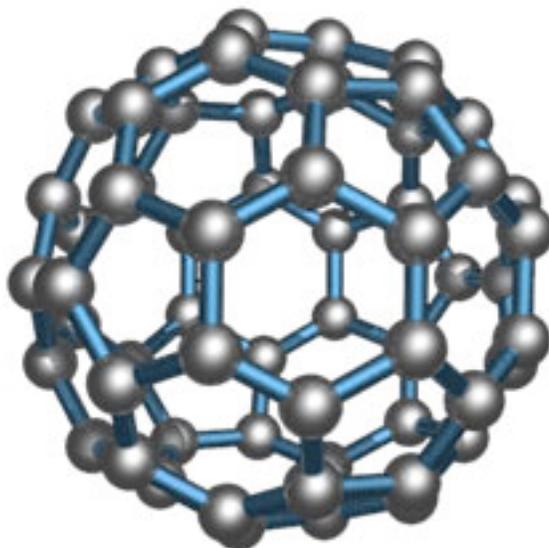
Stephanie Chan
Peter Han
Steven Lin
Amisha Patel

Group IV

Ji Seok Choi
Levey Hao
Bianca Manzano
Danielle Crumley

Lab Schedule by Group

	Session I July 10	Session II July 12	Session III July 17	Session IV July 24	Session V July 26	Session VI July 31
Group 1	Lab 1 RH 481	Lab 2 NS II 1416	Lab 5 FHR B140	Lab 4 FRH 1126	Lab 3 NS II 1446	Lab 6 RH 450
Group 2	Lab 2 NS II 1416	Lab 3 NS II 1446	Lab 6 RH 450	Lab 5 FHR B140	Lab 4 FRH 1126	Lab 1 RH 481
Group 3	Lab 3 NS II 1446	Lab 4 FRH 1126	Lab 1 RH 481	Lab 6 RH 450	Lab 5 FHR B140	Lab 2 NS II 1416
Group 4	Lab 4 FRH 1126	Lab 6 RH 450	Lab 3 NS II 1446	Lab 2 NS II 1416	Lab 1 RH 481	Lab 5 FHR B140



Lab 1

Fourier Transform Infrared Spectrometry

Teaching Assistant: Hyun Min Kim

Lab Room: RH 481

Fourier Transform Infrared Spectrometry

Analysis of MBTE in gasoline and ethanol in both vodka and mouth-wash

Fourier Transform Infrared (FT IR) spectrometry is a powerful technique that allows one to qualitatively identify molecules as well as quantitatively analyze their amount in a sample. This technique can also reveal the interactions between molecules and their environments. In this experiment we will quantitatively analyze MTBE in gasoline and ethanol in both vodka and mouthwash.

MTBE (methyl tertbutyl ether) is one of a group of chemicals commonly known as oxygenates because they raise the oxygen content of gasoline. MTBE is produced in very large quantities (more than 200,000 barrels per day in the United States in 1999). In California, since June 1996, virtually all gasoline sold has contained MTBE as its primary oxygenate in order to meet attainment levels of carbon monoxide.¹ However, there has been controversy over the use of MTBE for making cleaner burning gasoline. The additive has been found to contaminate ground water supplies by release from leaking gasoline storage tanks. MTBE has been classified as a possible human carcinogen and drinking water standards for this compound are being established. As a result, MTBE is being phased out as the major oxygenated additive and other compounds such as ethanol are being considered as alternatives. However, small quantities of MTBE are typically found in gasoline, even where it is not the major oxygenate. The amount of MTBE in gasoline samples will be determined in Experiment I.

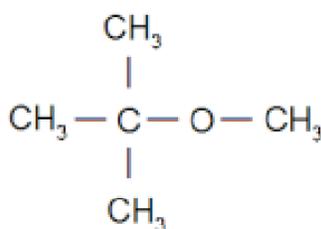


Figure 1: MTBE

Ethanol is a nervous system depressant with a broad variety of physiological effects based on the blood alcohol level. It is found in various amounts in different alcoholic beverages and other household items. Ethanol content is most commonly described in terms of proof, which is just the ethanol volume percentage multiplied by 2. The potency of an alcoholic beverage used to be tested by putting it on gunpowder and burning it for proof it was at least 50% ethanol by volume. In Experiment II, the amount of ethanol in vodka and mouthwash will be measured.

Background

What is FTIR?

The technique of IR Spectrometry takes advantage of the fact that almost every molecule strongly absorbs IR radiation and that the degree of absorption is proportional to the molecular concentration. The wavelength range of the IR region extends from about 0.78 μm to 1000 μm , with the relation between energy (E), wavelength (λ) and frequency (ν) shown below:

$$E = h\nu = \frac{hc}{\lambda} \quad (1)$$

$$c = \lambda\nu \quad (2)$$

In Equations 1 and 2, h is Planck's constant ($6.626 \cdot 10^{-34}$ J sec), and c is the speed of light in a vacuum ($3.00 \cdot 10^8$ m/s). In IR techniques, the absorption or transmission of the IR radiation is commonly measured vs. wavenumber, which is just the reciprocal of the wavelength, expressed in units of cm^{-1} . Thus the range of wavenumbers corresponding to the IR spectrum would be about 12,800 to 10 cm^{-1} . This is broken down into three main IR regions: near-IR (12,800 to 4000 cm^{-1}), mid-IR (4000 to 200 cm^{-1}), and far-IR (200 to 10 cm^{-1}). The most commonly scanned wavenumbers are from 4000 to 670 cm^{-1} , which encompass absorptions by the majority of common organic functional groups. This range of energies causes vibrational excitation in molecules. For a molecule to absorb IR radiation, it must change its dipole moment upon vibration, and the frequency of the radiation must exactly match the natural vibrational frequency of the molecule, resulting in a change in the amplitude of the vibration. Some simple molecules (O_2 , N_2 , etc.) have no fluctuating dipole moment, and so they do not absorb IR radiation. But many vibrations of MTBE and ethanol change the dipole moment; such vibrations are said to be IR active.

There are two fundamental types of molecular vibrations: stretching and bending. Stretching consists of a change in the distance along the axis of a bond between two atoms. Bending consists of a change in the angle between two bonds. There are four types of bending vibrations: rocking, twisting, wagging and scissoring. Organic functional groups have particular absorption peaks that can be used in qualitative analysis, varying only by the molecular environment. For example, the "ether band" of MTBE around 1092 cm^{-1} is easily distinguishable from absorptions by other components of gasoline. From quantum theory, the vibrational states are quantized and the allowed vibrational transitions are those in which the vibrational quantum number changes by unity. The more atoms there are in the molecule, the more complicated the IR spectrum becomes due to increased vibrational coupling and possible overtone peaks and combination bands. These effects create a unique IR absorption spectrum for each molecule that can be used as a fingerprint in qualitative experiments.

Quantitative analysis with FTIR

Infrared spectrometry can be used for quantitative analysis because band intensities are related to the concentration and path length of the sample through the BeerLambert Law, shown in the equation below.

$$A = \epsilon \cdot l \cdot C \quad (3)$$

In the BeerLambert Law, A is the Absorbance, ϵ is the molar absorptivity in $L/(\text{mol}\cdot\text{cm})$, l is the path length in cm and C is the concentration of analyte solution in mol/L . If the absorbances of a series of known standard solutions are measured, a plot of Absorbance vs. concentration can be made and least-square analyzed. Following the expected linear dependence format, $A = \text{slope} \times C + \text{offset}$, the slope of the linear plot would be equal to ϵl , allowing determination of the molar absorptivity if l is known (typically 1 cm). Also, an unknown solutions concentration can be determined after its absorbance is measured and applied to the linear least squares fit.

How the IR spectrometer works

Most IR instruments used today are of the Fourier Transform type. As shown in the Figure below, an IR source emits IR light that is passed through an interferometer and incident on a sample. The transmitted IR intensity is measured by a detector. A laser beam (632 nm) is used to trace the beam path and helps sample alignment. While taking data, the movement of the moving mirror in the interferometer can be observed by looking through the window on the spectrometer.

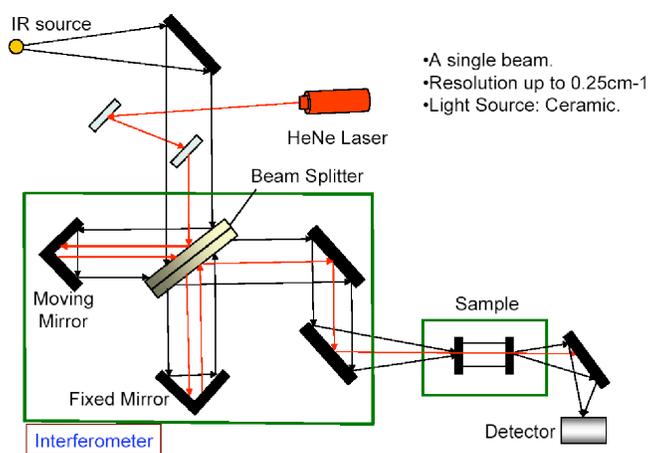


Figure 2: The FTIR spectrometer (Jasco 615)

Experiment I

In this experiment, you will quantify the amount of MTBE in gasoline from its absorption of the infrared radiation transmitted through the solution. The "ether band" of MTBE around 1092 cm^{-1} is easily distinguished from other absorptions due to the hydrocarbon components of gasoline. A series of MTBE/hexane standards can be used to prepare a linear calibration plot of absorbance at the ether band vs. concentration of MTBE. From this plot, the concentration of MTBE in a sample of gasoline can be derived.

Experimental procedure

Note: Detailed instructions on the start up, use, and shut down of the Jasco FT/IR615 instrument are provided in the handout near the machine in the lab.

1. In the fume hood, prepare a stock solution of 2% (volume : volume) MTBE by carefully adding hexane to 1.0 mL of MTBE until you obtain a total volume of 50.0 mL in a volumetric flask. There are volumetric pipettes available for adding 1.0 mL of the MTBE.
2. From this stock solution, make five solutions corresponding to 0.2%, 0.6%, 0.8%, 1.0%, and 1.6% MTBE by taking 1.0, 3.0, 4.0, 5.0, and 8.0 mL respectively of the stock solution and adding hexane to a total volume of 10.0 mL in volumetric flasks. Be sure to label each flask with tape. Close the flasks after the preparation to avoid evaporation.
3. Dilute the gasoline sample with hexane to make a 10% (volume : volume) solution by adding hexane to 1.0 mL of the gasoline to a total volume of 10.0 mL of solution. Label the flask and close it.
4. Set the spectrometer resolution to 1 cm^{-1} and the number of scans to 16 by clicking on Measure and then Parameters.
5. Using a plastic pipette, flush the transmission IR salt crystal cell with the hexane solvent several times, then fill with hexane. After that, load this cell into the spectrometer compartment.
6. Take a background spectrum of the hexane solvent and save this spectrum for later use. To do a single beam spectrum, click on Measure then Parameters and under vertical axis choose single for the background and abs for the sample. The spectral analysis software will then automatically ratio the sample spectra with that of the most recent background spectrum.
7. Now take the cell out and flush it with the standard solution you are going to use next. After that fill it with the standard solution and place it back into the spectrometer. Take a spectrum for your first standard and save it.

8. Scale the spectra to focus on the ether peak around 1092 cm¹. Do this by clicking on View then Scale and type in the desired x and y axis ranges. Record the absorbance of the ether peak by moving the red bar to the appropriate peak. The absorbance is listed on the computer screen. Or, you may use Peak Find to locate all peaks and choose the appropriate one from the Table.
9. Repeat steps 7-8 for your remaining MTBE standard solutions.
10. Now, record the spectrum of the gasoline sample and make any necessary dilutions so the absorbance of the ether band falls on the calibration curve. Determine the absorbance of the sample from the same ether peak used in the standards as you did in step 8.

Data Analysis

1. Make a Table of MTBE% concentration vs. Peak Absorbance measured at the top of the ether band at 1092 cm⁻¹ for the standard solutions.
2. Develop a Beer-Lambert Law plot for the MTBE in hexane standards and perform a least squares analysis of the linear best fit line on a computer or by hand on graph paper if a computer is not available. This will give you a dependence in the form:

$$Absorbance = slope \times C + offset, \quad (4)$$

3. Using the slope and offset parameters determined from your fit, calculate the % MTBE in the diluted gasoline sample.
4. Calculate the volume percent of MTBE in the original undiluted gasoline sample. Make sure you take into account the various dilutions.
5. Assign the principal bands in the spectra of MTBE and hexane to the functional groups responsible for these absorptions.

Experiment II

Determination of Ethanol in Vodka and Mouthwash

This part of the experiment will show that infrared spectroscopy can be carried out in water solutions using appropriate infrared-transmitting, but water-insoluble, crystals using the technique of attenuated total reflectance (ATR) FTIR. You will use this technique to determine the ethanol concentration in vodka and mouthwash (Listerine).

This technique allows you to quantitatively measure the absorbance of ethanol in water, even though water is a very strong absorber of infrared radiation itself.

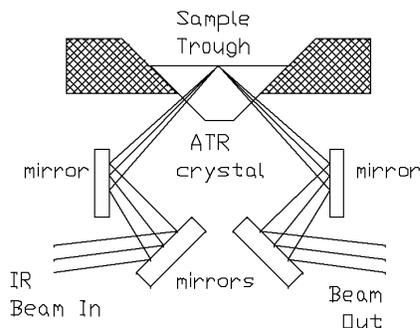


Figure 3: Schematic diagram of single-bounce ATR accessory.

As seen in Figure 3, in the ATR technique the sample is placed on an internal reflection element and the IR beam is directed into the element. It strikes the internal crystal-air interface at an angle greater than the critical angle, and as a result undergoes internal reflection inside the crystal. Most radiation is reflected at the point of internal reflection, but a small fraction is absorbed by molecules present at the surface of the ATR crystal. This absorption of infrared radiation can then be detected and measured.



Figure 4: Schematic diagram of multiple reflections inside a multipass ATR accessory

Increased sensitivity can be obtained by using a multipass ATR accessory. Figure 4 shows a schematic of the light path in such a device; the increased number of internal reflections leads to a proportional increase in the absorbance and hence in the sensitivity.

Experimental procedure

1. Prepare a 10 % (by volume) 95% ethanol in water solution by adding nanopure water to 5.0 mL of ethanol to a total volume of 50.0 mL in a volumetric flask.

2. Now place the liquid multi-pass ATR accessory in the sampling compartment. Be sure not to turn any of the screws on the accessory as they have been tuned to make sure the infrared beam passes into the crystal and back out to the detector properly. When properly aligned, you should be able to see red dots where the HeNe laser is reflecting at the crystal surface along the center of the crystal. Try to count the number of reflections you can see in the crystal. You may want to do this in the dark, since it makes the spots easier to see.
3. Carefully fill the top of the crystal with nanopure water using a pipette (DO NOT SPILL WATER IN THE SAMPLE COMPARTMENT). Take a background absorbance spectrum using 16 scans and 1 cm^{-1} resolution. Remove the water carefully with a plastic pipette and then dab the trough with clean, lint-free tissue. Do not exert any pressure on the glass surface during this procedure.
4. Now fill the ATR accessory with the 10 % ethanol sample. Take a spectrum of this sample and then take another scan immediately afterwards for reproducibility. Scale the spectra around the alcohol peak near 1044 cm^{-1} . Find the absorbance at that peak and record it in your lab book.
5. Prepare a set of standard solutions of 1 % , 3 % and 5 % ethanol in nanopure water using the 10 % ethanol stock solution in 10.0 mL volumetric flasks. Take spectra of all of them using the multi-path cell. Find the absorbance of each solution as you did for the 10 % sample in step 4.
6. Prepare a 10% dilution of vodka with water in a 10.0 mL volumetric flask. Record the spectrum of the diluted vodka sample as before and make any necessary dilutions so the absorbance falls on the calibration curve.
7. Prepare a 25% dilution of Cool-mint Listerine in a 10.0 mL volumetric flask (i.e, take 2.5 mL Listerine and add water until the total volume is 10 mL). Record the spectrum of the resulting sample as before and make any necessary dilutions so the absorbance falls on the calibration curve.
8. Get a metric ruler and measure the length and thickness of the crystal. Do not touch the crystal with your fingers during the measurement.

Experimental procedure

1. Calculate the theoretical number of reflections, N , along the crystal given the formula

$$N = l \cot \Theta / 2d \quad (5)$$

where l is the crystal length, Θ is the angle of incidence (determined by the optical configuration and provided by the manufacture of the ATR accessory) and d is the thickness of the crystal.

2. Develop a Beer-Lambert plot for the ethanol in water standards. Use the least squares fit to determine the % ethanol in the diluted vodka sample, as well as for the Listerine. Follow the same instructions as the plot made in Experiment I.
3. Calculate the volume percent of ethanol in the original undiluted vodka and Listerine samples. Make sure you take into the account the various dilutions.
4. Determine the proof of the original vodka sample.

Group Discussion Questions

1. How does the MTBE % determined in your gas sample compare to the suggested % for gasoline provided by government. Watch units for comparison! Your value is in v/v % MTBE in gasoline whereas the government standard from the Clean Air Act Amendments in 1990 is: "a minimum of 2 % O by mass (or w/w %)"

Data needed:

quantity	value
Density of gasoline	0.66 g/mL
Molar mass of MTBE	88.15 g/mol

2. Convert the concentration of MTBE in your gas sample from v/v% to molecule/mL. If the concentration of MTBE is 1 molecule/mL, what would the absorbance be? Calculate the percentage of IR light that is absorbed by the sample by the following relationship:

$$\%(absorbed) = (1 - 10^{-A}) \times 100\% \quad (6)$$

3. Compare the proof of vodka you determined experimentally with that stated on the bottle. Calculate the percent relative error (% re) assuming the value on the bottle is A , and your value is X :

$$\%(relative) = \frac{|A - X|}{A} \times 100\% \quad (7)$$

4. What other simple experimental techniques can you think of to determine the ethanol content of an alcoholic beverage?
5. If an average drunk human contains 5 L of blood, then how many mL of ethanol are in their blood when their BAC is at the legal limit in California (i.e., BAC = 0.08%)?

6. Compare the volume % of ethanol in vodka vs. mouthwash. Is it possible to determine the volume of mouthwash required to be imbibed to have the legal blood alcohol limit in California (see Problem 5 for help). What other potential problems would you have from accidental swallowing of mouthwash?

Lab 2

The Nature of Light

Teaching Assistant: Hrant Seferyan
Lab Room: NS II 1416

The Nature of Light

In today's experiments, we will learn about the dual nature of light. Although light may be described as a traveling wave propagating through space, we can also discuss its behavior in terms of the amount of energy imparted in an interaction with some other medium. In this case, we can imagine a beam of light to be composed of a stream of small lumps or *quanta* of energy, known as *photons*. Each photon carries with it a precisely defined amount of energy. This energy depends only on its wavelength or frequency.

To understand the operation of the *laser* and other light sources, we need to appreciate the unique character of the light emitted from gases and solids. All radiating bodies when viewed by the naked eye appear to possess a characteristic color: sunlight is white; a piece of hot iron may be orange-red; a sodium street lamp is yellow. If the light from any of these sources is passed through a prism, it spreads out in a series of component colors known as a *spectrum*. Sunlight appears as a continuous band of colors ranging from red through violet, a piece of iron also shows a continuum from dull red to orange, a sodium lamp displays a series of bright, narrow lines. Whether the spectral distribution is a *continuous spectrum* or in *discrete spectral lines* depends on the nature of the source and the temperature of the source.

Experiment I

White Light and Laser Light: Color, Energy, Wavelength

In this experiment, we are going to make a simple spectrometer, using a glass prism, rulers and a detector. The idea behind the commercially available scientific (thousands of dollars worth) spectrometers is almost as simple as the one we will make now in the lab.

First, we will understand the concept of monochromatic light, how it behaves as it refracts in different materials. Then we will see that white light is nothing more but collection of different colors. Then we will use the idea of dispersion in the glass prism to make a simple spectrometer.

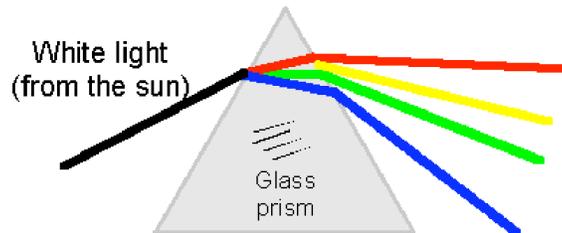
- What is "white light"?

Regular light from the sun or from a light bulb really contains all the colors of the rainbow. But you have to split it up to see this.

- Can light be split?

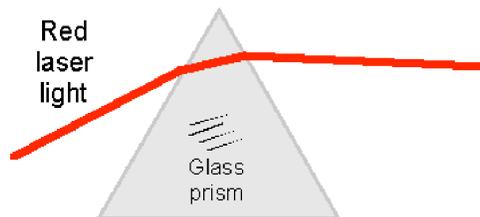
Yes! You can split up white light into its colors with a prism (raindrops act like tiny prisms when they make a rainbow in the sky, and a CD can

break the light up into colors because it has fine grooves like a diffraction grating or a hologram)



- So, what's a laser?

A laser is a special source of light of only one pure color (or *wavelength*). You can't break up laser light into other colors.



Experimental procedure

1. Use a prism to observe the dispersion of light in the prism. Use two different sources: He:Ne laser, and a white light continuum. Observe the differences: white light generates a nice rainbow on the screen. He-Ne laser generates only a single dot. Can you explain the difference?
2. Use a commercial monochromator and try to pass the Hg lamp radiation through it. Scan the monochromator to observe various sharp spectral lines (colors) contained in the spectrum of light emitted by the lamp. Can you explain the observation?
3. Now, with the help of the TA use a prism to make a monochromator. Use a Hg lamp to calibrate your set up. Use different sources to check the functionality of your set up. Use a He:Ne laser to measure its wavelength. How accurate is your measurement?

Experiment II

Double-slit experiment: Light is a wave

The *double-slit experiment* or two-slit experiment consists of letting light diffract through two slits producing fringes on a screen. These fringes or interference patterns have light and dark regions corresponding to where the light waves have constructively and destructively interfered. The experiment can also be performed with a beam of electrons or atoms, showing similar interference patterns; this is taken as evidence of the "wave-particle duality" predicted by quantum physics. Note, however, that a double-slit experiment can also be performed with water waves in a ripple tank; the explanation of the observed wave phenomena does not require quantum mechanics in any way. The phenomenon is quantum mechanical only when quantum particles - such as atoms, electrons, or photons - manifest themselves as waves.

Importance to physics

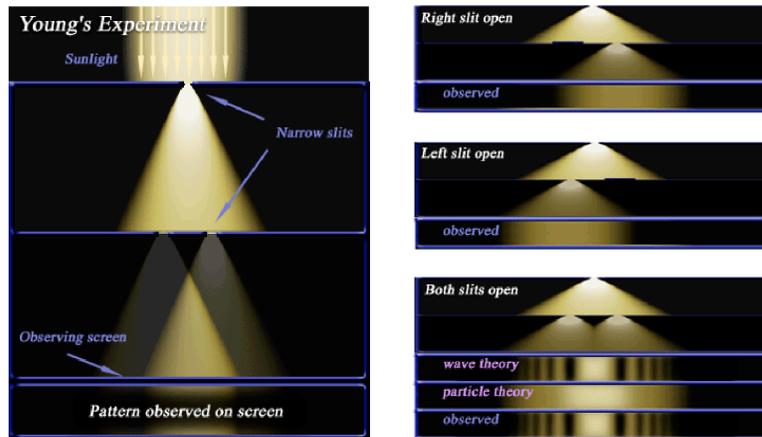
Although the double-slit experiment is now often referred to in the context of quantum mechanics, it was originally performed by the English scientist Thomas Young some time around 1805 in an attempt to resolve the question of whether light was composed of particles (the "corpuscular" theory), or rather consisted of waves traveling through some ether, just as sound waves travel in air.

The interference patterns observed in the experiment seemed to discredit the corpuscular theory, and the wave theory of light remained well accepted until the early 20th century, when evidence began to accumulate which seemed instead to confirm the particle theory of light.

Explanation of Experiment

In Young's original experiment, sunlight passes first through a single slit, and then through two thin vertical slits in otherwise solid barriers, and is then viewed on a rear screen. When either slit is covered, a single peak is observed on the screen from the light passing through the other slit. But when both slits are open, instead of the sum of these two singular peaks that would be expected if light were made of particles, a pattern of light and dark fringes is observed.

This pattern of fringes was best explained as the interference of the light waves as they recombined after passing through the slits, much as waves in water recombine to create peaks and swells. In the brighter spots, there is "constructive interference", where two "peaks" in the light wave coincide as they reach the screen. In the darker spots, "destructive interference" occurs where a peak and a trough occur together.



Quantum version of experiment

By the 1920s, various other experiments (such as the photoelectric effect) had demonstrated that light interacts with matter only in discrete, "quantum"-sized packets called photons. If sunlight is replaced with a light source that is capable of producing just one photon at a time, and the screen is sensitive enough to detect a single photon, Young's experiment can, in theory, be performed one photon at a time – with identical results!!!

If either slit is covered, the individual photons hitting the screen, over time, create a pattern with a single peak. But if both slits are left open, the pattern of photons hitting the screen, over time, again becomes a series of light and dark fringes. This result seems to both confirm and contradict the wave theory. On the one hand, the interference pattern confirms that light still behaves much like a wave, even though we send it one particle at a time. On the other hand, each time a photon with a certain energy is emitted, the screen detects a photon with the same energy. Under the Copenhagen Interpretation of quantum theory, an individual photon is seen as passing through both slits at once, and interfering with itself, producing the interference pattern.

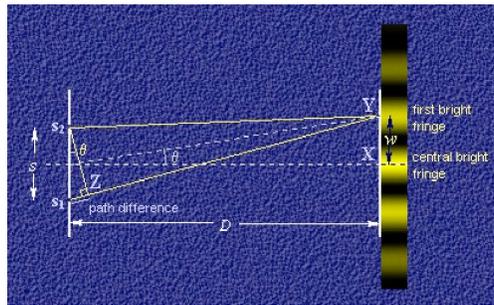
A remarkable refinement of the double-slit experiment consists of putting a detector at each of the two slits, to determine which slit the photon passes through on its way to the screen (If the photon or electron passes through only one slit - which it must do, as, by definition, a photon or an electron is a quanta, or "packet" of energy which cannot be subdivided - then logically it cannot interfere with itself and produce an interference pattern). When the experiment is arranged in this way, the fringes disappear. The Copenhagen interpretation posits the existence of probability waves which describe the likelihood of finding the particle at a given location. Until the particle is detected at any location along this probability wave, it effectively exists at every point. Thus, when the particle could be passing through either of the two slits, it will actually pass through both, and so an interference pattern results. But if the particle is de-

tected at one of the two slits, then it can no longer be passing through both - it must exist at one or the other, and so no interference pattern appears.

The many worlds interpretation states that the particle not only goes through both slits but that it is detected at every possible final location as well – but in different, mutually unobservable worlds.

Conditions for interference

A necessary condition for obtaining an interference pattern in a double-slit experiment concerns the difference in pathlength between two paths that light can take to reach a zone of constructive interference on the viewing screen. This difference must be the wavelength of the light that is used, or a multiple of this wavelength. If the beam from a Sunlight is let in, and that beam is allowed to fall immediately on the double slit, then the fact that the Sun is not a point source degrades the interference pattern. The light from a source that is not a point source behaves like the light of many point sources side by side. Each can create an interference pattern, but the interference patterns of each of the many-side-by-side sources does not coincide on the screen, so they average each other out, and no interference pattern is seen. The presence of the first slit is necessary to ensure that the light reaching the double slit is light from a single point source. The path length from the single slit to the double slit is equally important for obtaining the interference pattern as the path from the double slit to the screen. Newton's rings show that light does not have to be coherent in order to produce an interference pattern. Newton's rings can be readily obtained with plain sunlight. More rings are discernible if for example light from a Sodium lamp is used, since Sodium lamp light is only a narrow band of the spectrum. Light from a Sodium lamp is incoherent. Other examples of interference patterns from incoherent light are the colours of soap bubbles and of oil films on water.



In general, interference patterns are clearer when monochromatic or near-monochromatic light is used. Laserlight is as monochromatic as light can be made, therefore laserlight is used to obtain an interference pattern. If the two

slits are illuminated by coherent waves, but with polarizations perpendicular with respect to each other, the interference pattern disappears.

Results observed

The bright bands observed on the screen happen when the light has interfered constructively where a peak of a wave meets a peak. The dark regions show destructive interference a peak meets a valley.

$$\frac{n\lambda}{d} = \frac{x}{L} \quad n\lambda = \frac{xd}{\lambda} \quad (8)$$

where

λ is the wavelength of light

d is the separation of the slits

x is the distance between the bands of light (also called fringe distance)

L is the distance from the slits to the screen

n is the order of maxima observed (central maximum is $n = 1$)

This is only an approximation and depends on certain conditions. It is possible to work out the wavelength of light using this equation and the above apparatus. If d and L are known and x is observed, then λ can be easily calculated.

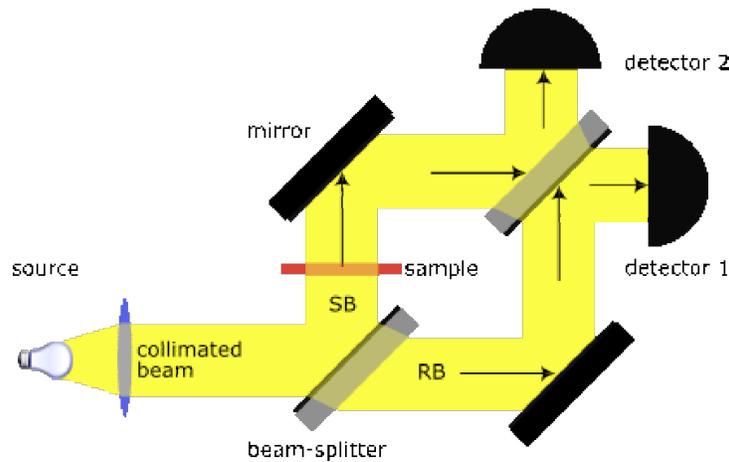
Experimental procedure

1. Use a He-Ne laser, an interferometer slit film and try to observe the fringe pattern on the screen. Experiment with different slit pairs to observe the most canonical pattern.
2. Try to attenuate the radiation with filters, and record it on the camera. Find the appropriate exposure time to record a sharp, crisp picture.
3. Attenuate the beam by a factor of 10, and increase the exposure by the same amount. What do you observe? What would you see if you attenuate it N times and increase the exposure the same amount of time?
4. Calculate the intensity of the laser at which photons hit the camera one by one. How far apart the photons should be from each other in space to be considered separate?
5. Set the camera for a long exposure time, and let it accumulate the pattern. Will you see the same interference pattern?

Experiment III

Mach-Zehnder interferometer

In this experiment we are going to construct a simple interferometer using a He-Ne laser. The idea of interferometer is very similar to the double slit experiment. A single coherent, light source is split into two arms, and overlapped together to create interference pattern. The Mach-Zehnder interferometer (named after physicists Ernst Mach and Ludwig Zehnder) is used to determine the phase shift caused by a small sample which is to be placed into one of the two collimated beams (thus having plane wavefronts) (then called sample beam (SB) as opposed to the reference beam (RB)) from a coherent light source. There are - in contrast to the Michelson interferometer - two detectors: 1 and 2.



Function

A coherent beam is split up by a beamsplitter and each one is reflected by a mirror. The two beams pass a second beam splitter and enter detector 1 and 2, respectively. There are some simple rules for phase shifts due to material (i.e. non-vacuum, which has a refractive index of exactly $n = 1$):

- reflection or refraction at a surface behind which is a medium with lower n causes *no* phase shift
- reflection at a surface behind which is a medium with higher n causes a phase shift of half a wavelength
- the speed of light is slower in medium with $n > 1$, specifically, its speed is:

$$\lambda_{mat} = \frac{\lambda_{vac}}{n} \quad (9)$$

This causes a phase shift proportional to $n \times l$, where l is the length traveled.

Given the above rules, mirrors, including the beamsplitters, have the following properties:

- a $\frac{1}{2}$ wavelength phase shift occurs upon reflection from the front of a mirror, since the medium behind the mirror (glass) has a higher refractive index than the medium the light is traveling in (air).
- let k be the constant phase shift incurred by passing through a standard glass plate on which a mirror resides
- a total of $2k$ phase shift occurs when reflecting off the rear of a mirror, since light traveling toward the rear of a mirror will enter the glass plate, incurring k phase shift, and then reflect off the mirror with no additional phase shift since only air is now behind the mirror, and travel again back through the glass plate incurring an additional k phase shift.

This effect of a sample can be measured with this setup as every slab of material will change the initial situation. Without a sample there is no phase difference for the two beams in detector 1, thus yielding constructive interference: both have incurred wavelength $+k$ phase shift due to two front-side reflections and one transmission through a glass plate. On the other hand, at detector 2 there is complete destructive interference: the lower route beam has experienced $\frac{1}{2}$ wavelength $+2k$ phase shift for its single front-side reflection and two transmissions through a glass plate, whereas the upper route beam has incurred 1 wavelength $+2k$ phase shift for its two front-side reflections and one rear-side reflection, thus yielding a phase difference of exactly half a wavelength, implying that the crest and troughs of the two waves cancel. Therefore, when there is no sample, only detector 1 receives light. If a sample is now placed into beam SB, there will be a variation in the intensities for 1 and 2, which allows the calculation of the phase shift.

Experimental Procedure

1. Use a He- Ne laser and a pair of lenses to expand the beam and collimate it. Make sure that the beam does not diverge over long distances.
2. Use a pair of mirrors, and beamsplitters and construct the interferometer according to the schematics above. In the perfect alignment regime you should see perfect cancelation at one of the detectors.
3. Detune the beam splitter and overlap the beams with the mirror. What do you observe? Why do you see fringe pattern?
4. At zero order alignment (when you see perfect cancelation), put a slab of glass in one of the arms. What do you see? Can you get an idea about the surface roughness of the glass?

Lab 3

Two-photon Microscopic Imaging

Teaching Assistant: Max Zimmerley
Lab Room: NS II 1446

Two-photon Microscopic Imaging

In today's experiments we will learn about a nonlinear optical mechanism that allows one to see distributions of molecules in a microscope. To do these experiments, ultrafast lasers that produce very short pulse are used. We will first make ourselves familiar with the laser set up. We will then use the laser pulses to visualize fluorescent samples in the microscope. Today's experiments show that fluorescence can be the result of 2-photon interactions, and that this mechanisms can be used to investigate our samples.

Experiment I

Getting Familiar with Ultrafast Lasers

In this experiment we are going to make use of an ultrafast laser. This laser delivers pulsed radiation. The duration of the pulses is about 3 ps ($1 \text{ ps} = 10^{-12} \text{ s}$), and the laser output is such that 76 million pulses are produced per second. This translates into a pulse repetition rate of 76 MHz.

This laser contains three important ingredients:

- A *gain medium* that produces light. In our case the gain medium is a sapphire crystal doped with Titanium ions. If we pump this crystal with 532 nm light, the crystal will absorb that light very efficiently, bringing the crystal in a higher energetic state. This excess energy is released in the form of fluorescence. The light emitted is in the range from 700 to 1000 nm and has thus a different color than the incoming pump light. This fluorescence will be used for the 'lasing' process
- A set of *reflectors* that capture the fluorescence light and send it back to the gain medium. The gain medium is thus place in between mirrors, forming a *cavity*, and part of its emitted fluorescence will arrive back at the crystal. This backreflection forms the asis of the stimulated emission process that makes laser action possible. To get the laser light out of the cavity, one of the mirrors in only partially reflecting, the so-called *output coupler*.
- A mechanism that synthesizes pulsed light. The laser light in the cavity is not automatically pulsed. In fact, without a certain mechanism in play, it is continuous, which we call *continuous wave* radiation. In this laser, the mechanism is called *Kerr-lens modelocking*. This is a nonlinear mechanism that gets more effective for higher light intensities. The highest intensities achievable in the cavity occur when all the light is pulsed. In other words, when we force the cavity to operate under conditions in which only modelocked light survives, we can push the cavity to the pulsed mode of operation.

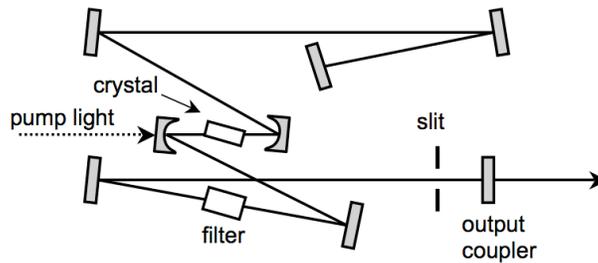


Figure 5: Layout of the Titanium:sapphire laser

Experiment 1.1

Open up the laser with help from the Teaching Assistant and try to identify the different components of the light source. Can you also identify the element that allows tuning of the laser wavelength?

Experiment 1.2

Detect the pulse train with a fast photodiode and visualize the signal on an oscilloscope.

- *What is the temporal difference between the pulses?*
- *Does the inter-pulse spacing correspond to the cavity length of the laser?*
- *Can you measure the width of the individual pulses with the oscilloscope as well?*

The pulse duration is an important parameter that needs to be characterized accurately before we start an imaging experiment. Because these pulses are too short to be measured directly using electronic devices, we will use the light pulse itself to sample its temporal width. We can do this with a device called an autocorrelator. In this device, two copies of the pulse are generated. It also contains a nonlinear element that is sensitive to the overlap of these two copies. When one of the copies is slid past the other as a function of time, the nonlinear element will produce a signal that contains information on the duration of the pulses.

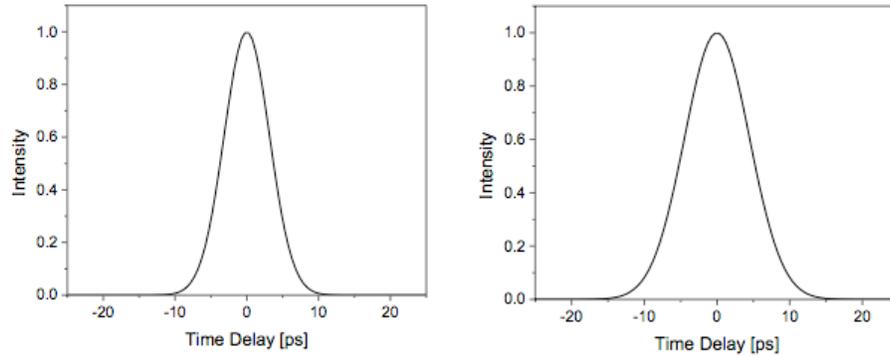


Figure 6: Autocorrelation of picosecond pulses. Left is shown a 10 ps pulse, whereas in the right panel the autocorrelation of this pulse is depicted. To retrieve the actual pulse width, one typically divides the full width half maximum of the correlation curve by 1.414.

Experiment 1.3

Use the autocorrelator to determine the temporal width of the laser pulses. The curve produced by the autocorrelator is a so-called auto-convolution of the actual pulse. Within certain assumptions, we can get the actual pulse duration by dividing the full width half maximum width of the autocorrelation curve by 1.414.

Experiment II

Getting Familiar with the Laser Scanning Microscope

In this experiment we will use a laser scanning microscope. In this microscope, the laser beam is raster scanned across the sample and the computer constructs the resulting image. The laser beams are scanned by means of galvanometric mirrors. These galvos can scan very fast, with image acquisition times up to one frame per second (512 x 512 pixels).

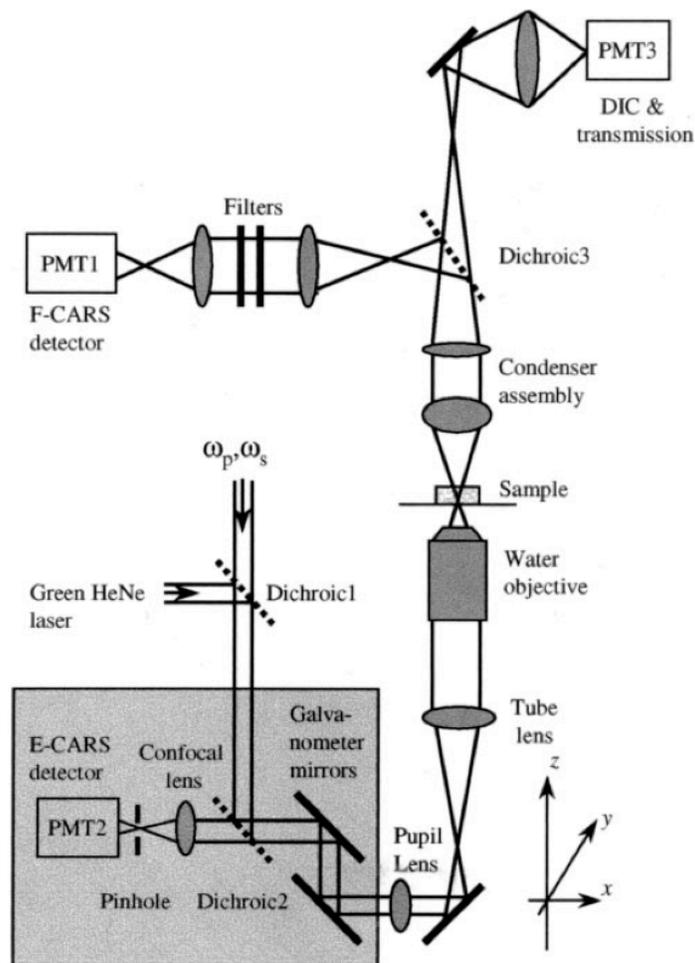


Figure 7: Layout of the microscope

The heart and soul of the microscope is the microscope objective lens. In this experiment we employ a 40x, 1.15 NA water immersion objective. It uses water as the immersion fluid to achieve better focusing properties. It focuses the light to a spot size that is about $0.3 \mu\text{m}$ wide and $1 \mu\text{m}$ long. Because of this special lens, we can resolve minute details in our samples.



Figure 8: Microscope objective

Experiment 2.1

Identify the galvanometric mirrors, the objective and the detector in the microscope. Familiarize yourself with the FluoView program.

Experiment 2.2

Put the sample with the $6 \mu\text{m}$ polystyrene beads on the microscope. Do not forget to immerse the lens with water. Scan the laser beam with the computer program in the transmission mode of the microscope. Save the resulting image on the computer. What do you see?

Experiment III

Two-photon Fluorescence Power Dependence

In regular fluorescence microscopy, a molecule absorbs one photon and subsequently emits one photon. In two-photon microscopy, a molecule absorbs two photons, followed by a regular one-photon emission. In this experiment we will examine the second process, which is only efficiently observed if one used pulsed lasers.

Experiment 3.1

Figure 5 shows the one-photon absorption and fluorescence spectrum of Rhodamine B. At what wavelength do you expect the strongest one-photon absorption and thus the strongest emission? Do you expect any one-photon absorption for a laser wavelength higher than 700 nm ? What is the maximum emission wavelength?

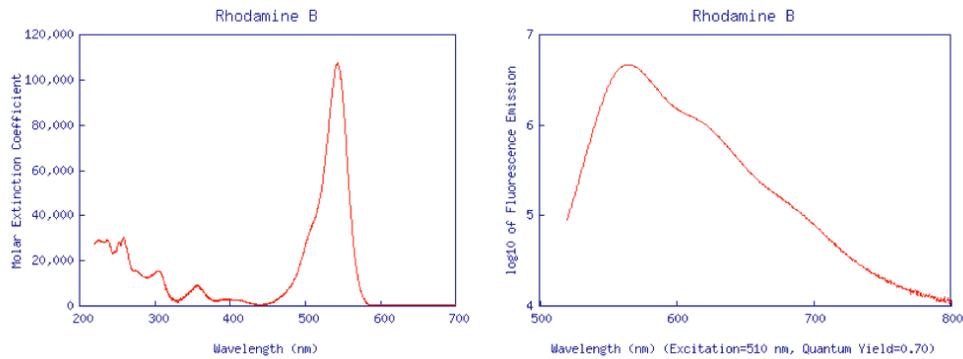


Figure 9: Absorption (left) and fluorescence (right) spectrum of Rhodamine B.

Experiment 3.2

Set the laser wavelength to 800 nm. Try to find the two-photon fluorescence signal from a solution of Rhodamine B. Set the PMT to 400 V. How much power do you have to send into the microscope to observe a strong signal.

Experiment 3.3

Vary the power of the incoming light on a scale from 30 mW to 100 mW in steps of 10 mW and measure the corresponding two-photon fluorescence power. Plot these results with power on the x-axis and fluorescence signal on the y-axis. What do you see?

Experiment 3.4

At constant power, measure the two-photon fluorescence signal at different excitation wavelengths between 750 and 850 nm. Plot the signal as a function of wavelength. Do you observe a trend?

Experiment IV

Two-photon Fluorescence Imaging

The two-photon fluorescence signal can be used to visualize microscopic samples. For this reason, the two-photon fluorescence imaging technique has found many applications in imaging of biological samples that contain fluorescent molecules (see Figure 6). In the experiments below we will use fluorescent polystyrene beads to examine the imaging capabilities of the microscope.

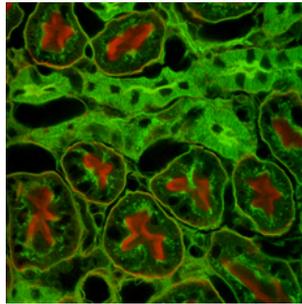


Figure 10: Tissue section labeled with fluorescent agents visualized with the two-photon fluorescence microscope

Experiment 4.1

Prepare a bead sample in agarose as follows:

- *Make a solution of pure water of 10 mL with 2% agarose by weight in a glass vial.*
- *Stir the solution vigorously. Place the vial in the microwave for 30 seconds.*
- *Cut a small well from a double sided sticky sheet and place it on a coverslip. Drop a little bit of the hot agarose solution in the well. Seal the well off with a coverslip.*

Image the 6 μm polystyrene beads in the xy -plane.

Experiment 4.2

Take a depth resolved (xz) image of the beads. Take also a 3D stack (xyz) of images and reconstruct the image using the FluoView program. What do you observe for the signal in the lateral and the axial dimensions?

Experiment 4.3

Image a couple of beads continually for a couple of minutes. Does the fluorescence intensity change over time? Can you think of a reason?

Lab 4

Imaging At the Nanoscale

Teaching Assistant: Danny Wan
Lab Room: FRH 1126

Imaging At the Nanoscale

The experiments in this laboratory are designed to introduce you to the tools of nanometer-scale microscopy. We will be learning to use an Atomic Force Microscope (AFM) and a Scanning Electron Microscope (SEM) to see and characterize materials which are too small to observe using standard optical microscopes.

Experiment I

Atomic Force Microscopy: Precision Imaging of Carbon Nanotubes

AFMs are a type of a Scanning Probe Microscope (SPM) in which a sharp tip is rastered across a sample to generate an image. At each position, the microscope makes a measurement and gradually builds up a 2D or 3D image. Different SPMs measure different physical parameters, and the AFM measures the force applied between the tip and the surface in order to map topography with a resolution of nanometers or even Angstroms. In these experiments you will learn how the topography images are produced and use an AFM to take topography images of single-walled carbon nanotubes (SWNTs).

Most AFMs measure force by deflecting a laser beam off the back side of the sharp tip (or cantilever). The cantilever bends when it contacts the sample, and the amount of bending is a measure of the force between the probe tip and the sample. AFMs use electronic feedback to move the cantilever and maintain a constant force between it and the sample.

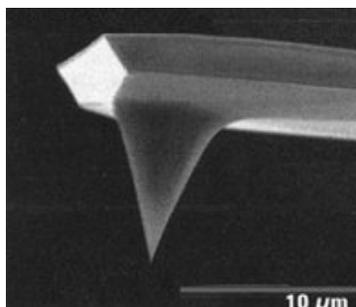


Figure 11: Tip of the AFM.

Experimental procedure

- 1. Prepare the Sample:** A number of samples have been set aside for your use. We will first pick one and inspect it under the optical microscope. Next, it needs to be loaded into the AFM sample holder. We must take particular care not to bump the sample into the AFM cantilever, since the cantilever is small and delicate and can be easily broken.
 - Use the Z Motor to ensure that the tip is completely retracted.
 - Remove the metal cylinder carefully.
 - Place the sample over the hole in the center of the cylinder.
 - Carefully slide the cylinder back into the mounted position under the cantilever.
 - Bring the Z Motor back down to where you can visually inspect that the cantilever is hovering above the sample.
- 2. Align the Photodiode:** To make a measurement, we will focus a red laser on the back of the cantilever and then capture the reflected beam onto a photodiode. Before bringing the cantilever close to the sample, we must make sure that the laser is hitting the cantilever and bouncing onto the detector.
 - With the tip suspended, first check to make sure the laser is on.
 - Open the red-dot alignment window in the AFM software.
 - Look at the green vertical bar and note the signal being measured (the sum value.) We want to make this signal a maximum.
 - Adjust the laser position in X and Y using the two knobs labelled Laser until the sum value reaches a maximum.
 - Next adjust the detector position in X and Y using the two knobs labelled Detector. The computer screen shows you where the laser beam is hitting the detector, and you want to get it centered in both X and Y.
- 3. Tune the Tip:** We will use a delicate, non-contact form of measurement in which the cantilever tip is constantly oscillating up and down. This vibration allows the cantilever to tap along the surface instead of dragging on it. The frequency of the vibration needs to be measured and controlled.
 - First double-check that the tip is still suspended.
 - Open the force curve window on the AFM software and select advanced.
 - Check that the drive amplitude is set to 100, the z-setpoint to 0, and the phase to 270 degrees.
 - Select Full auto-tune and allow the AFM to complete its cycle.

- Select Tune Amplitude.
 - Click Set and confirm your settings if they appear correct.
4. **Tip Approach:** Finally, were ready to bring the cantilever down onto the sample. We will manually move it close and then let the software take over to do an auto-approach. The manual method is much faster, but well manually crush our sample if we adjust too far. So its important to monitor the tip-sample distance by eye and stop once weve adjusted far enough.
- Use the focus buttons (in the stage menu) to adjust the camera focus onto the sample.
 - Manually lower the tip towards the sample by pressing the button labelled z-down.
 - Refocus on the sample as necessary as it moves.
 - Bring the cantilever further and repeat until the sample and tip are within the same depth-of-field so that they are in similar focus.
 - Once you can see both the cantilever and sample in the same video image, the cantilever is close enough. Next open the tip menu and hit the auto-approach button.
5. **Scan:** Once the system is aligned and tuned correctly the system is ready to take images.
- The scanning parameters of interest are the scan size and the speed. Both will affect the resolution of your image. Typical parameters are a 20 micron scan size and a speed of one Hz.
 - Click Scan to begin scanning.
 - The electronic feedback must be adjusted to obtain a high quality image. Good starting parameters are Gain: 5, Proportional: 10, and Derivative: 0. If the signal is oscillating like a sine wave, then lower the Integral gain. Otherwise, keep it as high as possible to maximize resolution.
 - To change the position a small amount, you may drag out the red box on the image and then right-click on it. This will immediately reset the position of the scanning.
 - Once you have a clean image of the sample surface, we will move the sample to image one of the nano-electronic devices on the chip. In order to move the cantilever a large distance, first retract the tip by hitting the Retract button THREE TIMES. Next, hit the X and Y arrow buttons to move the sample around to a new position. When youve selected a new position, use the auto-approach as you did before.

- Scan first along the electrodes, and then rotate the orientation to a 270 deg scan angle. This makes the cantilever travel parallel to the electrodes for better surface detail.
 - While the microscope is scanning, use the tip manual up and down arrows to align the green line with the center point. (Move the tip opposite to where you want the line to go).
 - When good images have been taken, be sure to save the files using the save dialog.
 - Its also possible to export the current PHA and TOP images using file >>export current image.
6. **Unload Your Sample:** When unloading, take care not to damage the AFM.
- Stop any scanning and retract the tip.
 - Lower the stage all the way.
 - Remove your sample and put it back in its storage box.
7. **Analyze Your Image:** If there is time before lunch, you will want to import one of your images into the data anlysis program. Because the image is a quantitative measure of topography, we can use the raw data to directly measure the heights of different objects. Use the line profile tool to measure the height of an electrode and one of the nanotubes you have found.

Experiment II

Scanning Electron Microscopy

Scanning Electron Microscopes (SEMs) work in a similar way to optical microscopes but use a beam of electrons instead of light. Televisions work in a similar way, shooting an electron beam at a fluorescent screen to light up the image. The SEM shoots an electron beam at a sample, scanning it back and forth and recording the number of electrons that bounce off.

Using electrons gives an SEM far greater resolution than an optical microscope because the electrons have much smaller wavelengths than visible light. At the same time, however, the SEM does not have the same resolution as an AFM. In this laboratory, you will learn to image using an SEM and compare the advantages and disadvantages of the two microscopes.

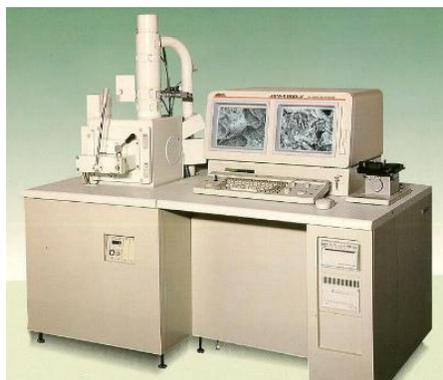


Figure 12: SEM microscope.

Experimental procedure

1. **Prepare the Sample:** As before, a number of samples have been set aside for your use. We will first pick one and inspect it under the optical microscope. Next, it needs to be loaded into the SEM sample holder. The SEM is more robust than the AFM, but loading is a little more complicated because the AFM works in air and the SEM requires a vacuum chamber.
 - First, hit the Vent button on the side of the SEM chamber. This puts air into the chamber so that we can open the door. (Always make sure that ten minutes have passed since the last measurement before venting. You can also use the IR camera to make sure that someone has not left a sample inside the chamber.)
 - Next, put on a pair of latex gloves to keep the SEM clean.

- Open the door to the SEM chamber and inspect the sample stages. Place your sample on some double sided tape on a sample stage. Press down at the corners to make the sample as level as possible. Place your stage into the holder.
 - If your sample is particularly tall, you should check that there is plenty of room for it when the door closes. In general, the z position of the door (the working distance) will read at least 10 mm. As you close the chamber door, you can watch on the IR camera to make sure you're not hitting anything.
 - Evacuate the chamber by hitting the Evac button.
 - Wait 5-10 minutes before proceeding to allow for evacuation of the chamber.
2. **Coarse Focus:** Before we can zoom in to high resolution, we must first adjust the electron beam and find a place on the sample to image.
- Open the SEM program if it is not already open.
 - Check that the magnification of the SEM is relatively low (less than x1000) and then turn on the filament. Press the SCAN2 button on the small console in front of the monitor. We will use this console to control many of the SEM features. Once the filament has turned on, press the Auto-focus button.
 - We will set the high voltage of the electrons to 1 kV. Depending on what you would like to image, you can set the beam as low as 0.1 kV and as high as 30 kV. For small carbon objects like the nanotubes, 1 kV is a good starting value.
 - Adjust the working distance to be 8 mm. If you need to move the stage very far, be sure to watch while using the IR camera to avoid hitting anything inside.
 - Many of the imaging features are automated. After adjusting the working distance, hit Auto-focus again. You can also choose Auto brightness and contrast (ABC) to improve the image.
3. **Select a Part of Your Sample:** The SEM chamber has two knobs for X and Y positioning. This moves the sample around (the beam is moved very small amounts electronically, using electric and magnetic forces).
- Move the stage to an interesting area of your sample. Increase the magnification slowly until it reaches x5000. You can continue to use the Auto-Focus and ABC as you zoom in.
 - Using the focus knob, adjust until the clearest possible image is found. The same knob can be used for COARSE and FINE focusing by hitting the focus button to toggle back and forth.
 - Center any small object in the middle of the screen.

4. **Fine Focus:** Before we can really zoom in farther, we will need to make sure the electron beam is lined up properly. An SEM has three different types of focusing and all three need to be adjusted to optimize the image. First, we will adjust the aperture, a mechanical hole which the beam passes through. Second, we will adjust the stigmatism, which makes the beam symmetric. In general, the aperture and the stigmatism should only need tiny adjustments in order to optimize the imaging.
 - Press the Wobble button. The image should repeatedly blur and possibly move back and forth on the screen.
 - There are two knobs on the upper cylinder of the SEM, up above the sample chamber, for adjusting the aperture. They should be adjusted until the image on the screen has virtually no motion in either direction (there will still be a blurring effect, though. We just want the object to not move up or down or side-to-side). Once the sample is not moving, turn the Wobble back off.
 - Now you may increase the magnification up to x10,000 and focus again.
 - Next, press the STIG button. The same knobs you've been using now adjust the stigmatism of the beam in X and Y. Adjust each independently, each time trying to get the focus of the image better. Turn STIG off and after refocusing the image should be much clearer than when you started. You can repeat the STIG and Focus adjustments a few times if necessary. Just remember to turn STIG off each time to return the knobs to brightness and contrast control.
5. **Image Your Sample:** It can take time and patience to adjust the parameters correctly to obtain a good image. Once everything is focused, you can move around and collect high resolution images. As you move, you may need to keep adjusting your focus.
 - Find the portion of the sample you wish to image and zoom in to about x10,000 - x15,000 nearby. Refocus as best you can in this area.
 - Zoom out for the image you wish to collect.
 - Switch from SCAN2 to SCAN3 mode and then press the FREEZE button.
 - Once the SEM is frozen, you can press the SAVE button to save your image. Then continue scanning.
 - SCAN4 goes even slower than SCAN3 and can give a cleaner image by averaging for a longer time, if you can stand the wait.
6. **Unload the Sample:** As with loading, take care to avoid damaging or contaminating the SEM.
 - Once you have taken your last image, zoom out and shut off the filament.

- Wait 5-10 minutes to allow the filament to cool down.
- Increase the working distance to above 10 mm.
- Put the latex gloves back on and vent the chamber.
- Remove the stage from the SEM, close and evacuate the chamber.
- Remove the sample from the stage.

Experiment III

Energy Dispersive X-Ray Spectroscopy (EDS): Elemental Mapping

When high energy electrons bombard a sample, as in an SEM, the incoming electrons can knock out core electrons and produce x-rays. Since each element of the periodic table has its own unique x-ray fingerprint, these x-rays can be used to identify what your sample is made of. In this experiment, we will use x-ray mapping to determine the elemental composition of a surface. SEM may not have the resolution of an AFM, but this compositional mapping is an important advantage.

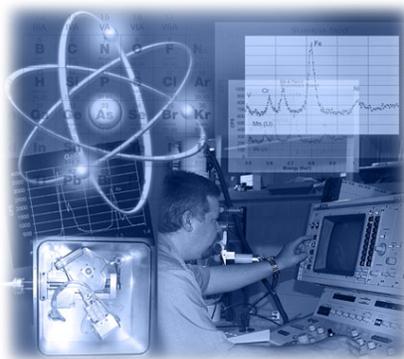


Figure 13: EDS

Experimental Procedure

1. **Check the Liquid Nitrogen (LN₂) level:** Check that there is LN₂ in the cooling vessel. If not, were in trouble. The LN₂ must be filled up at least six hours prior to using EDS in order that everything can cool down.
2. **Load and Image a New Sample:** Follow the same procedures as with loading a sample for SEM imaging. This time, we will image one of the small white beads set aside for your use.
 - Load your sample. The working distance must be kept at 10 mm or greater for X-Rays to hit the detector.

- This time, we will use a much higher accelerating voltage in order to generate lots of X-Rays. Set the beam to 20 kV.
 - Focus on your sample as before. Set the spot size to 50 and refocus.
3. **Acquire an X-Ray Spectrum:** The EDS mapping uses a different software program which runs in parallel with the SEM.
- Open the Noran System SIX software and create a folder for your project. Choose the Spectrum mode. (Also, turn off the IR camera if it is on, since EDS cannot be operated at the same time.)
 - Once the x-ray detector is running, the screen shows you how many x-rays are being detected. You should be reading about 1500-2000 counts/sec. If not, the spot size of the SEM might need to be increased. The dead time of the detector should read slightly above 20%.
 - In the EDS software, click on Acquisition Properties. Most of the parameters have already been set for you, and we will not go over what they all do. You should see that the Live Time Limit is 30 and the low energy cutoff is 100. Check that the max KeV matches your accelerating voltage.
 - Next, click Microscope Parameters and type in the microscope parameters which match the SEM screen. Remember to update this if you go back to the SEM software and change your parameters.
 - Finally, make sure the SEM is not in FREEZE mode and then press the GO button in EDS. The software will automatically start measuring x-rays and categorizing them according to their energy. The software plots a histogram of the x-rays, with peaks showing the most commonly-observed energies. Then, it starts to assign each peak to a different element of the periodic table. These assignments are not necessarily correct and you should check to see if they are reasonable.
 - Once you have acquired long enough that the spectrum is not changing, assign a name to the spectrum and save it.
 - Click the quantify button to analyze your spectrum and check that it is reasonable. If you have correctly identified all of the elements, the total should add up to 100Z%.
4. **Elemental Mapping:** Next, we will change to a mode that can take a picture element-by-element. This can give you an elemental composition of all the features in your imaging area. In the worst cases, though, it can take nearly an hour to obtain a good image.
- First, return to the Acquisition Properties page, where we will change some of the settings. Choose the smallest allowed Resolution and set the Dwell Time to 400-600 microseconds. Next, set the Number of Frames to 30. The software will calculate the Frame Time, which is an estimate of the total time necessary to complete a good image.

- Click on Acquire an Image.
- Select the elements you wish to map based on the spectrum you collected. It can also be useful to select an element that is not present, because this provides a background level for comparison.
- Start the acquisition and let the images build up over time. If you decide to add in another element, you will have to restart the acquisition.
- Save the resulting images.

5. **Unload your Sample:** Take care not to damage the SEM.

- Save your project.
- Exit the Noran System SIX software and turn the IR camera back on.
- Follow the procedure for unloading a sample from the SEM. Dont forget to wear your gloves!

Lab 5

Millikan Oil Drop Experiment

Teaching Assistant: Wendong Xing
Lab Room: FRH B140

Millikan Oil Drop Experiment

The purpose of the experiment described below is observation of the quantization of electrical charge in nature and measurement of the electron charge. This experiment was originally carried out by Robert Millikan (1909) and, according to a recent survey by New York Times, is considered to be one of the most beautiful experiments in science. The experiment relies on carefully balancing the gravitational and electric forces on tiny charged droplets of oil suspended between two metal electrodes. Knowing the electric field, the charge on the droplet can be determined. Measurement for different droplets (when carried out properly) show that their charge is always a multiple of the same number, the charge of a single electron.

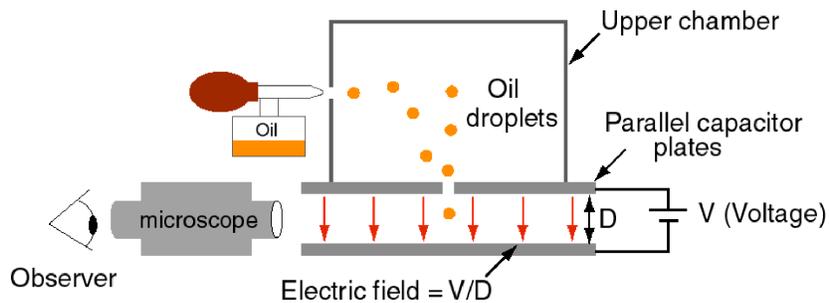


Figure 14: Layout of the Millikan experiment.

The setup of the experiment is shown in Figure 14. Oil drops are introduced into the upper chamber with an oil spray-atomizer, and are allowed to fall through a small opening in the upper plate of the capacitor. At this point the voltage applied to the capacitor is zero. The falling oil drops can be seen through a microscope focused onto the region just below the opening through which the droplets enter the capacitor. Then, a voltage is applied to the capacitor. As a result, some drops will slow down, some will fall faster, and some will reverse the direction of their motion. This is because the droplets tend to get charged through friction with the nozzle of the atomizer as they are sprayed, and the presence of these charges results in extra (electrostatic) forces acting on them. The motion of the charged droplets can then be controlled by changing the voltage applied to the capacitor. Normally, one drop is selected, and its speed is measured in the capacitor's electric field and gravitational field. Using these measurements, the electrostatic forces acting on the droplet (and, consequently, charge) are calculated. The velocity of a droplet is determined by measuring the time it takes for the droplet to travel between two chosen reference points, defined, for example, by the grid in the eyepiece of the microscope.

Motion of the Drops

One has to carefully consider all forces acting on the charged droplet in order to be able to determine the magnitude of the electrostatic force. The equation of motion of the oil drop can be written in the following form (we will take down as the positive direction):

$$m \cdot a = F_e + F_g + F_s \quad (10)$$

Where m is the mass and a is the acceleration of the droplet. Terms on the right-hand side are the electrostatic F_e , gravitational F_g and air-friction forces F_s correspondingly. These can be expressed in the following way:

$$\begin{aligned} F_e &= E \cdot q & (\textit{E} \text{ is the electric field strength, } q \text{ is the charge of the droplet}) \\ F_g &= m \cdot g & (\textit{m} \text{ is the mass of the droplet, } g \text{ is the gravitational constant}) \\ F_s &= -k \cdot v & (\textit{v} \text{ is the speed of the droplet, } k \text{ is the air viscosity-factor that} \\ & & \text{depends on the size of the particle as well as the temperature} \\ & & \text{and pressure of air}) \end{aligned}$$

The electrostatic and gravitational forces are constant, whereas the friction force is proportional to the speed of the particle. Therefore, regardless of the initial state of motion of the droplet, F_e and F_g will accelerate it until F_s is large enough to counteract them, such that the acceleration is zero:

$$m \cdot a = 0 = E_q + m \cdot g - k \cdot v \quad (11)$$

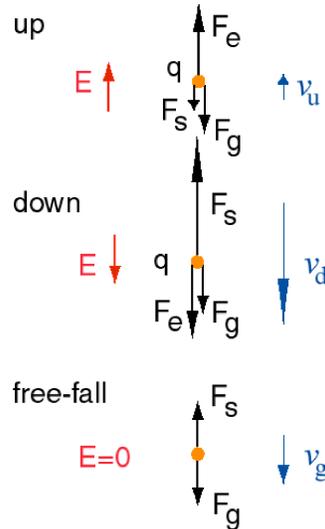


Figure 15: Forces involved in the Millikan experiment

This situation is illustrated in Figure 15 for two different polarities of the electric field and the case when the electric field is zero. Under these conditions the droplet is moving with constant (terminal) speed given by:

$$v = \frac{E \cdot q + m \cdot g}{k} \quad (12)$$

The time required for the droplet to reach this speed is on the order of m/k , a very small number for small (micrometer-scale) droplets. Therefore, during the experiment only the constant-velocity motion is observed. This constant velocity is determined (in part) by the charge q , and, if one measures this velocity, and if parameters E , m are known, k are known, one could find the value of q . E is simply V/D , where D is the distance between the plates of the capacitor and V is the voltage applied to the plates. However, the size of the droplet is normally not known, which means that m and k are not known either. To find m and k we have to look at how they depend on the size of the droplet. If the droplet is roughly spherical in size (a realistic assumption), then:

$$\begin{aligned} m &= 4\pi\rho r^3/3 & (\rho \text{ is the density of oil, } r \text{ is the radius of the particle}) \\ k &= 6\pi\eta r & (\eta \text{ is the viscosity of air}) \end{aligned}$$

Calculation of the charge

The values of parameters ρ and η are known, so that only r is needed to find m and k . This can be done if two measurements of the terminal velocity v_1 and v_2 are done for two different electric fields E_1 and E_2 (for the same droplet). One then has the system of equations:

$$E_1 \cdot q + m \cdot g = k \cdot v_1 \quad (13)$$

$$E_2 \cdot q + m \cdot g = k \cdot v_2 \quad (14)$$

These equations can be used to exclude q and obtain a simple equation for r , which then is used to find m and k , and, ultimately, q . During the experiment, E_1 and E_2 are chosen such that the droplet is raised when one electrostatic field is applied, and lowered for the other. This results in a cyclic motion of the droplet, which allows the speed to be measured at every step of the cycle. Averaging of many measurements minimizes the random errors associated with the measurements and is essential for obtaining the accurate value of the charge. Two choices for E_1 and E_2 are convenient:

- a $E_1 = 0$, so that the droplet is allowed to fall, $E_2 < 0$, so that the droplet is raised by the electric field.
- b $E_1 = -E_2$, so that the droplet is driven by the electric field at both stages of the cycle.

case (a)	case (b)
we have ($E_2 = -E$, where E is a positive number; v_g and v_u are the terminal velocities for free-fall and going up in the electric field correspondingly, see Figure 2):	we have ($E_1 = E = -E_2$, where E is a positive number; v_d and v_u are the terminal velocities for going down and up in the electric field correspondingly):
$m \cdot g = k \cdot v_g$	$E \cdot q + m \cdot g = k \cdot v_d$ $-E \cdot q + m \cdot g = k \cdot v_u$
which is equivalent to:	so that
$4\pi\rho g r^3 / 3 = 6\pi\eta r v_g$	$2m \cdot g = k(v_d + v_u)$
which gives:	which gives:
$r = \sqrt{\frac{9\eta_0 v_g}{2\rho g}}$	$r = \sqrt{\frac{9\eta_0 (v_d - v_u)}{4\rho g}}$
The charge is then found by first calculating and then plugging it into:	The charge is then found by:
$q = k \frac{v_g - v_u}{E}$	$q = k \frac{v_d - v_u}{2E}$

The presented calculations are generally correct. However, one needs to include various corrections to η to obtain accurate values for q (see Appendix A).

Questions to think about

- Without any electric field applied, how does the terminal speed depend on the size of the particle?
- Why is oil used for creating droplets rather than any other fluid?

Experimental Procedure

As discussed above, the experiment consists of raising a tiny, electrically charged oil drop in an electric field and then lowering it again. To raise it you apply a constant electric field on the drop that forces it upward. To lower the drop you can either turn off the electric field and just let it fall or you can reverse the field and force it downward. Generally you raise and lower the drop over a fixed distance, d , and measure the rise and fall times t_r , and t_f , respectively. You need to know the electric field as well. This is just the voltage on the capacitor plates, V , divided by the distance between them, D . The raw data in the measurement

consists of the 5 quantities, d , t_r , t_f , V and D . Generally you establish and measure d and D once and for all at the beginning of the experiment. D is set by the apparatus and is equal to 3.01 ± 0.03 mm. V is established and recorded for each drop and the same voltage (except for the sign) is used to raise and lower the drop if you choose to force it down. The two t 's should be measured many times for each drop; 12 is not overdoing it. Minimizing random errors and keeping track of them is one of the two most important ingredients of a successful oil drop experiment. If you make N measurements of one of the t 's, the best estimate of t will just be the mean (or average) of those measurements. The uncertainty in t will be the standard deviation of the N measurements divided by \sqrt{N} . You want to make N large to get a good estimate of the standard deviation of the measurements and to drive the uncertainty of the mean down.

The other important ingredient of a successful experiment is the selection of really small drops because they tend to have the fewest number of charges on them. If drops have 1, 2 or just a few charges on them, a 10% precision in the charge measurement will show you charge quantization. To see the difference between 100 and 101 charges, you have to measure the charge to a few parts in 1000, a much harder task.

The whole game here is to determine the q on a bunch of different drops. To measure the charge on the drops you want to have drops with only a few charges on them, and the uncertainty in the values of q you derive must be smaller than the charge quantum. If the errors are bigger than that, the charge will look continuous. Needless to say, *Mathematica* (or whatever similar thing you like) makes a world of difference to the labor involved in this.

Appendix A

Corrections to η due to the droplet size, temperature T and pressure P of air.

The formula for the air friction force above was given assuming that the air that the droplet is moving through is a continuous substance. A real gas is not a continuous medium but a swarm of particles that must fly for a distance called the mean free path before they become aware of conditions in their neighborhood. Thus a real gas is less able to organize resistance to an object moving through it than a continuous substance would be. The difference starts to become important only when the moving object is small, meaning comparable with a mean free path or smaller. Thus the resistance force on a small object moving through a gas is less than what you would calculate based on a measurement of the viscosity made with a big object. The oil droplets are normally less than 1 μm in diameter sphere and the mean free path in the surrounding air has been measured as 0.0673 μm . The correct value of η is given by:

$$\eta = \frac{\eta_0}{1 + \frac{b}{rP}} \quad (15)$$

Here r is the radius of the droplet, P is the air pressure in the room in torrs (mmHg); and $b = 5.908 \times 10^{-3}$ torr-cm. η_0 is the value of viscosity that would be observed for large objects, and is given by:

$$\eta_0 = 1.81804 \cdot 10^{-4} \left(\frac{273.16 + T}{293.16} \right)^{3/2} \left(\frac{273.16 + T + 110.4}{293.16 + 110.4} \right) \quad (16)$$

The units of the viscosity as given in are $\text{gm cm}^{-1} \text{s}^{-1}$; T is the Celsius air temperature. The constant out in front is the viscosity at $T = 20 \text{ C}^\circ$.

Both temperature and size-dependent correction have to be taken into account to obtain good results. For example, for $r = 1 \mu\text{m}$ and $P = 760$ torr, the correction to η is almost 8 %. This size-dependence modifies the equations for r such that one obtains the following expressions for r :

In the free-fall case (a):

$$r = \sqrt{\frac{b^2}{4P^2} + \frac{9\eta_0 v_g}{2\rho g}} - \frac{b}{2P} \quad (17)$$

In the case when the field helps to push the droplet down (b):

$$r = \sqrt{\frac{b^2}{4P^2} + \frac{9\eta_0(v_d - v_u)}{4\rho g}} - \frac{b}{2P} \quad (18)$$