

A Size and Scale Laboratory Experiment for Introductory Nanotechnology

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A Size and Scale Laboratory Experiment for an Introductory Nanotechnology Course

1 Abstract

A size and scale laboratory experiment has been developed for an associate level course in nanotechnology. This lab will assist students in conceptualizing the size of particles by completing three exercises: 1. Physically measuring an oleic acid molecule. 2. Comparing the molecules length to other nano-sized objects by creating an enlarged scale which is then compared to familiar objects at normal scale. 3. Examine the quantum effects of quantum dots to introduce students to the unique properties of nanoparticles. This paper details these three exercises and evaluates their effectiveness in teaching students about the physical meaning of measurements with "micro" or "nano" as prefixes.

2 Introduction

The implementation of the principles of nanotechnology have not always been a scientific endeavor. The use of gold and silver nanoparticles in the glazing of pottery was first seen in the work of ancient artisans to give a sparkly luster to their work [1]. Through the study of phenomena such as this, progress in the field of nanotechnology has been made through the measurement, observation and manipulation of small particles. Tools such as the Scanning Electron Microscope, Tunneling Electron Microscope, and Atomic Force Microscopy have been developed and are used to further the study of objects that cannot be resolved with optical microscopes. These tools have also been used to realize a prediction of Richard Feynman. Feynman in his famed 1959 talk, Theres Plenty of Room at the Bottom, predicted the ability to manipulate single atoms to produce tiny machines and new materials [2]. Don Eigler showed that this was possible by using a scanning tunneling microscope to spell out the IBM logo with 35 Xenon atoms [3].

Before scientists had the ability to manipulate single atoms, advances in the study of the size of nanoparticles were made by Nobel Prize winner Richard Zsigmondy, who studied nanomaterials with sizes down to 10 nm using an ultramicroscope, which could resolve particles smaller than the wavelength of light. Zsigmondy also coined the term "nanometer" for describing the size of a particle [4].

This paper has been written to discuss a Size and Scale laboratory experiment that was developed, in conjunction with lecture and virtual reality simulations, to help students

understand the physical meaning of a nanometer. Born from the predictions and discoveries of many scientists like Feynman, Eigler and Zsigmondy, nanotechnology deals in dimensions from 1 to 100 nanometers [5]. A size that can be difficult to conceptualize. To help students with this task a laboratory experiment was designed as of an associate level course in nanotechnology. This experiment merges three common experiments into a single exercise to help students comprehend the physical size of nanoparticles, and introduce to them a few unique properties these particles may possess.

3 Theory

A nanotechnology curriculum must be presented to a student in a way that builds a solid foundation that prepares them for a future in nanotechnology. These topics may include an introduction to atomic structure, unique properties of materials on the nano scale, using those properties to fabricate materials, and putting those new products to work in industry. Even though it appears these topics cover a vast number of disciplines, studying the structure of materials on the atomic level and how their size and scale give them unique characteristics is one of the foremost principles of nanotechnology.

The laboratory experiment that was developed is a three-part experiment that teaches size and scale and introduces a few of the unique characteristics that small things may possess. Each part consists of a commonly used experiment that the students will perform as a single exercise to build a complete picture of size and scale that they can call upon when learning more complicated concepts.

The experiment begins by proving to a student that they can measure the length of a molecule using simple methods. This has been done many times and is not new, but is a simple way to introduce the nanoscale. Part two helps with the visualization of the nanoscale through pictures and calculation. The final part expands the students new understanding of the physical nature of a nanometer and lets them experiment with quantum dots. This will show the student that objects this small can have interesting properties and let them observe these while gaining an understanding of how quantum dots work. This will be a good place to introduce a few principles that will be important in nanotechnology, atomic structure, photon emission, semiconductors, and the particle in a box. Part one begins with a pre-lab questionnaire. Questions about unit conversion, ratios, and chemical solutions prepares the student to begin the process of measuring the length of an Oleic acid molecule [6]. The hope is, that the student will answer these questions completely and correctly before they begin the experiment. This will help them focus on the measurement process in the next step, rather than algebraic issues that may arise from lack of preparation.

The student will then exploit a property of Oleic acid molecules that will make it possible for them to measure the length of the molecule. The Oleic acid molecules can be arranged in a monolayer, which is an ordered layer only one molecule thick with no empty space between adjacent molecules. Due to the hydrophilic and hydrophobic nature of the ends of the molecule, the Oleic acid will essentially stand straight up on the surface of the water. Using the surface area of the monolayer and the total volume of the molecules making up that layer, the student will calculate the thickness, or length of the molecule, using the formula for the volume of a cylinder [6, 7, 8].

To make the lab possible the student will create an Oleic acid monolayer that has a surface area small enough to fit on a laboratory table. The volume of molecules contained in one drop from a dropper is about two hundred times larger than needed. However, if the Oleic acid is diluted a monolayer with an appropriate size is created. When the Oleic acid/alcohol mixture hits the water, the alcohol will dissolve into the water leaving the Oleic acid behind on the surface [6].

The surface area of the monolayer can be measure by sprinkling a fine powder uniformly on the surface of the water before dropping the drop of Oleic acid/alcohol mixture on the water. As the Oleic acid spreads out into a monolayer, it will push the fine chalk dust outwards keeping it from penetrating the monolayer. The monolayer can be detected as the part of the water that is free from chalk dust. The student can then find the average diameter of the Oleic acid monolayer, the volume of acid contained in a single drop of acid/alcohol mixture, and calculate the height of the monolayer [6, 7].

This measurement will introduce the student to the nanometer scale. The next step is to help the student conceptualize what this physically means. To make micro- and nano-scale measurements as commonplace as the centimeter, meter, and kilometer the student will perform several calculations and visualize several objects on an enlarged scale.

Visualizing the nanoscale will be done in part two of this laboratory experiment through pictures and calculation. Part one proves they can make a nanoscale measurement, but one-billionth of a meter is hard to imagine. Several calculations will allow the student to create a picture in their minds of the scale at which they will be working. Like comparing the size of something to a bus or a fly, it is common to create visualizations to help describe macro-size objects. Why not do this for micro-sized things as well?

The student will begin by imagining that the diameter of a thin human hair is enlarged to the size of the empire state building. A 17m hair becomes 443 meters tall. From there the student will "enlarge" a red blood cell, bacteria, and virus, then compare how large a nanometer would be on this scale to the other objects [9, 10].

Part Three. Now that an understanding of the physical nature of micro and nano objects has been gained, the student will look at the quantum effects of nano objects, Quantum Dots. The student will learn that objects this small can have interesting properties and will observe these properties while gaining an understand of how quantum dots work.

The particle in a box problem is hard to visualize for students due to the lack of analogous real world examples. However, here, the student will be introduced to a great example that is becoming more common. Quantum Dots. To do this, a few concepts need to be briefly discussed to provide a more comprehensive understanding. The student will read about semiconductors, band theory, and the particle in a box then learn how these concepts, together, describe quantum dots. The student will then use their new knowledge to experiment with and discuss the emission spectra they will observe and relate it to size and scale.

The student will start by reading about semiconductors and learn that these are real world particles in a box because the electron has difficulty getting outside of the semiconductor. Discussing and observing the Quantum Dots will show how changing the size of the dot is analogous to changing the size of the box in the particle in a box. The student will prove to themselves how this change in size changes the energy of the particle and correlates to a shift in the peak wavelength of the emission spectra [11].

The particle in a box teaches us that energy levels are quantized and inversely proportional to the square of the length of the box. That energy can be represented by:

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \tag{1}$$

Eq. 1. The energy of a particle in a certain excited state n. Where n=1,2,3...[11]

where n=1,2,3 ... correspond to the ground state, first excited state, etc [11]. The equation used to determine the energy of a quantum dots is extremely similar. The nature of a semiconductor forces us to account for not one energy term, but three[11]. First, our energy equation needs to account for the mass of two particles, an electron (m_e) and a hole from the absence of an electron (m_h) . The third term is the energy of the semiconductor bandgap (E_g) which will be discussed in more detail later (see appendix B).

$$E_{\text{quantum dot}} = \frac{\pi^2 \hbar^2}{2m_e R^2} + \frac{\pi^2 \hbar^2}{2m_h R^2} + E_g \tag{2}$$

Eq. 2.	The energy	of a quantum	dot	[11]	1
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where for the quantum dots the electron mass $m_e = 7.29 \times 10^{-32}$ kg, the hole mass $m_h = 5.47 \times 10^{-31}$ kg and the gap energy $E_g = 1.34$ eV [11]. To ensure the student understands where these terms come from they will read a brief explaination about semiconductors, since quantum dots are just tiny semiconductors that take on some of the same special properties of atoms because of their size.

After reading about semiconductors the student should now have a qualitative understanding of doping and why it changes the conductance of a material. A brief discussion of what conductance is on an atomic level and how band gap energy is related is addressed in the laboratory experiment (see appendix B).



Figure 1: Figure showing how the forbidden gap limits the flow of electrons.

From the figure above the student will see that the valence and conduction bands of a conductor overlap, but the forbidden gap of an insulator is large enough that no electrons can reach the conduction bands. For a semiconductor, the forbidden gap can be small enough that just a change in thermal energy can allow electrons to go from the valence band to the conduction band, allowing the material to conduct when a potential difference is applied [12].

The final step is discussing photon emission and then relating semiconductors, band gap, and photon emission to quantum dots(see appendix B).

The nature of quantum dots allows them to behave in a manner similar to atoms and semiconductors. When you dope a semiconductor, you are changing the amount of energy required for an electron to cross a band gap. This is like forcing an atom to have only one discrete energy level so that it emits a photon of a very specific wavelength. For a quantum dot, changing the band gap is literally changing the size of this Nano-sized semiconductor. This relationship between the size of the quantum dot and the emission spectra will be explored in this laboratory experiment.

4 Experiment Design/Results

Thus far, three student trials have been completed. Students 1, 2, and 3 are all physics students, and upperclassman. As the students were completing the experiments they were encouraged to record all their data as indicated within the exercises. They were also asked to critique the experiments so those notes could be used in the future to improve the experience. It should also be noted that Students 1 and 2 worked together, while Student 3 worked alone at a later time. Students 1 and 2 took 2 hours to complete the experiments together and Student 3 took 3.5 hours to complete the experiments while working alone.

Part one consisted of pre-lab questions and measuring the length of the oleic acid molecule. Students 1, 2 and 3 were able to answer all of the pre-lab questions successfully. There seemed to be no issue with unit conversion, knowing an equation for volume, answering questions about the height of a monolayer when volume and diameter are known values, and general algebraic word problems involving mixtures/solutions. As the students proceeded to the Oleic acid portion of the experiment it was observed that the students were using slightly different measurements throughout the lab. For example, the students were asked to measure out 1ml of liquid and count the number of drops to do so. There was a difference of 10 drops between the students. Which led to a 84% difference between the calculated value of the volume of a single drop of liquid between the students.

	Student 1	Student 2	Student 3
Drops to make 1ml	56	56	46
Volume of one drop	0.01786 ml	$0.01785 \ {\rm ml}$	0.0213 ml

Table 1. Table showing student measurements: Volume of Oleic acid in one drop of solution, and number of drops of solution to make 1ml.

Once the Oleic acid/alcohol mixture was measured a single drop was placed into a shallow pool of water that had been dusted with chalk. The alcohol dissolved into the water and the acid spread out on the surface as a monolayer. The student measured the diameter of the monolayer in several places to get an average. Then used their calculated value for the volume of acid in that drop along with the diameter of the monolayer to calculate the length of the Oleic acid molecule.



Figure 2: Left: Student dropping one drop of Oleic acid/alcohol solution. Right: Figure showing how too much chalk dust on the water's surface can create a poor monolayer.



Figure 3: General materials used in Oleic acid experiment.

Creating a uniform layer of chalk dust proved to be difficult for all three students, and had to be repeated to get an intelligible result. Using fine sandpaper and a stick of chalk would not create a uniform layer of dust on the waters surface that allowed the Oleic acid to spread evenly and uniformly. A circular shape was expected so that a diameter could be measured. This measurement proved difficult for all three students and made them unsure of their results.

Calculating the length of the Oleic acid molecule then becomes an algebra exercise. The students are asked to find the average diameter, the surface area, and the thickness of the monolayer they have created, using the previously calculated volume of Oleic acid per drop. The students results are shown below. It should be noted that student 3 made an algebraic error when finding their final solution. If corrected they would have found a length of .78 nm. This demonstrates that minor errors in measurement can lead to significantly different results from student to student.

	Student 1	Student 2	Student 3
Length of Oleic Acid	Trial 1: 1 nm	Trial 1: 1nm	16.3 nm
Molecule	Trial 2: 1.5 nm	Trial 2: 1.5 nm	
Actual Length	$\approx 1.97 \text{ nm}$		

Table 2. Table showing student measurements: Measured length of Oleic acid molecule.

Part two of the size and scale laboratory experiment consisted of an algebraic exercise that was designed to give students a better understanding of the physical relationship between micro and nano-sized objects. In general, it was completed by the students with only a few algebraic errors from student 3, who was working alone. When enlarging the scale at which the objects were seen, the students all used the same mathematical approach. Student one said that they would like to have seen a connection to the Oleic Acid experiment and been asked a question about an enlarged Oleic acid molecule. Student three said this portion of the experiment did not solidify the comparison of size as he had hoped.

The quantum dot experiment consisted of using software to view the different colors (emission spectra) emitted from several vials of quantum dots and relate the peak wavelengths to the diameter of the quantum dot. Once the student read through several pages of theory, explaining why their size determines the wavelength that is emitted, the data collection process began. All three students made the comment that they have read or been taught most of this theory before and that their background aided in their understanding of the material. They all suggested the theory be simplified so an audience of new science students would be able to fully understand the material without any prior experience in this field.

During the process of writing the quantum dot experiment, an updated version of Ocean View software and fiberoptic cable hardware was used to view the emission spectra and write the instructions for future students. When the trials began the students had to use an older version of the software that was available to them on the laboratory computers. It did not hinder the process or collection of data and the students adapted quickly. It should be noted that the software instructions in the laboratory writeup (see appendix B) must be rewritten to accommodate the software that is available to all students. These students used Ocean Optics Overture spectroscopy software during their trials. Although the 3 student captured nearly identical data, the difference in the layout of the displayed emission spectra data between software versions can be seen below.



Figure 4: Figures showing different graphs produced from different versions of the same spectroscopy software.

The software instructions asked the student to become familiar with the different features available to them. Connecting the hardware, creating a graph of the spectra, scaling the graph to show appropriate data, creating an Excel spreadsheet, viewing peak wavelengths, and saving a graph of the emission spectra was outlined to assist the students. The students were then asked to place their wavelength data for each vial into Excel along with a graph showing peak wavelengths. Then they were to use the equations provided in the laboratory write up to solve for the radius of the quantum dot using the peak wavelengths they found. Then the students were asked to calculate the percent error between their experimental values and known values of the radius of each quantum dot. Finally, plot the quantum dot radius verses the emitted wavelength for each vial and write a brief explanation of the relationship they see.



Figure 5: Quantum Dots laboratory materials setup, and fluorescing quantum dot solution.

5 Conclusion

This laboratory experiment had three parts that were designed to work together to give a student a better overall understanding of size and scale. Based on the results of the three students who have completed this laboratory experiment a few modifications need to be made to increase the effectiveness of this experiment, teach the concepts more clearly, and improve the continuity between the three sections of the experiment.

It was clear that the Oleic acid experiment was more accessible to each student. Each student was able to perform the experiment without any clarification or additional instruction. This is due to the plethora of similar experiments that have been created and compiled into this part of the experiment, although a more efficient way of distributing chalk dust on the waters surface would eliminate frustration on the students part.

Scaling up macro and micro sized objects in part two has merit but needs revision to become more effective. Showing several pictures after the students calculations that depict the enlarged objects, including an Oleic acid molecule, may help make a connection between parts one and two.

The quantum dot data collection went very smoothly, and all three students were able to build a spreadsheet with their data and results without issues. It is possible that a freshman or sophomore may experience more difficulties when reading the theory and collecting data due to less experience in a laboratory setting.

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Appendices

A Materials

- 1. Part 1: Oleic Acid Molecule Lab
 - Safety Goggles
 - Rubber Gloves
 - 0.50 ml of Oleic Acid
 - Chalk or Lycopodium Powder
 - 100 ml of Methyl Alcohol
 - Calibrated Pipette with Rubber Bulb
 - 100 ml Graduated Cylinder
 - 10 ml graduated Cylinder
 - dropper with rubber bulb
 - Sandpaper (if using chalk)
 - Large Tray (approximately 30x30 inches)
 - 1 Liter Beaker
 - Water to Fill Trays
 - Standard Ruler
- 2. Part 2: Scaling/Enlarging
 - Standard Calculator
- 3. Part 3: Quantum Dots
 - Cenco Physics/Nanosys Experiment Guide: College 175118 CENCO Quantum Dots
 - Ocean Optics, Overture, Spectroscopy Software (approx. \$200-\$3000 depending on license and installation agreement)
 - Ocean Optics Red Tide Spectrometer (approx. \$1200-\$1800 each)
 - Lab-grade Bifurcated Fibers (approx. \$ 300-400 each)
 - Quantum Dots Vials (approx. \$300 for a kit of 4(1ml))
 - Light source: 405 nm
 - 2 Support Stands (approx. \$80 each)
 - 2 3-prong extension clamps (approx. \$50)
 - Excel or other Spreadsheet Program

B Size and Scale Laboratory Experiment

Prelab Questions:

Carefully read the laboratory manual and answer the following questions before coming to class. Once you have read the entire lab write-up and answered the questions correctly you may begin the experiment.

- 1. "How many milliliters (ml) are there in 6.3 cubic centimeters (cm3)" [6]?
- 2. "What equation gives the relationship between the cross-sectional area (A), the volume (V) and the length (L) of a cylinder" [6]?
- 3. "If the area of a monolayer of BBs is 23.6 cm^2 and the total volume of the BBs is 35.4 ml, what is the approximate diameter of a single BB" [6]?
- 4. "What is the shape of an oleic acid molecule, according to the lab write-up" [6]?
- 5. "If the diameter of a human hair is 0.00624 cm and the diameter of a typical atom is 2.40x10-8 cm, how many atoms laid end-to-end would it take to make a length equal to the hair diameter" [6]?
- 6. "If you wanted to make a dilute solution of oleic acid in alcohol containing 0.5% acid by volume, how much acid should I add to a volume of alcohol equal to 20 ml" [6]?
- 7. How many Angstroms are one centimeter (cm)?

Introduction

"Atoms are incredibly small. You might think that it would be impossible to measure the dimensions of an atom or molecule using simple lab equipment but it isnt! In this lab you will exploit a property of oleic acid molecules that will make it possible for you to measure the length of the molecule" [6].

Precautions and Safety Considerations

"The methyl alcohol you will be using in this lab is a poison and must not be ingested. It is flammable, so it must be kept away from all ignition sources. As with all chemicals, the oleic acid and alcohol should be contained and not spilled on skin or clothing. Protect your eyes with goggles and your hands with gloves. OLEIC ACID WILL STAIN certain types of clothing" [6].

"In part of the lab you will spread chalk dust on the surface of the water. Do not breath in the chalk dust. Be careful not to spill the oleic acid or the oleic acid and water mixture on the floor since it will become extremely slippery and potentially dangerous. If a spill occurs, immediately clean it up with paper towels and discard the used towels in the wastebasket" [6].

"The pipettes used to measure the oleic acid have a small piece of cotton at the top of the glass tube. The purpose of the cotton is to keep liquid from escaping from the end of the glass tube. If you suck too much oleic acid into the pipette do that some reaches the cotton, the pipette will become useless and will have to be thrown away!" [6].

Theory

"Since molecules are so small, we will not be able to measure them in any conventional way with a ruler. Instead we will have to use a technique that will work even though we cannot see or touch an individual molecule. If the molecules can be arranged in a monolayer(an ordered layer only one molecule thick with no empty space between adjacent molecules), and if the surface area of the layer and the total volume of the molecules making up the layer can be measured, then the thickness of the monolayer can be calculated from the formula:"[6]

 $MonolayerThickness = \frac{Volume}{SurfaceArea}$

This formula can be derived from the equation describing the relationship between volume, surface area, and length.

"Oleic acid molecules have the property that they will form a monolayer if placed on the surface of water! So the experiment involves measuring out a very small volume of oleic acid molecules, then gently dropping the molecules onto the surface of a pool of still water and measuring the area off the monolayer surface. From other experiments it is known that the shape of an oleic acid molecule is approximately cylindrical, and the length of the cylinder is much larger than the diameter. It turns out that the molecules in the monolayer arrange themselves so that the cylinders are all standing straight up. Thus, our measurement of the monolayer thickness is really a measurement of the length of the oleic acid molecule" [6].

"(NOTE: Oleic acid acts in some ways like oil. To prevent oil from our hands from interfering with the experiment, try to avoid touching with ungloved hands anything that will eventually come in contact with the oleic acid: the insides of graduated cylinders, beakers, trays etc.)"[6].

"To make the lab possible we need to have a monolayer surface area that is small enough to fit comfortably on a laboratory table. The volume of molecules contained in one drop from a dropper is about two hundred times larger than needed. However, if the oleic acid is diluted in methyl alcohol, when the oleic acid/alcohol mixture hits the water, the alcohol will dissolve into the water leaving the oleic acid behind on the surface. Thus, a mixture that is about 200 parts alcohol to 1 part oleic acid will be needed" [6].

"The surface area of the monolayer can be measure by sprinkling a fine powder uniformly on the surface of the water before dropping the drop of oleic acid/alcohol mixture on the water. As the oleic acid spreads out into a monolayer, it will push the fine chalk dust outwards keeping it from penetrating the monolayer. So the monolayer can be detected as the part of the water that is free from chalk dust"[6].

- 1. Materials and Equipment
 - Safety Goggles
 - Rubber Gloves
 - 0.50 ml of Oleic Acid
 - Chalk or Lycopodium Powder
 - 100 ml of Methyl Alcohol
 - Calibrated Pipette with Rubber Bulb
 - 100 ml Graduated Cylinder
 - 10 ml graduated Cylinder
 - dropper with rubber bulb
 - Sandpaper (if using chalk)
 - Large Tray (approximately 30x30 inches)
 - 1 Liter Beaker
 - Water to Fill Trays
 - Standard Ruler

Measuring the Size of Oleic Acid Molecules

"Since we are using chemicals, we need to put on safety goggles and gloves. Be sure to adjust the straps of the goggles so that they are comfortable an neither too tight note too loose." [6].

Experiment

Prepare the dilute solution of Oleic acid in methyl alcohol

"We want to dilute the Oleic acid to a 0.5%, i.e. 5 parts in 1000 or 5:1000. To do this we will add .50 ml of Oleic acid to 100 ml of methyl alcohol. The 0.50 ml of acid will be dispensed from a calibrated pipette, and the 100 ml of alcohol will be measured in a 100 ml graduated cylinder" [6].

- 1. "Fill a 100 ml graduated cylinder with methyl alcohol. You measure volumes with a graduated cylinder by letting the bottom of the center of the liquid surface reach the graduation line" [6].
- 2. "Carefully draw some Oleic acid into the cylinder of the pipette using the rubber bulb. Remember that the pipetter will be ruined if you suck oleic acid into the cotton at the upper end of the glass tube. Be careful to hold the bottom of the pipetter always below the surface of the acid so that no bubbles are sucked into the pipette. Make sure you know what each line designation on the pipette represents. Although you will only release 0.5 ml of acid into the alcohol, draw about 0.6 to 0.7 ml" [6].
- 3. "Using the graduations on the pipette, carefully release 0.5 ml of oleic acid into the graduation cylinder filled with the methyl alcohol. Release the remaining oleic acid in the pipette back into the bottle" [6].
- 4. "Stir the mixture with a glass stirring rod many times to mix the chemicals" [6].

"Now you have a great quantity (100.5 ml) of a dilute oleic acid/alcohol mixture. You will only use a small amount of this in the experiment" [6].

Volume of Oleic Acid Mixture in One Dropper

"We will select a small volume of the oleic acid mixture by using a dropper. We will need to determine the volume of a drop of mixture released by the dropper. To do this, we see how many drops it takes to make exactly 1 ml of mixture, and then we will divide 1ml by the number of drops to determine the volume of one drop" [6].

- 1. "Take the 10 ml graduated cylinder and carefully count how many drops from the dropper it takes to fill it to 1 ml. You may want to practice making a few drops before you start to fill the cylinder. Remember, you measure volumes with a graduated cylinder by letting the bottom of the center of the liquid surface reach the graduation line. Record the number of drops here:"[6].
 - -"Number of drops to make 1 ml:_____"[6].
- 2. "Divide 1ml by the number of drops to determine the volume of 1 drop, and record your result here:"[6]
 - "Volume of one drop of oleic acid/alcohol mixture:_____ ml"[6].
- "The volume of oleic acid in the mixture is only 0.50% of the mixture volume. So multiply the volume of one drop by 0.005 to obtain the volume of oleic acid inside one drop, and record your result here:"[6] "Volume of oleic acid in 1 drop of oleic acid/alcohol solution:______ ml"[6].

Surface area of an oleic acid monolayer

"Now you are ready to prepare the water layer and spread fine chalk dust over it. Before you being, however, it is important to realize that the chalk particles are typically hundreds or thousands of ties larger than the thickness of the oleic acid monolayer. If your body were the size of the oleic acid molecules, the chalk particles would appear to be mountains floating on the liquid surface. You need to take care to make small chalk particles, to not put too many on the liquid surface, and not to clump many particles together. Most students who obtain poor results for this lab make the mistake of using too much chalk dust on the surface of the water" [6].

"Follow the procedure below, and when you are finished you will be ready to make the monolayer of oleic acid and measure its surface area" [6].

1. Your tray needs to be very clean in order to get good results. Before doing anything, thoroughly clean the tray with alcohol and paper towels. After cleaning, be very careful to keep the tray clean. Dont put anything in it other than what the instructions say, and dont touch the inside surface of the tray with ungloved hands.

- 2. "Take the large 1 liter beaker and get enough water from the faucet to fill the tray to about $\frac{1}{2}$ inch (1 to 1.3 cm) depth" [6]. Make sure the tray is level.
- 3. "Hold the chalk and sandpaper about a foot above the water and gently sand off some of the chalk so as to lightly cover the water surface. The goal is to end up with the water surface looking like it is covered in a very fine layer of very fine dust. Use only enough chalk so that you can just see the chalk on the water surface. Too much chalk will prevent the oleic acid from spreading into a monolayer. If the chalk clumps together on the water surface, you have used too much chalk. If you can clearly see individual chalk particles on the surface, the chalk particles are too large. Also, be careful not to breathe the chalk dust"[6].
- 4. "You can now drop a single drop of oleic acid/ alcohol mixture into the center of the tray. Remember to release the drop at a height of about 1 cm about the liquid surface" [6].
- 5. "After the circle of oleic acid stops shrinking, measure its diameter at about 5 points space uniformly around the edge, and record your values here[6]:Diameter of the monolayer (cm)
- 6. Put another drop of the mixture into the center of the oleic acid film. You have roughly doubled the volume of the oleic acid film. Since the thickness should be fixed at one molecule thickness, the area should have also doubled. A circle with twice the area has about 1.4 times the diameter of the smaller circle.

Has the area of your circle about doubled?

7. Now find the average of the five diameter measurements above, and record your result here using 3 significant figures.

"Average diameter of the oleic acid monolayer" [6].: ______cm

- 8. Calculate the area of the circle and record your result: "Surface area of oleic acid monolayer" [6].: cm^2 .
- 9. "Using your volume of oleic acid in your drop and the measured surface area of the monolayer, calculate the thickness of the oleic acid monolayer and record it here" [6]:

"Thickness of the oleic acid monolayer" [6].:_____ cm.

The Angstrom Unit of Length

"Although atoms dont have well defined edges, we can talk about their sizes. For example, the size can be taken to be equal to the spacing between adjacent atoms in a crystal. The atoms of the various elements vary in size by about a factor of four. The size of the smallest atom, hydrogen, is about $1x10^{-8}$ cm. The unit of length called the Angstom is defined to be $1x10^{-8}$ cm, and is the convenient length unit to use when dealing with atoms or molecules. It is named in honor of Anders Jons Angstrom (1814-1874), a Swedish physicist who made important contributions to the study of the wavelength of light emitted by various atoms" [6].

1) Convert the length of the oleic acid monolayer from centimeters to Angstroms:

Angstroms

Final Steps: Clean up!

- 1. Empty the water from your tray into the designated container or sink[6].
- 2. "Dry the tray with a clean paper towel after removing any chalk dust that remains" [6].
- 3. "Rinse out the 100 ml and 10 ml graduated cylinders that contained the oleic acid/alcohol mixture" [6].
- 4. "Throw away your glass pipette and place the bulb from it and your dropper in the designated area" [6].
- 5. "Wipe your table with paper towels to clean up any water that may have spiled on the table" [6].

Part Two: Putting it into Perspective!

The size of the Oleic acid molecule that you calculated above is difficult to imagine or even compare to macro-sized objects that we are used to seeing every day. To put things into perspective we are going to blow things up.



Figure 1. Showing size comparison of micro-sized objects that have been enlarged to a macro-level scale[9].

Lets imagine we can scale up a thin human hair to the size of the Empire State Building. Our new scale will make a $17\mu m$ hair 443 meters tall[9]! If we continue knowing this scale, then we can predict the size of other objects as well. Fill in the blanks below to see how big each object would be on an empire state building sized scale.

1. If a red blood cell[9] is about 6 μm in diameter, it would become

_____ meters tall.

2. A small bacteria cell[9] is about $0.5\mu m$ in diameter, which puts it at

_____ meters tall on our blown-up scale.

- 3. A virus, which can be around 100nm in diameter, is how many times smaller than our bacteria? How tall on the buildings scale?
- 4. This leads to the conclusion that 1 nanometer is going to be just[9]

_____ off the ground!

5. How many one-nm objects, like the Oleic Acid molecule, would it take to span across our $17\mu m$ hair?

Part Three: Particle in a Box

Theory

The particle in a box problem is hard to visualize. This is because there is not a good real world example of a particle in a box. However, there is one good example that can now be used: Quantum Dots. Quantum dots are small semiconductor particles. By observing the emission spectra of different sizes of Quantum Dots, the effects of quantized energy levels can be observed[11].

As you remember, the particle in a box taught us that energy levels are quantized and inversely proportional to the square of the length of the box. That energy can be represented by:

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

Eq. 1. The energy of a particle in a certain excited state n. Where n=1,2,3...[11]

The equation used to determine the energy of a quantum dots is extremely similar. The nature of a semiconductors forces us to account for not one energy term, but three. First, our energy equation needs to account for the mass of two particles, an electron (m_e) and a hole from the absence of an electron (m_h) . The third term is the energy of the semiconductor bandgap (E_g) [11]:

$$E_{\text{quantum dot}} = \frac{\pi^2 \hbar^2}{2m_e R^2} + \frac{\pi^2 \hbar^2}{2m_h R^2} + E_g$$

Eq. 2. The energy of a quantum dot. Where $E_g = 2.15x10^{-19}J$, $m_e = 7.29x10^{-32}kg$, $m_h = 5.47x10^{-31}kg$, and $\hbar = \frac{6.626x10^{-34}J_{*s}}{2\pi}$, R=Radius of the Quantum Dot [11].

To understand where these terms come from a brief discussion of semiconductors is required. After all, quantum dots are just tiny semiconductors that take on some of the same special properties of atoms because they are so small.

Semiconductors

Semiconductors are materials which have a conductivity between conductors (generally metals) and insulators (such as most ceramics). They can be made from pure elements like silicon or germanium, or compounds such as gallium arsenide or cadmium selenide [12]. In a process called doping, small amounts of impurities are added to pure semiconductors which will both change its conductance and cause them to conduct electricity under some conditions but not others, making them a good medium for the control of electrical current. A change in the applied voltage or current, temperature, or the intensity of light can change the conductance of semiconductors, allowing electrons to flow [12]. When impurities are added to a pure substance like silicon, the conductance is generally increased. This is because there has been a change to the crystalline structure of the atoms. In our example below, Silicon has 4 valance electrons per atom and its 2-dimensional crystalline structure looks like this[12, 13]:



Figure showing the Silicon crystal lattice and the covalent bonds between electrons.

By doping the silicon semiconductor with an atom that has one extra valence electron we end up replacing a small percentage of the silicon atoms with the new atoms containing 5 valence electrons[12, 14].



Figure showing a doped Silicon crystal lattice with an extra electron.

This extra electron is not held in place with the same forces as the ones paired in covalent bonds and is able to move about the crystalline structure more freely, causing an increase in the electric conductivity of the semiconductor. This is because once the extra electron starts moving about the lattice it leaves behind an empty, low energy quantum state, or hole, that wants to be occupied, causing a flow of electrons from the adjacent silicon atoms[11, 12, 14].

Band Theory

As stated above, a semiconductor is something that has a conductivity somewhere between a conductor and an insulator. Now that we know how a semiconductors conductance can be changed with doping, lets look at what conductance is on the atomic level.

Atoms consist of a nucleus, and electrons that orbit around it. These orbits are in discrete shells. An atom such as sodium has two electrons in the inner shell, eight in the next shell and one its outermost shell. The outermost electron is in a shell that is referred to as the valence band or valence shell. This single electron is very loosely held and contributes to the reactivity of sodium, and with a potential difference this electron is free to move. This band will also be referred to as the conduction band[11, 12, 14].

The valence band and the conduction band are not always the same thing, however! Pictured below is a similar diagram, but of a chlorine atom. Notice that chlorine has 7 electrons in its valence band, but this time they are very tightly held and do not have enough energy to become conductors in their current position. To become conductors, they have to move to the conduction band that is in the next shell. Right now, there are no electrons in this conduction band. For an electron to get promoted to the conduction band it needs to cross a what is called the forbidden gap[11, 12, 14].



Figure showing the relationship between the forbidden gap, and the valence and conduction bands of an atom.

We know that electrons have discrete energy levels. To move to the conduction band an electron will need a specific amount of energy. For insulators, this is actually a very large energy gap to overcome. Below is a good visualization of the relationship of the conduction and valance bands for insulators, conductors, and semiconductors[11, 12, 14].



Figure showing the flow of electrons in insulators, semiconductors and conductors. The ability for electrons to go from the valence band(green) to the conduction band(yellow) depends on the size of the forbidden gap. The "larger" the forbidden gap, the more energy it takes for electrons to cross. Electrons have difficulty crossing the forbidden gap in insulators but cross with ease in conductors.

From the figure above, you can see that the valence and conduction bands of a conductor overlap, but the forbidden gap of an insulator is large enough that no electrons can reach the conduction bands. For a semiconductor, the forbidden gap can be small enough that just a change in thermal energy can allow electrons to go from the valence band to the conduction band, allowing the material to conduct when a potential difference is applied[11, 12, 14].

Quantum Dots

The background information above is the basis for understanding how and what quantum dots are. As previously stated, quantum dots are semiconductors. They are also a real example of a particle in a box.

When an atom absorbs a discrete amount of energy, an electron gets promoted to an excited state, falls back down, then emits a photon. The wavelength, or color, is directly related to how much energy the electron gained. The amount of energy it takes to get promoted to an excited energy state is called band gap energy. This is exactly what is happening in semiconductors. The band gap for a semiconductor is the amount of energy required for an electron to go from the valence band to the conductance band. The nature of quantum dots allows them to behave in a manner similar to atoms and semiconductors[11]. When you dope a semiconductor, you are changing the amount of energy required for an electron to cross a band gap[12, 14]. This is like forcing an atom to have only one discrete energy level so that it emits a photon of a very specific wavelength[12, 14]. For a quantum dot, changing the band gap is literally changing the size of this "Nano-sized" semiconductor. This relationship between the size of the quantum dot and the emission spectra is that we will explore in this laboratory experiment. Materials Needed:

- Particle in a box experiment
- Flashlight
- Metal Support Stands
- OceanOptics Spectrometer and Fiber Optic Cable
- Ocean View Spectroscopy Software
- Excel or Similar Spreadsheet program

Procedure

- 1. Plug in the Ocean optics fiber optic cable into the Red Tide spectrometer. Then plug in the red tide unit to the computer via the USB cable provided.
- 2. Open the OceanView/Spectra Suite software.
- 3. Click "Spectroscopy application wizards".
- 4. Click the "Fluorescence" button
- 5. Click "Active acquisition".
- 6. Ocean view will then ask you to store data from the light that is coming in from the background. This includes the ceiling lights, and the flashlight we will use to illuminate the quantum dots. By doing this, the software will filter out the background light and give us data from only the quantum dots. Shine the flashlight into the optical cable from a few feet away to get a good reading on the graph. Make sure the intensity isnt too high. Once you are satisfied with how your graph looks, click finish.
- 7. Now take time to toggle over the icons at the top of the graph so you can scale your data/graph to fill the viewing window.
- 8. Notice there are 2 tabs open. One for "view minus background" and one for "view". Compare the two to see why filtering out the background spectra helps us view the quantum dot spectra.

- 9. If you click on the graph near a peak you can see the wavelength displayed on the lower left-hand part of the graph.
- 10. A spreadsheet containing the data points from each graph can be found by using the "view result in table form" button near the top of your graph.

Now that you are familiar with the operation of the software we can collect some data.

- 11. Clamp your quantum dots upright, very gently, on a metal stand or any place that will give you easy access to the underside of the vials.
- 12. Position your fiber optic cable so that it also is on a metal stand and pointing at the quantum dot vials. You will need to be able to adjust the position of the cable to view all the vials throughout the experiment.
- 13. Using the provided flashlight, illuminate the underside of one of the vials so that the flashlight is perpendicular to the optical cable. Point the optical cable directly at the vial, getting it as close as possible. You should see the emission spectra on your computer.
- 14. Take a screen shot of the graph and copy/paste it into excel, making sure to label it with the peak wavelength from that vial.
- 15. The peak wavelength can be found from the spreadsheet data in the software. Copy and paste that data into Excel next to its corresponding graph screenshot.
- 16. Using the equation for the energy of a Quantum Dot ($E_{\text{quantum dot}} = \dots$) found above, calculate the radius(R) of the Quantum Dots for each vials and put it in your spreadsheet. Be sure your answer is in Nanometers [11]. Please note that the energy of the quantum dot can also be defined as $E_{\text{quantum dot}} = \frac{h*c}{\lambda}$ where h is Planck's Constant, and λ is the peak wavelength of a quantum dot vial and c is the speed of light.
- 17. Calculate the percent error between your measured wavelength and dot radius verses the actual values provided by your instructor for each vial. Place this data in your spreadsheet[11].
- 18. "Plot the quantum dot radius verses the emitted wavelength for each vial, on a single graph in Excel. What relationship do you see" [11]?
- 19. "What happens if the radius of the quantum dot gets very large (approaching infinity)"[11]?