Chapter 20

Surface Chemistry: Bubbles and Films
Introduction

The calming effect of oil on rough water has been known for thousands of years. Benjamin Franklin reported some of the earliest scientific experiments on the effect of oily films on water. His famous experiment on the pond on Clapham Common was described thus: "...the oil, though not more than a teaspoonful, produced an instant calm over a space of several yards square, which spread amazingly, and extended itself gradually 'til it reached the lee side, making all that quarter of the pond, perhaps half an acre, as smooth as a looking glass."\(^1\)

The strange and unusual behavior of liquid surfaces has stimulated chemists and physicists alike to try to find explanations for the spreading of oil on water, the calming effect of oil on rough water, etc. The study of the chemistry of surfaces has proved to be so fruitful and of such practical importance that it has become a separate discipline called surface chemistry. The real challenges in the surface chemistry of liquids involve, for example, research in the dynamics of the interactions of the oceans with the atmosphere, research on biomembranes in plants and animals, and research on the environmental consequences of large-scale oil spills in the ocean.

The containment of oil spilled in the ocean, or indeed in any aquatic environment, is extraordinarily difficult. The removal of oil spread over ocean and land surfaces is even more difficult. Nowhere were these problems more evident than in the recent massive oil spill from the supertanker Exxon-Valdez in beautiful Prince William Sound off the coast of Alaska. The March, 1989 Exxon-Valdez disaster tragically demonstrated the enormous risks inherent in the large-scale production and transportation of fossil fuels. The calming effect of oil on rough water turns into environmental nightmare when a teaspoon of oil becomes ten million gallons of Alaskan crude!

Background Chemistry

A surface may be defined as the place where two different phases meet. The interfacial region between gases and liquids, immiscible liquids, liquids and solids, and immiscible solids may all be called surfaces. Surface chemistry is a rich and fascinating area of science because most chemical transformations take place at interfaces. Extreme changes in many chemical and physical properties occur at surfaces. Atoms, molecules, and ions at and around a surface exist in a very different environment than those deep within the bulk material. The inequality of forces and the close proximity of different species lead to an enormous variety of unusual and useful chemistry. The emphasis in this series of laboratory experiments is on the surface chemistry of liquids, particularly the interface between aqueous solutions and air. A knowledge of the water-air interface is central to understanding the beauty of bubbles, much of the biology of plants and animals, and the way our water planet works.

First let us consider the interface between bulk pure water and air. A water molecule that is in the interior, remote from the surface, is completely surrounded by other water molecules. The water molecules are attracted to each other by intermolecular hydrogen bonds that are continuously forming and breaking as the molecules collide. On a time-averaged basis, each water molecule experiences a symmetrical force field that has the same magnitude in all directions. The direction in which any water molecule moves is determined solely by momentum exchanges with colliding molecules and is therefore random.

The molecular picture near the water-air interface is very different. A water molecule that is approaching the interface in its random thermal motion experiences an increasingly unsymmetrical force field. As it moves closer to the surface, the number of water molecules on its interior side remains the same, but the number of exterior water molecules decreases rapidly. The water molecules in the dynamic surface layer are continually being attracted inward and, of course, are continually being replaced by molecules diffusing from the interior. The surface layer, which is perhaps two or three molecules thick, is therefore in a continual state of tensile strain, and the restoring force is called the surface tension. For a flat surface the surface tension is defined as the force acting parallel to the surface and at right angles to a line of unit length anywhere in the surface. The SI unit of surface tension is newton per meter (N m⁻¹). The magnitude of the surface tension of a pure liquid in equilibrium with its vapor and air is dependent on the magnitude of the intermolecular attractions in the liquid. Water has a relatively high surface tension because of its relatively strong hydrogen bonding, whereas ethanol has a much smaller surface tension because of its weaker hydrogen bonding.

One of the most important practical consequences of surface tension is that a liquid spontaneously tries to shrink (minimize) its surface. A drop of any liquid in equilibrium with its vapor and in the absence of external forces spontaneously assumes the form of a sphere. This shape corresponds to the minimum surface area for a given
volume of liquid. Work must be done on a drop to increase its surface area; therefore, the surface molecules are in a state of higher free energy than those in the bulk interior of the liquid.

It is important to emphasize that the phenomenon of surface tension is a consequence of two molecular properties of liquids: \textit{intermolecular attraction} and \textit{rapid molecular motion}. The thin surface layer is undergoing constant depletion and replenishment as molecules move out of and into it. The average residence time of a water molecule in a water surface layer is about a microsecond ($10^{-6} \text{ s}$ at $25^\circ \text{C}$). Unfortunately, there are many descriptions of surface tension in the literature that are misleading because they do not emphasize the molecular dynamics. One common analogy for surface tension is that the surface of a liquid is like a "skin." The skin is said to be like that of the stretched rubber skin of an inflated balloon. This picture is a bad analogy because the molecules in the rubber membrane remain fixed in the surface in a continuously strained condition, whereas in a liquid surface there is always tremendous fluidity.

The introduction of other substances into the water-air system complicates the chemistry considerably. These multicomponent systems, however, are most interesting because they represent most of the actual, practical examples of surface chemistry. It is generally impossible to predict theoretically what will happen at the surface in complex systems. Often the best approach to complex systems is to carry out experiments and then try to explain and interpret the results. One special type of binary liquid system that merits special attention is the presence of insoluble oily materials at the water-air interface. This type of system is important in food processing (e.g., salad dressings), crude oil production, oil spills, biological membrane formation, fabric cleaning, and the survival of flora and fauna. The behavior of oily materials at aqueous surfaces depends very much on the chemical structure of the material. Nonpolar substances consisting of carbon and hydrogen (e.g., motor oil) are immiscible and not soluble in aqueous solutions. These substances are said to be \textit{hydrophobic}, or water-hating, substances. Polar substances (e.g., ethanol) that can interact strongly with water are said to be \textit{hydrophilic}, or water-loving, substances. The balance of the hydrophobic and hydrophilic characteristics in a particular molecule determines to a large extent its surface chemistry. A good example is motor oil, which in the unused state is a homogeneous mixture of hydrophobic hydrocarbons. Used motor oil, however, has been drastically oxidized by high-temperature engine reactions with air to become partially hydrophilic in character. The difference in the surface activity of the oil upon water is quite dramatic.

The experimental breakthrough in the study of oily materials on water came in 1891 when Fräulein Agnes Pockels (in her kitchen) developed an original and elegant method of manipulating oils on water. Her technique involved a trough filled to more than the brim with water and the use of "barriers" that were swept across the surface to control the extent of an oil film. Pockel's letter to Lord Rayleigh\footnote{Pockels, A., \textit{Nature} 43, 1891, p. 437.} stimulated a century of extraordinarily fruitful research in surface chemistry. The trough method she developed was refined, quantified, and extended by Rayleigh, Langmuir, Blodgett,
and many others, and has achieved a recent renaissance with the advent of computer-controlled barrier systems. Rayleigh proposed that the films were only one molecule thick; Langmuir made a giant step in showing that long-chain fatty acid films were oriented with the hydrophilic acid group in the water and with the hydrocarbon tail stuck vertically out into the nonpolar air. The cumulation of all the intense research on the surface properties of molecules with hydrocarbon tails and polar heads has been the basis for understanding the chemistry and biochemistry of detergents and biological membranes.

Soap molecules have played a central role in the development of aqueous surface chemistry. These molecules are salts of long-chain acids. A typical example is sodium palmitate (made from palm oil):

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{O} \\
\text{H} & \quad -\text{C} & \quad -\text{C} & \quad -\text{C} & \quad -\text{C} & \quad -\text{C} & \quad -\text{C} & \quad -\text{C} & \quad -\text{C} & \quad -\text{C} & \quad -\text{C}^+ \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} & \quad \text{O}^- & \quad \text{Na}^+ 
\end{align*}
\]

The long hydrocarbon tail of the molecule is nonpolar (hydrophobic), and the anionic head is quite polar (hydrophilic). In general, soap molecules are called surfactants,—i.e., they are surface-active agents. They can be anionic (as in sodium palmitate) or nonionic or cationic, depending on the charge on the tail. The dissolution of a surfactant in water produces a series of bizarre molecular arrangements. The hydrophobic tail is "squeezed out" by water molecules that are strongly hydrogen bonded, yet the polar tail is strongly bonded to water. The result is cooperative and oriented gathering (aggregation) of molecules both in the bulk aqueous solution and at the surface, as shown in Figure 20.1.

![Figure 20.1 Aggregation of Palmitate Ions](image)

Figure 20.1 Aggregation of Palmitate Ions
The surface tension of aqueous solutions of surfactants is much smaller than that of pure water. The molecular explanation is that the hydrophobic tails resist moving into the aqueous interior, whereas the hydrophilic heads strongly attract water molecules and slow down the return of the water molecules into the interior. Surfactant molecules reduce the aqueous surface tension while at the same time maintaining the flexibility and tremendous fluidity of the interface. A lowered surface tension produces bubbles, films, and froths in agitated solutions containing soap molecules.

When air is blown or shaken into a soap solution or when a wire frame is dipped and pulled out of a soap solution, beautiful soap films and bubbles are formed. Films and bubbles are bilayers of surfactant molecules, sandwiching water and counter ions, as shown in Figure 20.2.

![Figure 20.2 Bilayers in Soap Films and Bubbles](image)

The gravitational effect on the bilayer gradually drains molecules downwards toward the bottom of the film, and the film begins to thin. Beautiful interference colors play on the surface and eventually disappear in blackness. The bilayer has become thinner than light itself. Suddenly the film breaks as the negative heads come close and repel each other. Drops fly away at 50 miles an hour . . . and the bubble is gone forever.

Most of what we know about soap bubbles was discovered by the remarkable Belgian scientist J.A.F. Plateau, whose great work, *Statique Expérimentale et Théorique des Liquides*, was published 30 years after he became blind. We owe a debt to Plateau's wife, whose diligent observations allowed Plateau to discern the fundamental geometries of bubbles and films. We now know that the geometry, and
most other properties, of soap bubbles and films is a direct consequence of the coupling of
intermolecular attraction and dynamic molecular motion at the surface of liquids. The
path of an individual soap molecule is totally unpredictable. The collective action of
billions of molecules completely determines the macroscopic shape of bubbles and films.
The perfect economy of space and the wonderful architecture of soap films is just one of
the many amazing phenomena exhibited by chemical surfaces. In this laboratory
module you have an opportunity to explore the world of surface chemistry and perhaps
even make a new architectural contribution to the collection of "beautiful rooms."
Pre-Laboratory Quiz

1. Give a definition of a surface.

2. Draw a simple picture to show that a surface molecule of water is different from a bulk molecule in the interior of the water.

3. What is the SI unit for surface tension?

4. What two properties of liquids give rise to surface tension?

5. What does hydrophobic mean?
6. Who developed the original trough technique for manipulating oils on water?

7. Draw a picture of a micelle in a surfactant solution.

8. Why is the "skin" analogy for surface tension misleading?

9. Which has the lowest surface tension: water or ethanol? Why?

10. Who discovered most of what we know about soap bubbles?
Laboratory Experiments

Flowchart of the Experiments

Section A. The Measurement of Surface Tension by Capillary Rise Techniques
   Part 1. The Surface Tension of Water
   Part 2. The Surface Tension of Ethanol
   Part 3. The Surface Tension of Soap and Detergent Solutions

Section B. Langmuir-Blodgett-Pockels Techniques and Oil Spill Chemistry

Section C. Some Properties of Soap Films

Section D. Minimum-Distance Networks and Soap Film Computers

Section E. Three-Dimensional Systems: Bubbles and Films on Frames

Section F. Free and Captive Bubbles and So Froth

Section G. Fun with Big Bubbles

Requires one three-hour class period to complete
Section A. The Measurement of Surface Tension by Capillary Rise Techniques

Goals: (1) To observe and measure the rise of liquids up a capillary tube. (2) To be able to calculate the surface tension of a liquid from an appropriate mathematical relationship.

Discussion: Measurements will be made on several pure liquids (e.g., water and ethanol) and on solutions containing surface-active solutes.

Section A. Part 1. The Surface Tension of Water

Before You Begin: Surface phenomena are extraordinarily dependent on the presence of small amounts of surface-active materials. Skin oils and many other contaminants can dramatically affect the results of surface tension measurements (particularly by this technique). Absolute cleanliness is necessary in order to achieve success in this series of experiments. Wash your hands before you start and make sure that all soap is removed — soap is a surface-active agent. All your apparatus should be cleaned and rinsed with distilled water. The capillary tube is particularly susceptible to contamination with oils and grease. Plastic wash bottles containing wash liquids (e.g., ethanol and distilled water) are at Reagent Central.

Experimental Steps: 1. Construct a straw clamp and stand using 2 straws, scissors, and a 1/4" office punch. Use a 96-well tray (RB) as a base.
2. Thoroughly clean a 24-well tray and rinse well with distilled water. Slap the tray on a clean paper towel to remove drops of water.
   NOTE: Avoid touching the sides of the wells with your fingers — skin oil will destroy the experiment.
3. Clean the narrow capillary tube by washing with a stream of ethanol followed by several washes with distilled water. Make sure that all the ethanol is washed out of the inside of the capillary tube. Handle the tube with a clean piece of dry paper towel.
4. Touch the end of the capillary tube to the clean towel and allow any liquid in the inside bore to be sucked out and absorbed by the paper. Do this at both ends. If there is still a liquid slug in the middle, shake the tube gently and then touch the paper towel to the end of the capillary.
5. Place the tube into the straw clamp. Do not allow the tube to touch any surface other than the straw.
6. Fill 1 well of the 24-well tray about 3/4 full with distilled water.
7. Lift the stand and clamp over the well so that the capillary tube gently enters the water. Make sure that the end of the tube is at least 0.5–1 cm under the surface of the water.

The water will rise up the capillary tube.

8. The next step is important and not easy to do. Hold a cutoff microburet over the hole at the top end of the tube so that good contact is made. Very, very gently squeeze the bulb in order to suck or blow the column of liquid up or down a little.

This technique will ensure that the liquid is really at equilibrium and at the maximum height it will rise to.

9. As illustrated below, carefully measure the height of the column of liquid (h) in the tube from the level of the liquid in the well.

- Record the measurement.

10. With a clean piece of paper towel, remove the tube, touch the end to remove the residual column of liquid, and replace it in the liquid in the well.

11. Repeat Steps 7 through 9.
   - Do you think that the capillary tube must be vertical? Why?
   - Would the water rise if the capillary were made out of a plastic, such as polyethylene?

*Calculation of the Surface Tension of a Liquid*

A liquid will rise up a narrow tube only if the liquid actually "wets" the tube wall — i.e., the contact angle is 180°. The surface tension of the liquid acting at the top of the column of the liquid in the tube holds the column up against the force of gravity pulling the liquid column down.
Let
\[ r = \text{radius of tube (cm)} \]
\[ \gamma = \text{surface tension (dyne cm}^{-1}\text{)} \]
\[ D = \text{density of liquid (g cm}^{-3}\text{)} \]
\[ g = \text{acceleration due to gravity, 980 cm s}^{-2}\]
\[ h = \text{capillary rise (cm)} \]

Then
\[
\text{Surface tension force} = \text{circumference of liquid column} \times \text{surface tension} \\
= 2\pi r \gamma \\
\text{Weight of liquid} = \text{volume of column} \times \text{density} \times \text{acceleration due to gravity} \\
= \pi r^2 h D g
\]

At equilibrium, the two forces are equal; thus,
\[ 2\pi r \gamma = \pi r^2 h D g \]
Rearranging and cancelling,
\[ \gamma = \frac{rhDg}{2} \]

and the unit of surface tension \( \gamma \) is dyne cm\(^{-1}\). To convert this value into an SI unit, multiply by \( 10^{-3} \), and the unit is newton per meter (N m\(^{-1}\)). The literature value for the surface tension of pure water (against air) at 25°C is 72 dyne cm\(^{-1}\), or 0.072 N m\(^{-1}\).

Ask your instructor for the radius of the tube and use 1.00 g cm\(^{-3}\) for the density of water.

- Calculate the surface tension of water from the average of your capillary rise measurements.
Would you expect the surface tension to increase or decrease if the temperature were raised? Why?

NOTE: If you do not know the radius of the capillary tube, then you can carry out the capillary rise experiment and assume the value for the surface tension of water (given earlier). The calculation will then enable you to find the average tube radius. You have calibrated the tube and can now use it to measure the surface tension of other liquids.

### Section A. Part 2. The Surface Tension of Ethanol

**Experimental Steps:**

1. Clean the capillary that you used in Part 1, only this time wash it thoroughly (inside and out) with ethanol from a wash bottle.

2. Wipe with a dry paper towel. Remove any residual ethanol by contacting the end of the tube with the dry towel. Do the same at the other end if necessary.

3. Dry a well in the 24-well tray with a microtowel and fill it about 3/4 full with ethanol (C₂H₅OH).

4. Carry out 2 measurements of the capillary rise of ethanol using the same technique used for water (Part 1).
   - Record the measurements.
   - Calculate the surface tension of ethanol given that the density of 95% by volume ethanol is 0.82 g cm⁻³.
   - In your record give a brief discussion of why the surface tension of ethanol is different from water. Give particular emphasis to the intermolecular forces in each system.

5. If you have time, it might be interesting to make a solution with a mole fraction of 0.5 water and 0.5 ethanol and measure its surface tension.

### Section A. Part 3. The Surface Tension of Soap and Detergent Solutions

**Experimental Steps:**

1. Select 1 of the soap or detergent solutions that are available at Reagent Central.
   - Make a note of the brand name, type, and concentration of the soap or detergent.

2. Fill a clean well about 3/4 full with the selected solution.

3. Wash the capillary tube with ethanol and distilled water.

4. Carry out 2 measurements of the capillary rise for the same soap or detergent solution using the standard technique.
   - Calculate the surface tension of the soap or detergent solution. Assume that the density of the solution is 1.0 g cm⁻³.
• In your laboratory record, give a brief explanation of your surface tension result.

• Would you expect the surface tension of an inorganic salt solution (say, 1 M NaCl) to be less than or greater than that for pure water? Explain.

• Do you think that changing the gas above a surface (say, by replacing air with dinitrogen) would change the surface tension?

• Do you think that the surface tension is related to the charge (i.e., anionic, neutral, or cationic) on a surface-active agent?

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**Section B. Langmuir-Blodgett-Pockels Techniques and Oil Spill Chemistry**

**Goals:**

1. To explore the surface activity of a variety of natural, synthetic, and modified hydrocarbon oils using a Langmuir-Blodgett-Pockels trough.
2. To investigate several strategies for oil spill containment and cleanup.

**Before You Begin:**

The observation of surface phenomena, in this instance on a water surface, requires considerable care and thought. The room lighting will often determine the appropriate viewing angles at which to see the various phenomena. In the first experiment explore all the possibilities. Once you first see the activity at the water surface, subsequent observations are very easy.

**Experimental Steps:**

1. Clean a plastic petri dish thoroughly with soap and water. Make sure that all the soap is rinsed away.

2. Fill the petri dish bottom about 3/5 full with room temperature water.

3. Place the dish onto a white surface (no lines in the background) in a position on the table where the surface can be viewed easily.

4. Try looking at the water surface from different angles until you can see the occasional specks of dust floating at the surface.

   NOTE: Once you have established a good viewing position, place the dish in roughly the same place for all experiments and make a mental record of where you are in relation to the light and the dish. The dish and water system is a simple Langmuir-Blodgett-Pockels trough (LBPT).

5. Obtain a container of lighter fluid.

   **CAUTION:** Make sure there are no flames in the room!

6. Open the container and use the pipet to drop 1 drop of the fluid into the center of the water surface in the dish.

7. Observe and make notes. Several interesting things are going to happen in a relatively short period of time. Watch carefully (in a good viewing position) until the hydrocarbon fluid disappears.

   • Record your observations!
NOTE: If everything went by too fast, all you have to do is place another drop onto the surface and repeat the experiment.

At this stage it is perhaps worthwhile to form a discussion group with your peers (and the instructor). Try to formulate explanations and interpretations of the complex sequence of phenomena you have just observed.

To help you do this, here are some thoughts. Lighter fluid is a homogeneous mixture of many hydrocarbons ranging from small molecules (e.g., C$_3$H$_6$) to large ones (e.g., C$_9$H$_{20}$). The fluid mixture is obviously volatile — it disappeared! The mixture consists of a range of compounds of different molar mass, each of which has a different vapor pressure (at the temperature of the water in the dish). The smaller molecules will evaporate faster than the larger molecules; therefore, the fluid composition changes as the fluid evaporates. The fluid is less dense than the water and is immiscible with water. The series of colored spectra that eventually appear in the fluid layer form when the layer thickness approaches the wavelength of visible light.

8. If you have time you might want to explore the effect of temperature on the surface behavior of hydrocarbons.
   - What would happen on ice-cold water?
   - How about the effect of substances dissolved in the water?
   - Would a seawater surface exhibit the same characteristics?

9. You can investigate the effect of waves on the fluid layer in the following way. Hold a cotton swab vertically close to the edge of the dish and dip it in and out of the water in a periodic motion.

10. Clean the dish and again fill it about 3/4 full with water.

11. Obtain a sample of unused (new) motor oil. Transfer some oil to the surface by touching a plastic stem (or toothpick) to the oil and then to the surface.
   - Describe and explain the behavior of the oil.
   - Why does the oil form a lens?
   - Does the oil disappear?
   - What happens if you make waves?

12. Design some simple experiments to explore the best way of removing the oil from the surface.
   - Would your idea work on a large scale?
   - What would happen if the water temperature were almost 0°C?
   - Why won't a cotton swab pick up the oil very easily? Try it!

13. Remove the oil (by your best method) and clean the dish thoroughly with soap and water.

14. Place the dish on the plastic surface against a white background.
15. Fill the dish with water until the water "piles up" above the plastic edges of the dish (as illustrated below).

16. Slip a straw over a glass rod. Hold the rod at both ends (use both hands). Place the rod and straw horizontally onto the edge of the dish and in the piled-up water. Pull the rod over the dish keeping the straw touching the edges of the dish. As you do this the surface will be swept clean, as shown below.

If you leave the rod "parked" on the surface at the end of the sweep, any surface contamination that was swept in front will stay enclosed. The sweep technique (invented by Pockels) is an extremely effective method of ensuring a clean surface.

17. You can now remove the contamination by quickly dabbing the end surface with a clean, dry paper towel.

18. Obtain the used-oil sample.

19. Using a thin plastic stem, transfer a small drop to the center of the water surface in the dish.

20. Observe carefully what happens.
   - Draw a picture in your record.
• Compare the behavior of the used versus new oil.
• Describe the color of the oil (view at a good angle!).

21. Now you need to do two things at once! Keep watching the oil at an angle at which you can see the color and push the rod and straw over the surface for about 3–4 cm. Then pull it back and push again (keeping it on the edges of the dish).
• Describe what you see in your notebook.

22. You now have an oil slick that has spread out over a considerable area. Design a way in which the slick can be removed from the surface. Experiment with microbooms (use cut pieces of straw or cotton or fishing line) to try to contain the slick.

If you sweep it, you are still faced with the problem of removing the swept oil. If you were in an ocean environment, the boom would have to be rather long!
• Describe your design in your lab notebook.

23. Make waves and observe the behavior of the oil slick.
• Record your observations.

24. Obtain a detergent solution and dip a clean plastic stem — i.e., not contaminated with oil — into it. Transfer the small volume of detergent solution to the middle of the slick.
• What happens?

25. If you have time, you might want to investigate the effect of ocean composition, temperature, waves, wind, and ships on an oil slick. To make a new slick, all you have to do is empty the dish, clean it thoroughly with soap and water, wash your hands thoroughly, and start again.

Section C. Some Properties of Soap Films

Goal: To use a soap solution to investigate some of the chemical and physical properties of bubbles and films.

Experimental Steps:
1. Obtain a piece of aluminum wire from Reagent Central.
2. Bend the wire to make a smooth ring (about 6 cm in diameter) with a handle at right angles to the plane of the ring. The ring should easily fit into the bottom of a petri dish.
3. Obtain soap solution from Reagent Central and fill the dish about 3/4 full — this is a special solution specifically formulated for making good bubbles and films. It is labelled as such.
4. Holding the ring by its handle, dip the wire ring into the soap solution and gently remove it.
5. Tilt the ring at an angle so that you can see the film that has formed on it. Use your hand lens to make observations on the nature of the film.
• How thick do you think the film is? Is there any way of measuring the thickness of a soap film?
• What are those weird wriggly areas?
• How does the film get around the wire?
• Are there any colors? Describe them.
• Do the colors change with time?
• How long does it take for the film to collapse?
• How does it collapse?

6. Dip again and make another film. Poke a straw through the film.
• Does it collapse?
• Is there a film inside the straw now?

7. Move the straw in a circular motion in the film.
• Describe what happens.
• How do the soap molecules move out of the way so quickly?
• Can a film be made on any type of material, e.g., a rubber band or a plastic ring?
• In your record draw several pictures to show the ring being lifted from under the surface of the soap solution and out into the air and explain why the film is a thick bilayer. Use the head and tail stick representation for individual soap molecules.
• Is the film on the wire ring the minimum surface area for a circle? Explain.

8. Tie a piece of thread very loosely across the wire ring so that it is attached on opposite sides of the ring.

9. Dip the ring with thread into the soap solution in the dish. Make sure that the thread is thoroughly wetted.
• Describe the result.

10. Poke the thread with a straw.
• Describe its action.

11. Break the film on one side of the thread with your finger or a dry glass rod.
• Interpret the action of the forces that must be acting on the thread.

12. Dip the ring and thread again and arrange the thread so that it forms a looped circle in the middle. Now, break the film inside the thread loop (but not outside).
• Describe and explain what happens.

13. Poke at the thread with a straw without breaking the outside film.
• What happens when you push the loop in toward the center of the ring?
You have seen in these simple experiments that soap films always try to form minimum-area surfaces. The reason is that soap and water molecules in the top and bottom surfaces of the film are more strongly attracted to soap and water molecules inside the film than to the air molecules (O₂ and N₂) outside the film. At the molecular level the film is a chaotic mass of continuously moving molecules that are being pulled into the inside of the film.

In the next few experiments you can investigate minimum-distance networks and soap film computers.

**Section D. Minimum-Distance Networks and Soap Film Computers**

**Goals:**

1. To be able to solve minimum-distance problems.
2. To deduce some of the mathematical relationships that govern soap network systems.

**Before You Begin:**

Before beginning to work with actual soap films, think about the following puzzle. There are 3 points that are spaced equally apart, forming an equilateral triangle. The puzzle is to connect all 3 points such that the sum of the lengths of all lines is the smallest possible — i.e., a minimum distance between all 3 points. The author has tried two ways, one of which is much shorter than the other. You can easily see if you have solved the puzzle by using a ruler to measure the total line length, as shown below.

These types of problems have become known as Steiner problems, after the nineteenth-century mathematician Jacob Steiner, who made a study of them. The soap film approach to solving Steiner problems was made famous in the 1940s by the mathematician Richard Courant. OK, let's solve the puzzle with a soap film computer!

**Experimental Steps:**

1. Empty the soap from the dish into the waste soap container. Rinse the dish. Turn it over and place it on the plastic surface.

   You are going to use it as a support for a glass sheet.

2. Obtain 2 glass or plastic sheets from Reagent Central. Place one of the sheets onto the dish (it will hang over the end). Form an equilateral triangle with 3 thumbtacks
placed about 1–2 cm apart in the middle of the glass sheet. Place the second sheet onto the tacks.

3. Grasp both sheets and press so that you can lift and carry them without losing or moving the tacks — no mean feat!

4. Dip the entire sandwich into the bucket of soap and then withdraw it. If you do this cleanly and avoid the froth, you will be presented with an answer to Steiner’s 3-point problem.

5. If you are careful (and lucky) you can lay the sandwich back down on the dish and use a ruler to measure the total line length and prove the answer is correct.

6. You might want to experiment with 3 point problems in which the triangle is not equilateral. Some typical minimum distances are illustrated below.

There is always a triple film junction with 120° angles, and in the limiting case, the triple junction degenerates and joins the tack that forms the 120° vertex.

7. Add a fourth thumbtack to see if you can create a 4-point (square) system that can be solved with a soap film computer. Some possibilities are,
You can see that there are 2 networks that have an equal probability of being answers. The soap system will inevitably adopt one of these 2 minimum networks. It is impossible to predict in advance which one will appear! You can actually push the network into the other minimum form by gently blowing on the intersection with a straw. The network will move through a point where 4 films actually come together and then adopt the more stable, minimum network. It is interesting to note that soap networks connecting an irregular quadrilateral can adopt minimum forms that when blown on adopt a shorter network. Both forms are minimum networks, but one is more minimum than the other!

- How could these minimum networks be shown in graphical form?

The mathematical formula governing the topology of Steiner's problems is that the number of points \( N_1 \) minus the number of 3-way junctions \( N_3 \), equals 2:

\[
N_1 - N_3 = 2
\]

The Steiner problems involve two-dimensional film networks, but it is possible to solve three-dimensional problems using the fact that soap films always tend to form a minimum area, as you will see in Section E.

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**Section E. Three-Dimensional Systems: Bubbles and Films on Frames**

**Goal:**

To extend the soap film computer concept to solve minimum-area problems in three-dimensional systems.

**Discussion:**

Observations and measurements will be made on several wire polyhedra.

**Experimental Steps:**

1. At Reagent Central there are numerous soldered wire frames forming both regular and irregular polyhedra. Select some of the simpler arrangements to begin with (e.g., the tetrahedron or cube).

2. Fill the large cup (or beaker) with soap solution and take it back to your place in the laboratory.

3. Use a towel to sweep any froth of small bubbles from the top of the soap solution.

4. Dip the frame (the entire polyhedron) into the soap solution and withdraw it slowly. The soap film computer (the frame) will adopt the minimum area bounded by the particular polyhedron that you are using.

5. Select several more complex polyhedra from Reagent Central and carry out Steps 3 and 4 with each. Selectively break a film and watch how the minimum surface responds. Redip to obtain the analog answer and use a straw to blow on various places in the films.
• Draw pictures of the minimum areas adopted by 3 different polyhedra. For each area, note how many films meet and where they meet — i.e., at points or lines — and note the angles formed in the process.

• Describe whether you can obtain alternative minima.

• Note the colors in the films. Describe color changes as the films drain.

NOTE: The minimum area inside a tetrahedral frame is

![Diagram of tetrahedral frame with handle and wire frame]

It is especially interesting to note that at the 4-way point, the angles are exactly 109° 28' 16". You will see later that this angle precludes the making of a regular froth of regular cells.

6. Generate a little froth on top of the soap solution and slowly dip a frame. If you are lucky, as you dip and withdraw the frame, you might catch a bubble in the middle of the minimum area.

7. Use a straw to enlarge the bubble (by blowing into it).

• Describe the intersecting points and angles, etc.

8. If you have time try constructing an irregular structure from a piece of wire. How about a helix form?

• Can you predict the minimum area for the structure that you made?

<table>
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<tr>
<th>Section F.</th>
<th>Free and Captive Bubbles and So Froth</th>
</tr>
</thead>
</table>

**Goal:**
To investigate some of the characteristics of free and captive bubbles and examine the pressure and area relationships in different sized bubbles.

**Before You Begin:**
Remember to draw pictures of what you see in the following experiments.
**Experimental Steps:**

1. Let's start with a very simple experiment and some simple questions. Blow a few free-floating bubbles.
   - Describe how you did that!
   - Why are free bubbles spherical in shape?
   - What determines the size of a free bubble?
   - Is there any limit to the size of a free bubble?
   - Why do bubbles fall?

2. Pour a little soap solution into a petri dish until the bottom of the dish is just covered. Poke the end of the straw into the soap and blow down the straw to make a captive bubble.
   - Describe its shape.

3. Poke the straw into the bubble and blow gently.
   - What happens to the bubble?

Now here is a very interesting question,

- Is the air pressure inside a large bubble greater or smaller than the air pressure in a small bubble?

The answer is smaller — which perhaps seems slightly paradoxical in view of the fact that the bubble got larger when you blew into it! Everyone knows, for example, that if you pump air into an automobile or bicycle tire, the tire expands and the pressure increases. In contrast, though, when you blow air into a bubble, the bubble expands and the pressure decreases. The explanation for this apparent paradox is that tires are far less elastic than soap bubbles, and the rubber allows stresses to build up. In contrast, a soap film never exerts a force of more than about 0.066 N m\(^{-1}\) (which is 2 times the surface tension of a soap solution because a soap film has 2 surfaces). The force is about the same for thin and thick bubbles and for small and large bubbles. A bubble simply expands until the force exerted by the air inside exactly balances the force within the film.

4. Test the pressure theory by blowing another hemispherical cap bubble on the dish.

5. Now place the straw about 0.5 cm away from the side of the bubble, blow with constant force, and observe the resulting curvature in the bubble.
   
   You are applying pressure to the bubble and it adopts a much larger curvature — i.e., smaller diameter curve.

6. Poke the straw into the soap solution in the dish and blow a captive bubble that occupies about 1/2 the dish. Remove the straw.

7. Blow another captive bubble in the other half of the dish.
• Describe what happens when the bubbles touch. Explain your observations by invoking an important property of soap films.

8. Poke the straw into one of the bubbles.
   • Why doesn't the bubble leak air out and go down?
   HINT: This is a trick question.

9. Now blow into the bubble to increase its diameter. Observe the curvature of the film that joins the two bubbles.
   • Why does the curvature go in that direction?
   • What angles are formed at the intersection of the bubbles?

10. Dip the straw in soap solution and lift it out. Keeping the straw vertical, blow gently down the straw to form a bubble on the end of the straw. Now stop blowing (and remove your mouth).
   • Explain why the bubble goes down.

11. Repeat Step 10, except this time when you stop blowing, quickly and smoothly place your index finger over the end. The bubble will stay. Now gently lower the bubble until it touches the soap in the petri dish. You can repeat the experiment as many times as you like — the change is subtle, but definitely real.
   • Explain what happens and particularly note any change in size.

When the spherical bubble changes to a captive hemisphere, there is no change in the amount of air. The volume of the spherical bubble must therefore equal the volume of the hemisphere, i.e.,

\[
\frac{4}{3} \pi r_s^3 = \frac{1}{2} \left( \frac{4}{3} \pi r_H^3 \right)
\]

where \( r_s \) and \( r_H \) are the radii of the sphere and the hemisphere, respectively. Upon rearrangement and cancellation,

\[
r_s = \left( \frac{1}{2} \right)^{1/3} r_H
\]

which means that the radius of the sphere is 79% of the radius of the hemisphere.

A very simple and effective method of keeping bubbles around for a long time in order to make observations is to blow the bubbles in the dish and then place the top on the petri dish.

11. Design an experiment to study the shape and angles of a multiple-bubble froth.
   • Can you see any pentangular dodecahedra?
Section G. Fun with Big Bubbles

Goal: To have Fun!

Before You Begin
Your instructor will demonstrate amazing technical skill by attempting to produce world-record bubbles. The author has produced bubbles that are about 12 ft in diameter. All you need is the big bubble machine, which may be purchased at your local toy store for a few dollars. (Or you can make one yourself — check with your instructor.)

Experimental Steps:
1. Play with the lab’s big bubble machine!
2. Can you put a bubble inside a bubble? Try it!
3. Can a person get inside a bubble?