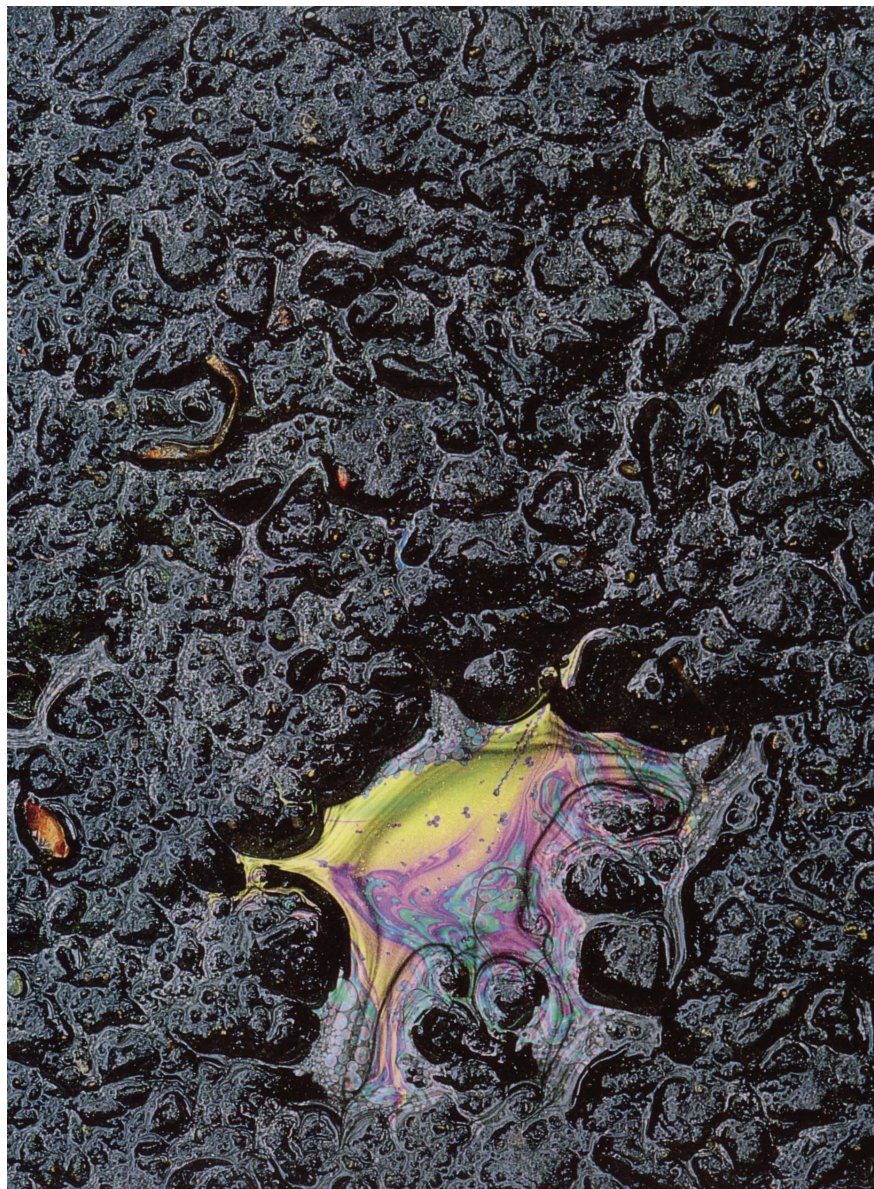


DO MOLECULES EXIST AND HOW SMALL ARE THEY?



by **Dr. Stephen Thompson**
Mr. Joe Staley
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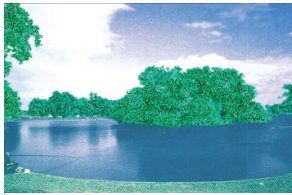
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

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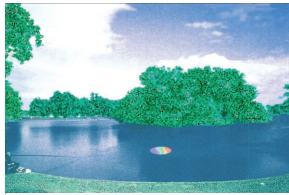
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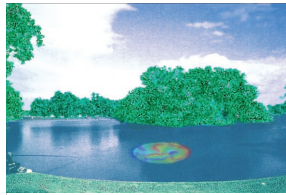
BENJAMIN FRANKLIN STILLS THE WAVES



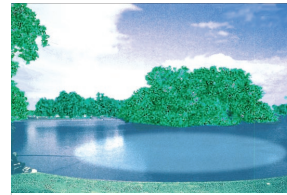
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Throughout his life Benjamin Franklin was interested in the calming effect of oil on turbulent water. In 1774, he described a series of experiments in which he poured oil on a pond in England. He observed that a teaspoon of olive oil poured on the surface spread to about one half of an acre. In an article in *Philosophical Transactions* 64, 1774, 445-460, he also reported, as seen in the excerpt given here:

Franklin searched for a scientific explanation of these phenomena because he was interested in the practical problem of saving the lives of sailors shipwrecked at sea in violent storms. He didn't realize that this simple experiment could actually be used to determine the size of olive oil molecules! Before determining their size, let's explore why olive oil molecules spread on water. This alone was fascinating to Franklin because on other surfaces, olive oil doesn't spread. How can this be?



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In 1989, when the Exxon Valdez grounded at Prince William Sound and spilled 10.8 million gallons of oil into the sea, the clean-up process was expensive and difficult because of the simple fact that oil spreads on water. Several methods to clean Prince William Sound were employed, including the use of a boom, as seen in the following picture. The boom can be pulled across the surface to collect the oil but is usually employed more as a guard to protect an area.

[450]

After this, I contriv'd to take with me, whenever I went into the country, a little oil in the upper hollow joint of my bamboo cane, with which I might repeat the experiment as opportunity should offer; and I found it constantly to succeed.

In these experiments, one circumstance struck me with particular surprize. This was the sudden, wide, and forcible spreading of a drop of oil on the face of the water, which I do not know that any body has hitherto considered. If a drop of oil is put on a polished marble table, or on a looking-glass that lies horizontally; the drop remains in its place, spreading very little. But when put on water it spreads instantly many feet round, becoming so thin as to produce the prismatic colours, for a considerable space, and beyond them so much thinner as to be invisible, except in its effect of smoothing the waves at a much greater distance. It seems as if a mutual repulsion between its particles took place as soon as it touched the water, and a repulsion so strong as to act on other bodies swimming on the surface, as straws, leaves, chips, &c. forcing them to recede every way from the drop, as from a center, leaving a large clear space. The quantity of this force, and the distance to which it will operate, I have not yet ascertained; but I think it a curious enquiry, and I wish to understand whence it arises.

Notice the color variation in the water. Describe the contaminated water. Are Franklin's observations similar to yours? Why or why not?

When oil is spilled on water, does it float on top, sink to the bottom, or get dispersed throughout the water?

What other methods have been used to clean up oil spills.
What new methods can you suggest?

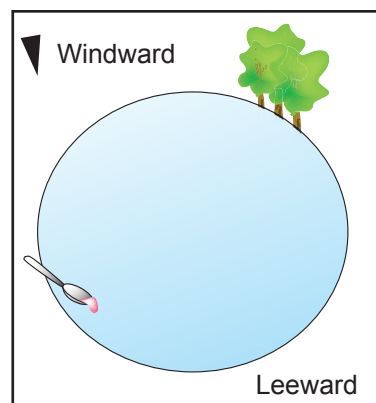
Read Benjamin Franklin's original discussion, which is included with your course resources.

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ON CLAPHAM POND-1

Benjamin Franklin was interested in the effect of pouring oil upon troubled waters. As a practical man he thought that the effect might help prevent ships from sinking and sailors from drowning. The following quotes are from the 1774 Philosophical Transactions of the Royal Society.

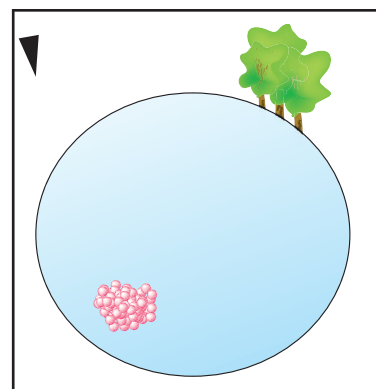
“At length being in CLAPHAM where there is, on the common, a large pond, which I observed to be one day very rough with wind, I fetched out a cruet of oil, and dropt a little of it on the water.”



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“I saw it spread itself with surprising swiftness upon the surface; but the effect of smoothing the waves was not produced...”

Why not?

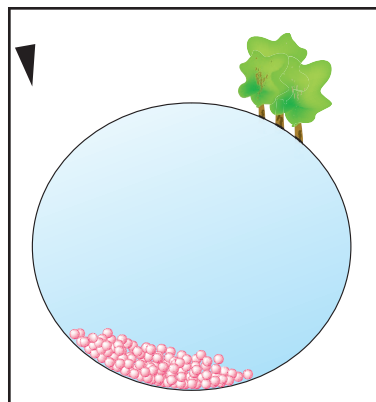


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“...for I had applied it first upon the leeward side of the pond, where the waves were largest, and the wind drove my oil back upon the shore.”

What would you have done next after getting this result?

Why do you suppose the wind pushed the oil upon the shore when the wind does not push the water upon the shore. Or does it?



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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

ON CLAPHAM POND-2

Visit a small or medium sized pond on a windy day. Observe the character of the waves both on the leeward and the windward sides. Repeat Franklin's experiments on both sides of the pond and describe your results.

"I then went to the windward side, where they began to form..."

Olive oil is attracted to the water. How does this experiment support this statement?

Olive oil is attracted to itself. How does this experiment support this statement?

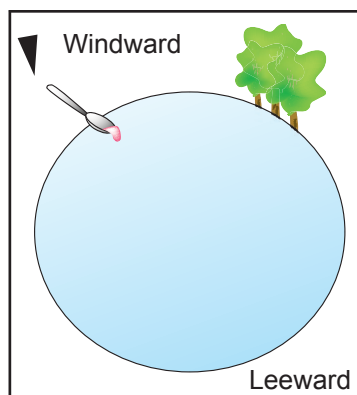
"...and there the oil, though not more than a tea spoonful, produced an instant calm over a space several yards square..."

What do you think would happen if the olive oil molecules were smaller than water molecules?

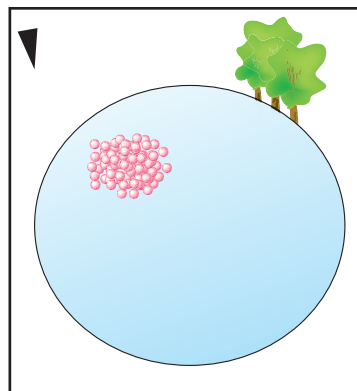
"...which spread amazingly, and extended itself gradually till it reached the lee side, making all that quarter of the pond, perhaps half an acre, as smooth as a looking-glass."

You might suppose that the oil spread because it was blown by the wind. Do you think that there might have been another reason why the oil spread?

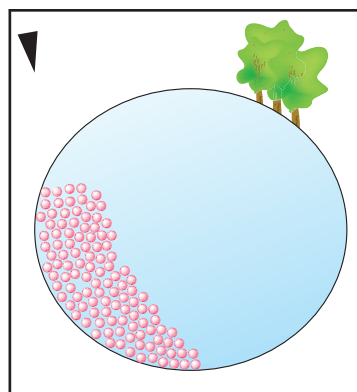
What do you think Franklin would have found if he had returned to look at the pond the next day? Why, from a molecular point of view do you think that?



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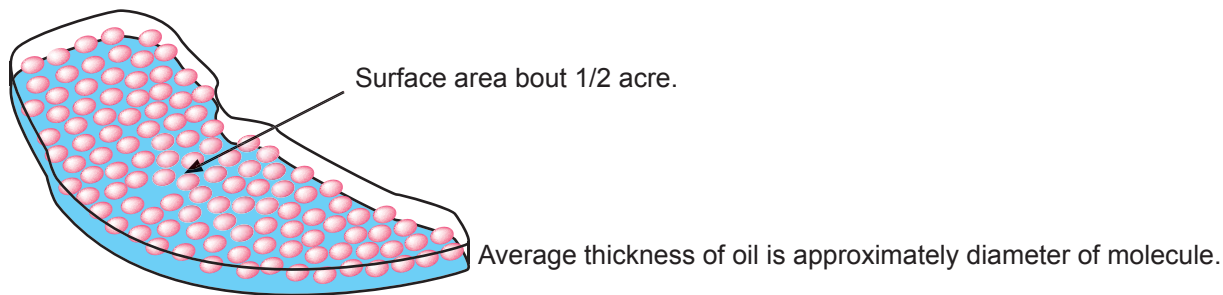
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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

SURFACE AREA CALCULATION



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One acre = 43,560 square feet = 4,840 square yards = 4047 square meters.

It is reasonable to approximate “perhaps half an acre” as 2000 square meters.
Call the surface area A
 $A = 2000 \text{ m}^2$
Call the diameter of the oil layer D .
Call the volume of the oil V .
From geometry, $V = AD$
But eighteenth century teaspoons in museums hold approximately two cubic centimeters, so we know that $V = 2 \text{ cm}^3$
Now we can put our facts together and see that $2 \text{ cm}^3 = 2000 \text{ m}^2 \times D$
You can finish the calculation.

Benjamin Franklin could have done this calculation but he did not. Why do you think that he did not? What implications would it have had for the development of science if he had?

A few years ago Professor Stephen Thompson of Colorado State University attempted to repeat Franklin’s experiment by dropping olive oil onto City Park lake in Fort Collins. It did not work. Why not?

We are assuming that the oil, after spreading to half an acre, was one molecular layer thick. Of what significance for our assumption is the fact that after spreading to half an acre the oil STOPPED spreading.

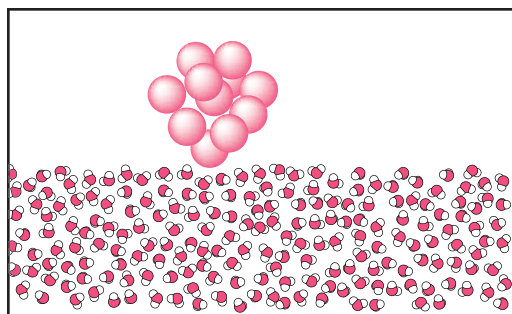
Calculate the number of molecules in Dr. Franklin’s teaspoonful.

DO MOLECULES EXIST AND HOW SMALL ARE THEY?

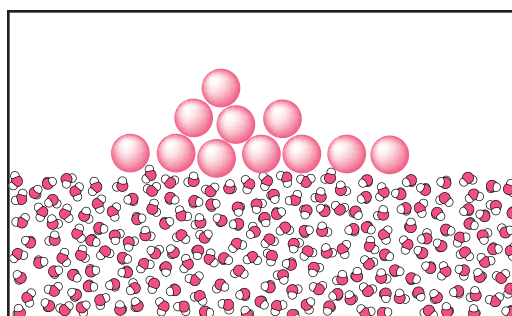
OIL ON WATER

If you look closely at the pictures on the right you will notice that the positions and/or orientations of (some of) the water molecules have changed. Did you try the experiment of placing a drop of oil on ice? Did the oil spread? Can you explain why the motion of the water molecules is necessary for the oil to spread? Could the spreading of the oil be simply due to the random motion of the water molecules? Could it be due to the weight of the oil pushing itself flat across the water?

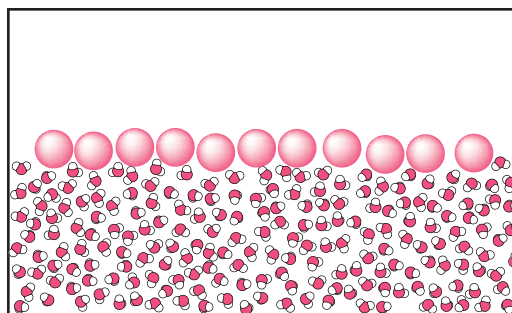
Did you try the experiment of placing a drop of mineral oil on water? Did it spread? How does that fact fit with the explanation of spreading as due to random molecular motion or to the weight of the oil?



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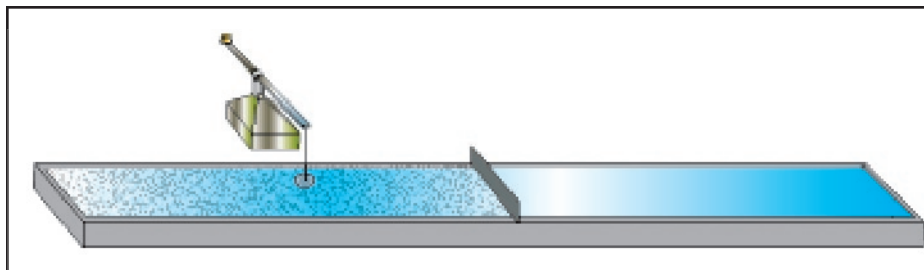
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AGNES POCKLES

In 1891 the famous scientist Lord Rayleigh (who won the 1906 Nobel Prize for the discovery of Argon) received a letter from an unknown German lady, Agnes Pockles. An English translation of the letter was published in Nature on March 12, 1891.

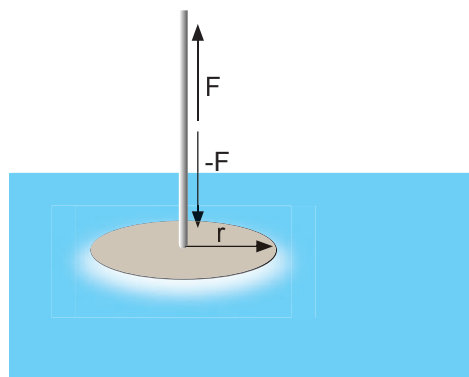
Pockles found experimentally that the surface tension of a saturated solution of sodium chloride was 15.4% greater than the surface tension of pure water. Can you give a molecular explanation for that fact?



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Agnes Pockles experimental apparatus for measuring surface tension.

The picture on the right shows Pockles' method of measuring surface tension. From this method, discuss why the units of surface tension are Newtons per meter. Devise another method of measuring surface tension.



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Among Pockles' results were the following:

“...that the surface layer of water can take up more of soluble substances than the internal liquid...”

and similarly

“...in which a thin disk of camphor, so hung that it is half immersed in the cleanest possible water surface, is cut through in the course of a few hours.”

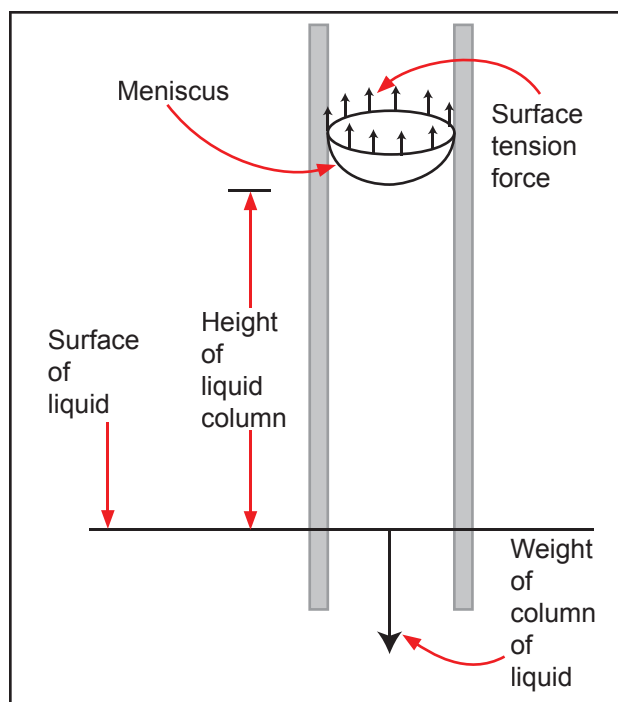
Explain what you can deduce about the molecular nature of water surfaces from these observations?

Read Ms. Pockles letter to Lord Raleigh, as translated and published in Nature, which is included in your course resources. Explain what you consider to have been her most significant or interesting results.

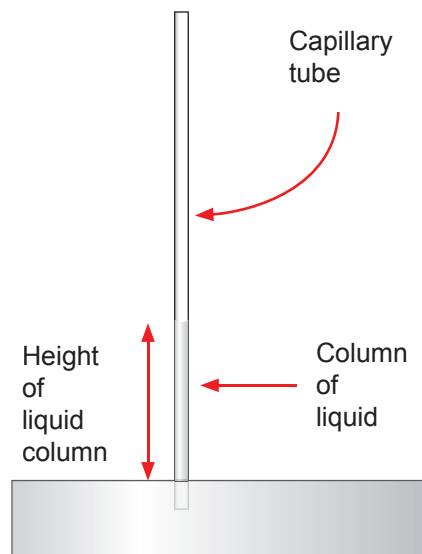
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

MEASURING SURFACE TENSION BY THE CAPILLARY METHOD

The Pockles method of measuring surface tension is rather difficult to use but here is a simpler method, although it still requires careful technique.



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Using the capillary method, measure the surface tension of different fluids, including distilled water, soapy water, tap water, an aqueous salt solution and ethanol. (The density of 95% by volume ethanol is 0.82g cm^{-3} .)

Why is careful attention to cleanliness essential for this measurement? When the liquid used is water, should the capillary tube material be hydrophilic or hydrophobic and what would happen if it were the opposite.?

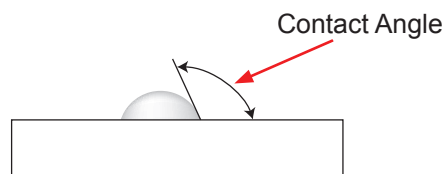
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

CONTACT ANGLES

We can often surmise the interaction between a liquid and a solid by observing the contact angle between a droplet of the liquid placed on the surface of the solid.

What can you determine about the relative hydrophilicity of the four surfaces illustrated in the drawings to the right? Assume that the droplet is made of water.

Place droplets of water on various surfaces, including both clean and dusty glass, different plastics and metals. Observe and draw the contact angles and discuss the hydrophobicity or hydrophilicity of the substances. Repeat the experiment with other liquids such as alcohol and various vegetable and mineral oils.



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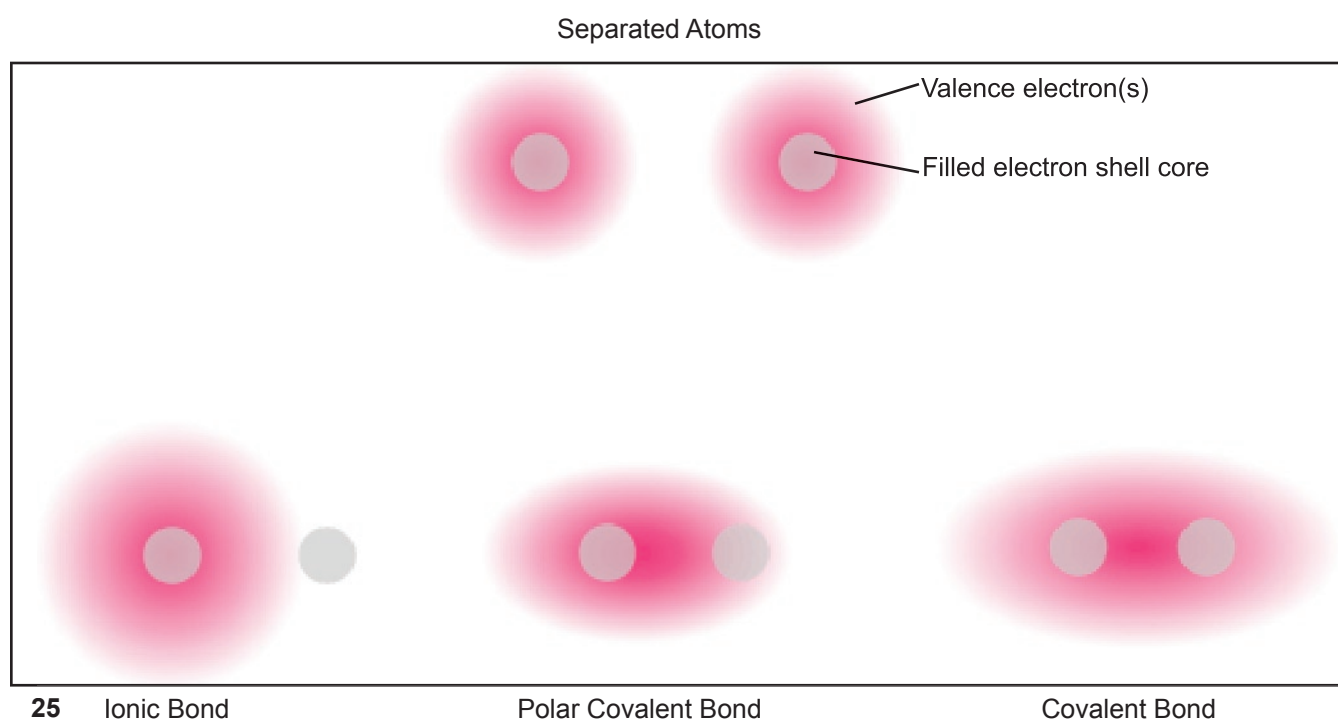


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DO MOLECULES EXIST AND HOW SMALL ARE THEY?

IONIC, POLAR AND COVALENT BONDS

Ionic and covalent bonds are two ideal types. Many bonds share characteristics of both ionic and covalent bonding. They are called polar covalent bonds and they tend to occur between atoms of moderately different electronegativities. In polar covalent bonds the electrons belong predominantly to one type of atom while they are still partially shared by the other type, as illustrated in the following pictures of the valence electron densities.



In the picture above, the separated atoms look alike. If, in fact, they are the same kind of atom, which of the three bonds shown is possible? Why only that one? What other type of bonding is possible between identical atoms?

DO MOLECULES EXIST AND HOW SMALL ARE THEY?

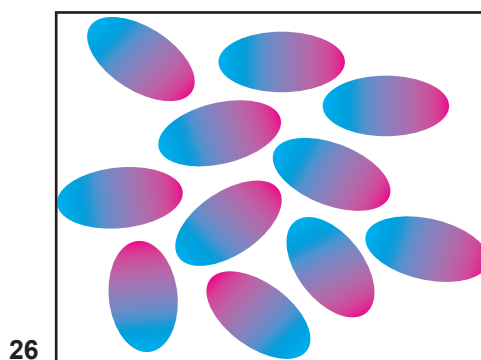
INTERMOLECULAR FORCES

In addition to covalent, polar, ionic and metallic bonding there are intermolecular forces which contribute to the structure of things. These include dipole-dipole forces, hydrogen bonding and London dispersion forces.

DIPOLE-DIPOLE FORCES

Many molecules are electric dipoles, that is, they have net positive charge on one part of the molecule and net negative charge on another part. Since opposite charges attract and like charges repel, these molecules will tend to orient themselves so that there is the most attraction and the least repulsion.

Why is dipole-dipole interaction more important in liquids than in solids?
Why is it more important in liquids than in gases?
Can homonuclear diatomic molecules such as H_2 , O_2 and N_2 have dipole-dipole forces?



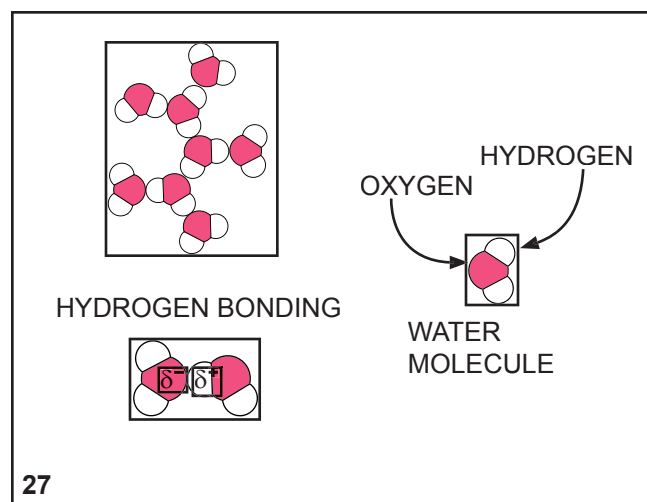
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DIPOLE DIPOLE INTERACTION

HYDROGEN BONDING

A particularly strong and important variety of dipole-dipole interaction is called hydrogen bonding. A hydrogen atom on one molecule is attracted to a highly electronegative atom in another molecule. Hydrogen bonding is strong both because of the high polarity involved and because the small size of the hydrogen atom permits a close approach between it and the electronegative atom.

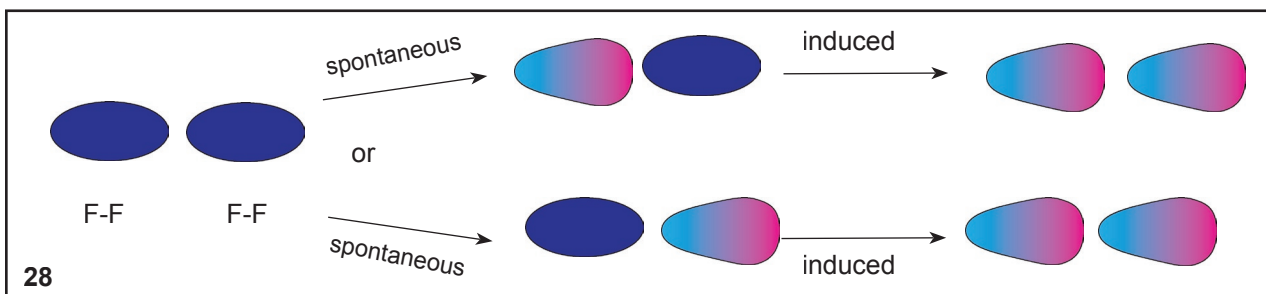
Hydrogen bonding is particularly noted between water molecules, but from the description given above you should be able to deduce other substances in which hydrogen bonding occurs.



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LONDON DISPERSION FORCES

Even nonpolar molecules have a random fluctuation of charge making the molecule temporarily polar. This then induces an opposite fluctuation in a neighboring molecule so that the two molecules have opposite charges on their near sides and attract each other.



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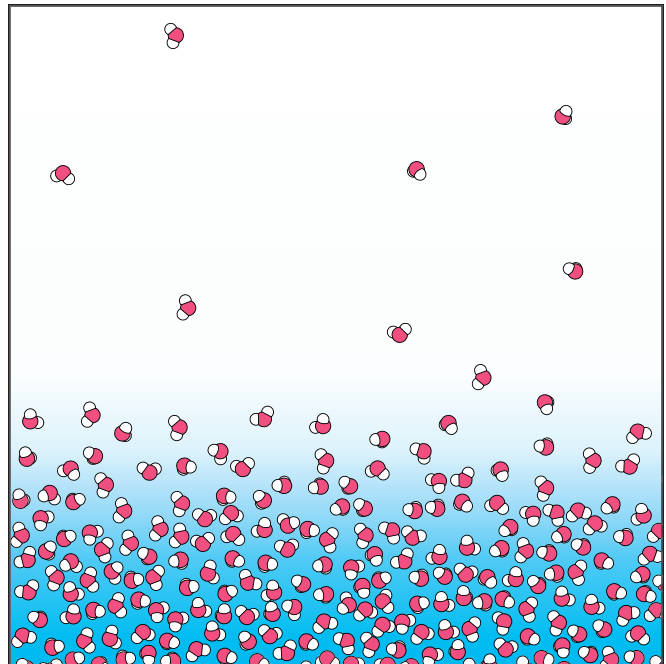
SURFACE TENSION

In the drawing on the right, circle a water molecule in the bulk of the water, a water molecule in the air and a water molecule in the surface layer of the water.

We know that it takes energy to evaporate water and that water molecules in air have a higher energy than water molecules in the liquid. What about water molecules in the surface layer?

What happens, in terms of energy, when we move more molecules from the bulk into the surface by stretching the surface layer?
What does this imply about the shape of a water/air interface, i.e. a surface?

The surface tension of water is 7.2×10^{-3} Newtons per meter. Multiply this by one square meter. What is the resulting unit? What kind of thing is that? (e.g. force, energy, viscosity,...?)



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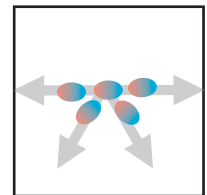
DISPELLING THE MYTHS

Some people may think of surface tension as implying some sort of skin or film on the surface, but we know that is almost the opposite of the truth.

A more sophisticated myth, because it is in the chemistry and physics textbooks, is that surface tension arises because, while a molecule in the bulk of the liquid is pulled equally in all directions by its neighboring molecules, a molecule on the surface is not pulled in the upward direction. This is a true statement about forces but its result is to keep the surface a surface and has nothing to do with surface tension.

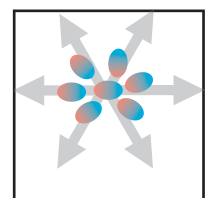
With the model of surface tension presented here it is possible to deduce whether surface tension would increase or decrease with increasing temperature, say from 300 K to 310K. Which is it?

In what direction is the resultant force on the surface molecule?



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Forces on a surface molecule.



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Forces on a bulk molecule.

DO MOLECULES EXIST AND HOW SMALL ARE THEY?

AMPHIPHILIC OIL ON WATER

What are the three types of inter-molecular forces involved in this system? (Hint: water-water (hydrogen bonding) is one.)

By referencing these three forces, how does palmitic acid spread into a monolayer? How do the relative strengths of these three forces compare to each other?

Does the surface tension of the water increase or decrease at the palmitic acid/water interface?

Using a similar molecular force description, why doesn't motor oil spread into a monolayer on water?

Draw a picture of what a "puddle" of motor oil on water might look like.

Draw a molecular picture of what the interface of the motor oil/water puddle might look like.

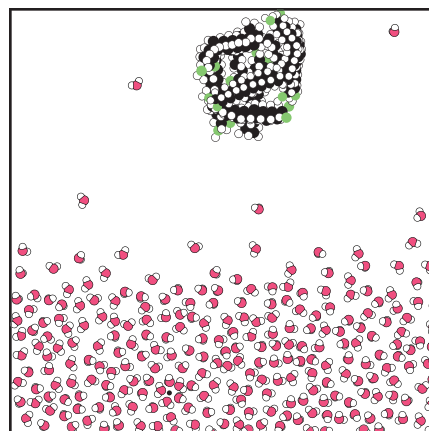
Why does the palmitic acid form a monolayer? Why don't individual palmitic acid molecules "break off" from the edges? (Or water penetrate the interior of the mono-layer, separating portions of it?)

Why is the constant molecular motion of the water surface necessary for the oil to spread? Incidentally, this is why oil will not spread to form a mono-layer on a glass surface.

Devise an experiment to show whether the time required for the oil to spread is dependent on the temperature of the water. What is your hypothesis?

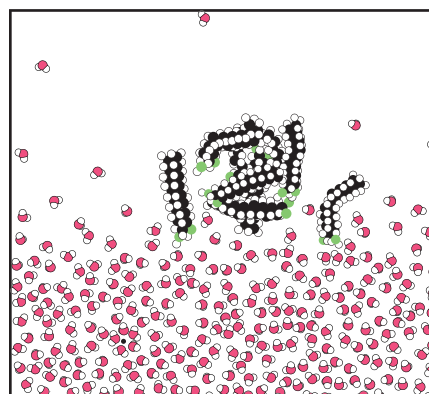
Perform the experiment. Report your results.

Why are there individual water molecules "floating" in the air above the surface?



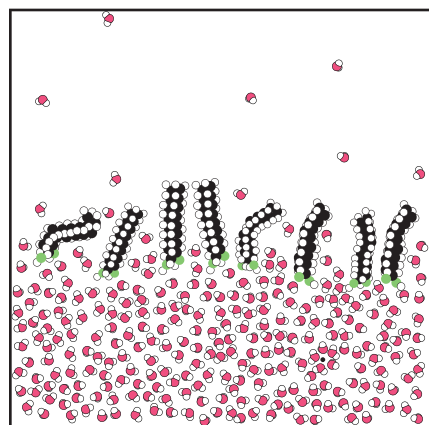
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A small drop of palmitic acid falling towards a water surface.



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The palmitic acid reaches the surface.



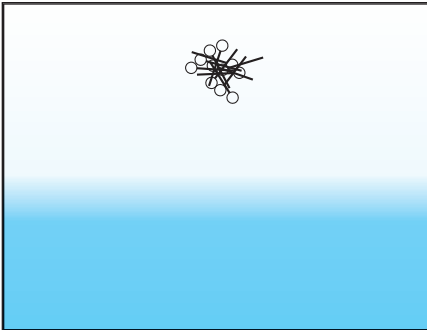
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The palmitic acid spread into a monolayer.

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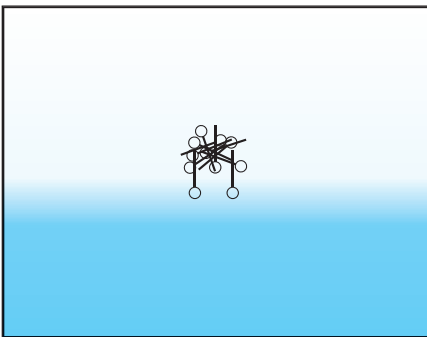
AMPHIPHILIC OIL ON WATER

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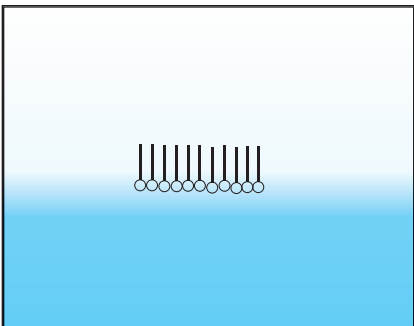


Using a simplified form such as the ones shown here - and it might be easier to put in the water with a blue marker- draw the sequence of molecular events if a drop of mineral oil were placed on water. Remember to modify the oil molecules to show that they are nonpolar.

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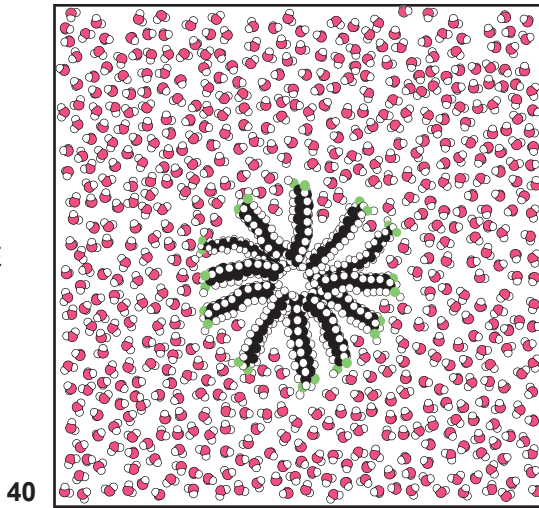
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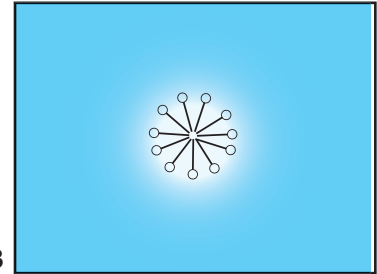
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AMPHIPHILIC OIL AND WATER

MICELLE

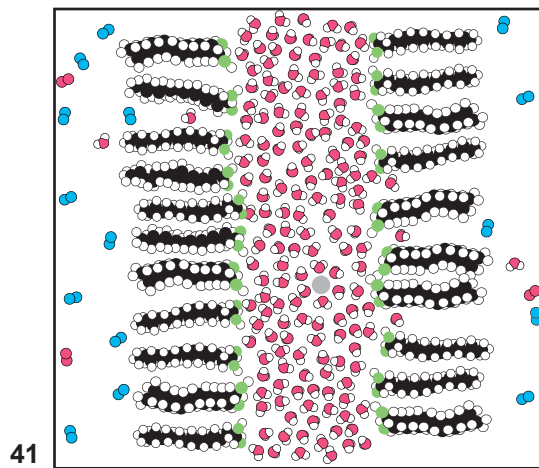


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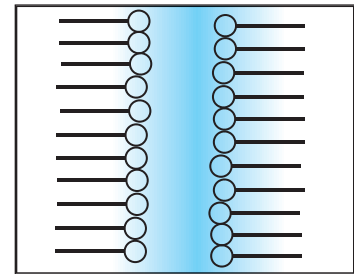


Investigate and describe occurrences of micelles, bilayers and vesicles. Give a molecular explanation for their occurrence and properties.

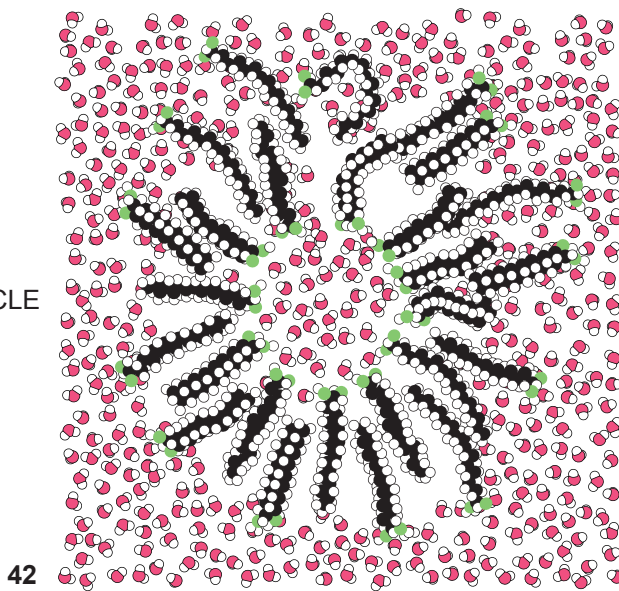
BILAYER



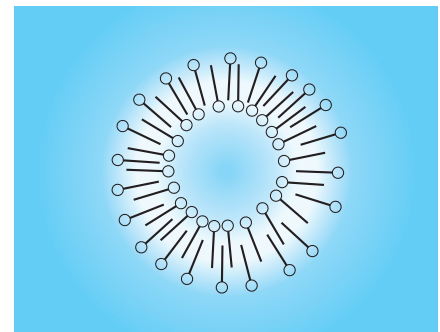
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VESICLE



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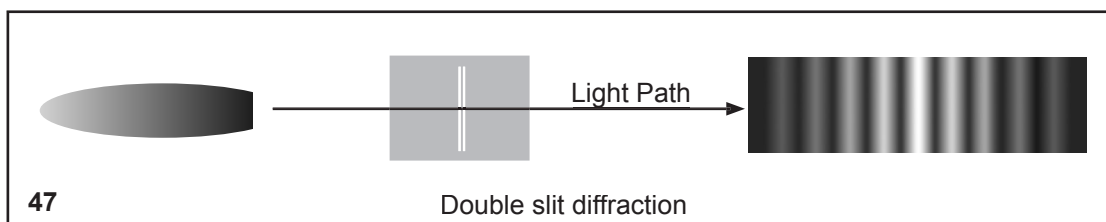
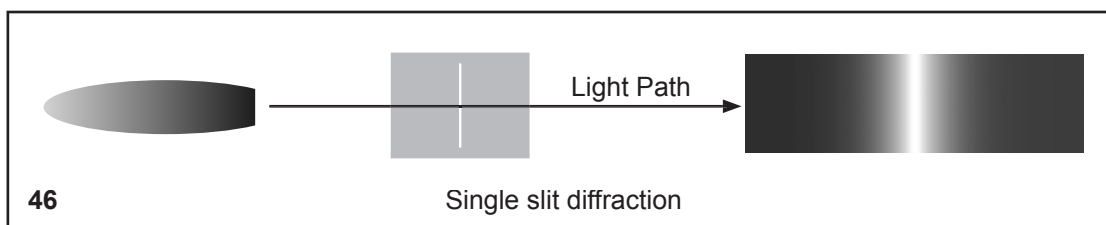
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

MODERN MOLECULAR IMAGING

We began investigating molecules through the simple technology of placing oil on water and we have seen Ms. Pockles device. But this is the 21st century and we can now look at molecules directly. Among the modern methods of seeing molecules we will look at x-ray diffraction, atomic force microscopy and the scanning tunneling microscope.

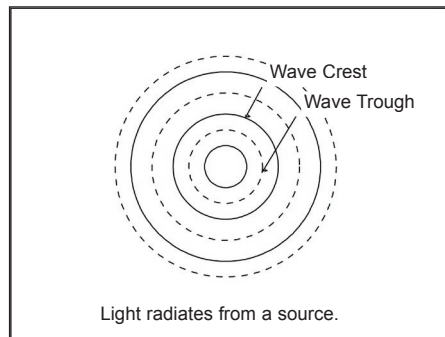
DIFFRACTION

Hold a sharp edge object, such as a pencil, at various distances away from a flat white surface in direct sunlight. From observing the shadows produced, what can you deduce about the nature of light?

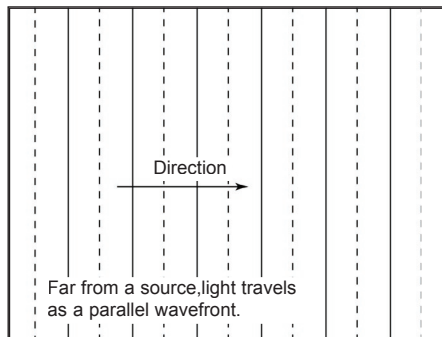


DO MOLECULES EXIST AND HOW SMALL ARE THEY?

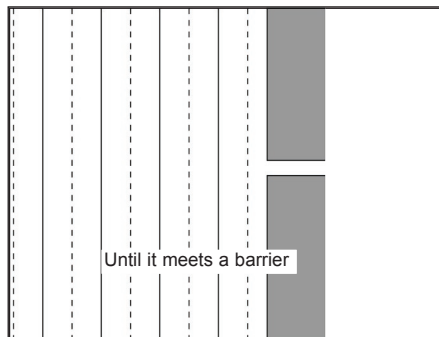
DIFFRACTION



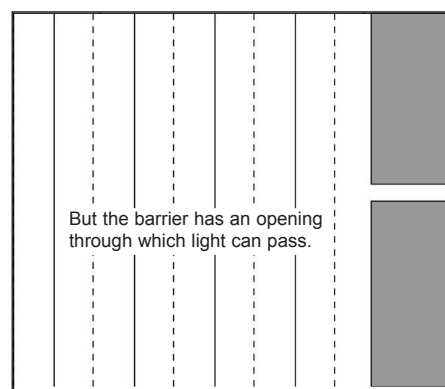
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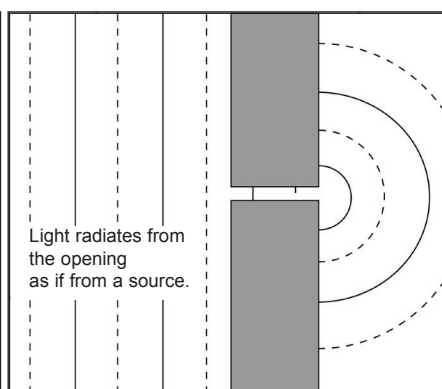
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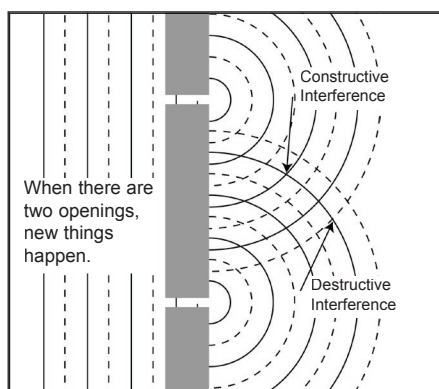
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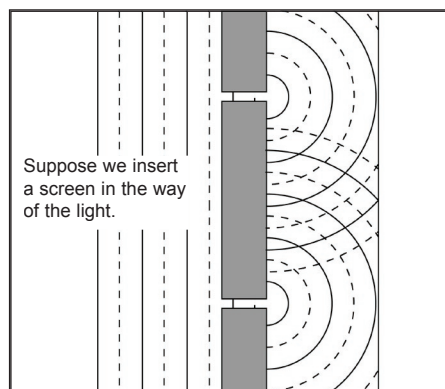
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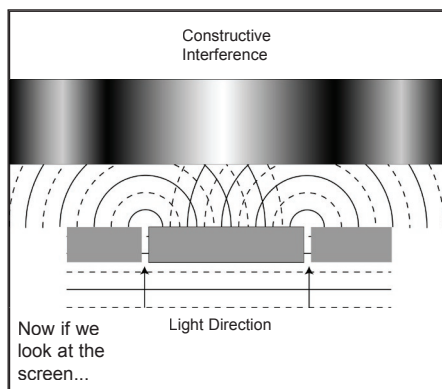
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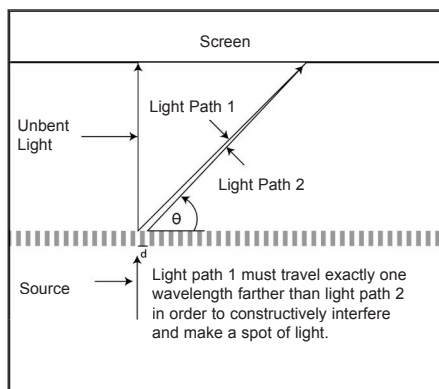
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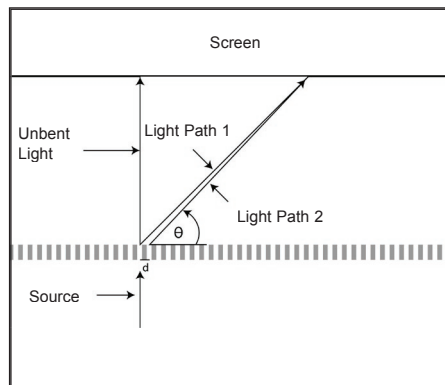
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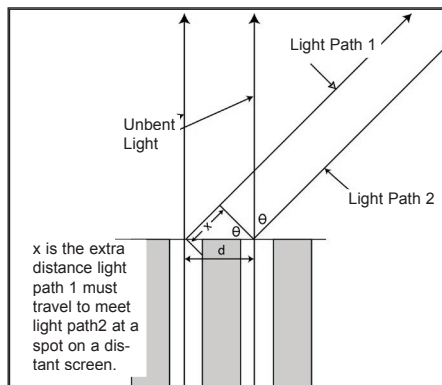
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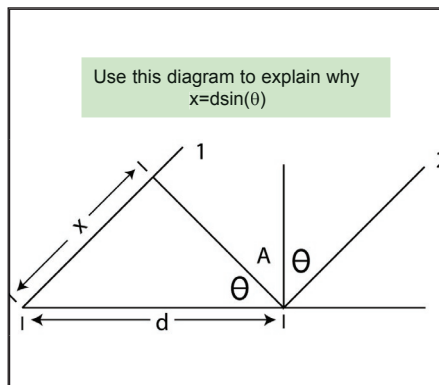
56



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58



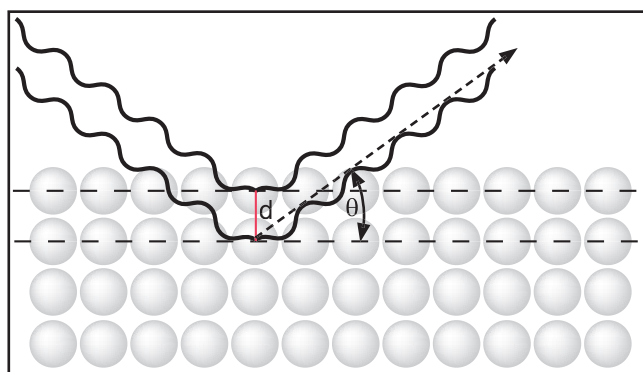
59

DO MOLECULES EXIST AND HOW SMALL ARE THEY?

X-RAY DIFFRACTION

There are several methods of X-ray diffraction but they all depend upon the wavelength of X-rays being the same order of magnitude, or smaller, than atomic sizes or the spacing between atoms.

Also, X-rays are reflected from the electron clouds of atoms and molecules, rather than from the nuclei.



60

In the picture above two x-rays arrive and are reflected from the substance at the same angle θ . When the angle is just right, the bottom wave will travel exactly one wavelength farther than to top wave and so the two waves will be in phase and interfere constructively, giving a dot on a screen. The relationship which connects the angle of reflection, the wavelength, λ , of the x-rays and the distance, d , between atomic (or molecular) planes is given by Bragg's Law.

$$n\lambda = 2d\sin(\theta)$$

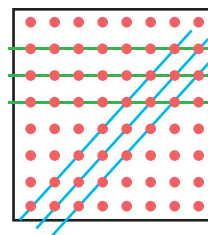
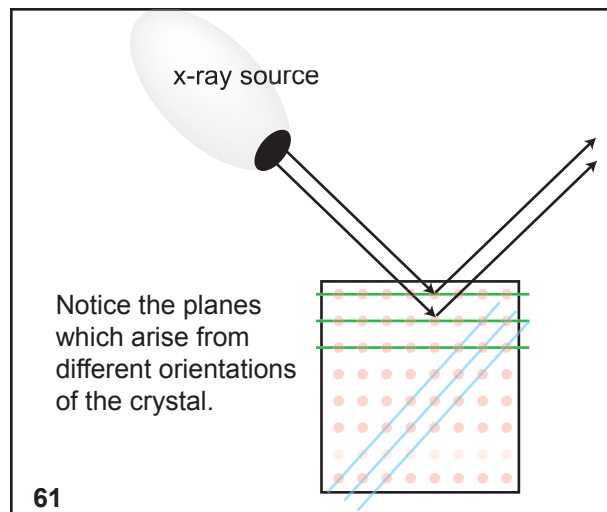
where n is a small positive integer.

When we are trying to find the separation d , which is effectively the atomic or molecular size, we solve the equation for d and then substitute experimentally determined values for λ and θ .

$$d = \frac{n\lambda}{2\sin(\theta)}$$

Compare the process of using x-ray diffraction for deducing crystal structure to the process of using a diffraction grating for spectroscopy. In what ways are the processes alike and in what ways do they differ?

Why can visible light waves not be used to measure atomic sizes?



62

Find some other planes in the pattern shown.

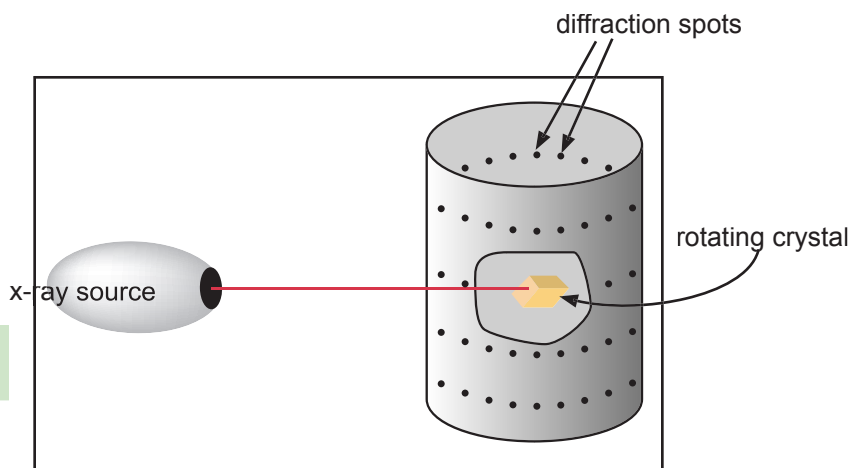
Suppose you could see at one meter wavelength. Describe, preferably by drawing, what the world would look like.

DO MOLECULES EXIST AND HOW SMALL ARE THEY?

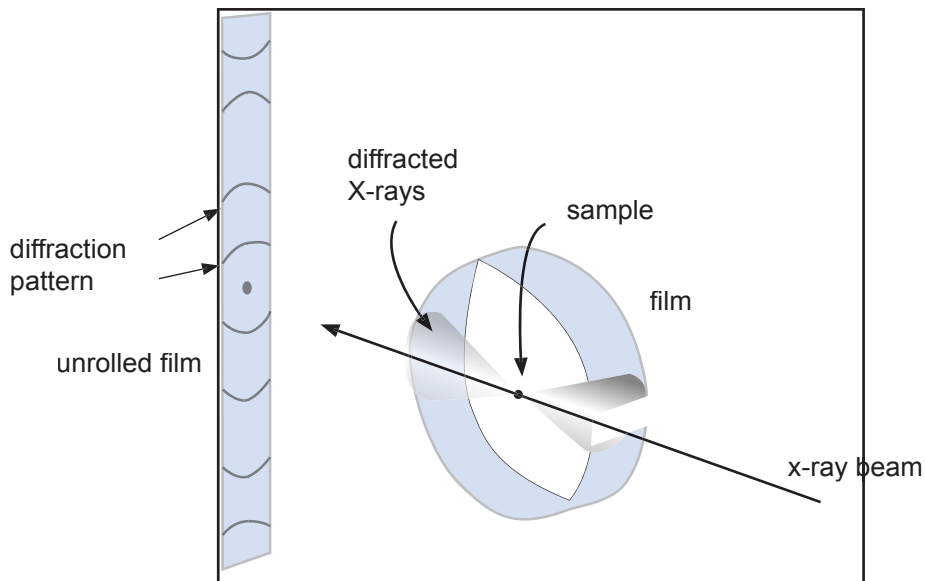
X-RAY DIFFRACTION

Explain why it is necessary to use a single crystal in the rotating crystal method?

How would you use x-ray diffraction to distinguish between glass and quartz?



63 Rotating Crystal Method



64 Powder Diffraction

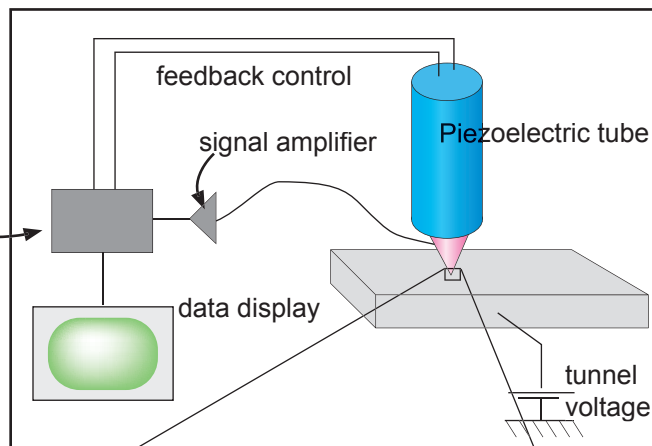
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

THE SCANNING TUNNELING MICROSCOPE

The scanning tunneling microscope (STM) measures the minute current between the atomic surface and the tip of a very fine probe. Because the current is very sensitive to the distance between the probe and the surface, the STM can recognize the bumps on the surface caused by single atoms.

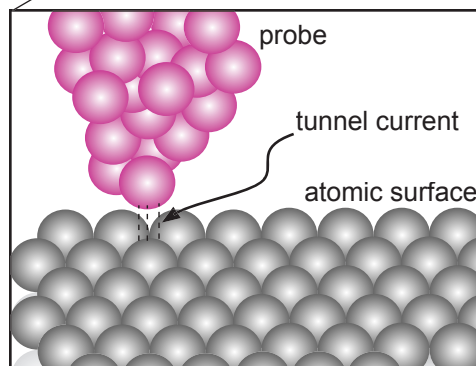
What limitations to the use of STM are implied by the necessity of using a tunneling current?

distance control
and scanning unit



65

The piezoelectric effect in some materials provides a transduction between electric currents and mechanical vibrations. Quartz exhibits the piezoelectric effect.

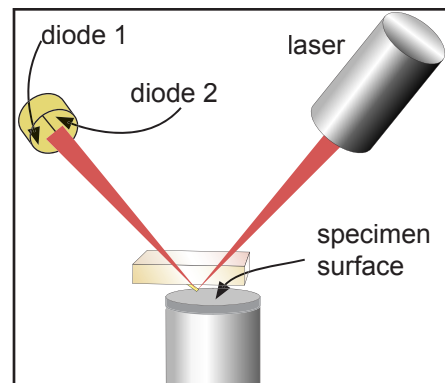


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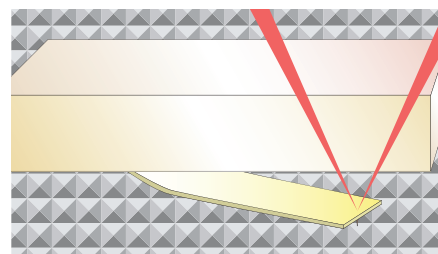
DO MOLECULES EXIST AND HOW SMALL ARE THEY?

ATOMIC FORCE MICROSCOPY

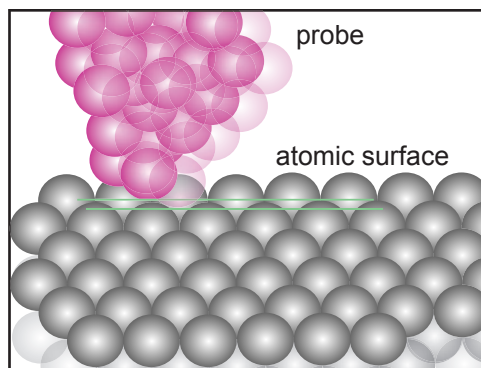
Atomic Force Microscopy relies upon direct contact, or near contact, between a finely pointed probe and an atomic surface. As the probe is moved across the surface, or vice-versa, the probe is pushed or pulled up and down by the variations in height between the top of an atom and the interstices between atoms. This motion is transmitted to a cantilever beam. The effect can be magnified several thousand times by a laser beam reflected off of the cantilever and measured by the relative strength of reception between two adjacent light measuring diodes.



67

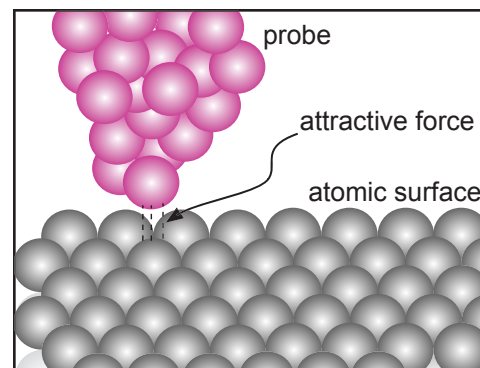


68



69

Contact Mode



70

Attractive Mode

There is a link on our website to another site which offers explanations of several other forms of modern molecular study techniques. Visit at least one of these sites, study the material and write an explanation of the process. Preferably draw it.