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TWO-DIMENSIONAL GASES, LIQUIDS AND SOLIDS[1]

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WE live in a world of three dimensions. We measure objects by their length, breadth and thickness. The position of a point can be described by three coordinates, x, y and z. We can not escape from the inside of a spherical surface except by passing through it, but if we are standing in a circle on a surface we escape from it by stepping over it.

It is amusing to try to imagine a fourth dimension. We can reason that if we could travel into it, we could escape from the inside of a sphere without going through its surface.

In the special theory of relativity, Einstein has given us reasons for looking upon time as a kind of imaginary fourth dimension which differs from any of the ordinary dimensions of space much as the number one differs from the imaginary number $\sqrt{-1}$.

In the general theory of relativity, there are suggestions that the effect of gravitation is to warp four-dimensional space-time in a fifth dimension, very much as we have to warp a map of Europe to make it fit onto a globe representing the earth.

Poincaré in an interesting book, "Science and Hypothesis," attempted in 1903 to trace the probable development of science on the earth if it had happened that the earth's atmosphere, like that of Venus, had been perpetually cloudy. Without ability to observe the stars and sun, mankind would have persisted for long in a belief that the earth is flat. If a pioneer among scientists had made the statement that the surface of the earth has no edge or boundary but yet has a limited area, he would have been disbelieved; for these two statements seem contradictory to those who believe in a flat earth. The difficulty disappears, however, if it is recognized that the surface of the earth is bent into a spherical surface by being warped in a third dimension.

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[1] Address delivered at the Mark Hopkins Centenary, Williams College, October 10, 1936.

When some forms of the relativity theory tell us that space has no boundaries and yet has a limited volume, we are similarly perplexed. The warping of our space in a fourth or fifth dimension, however, can remove these difficulties, at least for some people (the newspapers say ten).

Many of you perhaps have seen the little book entitled "Flatland," written in 1885 by an author who gives the name A. Square, but who is said to be Edwin A. Abbott. A race of people is pictured who live in two dimensions. One of the inhabitants argues that there can be no third dimension, just as we argue that there can be no fourth dimension.

Of course, no one can seriously maintain the existence of a real fourth dimension of space, which is like the three that we already are familiar with.

To-day, however, I propose to tell you of a real two-dimensional world in which phenomena occur that are analogous to those described in "Flatland." I plan to tell you of the behavior of molecules and atoms that are held at the surfaces of three-dimensional solids and liquids. The chemist has long described molecules that are held in this way on surfaces as adsorbed molecules. I will show you that we can have adsorbed films which really constitute two-dimensional gases, two-dimensional liquids and two-dimensional solids.

Hydrogen and carbon combine to form a very interesting class of substances called hydrocarbons. Most of these are stable and relatively inert. A good example of a compound of this kind is a substance called hexadecane, which has a formula $C_{16}H_{34}$, the carbon atoms being arranged in a long chain. Purified mineral oil, such as petrolatum, is a hydrocarbon having similar properties. It is not appreciably volatile and is insoluble in water.

When a drop of such a liquid is placed upon water, it floats on the surface as a lens which has a definite circular boundary where oil, water and air meet. Although the force of gravity tends to make the oil spread out over the water in a thin film, the lenses formed by petrolatum are about 4 mm thick. There must therefore be a force of considerable magnitude which prevents the oil from spreading. Measurements show that this force amounts to about 12 dynes per cm.

There are large numbers of oils and fats, however, which when placed on water spread out to form extremely thin films of the order of 10^{-7} cm thick. It is found that the general characteristic of all such substances that spread is that they contain in their molecules certain groups of atoms which have an affinity for water and are therefore called *hydrophilic*. The most common of these groups is the $-OH$ group or the $-COOH$ group. If such a group is substituted for one of the hydrogen atoms in each of the molecules of a lower hydrocarbon, the effect is to increase the solubility of the substance in water.

The substances that spread as thin films upon water are thus substances whose molecules possess a composite surface, most of the molecule having very little affinity for water, thus being *hydrophobic,* while another portion of the molecular surface is hydrophilic. By spreading on the surface of the water, the molecules can thus arrange themselves so that the hydrophilic portion of each molecule comes into contact with water without bringing the hydrophobic portion in contact with the water. In the common fatty acids, the COOH group is at the end of the long chain. Thus when the molecules spread over the surface of the water, they become oriented on the water so that they are approximately vertical with their heads (hydrophilic groups) in the water and their tails (hydrophobic groups) packed side by side above the layer that contains the heads.

Because of the affinity of the hydrocarbon parts of the molecules for each other, the molecules spread on the surface of the water only far enough for their heads to come in contact with the water. The surface tension of the water, therefore, is not decreased unless enough fatty acid is added to cover completely the surface with a monomolecular film. By measuring the volume of oil required to form a film covering a given area, the thickness of the film can be calculated. This thickness is evidently the length of the molecules, since these are arranged nearly vertically in the film.

By placing a known number of molecules on the surface and measuring the area to which the film spreads before the surface tension is lowered below that of pure water, the area per molecule can be measured. This gives the cross-section of the molecule. These experiments enable us to find the shapes of the molecules, and prove that the molecules of the higher fatty acids such as stearic acid $C_{17}H_{35}COOH$ in a film on water have a cross-section of about 20×10^{-16} sq cm or an average diameter of about 4.5×10^{-8} cm; while the length of the molecule is about 24×10^{-8}, or more than five times the diameter. This is quite in accord with the known chain-like arrangement of the carbon atoms.

Experiments of this kind are best carried out by using a large shallow tray which is filled to its brim with water. Movable strips of metal placed across this tray serve as barriers to confine the film that is produced by adding oil to the surface. To measure the force F per unit length which the film exerts on the barrier, one of the barriers is replaced by a floating strip of paper made waterproof by paraffin, which is attached to the vertical pointer of a balance placed above the tray. The leakage of the film around the ends of the floating barrier is prevented by connecting the barrier with neighboring points on the rim of the tray by paraffined silk threads which float on the surface of the water. The balance is adjusted so that it reads zero when there is clean water on both sides of the barrier. A definite minute amount of a substance such as a fatty acid is placed on the water on one side of the floating barrier by applying measured drops of a dilute solution of the substance in a volatile solvent, such as benzene. The film is confined to any desired area by a second barrier which extends across the tray. Dividing the area between the fixed and floating barriers by the number of molecules which have been placed on the surface, we obtain the area per molecule which we denote by a. The weights which must be placed on the pan of the balance in order to hold the floating barrier in a fixed position give us the force F (per unit length) exerted by the film. By progressively changing the area by moving the second barrier, the force F may be measured as a function of a, the area per molecule.

An elementary experiment in physics consists of establishing the validity of Boyle's law (which states that the pressure of a gas is inversely proportional to its volume) by placing a gas in a cylinder in which there is a movable piston by which any desired force can be applied. An equation which expresses the pressure in terms of the volume and temperature is called an equation of state. For ideal gases it is found in this way that

$$pv = kT \tag{1}$$

where p is the pressure, v is the volume of the gas divided by the number of molecules, T is the absolute temperature, and k is a universal constant 1.37×10^{-16} when expressed in the usual units. It is sometimes more convenient to express this equation in terms of n, the number of molecules per unit volume of gas. The equation then takes the form

$$p = nkT. \tag{2}$$

I hope you see the close analogy between the experiments in which a gas is confined in a cylinder having a movable piston and the experiment in which we place a monomolecular oil film on the surface of water in a tray, which is provided with a floating barrier which can exert any desired force on the film. The floating barrier thus corresponds to the piston in the three-dimensional experiment. We may thus look upon an equation which gives F in terms of a as the equation of state for the two-dimensional film on the surface of the water.

The justification for regarding the film as having only two dimensions is that it consists of a single layer of molecules, so that the motions of the barrier do not cause the molecules to climb up on one another and so move into the third dimension.

With this concept of the molecules existing in a two-dimensional film, it is possible by well-established principles of thermodynamics to show that if the absorbed molecules do not exert any force on one another, they should behave as an ideal, two-dimensional gas; and that the equation of state of this two-dimensional gas should be given by

$$Fa = kT \tag{3}$$

where k has exactly the same value as is found for a three-dimensional gas. You see the form of this equation is the same as that of Eq. (1), the force F corresponding to the pressure p, the area per molecule a corresponding to v.

It is often convenient to describe a monomolecular film in terms of σ which may be defined as the number of molecules per unit area, which is evidently the reciprocal of a. Thus the equation of state can also be written

$$F = \sigma kT. \tag{4}$$

This equation is evidently entirely analogous to Eq. (2).

Films produced on water by non-volatile and insoluble fatty acids have properties which indicate that they are two-dimensional liquids and solids rather than gases, for they do not spread indefinitely; the value of F becomes practically zero when the surface concentration σ falls to some definite value. This is just what would happen in the three-dimensional experiment with the cylinder and piston when the cylinder is completely filled with a liquid. If we apply considerable pressure to the piston, the volume decreases only a very little; and if we lower the pressure, the volume does not increase indefinitely. The molecules of the two-dimensional film are held together by cohesive forces which originate from the interaction by the hydrocarbon chains, which by themselves tend to draw the film into a lens just as they do in a case of a pure hydrocarbon.

Solids and liquids in a three-dimensional world do not differ very greatly in volume or density nor in compressibility. The main difference is that a solid has the property of rigidity; that is, it can withstand shearing stresses. Oil films on water which are not two-dimensional gases can be described as condensed films, for the molecules are tightly packed against one another either because of external pressure or because of the cohesion between the molecules. These condensed films can exist in a solid or liquid state. This can be shown by their enormous differences in withstanding shearing stresses. For example, if particles of talc are dusted upon a liquid film, these particles circulate freely over the surface if one blows lightly upon the surface. In the case of solid films, however, the talc particles are held rigidly in definite positions on the surface by the rigidity of the film. Many intermediate states can be observed, for example, where the talc particles will move only slowly even when a considerable force is applied by a strong blast of air. Such films evidently constitute a two-dimensional liquid of high viscosity.

We have recently constructed a simple apparatus to determine these mechanical properties of condensed films. A light aluminum disk is suspended at its center by a fine tungsten wire from a support which permits the rotation of the tungsten wire around its axis. This disk is lowered until it comes in contact with the surface of the water in the tray. An oil film is then placed on the water and subjected to any desired pressure by means of a barrier. The upper end of the tungsten wire is then rotated through a definite angle. If the film is liquid, the disk will also rotate through the same angle, and the length of time that it takes to do so is a measure of the viscosity. If the film has the properties of a two-dimensional solid, the rotation of the support will cause only a small elastic rotation of the disk, which corresponds to an angular displacement very much less than that of the support.

Experiments of this kind show that films of stearic acid on pure water, even if it is made alkaline by potassium hydroxide, are always liquid. Many previous investigators have found that such films on alkaline water are solid. It now appears that the observed rigidity was caused by extremely minute traces of impurities of divalent or trivalent elements in the water. One part in one hundred million of such impurities may be sufficient to make stearic acid films solid.

The films that I have been speaking of are those that form at the free surface of water; that is, at an interface between water and air. Such films have been quite extensively studied in recent years by a number of investigators.

If a thick layer of a pure hydrocarbon is placed upon water, the interface that forms the boundary between the hydrocarbon and the water is also a surface in which molecules can become adsorbed. The properties of these interfacial films are simpler than those of films on the free surface of water and exhibit in a more striking way the three possible states of a two-dimensional film (solid, liquid or gas). These films are also perhaps of greater fundamental interest, for their study throws light on many problems of biology, particularly those that characterize the walls of living cells.

The investigation of these interfacial films has been greatly facilitated by several new experimental techniques which have recently been developed by Dr. Katharine B. Blodgett. I can illustrate these by telling you what happens when a small amount of stearic acid is dissolved in a non-volatile hydrocarbon, such as petrolatum, and a drop of this is placed on alkaline water.

If only one part of fatty acid in several million parts of petrolatum is used, the drop remains as a globule on the surface; but the contact angle that the water makes with the oil gradually changes as the stearic acid slowly diffuses to the interface.

If one part in a hundred thousand is used, it is observed that the drop increases in size at first slowly, then with increasing rapidity; until quite suddenly it reaches a limiting size and stops spreading. The area to which the drop sureads is proportional to the amount of stearic acid that is placed in the drop but is independent of the amount of petrolatum that is in the drop. This proves that on alkaline water every molecule of stearic acid goes to the interface; the area per molecule is found to be 90×10^{-16}, or four and one half times as great as the area occupied by a stearic acid molecule in a condensed film on a free surface of water. If the drop of petrolatum containing stearic acid is allowed to spread on water which already has a film of stearic acid on it held under slight compression, the drop spreads to a considerably smaller area. Such experiments prove that the interfacial film has the properties of a two-dimensional gas which has an equation of state

$$F(a - a_0) = kT, \tag{5}$$

in which the constant k has the same value as it does in Eq. (3) and a_0 has the value 57×10^{-16}. Such a correction to the equation of state for an ideal gas is exactly analogous to the correction in the equation of state for three-dimensional gases when allowance is made for the volume that is occupied by the molecules.

If now we increase the concentration of the stearic acid in the petrolatum still more so as to have a few parts per thousand instead of per hundred thousand, the drop of the solution when placed on the alkaline water spreads almost instantaneously to a film so thin that iridescent colors appear which are formed by the interference of light reflected from the upper and lower surfaces of the thin layer of oil. These colored films are very convenient to work with, for the color enables us to determine accurately the thickness t; so that, if we have solutions of known concentration n (molecules per cm^3), we can calculate a by the equation

$$a = 1/nt. \tag{6}$$

The method of finding the thickness of the film from the color consists in matching the color of the film against that of a *comparison film*. A *comparison oil* was first made by oxidizing a white mineral oil, or even a lubricating oil, by heating it in an open dish on a hot plate until it smokes. During this process drops of oil are removed from time to time and placed upon a clean water surface. At first the drops form lenses. As oxidation proceeds the lenses spread out into colored films. The oxidation is continued until the films become so thin that the color nearly disappears. A drop of known volume (from a calibrated pipette) is then placed on water in a large tray. By moving a barrier the area of this oil film can be decreased and therefore its thickness can be increased and as this is done the color changes from the original faint yellow to a series of other colors. In this way the color can be brought to match that of any other colored film whose thickness it is desired to measure. This method furnishes us with an extremely accurate and rapid method of measuring a, the area per molecule.

If the water upon which the oil globule is allowed to spread is acid instead of alkaline, the results are strikingly different. No spreading occurs at 25° C. unless the concentration of stearic acid in the petrolatum exceeds 0.0032 parts by weight. For concentrations above this, however, the area to which the drop spreads increases linearly and very rapidly with the amount of the stearic acid in the drop. The rate of increase of this area with this concentration enables us to calculate the area per molecule by the equation

$$a = 1/(n - n_0)t, \qquad (7)$$

where n_0 is the critical concentration which is just sufficient to cause spreading.

With water that is fairly strongly acid, at temperatures above about 25° C., the area per molecule is found to be 53×10^{-16} cm^2, which is only a little more than half that observed with alkaline water. Measurements made with different external pressures applied to the film prove that this film is also gaseous and has an equation of state given by Eq. (5) with the value $a_0 = 20 \times 10^{-16}$.

The fact that a certain critical concentration n_0 is necessary on acid water before spreading begins indicates that the two-dimensional gas film at the interface is soluble to some extent in the petrolatum. We have here a case where the inhabitants of Flatland have learned to travel out into three dimensions. As long as they remain in Flatland they behave as a perfectly normal two-dimensional gas, but when they are crowded too much they escape into the third dimension and thus show an entirely different behavior.

On acid water at a lower temperature than a certain critical temperature of about 20° C the interfacial film of stearic acid condenses to a two-dimensional liquid, so that the area per molecule suddenly drops from 53 to 20. Very striking color changes are thus often produced by a change of a few tenths of a degree in the temperature of the water on which the oil is allowed to spread. This temperature thus corresponds to the boiling point of a two-dimensional liquid.

A comparison of these results with acid water and with water made alkaline with potassium hydroxide proves that the adsorbed molecules at the interface of alkaline water consist of molecules of soap, that is, of potassium stearate; whereas on acid water they consist of molecules of stearic acid. The large increase in a_0 from 20 to 57 units proves that the soap molecules surround themselves with a single layer of tightly bound water molecules; in other words, become hydrated; but this does not occur with stearic acid molecules.

Recently C. N. Moore and I have been investigating the intermediate field between acid and alkaline water, using solutions that are either neutral or very slightly acid or alkaline. We have also studied the effects of small amounts of calcium, magnesium, sodium and potassium salts in water. We find that in solutions which approximate closely to sea water in composition particularly interesting phenomena are observed. The area per molecule a and the value of n_0 which correspond to the solubility of the film are so remarkably sensitive to slight changes in acidity and alkalinity that the carbon dioxide of the air, which amounts to only a few hundredths of one per cent., produces great changes in these quantities. Sodium and potassium salts greatly increase the area per molecule and so make the film gaseous, whereas calcium and magnesium tend to bring this area down to 20 units and make the films solid. Calcium and sodium thus have an antagonistic action on the properties of these films.

The biologist has found that the permeability of the walls of the cells and many other properties are enormously affected by the ratio of the concentrations of calcium and sodium salts in the surrounding medium.

We are thus led to believe that interfacial films formed between a hydrocarbon which contains stearic acid and an underlying aqueous solution have properties which are in many respects very similar to those of a cell wall. In these experiments we have the advantage, however, that we can make this artificial cell wall cover a square foot if desired; we can study in detail properties which would be very difficult to measure on a living cell. By quantitative studies we can derive fundamental laws that govern these changes in properties. We hope by following up this work we shall be able to establish some principles that will be of great use to the biologist in understanding the complicated dependence of living cells upon the composition of the surrounding medium.