

Plate 2.—Film of olive oil at the beginning of its evolution upon pure water (less than one second after the deposition of the drop).

The center is thick (rings and interference colors), the border thin (brown of the first order, 100μ , then paler and paler white). The film is, however, already pierced with circular holes, yet small and rare at the center, large and fused together at the edge.



Plate 1.—Boat en route in black tray on water powdered with talc.

A large wake of camphored water free from talc is very visible at the rear of the boat. The operator contracts or expands the free surface by changing the position of the strip of paper placed across the tray.

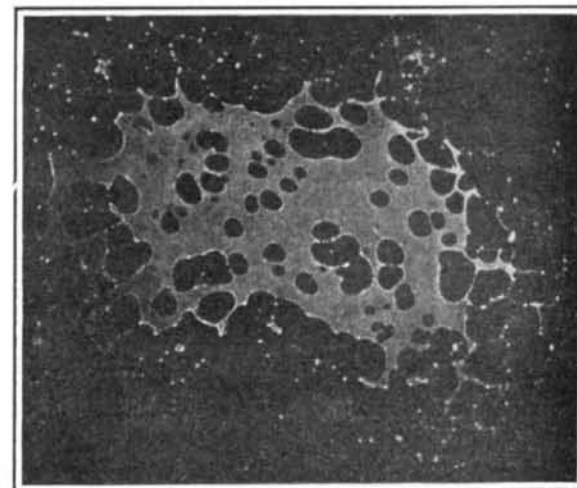


Plate 3.—Film completely extended, age about two seconds.

Its spread has reached the phase when first-order tints appear. A general shrinkage is taking place everywhere. The central black spots have increased in size and fused together; their borders are much broken up and are surrounded by various sized droplets.

Oil Films on Water and on Mercury*

A Study That Tells Us of the Discontinuity of Matter and the Size of Molecules

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CERTAIN phenomena of daily observation are of great interest to the physicist. Especially so is the expansion of oil over the surface of water or of mercury. I have studied this matter for a long while and from all my observations several unexpected facts stand out.

Films of oil tell us with the greatest nicety of the discontinuity of matter, and the dimensions of molecules. They also give us valuable information as to the field of molecular action. For our observations we will find that there is no need of complicated apparatus; basins, paper, threads of glass, a pipette, a sieve with some talc powder, and finally some oil and benzole suffice for the greater part of the experiments. As to measuring instruments, a double decimeter will do, although its divisions be a million times greater than the diameter of the molecules. Though it seems like measuring microbes with a surveyor's chain, we will see that the measures not only can be made but made with great precision, because of a very remarkable peculiarity of films of the thickness of one molecule. We will yet further see that the smallest variation in homogeneity engenders considerable differences in the surface tensions, causing the molecules to become exactly equidistant.

I. THE LIMIT OF THE EXPANSION OF OIL OVER WATER.

We will first look at an experiment of elementary simplicity yet fundamental. Let us pour some water into a photographic tray and then remove all the impurities from the surface by placing upon it just a sheet of thin paper. Then I scatter on the surface a little talc powder and place upon it a trace of oil by means of a very fine capillary tube. The oil spreads out rapidly from the talc in a circle, since the normal surface tension of the water is considerably lowered. But if there is very little oil, such as the capillary will take up by just touching the stopple of the bottle, the expansion stops suddenly, so that we have a circle of oil surrounded by free water.

Yet is the water really free? Perhaps there are traces of impurities which stop the extension of the oil. This is not the case.

Let us touch with a trace of oil another point distant

from the first one touched; a new circle forms and extends outward from the talc, but the first one is in no way affected. No equilibrating impurity exists outside of the first circle, otherwise its surface would have been deformed and diminished. There is therefore a real limit to the extension of oil upon water. And when that limit is reached the surface tension is both that of pure water and of oiled water.

Let us throw upon this water some grains of camphor dust. At once we see the grains in lively motion, but everywhere with apparently the same speed whether within or without the oiled region.

We may proceed differently. First spread over the water a sheet of oil, powder it, and then try to enlarge a little portion of the oil film by means of a strip of paper placed across it and over the edge of this dish. At once the whole surface is covered, since the layer of oil was somewhat thick. But there always comes a time when the extension stops; the oiled region marked by the talc remains behind, although there is a surface of water free from both talc and oil. The limit is extremely



Fig. 1.—Camphor boat (natural size).

c, grain of camphor at stern;
m, mast amidship.

clean cut and we have side by side two surfaces with the same surface tension—one of free water, the other of oiled water at its maximum extension.²

If at this moment a little camphor dust is scattered on the surface, the grains will be seen in active motion. In getting out of the way of the talc they act like little tadpoles. If the surface is reduced to one half all motion stops suddenly and the talc gathers around each particle of camphor. We may put upon the water a little tin boat such as I devised in 1888,³ and which is shown full size in Fig. 1. A little fragment of camphor is stuck with wax in a notch in its rear. A little mast bearing a streamer is fixed in the middle. This little boat,

²In 1891, Mlle. Pockel pointed out to Lord Rayleigh in a letter published in *Nature* (English) on the 12th of March, p. 437, some experiments relating to these facts. In enlarging progressively a surface of oil upon water or of water soiled with any other impurity, the tension of that surface varies continuously (abnormal condition); it increases slowly at first, then very rapidly, and reaches a maximum. Any further extension from the maximum point leaves the tension invariable (normal condition). If Mlle. Pockel had scattered an inert powder upon that surface to render it visible, she would have realized that, as soon as the maximum is reached, the oil would extend no further.

³See *La Nature*, April, 1888.

placed upon the water, moves rapidly and continuously so as to be seen from all parts of a room (plate 1).

I used this device the nineteenth of April, 1912, in Paris before the Société de Physique. Placed at first upon water with a film of oil at its maximum extension it traveled just as on pure water, leaving in its rear a large wake; the talc was thrown out with a marked vibration whenever it came in contact with the camphor, just as if the camphor corresponded to the propeller of the boat. I diminished the surface. At once the wake became smaller. The boat slowed up. I made the surface yet smaller. The boat stopped. I increased the surface, the boat again moved.

We may thus, by the simple movement of a capillary barrier (strip of paper), show to a whole audience the effect of sudden and considerable changes which the surface tension of water undergoes when covered with a film of oil of the critical thickness. It is a very simple experiment and very effective. Therefore, it is particularly interesting to know what thickness the film of oil must have at this remarkable phase.

II. THE THICKNESS AT MAXIMUM EXTENSION.

(1) *Experimental measures.*—Lord Rayleigh, in his admirable experiments of 1890, tried to find what is the minimum quantity of oil necessary to stop the movement of the camphor⁴ and found an extremely small value, a thickness of about 1.6μ . In 1891 he published the letter of Mlle. Pockel, which we have just mentioned, and in the following year⁵ showed the stopping of the movements of the camphor by a greasy body is due, as the law discovered by Mlle. Pockel led him to see, to a sudden fall in the surface tension of water when the grease layer has the right thickness. In 1899 he published a curve showing the relation between the surface tension and the quantity of oil⁶ and showed that the proportion of oil when the surface tension of the water begins to fall is about one half that at which the camphor movements stopped. The thickness is therefore $1.6/2$ or 0.8μ . But Lord Rayleigh gives it as simply 1μ .

We may obtain a yet greater precision by a method using drops of a standard solution of oil in a volatile solvent. I prepare a standard solution of oil in pure benzole. I use a solution containing exactly 1 cubic centimeter of pure oleine (trioleate of glycerin) per 1,000 cubic centimeter of benzole and a pipette giving 50 drops of this solution per cubic centimeter. Thus a drop contains $1/50000$ of a cubic centimeter of oil, and I place two of these drops upon the water. As soon

⁴Proceedings of the Royal Society, 47, March 27th, 1890. A French translation of the article will be found in *Conférences et allocutions de Sir William Thomson* (Lord Rayleigh), translated by Lugol (1893), p. 48.

⁵Philosophical Magazine, 33, p. 366, 1892.

⁶Philosophical Magazine, 47 and 48, 1899. In obtaining this remarkable curve, Lord Rayleigh appears to have supposed implicitly that the oil on the water always forms a continuous and homogeneous film, even when its surface is much diminished; for example when he gets the quotient of the weight of oil by the surface occupied. This is proper only when the diminishing of the surface is small, say in the ratio of 1 to 1.3. Beyond this limit this process is in error, for the surface begins to assume a globular form, finally becoming a veritable mass of foam. We will speak of this later on.

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¹This article gives a summary of all my researches upon oil films published since 1903; it includes also several new results relating especially to films on mercury and the interpretation of certain observed facts with them. The greater part of the figures have not before been published. The following is a bibliography of my earlier researches: *Recherches sur les lames très minces, liquides ou solides* (Proc.-verb. Soc. Sc. Phys. de Bordeaux, November, 1903); *Membranes de coagulation par simple contact de l'albumine avec l'eau* (l. c., January, 1904); *Comparaison de l'épaisseur critique des lames très minces avec le diamètre théorique de la molécule* (l. c., April, 1904); *De l'épaisseur critique des solides et des liquides réduits en lames très minces* (Bull. des séances de la Soc. franc. de Phys., p. 24, 1904); *Recherches sur les lames d'huile étendues sur l'eau* (J. de Phys., September, 1912, p. 699); *Sur un procédé de fixation des figures d'évolution de l'huile sur l'eau et sur le mercure* (Journ. de Phys., October, 1912). Several physicists have honored me by taking an interest for several years in my researches into molecular physics which has greatly encouraged me in carrying them out. I especially wish to mention M. Ch. Ed. Guillaume, president of the Société de Physique and M. M. Brillouin, professor at the Collège de France.

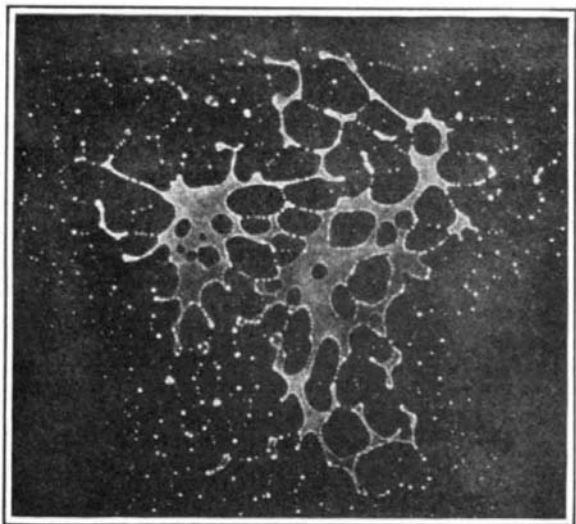


Plate 4.—Very advanced stage in the breaking up and contraction of an oil film by the fusing of the black film and droplets into drops of various sizes.

This film is about three seconds old.

as they touch the water, the drops spread over the whole surface; the evaporation of the benzole is almost instantaneous and leaves a residue of oleine equal to $2/50000$ or 400×10^{-7} cubic centimeter. Earlier measures showed me that this quantity of oil could not cover all the surface of the tray (625 square centimeters). I blow upon it to gather the invisible film of oil at the farther end of the tray and then scatter upon the nearer end a light veil of powder with the sieve. The talc thus falls upon the free surface of water *E* (Fig. 2); it scatters, carried by my blowing, but you see it stops abruptly along the barrier *TT'*, which though invisible was sharp, and marks the edge of the oil film *H*. The stoppage is of striking sharpness.

I now apply to the portion of water uncovered with oil a band of paper *BB'* (Fig. 3), in order to have a straight capillary border. I now make this barrier approach gently the border of talc which straightens, as is indicated in the figure.⁷ If the barrier is moved a little farther, the talc grains just at the limit of the oil, and more or less distant from each other because they are slightly oily, we see undergo an abrupt closing up between the oil and the paper. Retreat the barrier, and all at once the same grains become free, again floating freely side by side. By means of these sudden changes and by moving the paper slightly back and forth, I can accurately, within a few millimeters, find the limit at which the oil is just slightly contracted, that is at the place where there is the first appearance of change in the tension. At this place I make my measure, determining once for all by my double decimeter rule the length of the film of oil.

(2) *Results.*—We thus get the area of the mean surface covered by the film. In the experiment made the eighteenth of April, 1912, it was 363.71 square centimeters. Now, this was produced by two drops of the oil solution; that is, by 400×10^{-7} cubic centimeters of oil. The thickness of the film was therefore:

$$\frac{V}{S} = \frac{400 \times 10^{-7}}{363.71} = 1.10 \mu\mu$$

with an approximation between 1.04 and 1.15 $\mu\mu$.

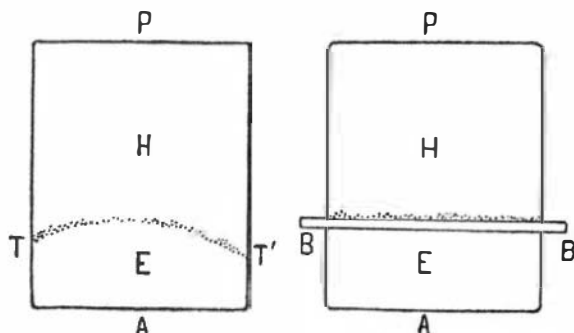
We can then state from this that the thinnest film of oil which can exist upon water is one and one tenth millionths of a millimeter. This thickness, almost identical with that found by Lord Rayleigh, is remarkably small. A simple comparison will give us a better idea of it.

Let us imagine a film of this thickness covering a globe 50 centimeters in diameter; let us enlarge in thought this globe until it has the actual dimensions of our earth. The film enlarged in the same proportion will acquire a thickness of only 26 millimeters, while the paper which covers the globe and upon which the world map was made will increase from its original thickness of 0.1 millimeter to 24 kilometers!

(3) *Comparison with molecular dimensions.*—But we may make better comparisons. In the molecular theory, the thinnest film of any substance which can exist is evidently made of a single layer of molecules; for it is impossible to conceive of a film thinner than a molecule except through the deformation or destruction of the molecule itself.

We possess to-day very numerous and exact determinations of the Avogadro constant, allowing us to calculate molecular dimensions. We have made the calculation for oil, or rather for the trioleate of glycerin. Using Perrin's value for Avogadro's constant, we found 1.13 $\mu\mu$ for the molecular diameter. The theoretical value of the diameter of a molecule thus calculated is practically identical with 1.10 $\mu\mu$, the experimentally

⁷It is yet better to collect the talc scattered upon the free surface by the band of paper itself.



Figs. 2 and 3.—Arrangement for measuring the limiting thickness of a film of oil.

H, film of oil; *E*, free water; *T T'*, barrier of powdered talc; *B B'*, band of paper.

measured thickness of an oil film at its maximum extension. The differences is only in the hundredths of a micron.

We know, therefore, that a film of oil at its maximum extension is formed of only a single layer of molecules.⁸ This remarkable fact is true of other films than those of oil, nor is it limited to liquid films. I have found it to be equally true for various solid substances, with this difference: it is the solid state itself which disappears at the critical thickness and not the surface tension, as with liquids.⁹ I therefore derive this general conclusion: the characteristic mechanical properties corresponding to certain states of a body, the surface tension of a liquid

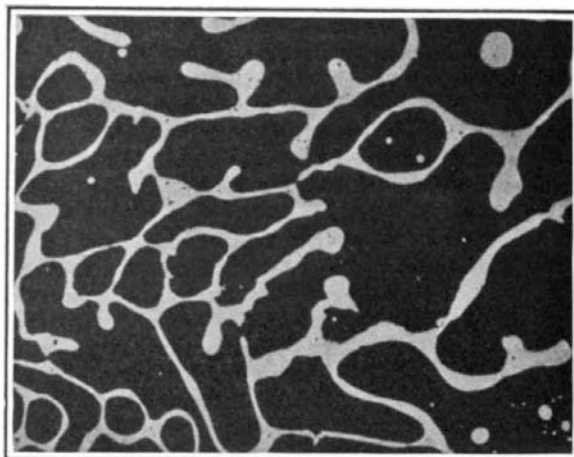


Plate 6.—Great Network of olive oil as generally formed after a long time by a very thick film.

The openings in the network are composed of great black fused films. Here and there are droplets.

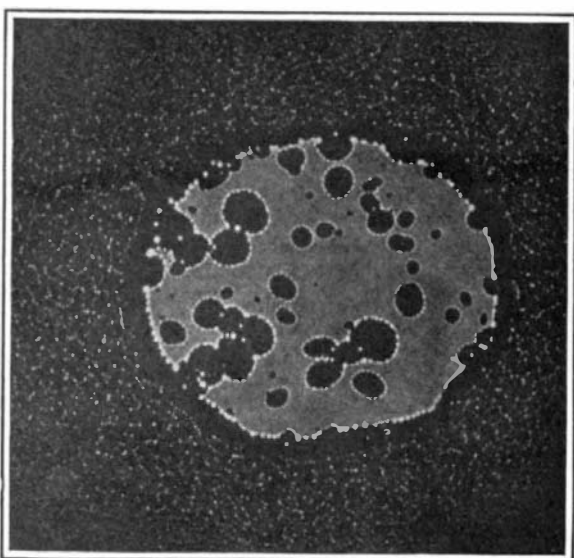


Plate 7.—Film of oleic acid upon mercury. Color, violet-rose (140 $\mu\mu$?).

The surface of the mercury had already received a drop of acid which had entirely contracted into droplets. The new drop expanded very slowly with clearly defined thick borders. These borders have already been transformed into chaplets of great drops such as are always found about the black spots which appear at various moments in the expansion of a film.

or the rigidity of a solid, persist almost intact down to molecular thicknesses, disappearing abruptly the minute we go further.

This fact has a general significance which we should appreciate. For the present, however, we will be content in seeing a new and direct demonstration of the discontinuity of matter and the reality of molecules; it is indeed a new method allowing us to measure the dimensions of molecules with a precision comparable with that of the best methods we have.

⁸Lord Rayleigh in the research cited above discussed this question, but the knowledge then of the value of Avogadro's constant was not so accurate.

⁹Devaux, l. c., 1904.

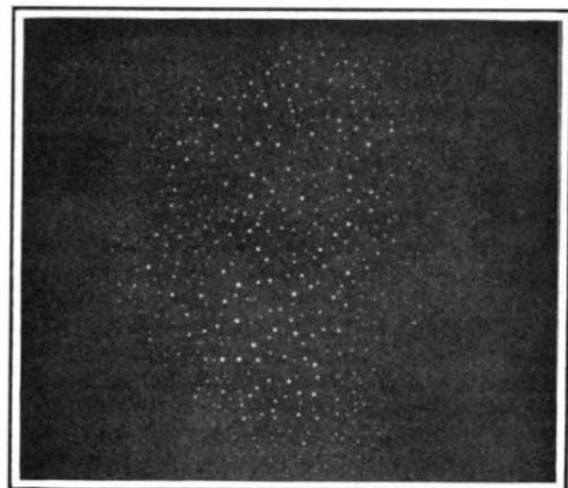


Plate 5.—Final Nearly (') stable state reached after 10 to 15 seconds.

The oil film seems reduced to a cloud of fine droplets scattered over the water. In reality, a very thin, continuous oil film exists between the droplets. The figure of equilibrium of oil on water is therefore discontinuous. (') I say "nearly" because the drops are still undergoing small displacements; they are approaching each other and fusing into larger droplets. This fusion is often hindered by an increasing viscosity, leading to an apparent solidification of the oil in contact with the air.

III. THE EVOLUTION OF LARGE DROPS OF OIL UPON WATER.

Instead of placing upon the water a very minute trace of oil, let us put there an ordinary drop of one to three hundredths of a cubic centimeter. We will now watch a series of phenomena as interesting as what we have just seen. Scarcely does the drop touch the water when it spreads out and covers the whole surface. But the film, of course, is very thick. It is hundreds of molecules thick and clearly visible, because it reflects light better than does water. Generally we see interference colors, at least at one phase of its extension. But this phase is always fugitive, especially with non-drying and fresh oils and when the surface of the water is very clean. This is the case with the present film.¹⁰ The evolution of a film lasts but 10 to 15 seconds; indeed the principal phases take place in the first 3 seconds. However, on water already oily, the formation is very much retarded and the film appears with a sharp circular border, as in plate 7. Soon its brilliant surface is pierced with black circular spots looking like holes, where the water appears as if free from oil. These spots, more or less numerous according to the kind of oil, gradually grow in size, and each one is finally surrounded by a band of small droplets similar to pearls (plate 3).

The first of these spots appears near the edge of the film, where it is thinner than at the center. They grow very rapidly and soon run together. The spots over the rest of the film subsequently behave in the same way (plate 4), so that finally the film is changed into groups of droplets scattered over the surface of the water which reappears as if free from oil, and uniformly dark (plate 5).

It is evident, however, that the surface of the water is yet covered between the globules by a very thin film of oil; and the persistence of this final phase shows that it remains in this discontinuous condition because the oil on the water is almost in static equilibrium. It is therefore necessary to distinguish two phases in the development of an oil film—the evolutionary phase, always fugitive, and the final static phase.

IV. THE STATIC PHASE OF OIL UPON WATER.

Let us consider especially this last phase, that of a very thin, continuous film extended over the surface of the water and studded or not with globules or disks. We will begin by establishing an important fact: the thickness of this continuous film depends upon the existence and dimensions of the globules. Because we find that when a film with minute globules exists beside one with great ones, the first always contracts at the cost of the second. Since, therefore, the tension is stronger in the former, we must conclude that the film with minute globules is the thinner.

With regard to the thickness of thin films, we are then led to distinguish four cases: the maximum and minimum thickness of films without globules; the maximum and minimum thickness of films with globules. Practically these reduce to three cases, since the maximum thickness of a film without globules is necessarily the same as the minimum thickness of one with globules.

(1) MINIMUM THICKNESS OF FILM WITHOUT GLOBULES.

We have already measured this thickness since it occurs in a film at its maximum extension and it is about 1.10 $\mu\mu$.

(2) MAXIMUM THICKNESS OF A FILM WITHOUT OR THE MINIMUM THICKNESS OF ONE WITH GLOBULES.

(a) Principle used in measuring films of a thickness

¹⁰The process of fixation of these films is peculiar and has been described in a special communication (l. c., October, 1912).

greater than that at the minimum: While the minimum thickness of oil films is easy to obtain and even to measure because of the sudden and considerable change in the surface tension for small variations in thickness, this is not the case for thicker films; for when we pass the critical thickness, the surface tension scarcely alters even for very great variations in the thickness of the film. It is therefore much easier to measure a film at its minimum thickness than at a greater thickness.

However, since it is always possible, by enlarging the film, to pass from a thicker to a thinner film, this difficulty can be avoided. We can then in any case choose an oil film without globules having the desired thickness, isolate a portion of the surface, S , then enlarge this to its greatest extension, S' . It will then have its minimum thickness. The ratio S'/S will be the ratio of the two thicknesses. Since the minimum thickness is known, we obtain the other thickness by multiplying by this ratio.

(b) Experimental procedure: In order to determine the greatest thickness of an oil film without globules, I proceed as follows: By means of a glass fiber, I place upon the water of my tray a drop of several tenths of a cubic millimeter. It expands into a film which contracts very quickly into a multitude of little droplets scattered over a black film. I now place a sheet of paper over the greater part of the surface and move it very slowly toward me. Immediately we see the globules over the rest of the surface grow into brilliant disks which finally break up into smaller drops. Repeating this partial wiping away several times, the globules one by one disappear, each momentarily becoming a disk, multicolored or of brilliant white. Finally the whole surface of the water appears black. But there are still very small droplets which may be made evident by slight enlargements made by jerking the dish. Each one gives a flash of light and then disappears. The final phase of the phenomenon requires acute observation, especially for some oils which produce particularly fine globules. In such cases I scatter a light veil of talc powder on the film, then extend the film slightly and at once we see the talc thrown out in little circles about each minute globule.

(c) Results: The following table shows results obtained by the process just described. It gives the ratio between the greatest and least thickness we can have with films without globules.

Trioleine.....	1.32	1.27	1.28
Olive oil.....	1.27	1.21	1.22
Linseed oil.....	1.18	1.15	
Nut oil.....	1.18		
Cod-liver oil.....	1.16		
Sheeps-foot oil.....	1.16		
Castor oil.....	1.53		

The ratio of the maximum to the minimum thickness for an oil film without globules varies a little from oil to oil, but it is always less than two: It is usually very close to unity, so that a film extended over water can have a maximum thickness but little superior to its minimum thickness. We may otherwise state this. A film thicker than one molecule cannot exist without nearly all the excess of oil forming into globules.

(d) The formation of foam in a very shrunken oil film: The last experiment explains a very curious and interesting fact. If we reduce an oil film from its maximum extension so as to diminish its surface to one tenth or one twentieth of its original area the film loses its bright aspect, becoming leaden and as if covered with an exceedingly fine foam. Microscopic examination assures us that the oil has changed into a multitude of droplets of various sizes, 10μ , 5μ , 1μ , and less. Working in the sunlight, I have seen the foam appear before the film has been reduced to one half its maximum extension.

This is a new and direct proof of what we have just learned, that as soon as an oil film is so much reduced in surface that it is more than one molecule thick, nearly all the excess of oil forms into globules.

(e) Variation of molecular distances: This extraordinary fact gives a new and interesting insight into the field of molecular action. It shows particularly that the forces which stretch out these films of liquids are due almost wholly to a single layer of molecules and that the surface layer. It is evident further that a film, if it is uniform, must be greater than one and less than two molecules in thickness. Now, everything indicates that a film is really uniform and homogeneous, since the least variation in its thickness gives rise to considerable differences of tensions which tend to re-establish everywhere a perfect homogeneity, and especially the equality of molecular distances. The difference between the states of least and greatest extension can be dependent then only on the distances between the molecules; if they are compact in the first case, they cannot be so in the second. At any rate, that is the interpretation given by M. Brillouin in a discussion which followed my communication.¹¹ The distance apart of the molecules in such films will be inversely as the square root of the surface. Accordingly, the square roots of the preceding

ratios give the relative molecular distances. This ratio ranges between 1.1 and 1.2.

It follows that as soon as the molecule of a monomolecular oil film are separated by from 1.1 to 1.2 their normal distances, they lose all power of lowering the surface tension of water. Conversely, as soon as the molecules are brought together, so that they are separated by 1.1 to 1.2 of their normal distances, they cause an abrupt and considerable fall in the surface tension of the water, making it practically the same as if it were a large body of oil. For beyond this limit the oil gathers into globules.

(f) Correction to the value of the normal molecular distance: The measure of the molecular distance 1.10μ , given above, corresponds to films at their greatest extension. The true distance in normal oil will be somewhat smaller, say $1.10/1.1$ to $1.10/1.2$ or 1.10 to 0.92μ . This correct distance differs decidedly from the theoretical value, 1.13μ , deduced from the measures of Perrin. Some day we will examine the cause of this difference.

(3) MAXIMUM THICKNESS WITH GLOBULES.

(a) Method of measurement: This measurement is especially difficult. After various attempts, I came to the conclusion that here the only certain method was to proceed by the extension of the films as in the previous case. In order to determine the maximum thickness, I isolate portions of great black spots (4.5 centimeter in diameter) which have appeared very slowly from a thick sheet of oil (plate 6). Then, first lightly powdering the surface, I enlarge it to its maximum extension. This operation is often hindered by the existence of very minute globules. In an instance where the globules were absent I noted that the maximum extension was obtained by about doubling the surface. It certainly was not tripled. We may say, then, that a film of oil at its greatest thickness, when the excess of oil has formed into disks in contact with it, is only about twice its least thickness.

In other words no continuous film will be stable on water when its thickness is greater than two molecules, whatever be the thickness of the masses of oil in contact with it. It will be necessary to await new measures before we truly know whether these films have a real thickness analogous to the maximum thickness without globules. That is, whether they are not formed of a layer of single molecules packed as closely together as possible.

(b) Discontinuity maximum: We are now in the presence of the maximum of the discontinuity of oil films upon water. We may easily have upon the water disks a millimeter or more in thickness. I have noted, for instance, that a cubic centimeter of olive oil placed upon water already heavily oiled forms a disk 30 millimeters in diameter and having an area about 7 square centimeters. Its mean thickness is therefore greater than 1 millimeter, and it is certainly 2 millimeters thick at its central part. Despite this thickness, the disk is surrounded by water on all sides, kept in stable equilibrium by an absolutely invisible film of oil having a thickness one millionth of that of the disk.

A simple comparison will show how peculiar is this discontinuous equilibrium of oil on water: Let us imagine our film enlarged one half a millions times; then our oil film at its maximum thickness would be 1 millimeter thick, and it carries instable equilibrium masses of oil whose thickness can reach and even surpass 1 kilometer (1,000,000 millimeters)!

(c) Comparison with the black film of soap bubbles: I have already, in calling attention to the evolution of a thick film of oil newly formed upon water, spoken of the constant appearance of black circles which grow larger and larger and merge finally into a continuous surface dotted with globules. It is odd that physicists have not been struck long since with the resemblance between these "holes" in the oil films and the black spots of soap bubbles. The mode of sudden appearance, the circular form, size, and progressive enlargement are very similar, and each hole is really occupied by an oil film whose thickness is comparable with that of the black spot of the soap bubble.

The holes in the oil film are, it is true, always more numerous, and further, they finally become surrounded with droplets and then flow together (plates 3 and 4). In reality, soap bubbles often show several simultaneous black spots, especially just before rupture. Further, and which is of special interest, Herbert Stansfield¹² has called attention to black spots in soap bubbles accompanied by collars of disks and granules which correspond to what occurs with oil films, only, since the soap bubbles are never horizontal, gravity necessarily pulls the thick portions away from where they appear. The confluence of the spots is not then peculiar to oil films.

The phenomena in the two cases are the same, the differences arising from the changed conditions under which the films are formed, an independent and two-faced skin in the case of a soap bubble, a skin adherent to and supported by water in the case of the oil film.

Accordingly, the study of the evolution of oil films throws light upon the final stages through which a soap bubble goes when it does not break. It becomes reduced to a black, very thin film, dotted with thick portions, either circular disks or droplets.

Further, similar, very large, black spots have been obtained in the films of soap bubbles by Reynolds and Rucker¹³ in their beautiful researches made between 1877 and 1893. Upon these films they determine the thickness of the black spots which were all found sensibly equal and equal to about 12μ . Johannot¹⁴ later showed that films could exist having a thickness one half as great, or 6μ .

We can now compare the thickness of oil and soap bubble films. In both instances we have black films formed from much thicker ones.





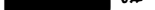
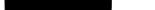
Black films of oil with a maximum thickness of 2 to 3μ .

Black films of soap bubbles, maximum thickness of 6 to 12μ .

These thicknesses are of the same order. Oil films are certainly always at least one half as thin as the thinnest soap-bubble films. This important difference must be due to the fact that in the case of oil films on water there is only one free surface.

TABLE OF RESULTS.

The following table gives a summary of the previous results and allows us to make useful comparisons.

THEORETICAL REPRESENTATION OF BLACK FILMS AND OF MOLECULES.		
Greatest and least thicknesses of stable oil films expanded upon water. The thicknesses are multiplied by one million (1 mm. represents 1μ .)		
	1.13 μ	Theoretical size of oil molecules (triolate of glycerine), ¹⁵ calculated from Perrin's data.
	1.10 μ	Minimum thickness of a stable oil film found experimentally.
	1.15 to 1.53 μ	Maximum thickness of a stable film without globules, or the minimum thickness of a film with globules, found experimentally.
	2 to 3 μ	Maximum thickness of a film in stable equilibrium with great globules or with masses of oil of 1 mm. or greater in thickness.
	6 μ	1st minimum thickness of film of soap-bubbles.
	12 μ	2nd minimum thickness of films of soap-bubbles or maximum thickness of the black spot.

V. OIL FILMS ON MERCURY.

Oil placed on mercury shows very similar results to those obtained upon water.¹⁶ There is still a very sharp limit to the extension, and the thickness of the films at the limits is sensibly the same. When the oil is abundant enough, it forms a thick colored film which grows rapidly with the production of black spots surrounded with globules (plate 7) and finally becomes a very thin film dotted with droplets. Other liquids (sulphuric acid, soap water, distilled water) give upon mercury analogous growths. We have therefore here a very general class of phenomena.¹⁷

VI. CONCLUSIONS.

We see now that a concept which at first seemed chimerical—that is, the reduction of substances to perfectly homogeneous films only one molecule in thickness—has become an experimental reality. And indeed these phenomena work spontaneously and are visible to you all whenever a drop of grease falls upon the water in one of the ordinary plates from which you eat, so that nothing is more common and banal than these extremely thin films.

The formation and stability of these films are automatic. The stability is so great that it is possible, without breaking the film, to distend it—that is, to separate progressively the molecules—until their reciprocal action is entirely destroyed, an operation which we could not perform upon liquids in bulk without leading immediately to rupture.

With our films, however, this is a most simple operation and always successful; it is only necessary to increase the free surface occupied by the film upon the water or the mercury. Thus we have become acquainted with the fundamental fact that the extension of the oil film is limited. As soon as the molecules are separated by a distance greater by one to several tenths of their normal distance they lose all reciprocal action, for they no longer diminish the surface tension¹⁸ of the water. We have

¹²A. W. Reynolds and A. W. Rucker, Proc. Roy. Soc. of London, 1877; Phil. Trans. ditto, pt. 2, 1881, 1883; Phil. Mag., vol. 19, 1885; Phil. Trans. Roy. Soc. of London, II, 1886; Wied. Ann., vol. 44, 1891; Phil. Trans. Roy. Soc. of London, vol. 184, 1895.

¹³Johannot, Phil. Mag., vol. 47, 1899.

¹⁴See Devaux, l. c., November, 1912.

¹⁵Devaux, Journal de Physique, November, 1912.

¹⁶Karl Fischer in his inaugural dissertation (Die geringste Dicke von Flüssigkeitsschichten, Munich, 1896), studied the extension of two oils and other liquids upon mercury. He gives numerous measures of the thickness of films before their rupture. The thinnest had thicknesses less than 3μ (rapeseed oil) and 1μ (sulphuric acid).

¹⁷A curious exception is found in oleic acid and in soap, the molecules of which when stretched over water can be separated some ten times the molecular distance. Devaux, l. c., 1904.

¹⁸Proceedings of the Royal Society, 1906, p. 311.

¹¹Meeting of the Société de Physique, May 3d, 1912.

called this phase the maximum extension. Conversely it suffices to bring them together, by contracting the surface slightly, in order to see the effect of the oil upon the surface tension of the water reappear and increase rapidly, so that the tension passes rapidly from that of pure water to nearly that of oil.

These facts allow us to enter directly the experimental study of the field of molecular action.¹⁹ They allow us to catch a glimpse of other mysteries to be discovered, other marvels to contemplate, and to delve into that domain of invisible elements of which visible matter is composed.

The little drop of oil has much more to show us. Who knows, indeed, but that it will bring us before long phenomena of the greatest importance, yet which at present we can not foresee?

Waste Pine Wood Utilization*

Some of the Products Obtained and Processes Employed

By John E. Teeple

THIS is an old, old industry. As far back as we have definite information, people were using tar on their cordage and pitch on their ships. Even Noah's ark you recall was "pitched within and pitched without," and the ark of bullrushes that supported the baby Moses was "daubed with pitch." We lack positive assurance that a pure pine pitch was used in these cases, but it may easily have been cypress pitch, which is not so widely different. Since the industry is such an old one, the chemist is not to be either censured or credited with its results until within the last thirty years, and more especially within the last ten or fifteen years. The method commonly used formerly was to pile the wood in large heaps, cover it with earth, and by burning a portion of the wood accomplish a destructive distillation of the remainder. The products were tar and charcoal, although some few attempts were made to recover the volatile spirit for use as an illuminant.

About thirty years ago the use of iron retorts was introduced, and this made possible the recovery of an unsatisfactory turpentine, a little of the natural pine oils, and considerable tar oil, creosote oil, pitch and pyroligneous acid, in addition to tar and charcoal. The turpentine had a vicious odor, but being in small amount, it could usually be worked off by persuasion. Tar was a standard commodity, but the trade soon began to differentiate between this retort tar and ordinary kiln tar, and the purchaser demanded a reduction in the case of the former, or refused it. Charcoal could be sold for household fuel, provided the plant was located in the neighborhood of a fair-sized city. Otherwise, it was used to fire the retorts. Gas was also at a time recovered and burned under retorts. When pitch was not readily salable it could be dissolved in the tar oils or creosote oils and sold as tar, but these various light and heavy distillation oils accumulated, and, depending on his ingenuity, the manufacturer worked them up into paint oils, mixed paints, insecticides, disinfectants, fungicides, embalming fluids, medicinal products, and so on until the catalogue becomes alarmingly long. This destructive distillation industry still exists. It is one of the two methods of treating wood to obtain Naval Stores that has been able to operate continuously under even the present very adverse conditions. Many improvements have been made in the type of the retort, in the regulation of heat, and in the separation and preparation of products for the market. In many cases the turpentine now obtained is of excellent odor and of surprisingly good quality, but its success has usually depended on the ability of the manufacturer to work up his oils into lines of specialties under carefully established trade names, and thus protect himself from too vigorous competition. He has improved his retort tar so that now it commonly commands the same price as kiln tar, and is sometimes quoted at a higher figure. With the present high prices ruling for acetate of lime, due to the strong demand for acetone, he is even proceeding in some instances to the manufacture of this product from his pyroligneous acid. A considerable part of these improvements has, of course, been due to chemists, but it must be admitted that a further very considerable part of the preparation of products for the market has been due rather to business men who are good observers, but were not primarily trained as chemists. It seems to me that the destructive distillation of wood is wrong in principle, with our present knowledge of its composition, but at the same time the fact that some of these plants have been continuously operating for many years indicates that they are not to be abolished with the speed that advocates of some of the newer processes have assured us.

Of other processes that have been suggested—distillation with superheated steam, extraction with rosin bath or tar and pitch bath, distillation with water, distillation

with hot gases, digestion with soda and application of vacuum have all had their trial in a commercial way, and a number of them have seemed to operate successfully for a while, due usually to special market conditions, but for the present these have all passed into history. It is very doubtful whether any of them will appear again, at least alone, even under improved conditions. While they lasted, each one found vigorous supporters and provoked much discussion. The question, for example, whether the steam should preferably pass upward or downward through a retort, was considered of considerable moment, but now it hardly arouses our interest. Some chemist usually took an active part in developing all of these processes, but the fact that none of them are operating to-day should not be laid entirely against him. In many cases he was responsible only for the laboratory results, and plants were constructed without the aid of chemical engineers, or, in fact, of chemists or engineers of any kind. In many other cases he had no first-hand knowledge of the industry himself, and relied on faulty information as to cost of wood and market conditions, supplied by men who were promoting the plants. In any case, in developing these processes the chemist and chemical engineer accumulated, and frequently put on record, a fund of very valuable information which is not at all lost, but which will have an important bearing on the future development of the industry.

In one important respect the chemist performed valuable service during this period of development. For the first time there was produced under his supervision a quantity of wood turpentine and pine oil sufficient to have an appreciable effect on the market. He succeeded in making a wood turpentine of a much higher and more uniform grade than had ever been attained before, and by his knowledge of its uses he overcame the prejudice against it, due to its different odor and different source, in enough places so that a firm and steady outlet on good prices was obtained for all that could be supplied. For the first time, too, there was a very considerable amount of the heavy natural oils of the wood, known as pine oil, to be disposed of. This had no regular market, and he succeeded in finding a use for it in a very wide range of industries, where it has so firmly established its value that at the present time the supply cannot begin to equal the demand.

The one other process which has apparently proved of value, and which is still in operation to-day under adverse market conditions in at least two or three plants, is that of extraction by means of a volatile solvent. This method was at one time very extensively employed, producing more naval stores from waste wood than all other systems combined. The amounts of turpentine and pine oil were large and of good quality, and one new product was added from the wood—rosin. This was ultimately refined to a grade approximately corresponding to F and G grades of gum rosin. At first, progress in marketing this was rather difficult, but the oils and tarry matters affecting its use were in part eliminated, and in part the customer was taught what changes were necessary in order to use it as satisfactorily as gum rosins, so that to-day again the demand exceeds the supply.

The worst feature, of course, in the development of this industry during the last few years has been the wide fluctuation in prices. In 1911, F rosin reached a high price of \$8.65 per barrel of 280 pounds, at Savannah: to-day it is \$3—scarcely more than one third of the high figure, and it has been lower. In 1911 turpentine reached a high price of \$1.07 per gallon at Savannah: to-day it is 38 cents and has been lower. Most of these plants were built on the assumption that turpentine would not go below 50 cents per gallon, nor rosin below \$5. These conditions were freely predicted at the time by people who had spent their lives in the naval stores industry, and so probably the chemist should not be blamed too much for the failure of processes to operate successfully at much lower figures, when he had based all his calculations on the higher figures and on the best judgment of people well informed as to conditions.

Now as to the future of the industry: Let us look first at the composition of the material with which we have to deal. Assuming that this is what we know as fat lightwood or as fat lightwood stumps, it contains rosin, turpentine, pine oil and the wood fiber. The problem is: In what way can all these products be extracted and placed on the market to bring the largest net amount to the manufacturer? In some places where the timber has been very largely the long-leaf pine, there is the additional factor of so locating his plant that he can entirely clear the land and largely enhance its value at the same time that he is furnishing his plant with raw material. In the future this will no doubt have an important bearing on the establishment of plants, but it will not be considered here. Suppose we have 5,000 pounds of very rich, fat lightwood stumps. Suppose this contains 20 per cent, or 1,000 pounds, of rosin; 40 gallons, or 300 pounds, of turpentine and pine oil, and 15 per cent, or 750 pounds, of water. This leaves nearly 3,000 pounds of wood fiber. Now, if we subject this 5,000 pounds of fat lightwood to destructive distillation, no matter how carefully, we shall not get all the turpentine and we get

only a small portion of the pine oil, before the rosin and the wood itself begins to decompose. The rosin would be valuable if we could get it, or its decomposition product, rosin oil. The pine oil would be valuable if we could get it, but before either the rosin oil or the pine oil leave the retort in any quantity they become thoroughly mixed with the tar and tar oils from the decomposition of the wood fiber, and there is no convenient way of ever separating them again in marketable conditions from the resulting mess. If we investigate any of the other methods that have been discussed above, we find an important loss in some one or more of the products originally present in the wood. If we digest with soda there is a very fair recovery of the turpentine and a moderately good recovery of the pine oil, but the rosin and resinates are not in good marketable condition, and it would be very difficult to get them in any condition for anything but very special markets. On the other hand, if we use a volatile solvent, properly selected and properly applied, we can recover nearly the whole of the rosin, turpentine and pine oil, and have left the wood fiber unchanged. The rosin, the turpentine and the pine oil will be in such condition that they can be made into the best grades it is possible to produce from wood. The wood fiber is free of rosin, and is in just the condition required for digestion to manufacture wood pulp. According to information and experiments it gives a good yield of a very strong-fibered pulp. Probably it will work up best into what is known as Kraft pulp, or undercooked pulp, and this 3,000 pounds of wood fiber remaining should furnish about 1,500 pounds of good marketable pulp.

Our wood fiber has two disadvantages as a source of pulp. In the first place it cannot be entirely freed from the charcoal and charred and burned wood, and in the second place it will not be entirely free from bark, but there is no question that it will produce a good grade of brown wrapping paper, and with this addition we have made a very complete utilization of our 5,000 pounds of wood. The difficulty heretofore has been that the naval stores manufacturer has approached the problem with the view of making the wood pulp plant an annex to his existing plant. The wood pulp plant is the more expensive, requires the more skilled labor, and is by far the more important, so that the rosin and turpentine production should be considered rather as an annex to the pulp plant, or, better still, the whole should be considered as one complete proposition. Many people have this combination of rosin, turpentine, pine oil and wood pulp in their minds at the present time. There is no doubt that it will be tried before long. It is only to be hoped that when it does receive its trial it will be under the supervision of men thoroughly acquainted with both the wood pulp industry and the wood extraction industry, and with the aid of the most competent chemical engineers there are available. In this way it can build on the mistakes of its predecessors, and it seems to me to stand an excellent prospect of success. There has too much good work gone into this industry, and there is too much accumulated information available, to allow it to languish. I feel sure it has an important future, and when its success ultimately comes, very large credit will be due to the chemist and chemical engineers who have made it possible.

A Test of Clean Milk Production

A WRITER in the *American Journal of Public Health* recounts a comparative test of clean milk production, made under the following conditions: Ten dairymen known by their low bacteria records to be expert clean milk producers were placed on ten dairy farms in the neighborhood of Philadelphia which were ordinarily equipped, and which had only fair records under the owning dairymen. The experts were given sterile cans and sterile covered buckets, with 5 inch openings. Under the conditions of the test they were to milk the cows on the respective farms once, and handle the milk until it was placed either in ordinary tanks of cold water or in ice water for cooling purposes; then, when the milk was transported to the milk stations, bacterial counts were to be made. The result of the test was that whereas the owning dairymen of the ten dairies had bacterial counts on April 5th of 60,000 as a minimum to 4,830,000, the counts on April 6th produced milk which had counts ranging from 800 to 7,000, with a maximum in one instance of 61,000, in which the expert complained that the barn had been swept just before he milked, raising much dust. The author concludes that the fundamentals of clean milk production, which were present in this test, are milking with dry hands into covered milk pails; proper washing and sterilization of milking pails and milk cans; cooling milk by placing cans in tanks of cold water or ice water; and regular laboratory tests of milk for bacteria and payment based on laboratory tests. The last is the essential stimulus to clean milk production. The author says he has revised his opinion in regard to the relative values of equipment and dairyman, so that the dairyman should count for at least 90 per cent, and equipment for the other 10 per cent in clean milk production.

¹⁹M. Brillouin so stated in the appreciation which this professor of the Collège de France gave upon my researches at a meeting of the Société de Physique on the 3d of May, 1912.

*The Journal of Industrial and Engineering Chemistry.