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XXXVI. *Investigations in Capillarity:—The Size of Drops.—The Liberation of Gas from Supersaturated Solutions.—Colliding Jets.—The Tension of Contaminated Water-Surfaces.* By Lord RAYLEIGH, F.R.S.*

The Size of Drops.

THE relation between the diameter of a tube and the weight of the drop which it delivers appears to have been first investigated by Tate †, whose experiments led him to the conclusion that “other things being the same, the weight of a drop of liquid is proportional to the diameter of the tube in which it is formed.” Sufficient time must of course be allowed for the formation of the drops; otherwise no simple results can be expected. In Tate’s experiments the period was never less than 40 seconds.

The magnitude of a drop delivered from a tube, even when the formation up to the phase of instability is infinitely slow, cannot be calculated *a priori*. The weight is sometimes equated to the product of the capillary tension (T) and the circumference of the tube ($2\pi a$), but with little justification. Even if the tension at the circumference of the tube acted vertically, and the whole of the liquid below this level passed into the drop, the calculation would still be vitiated by the assumption that the internal pressure at the level in question is atmospheric. It would be necessary to consider the

* Communicated by the Author.

† Phil. Mag. vol. xxvii. p. 176 (1864).

curvatures of the fluid surface at the edge of attachment. If the surface could be treated as a cylindrical prolongation of the tube (radius a), the pressure would be T/a , and the resulting force acting downwards upon the drop would amount to one-half (πaT) of the direct upward pull of the tension along the circumference. At this rate the drop would be but one-half of that above reckoned. But the truth is that a complete solution of the statical problem for all forms up to that at which instability sets in, would not suffice for the present purpose. The detachment of the drop is a *dynamical* effect, and it is influenced by collateral circumstances. For example, the bore of the tube is no longer a matter of indifference, even though the attachment of the drop occurs entirely at the outer edge. It will appear presently that when the external diameter exceeds a certain value, the weight of a drop of water is sensibly different in the two extreme cases of a very small and of a very large bore.

But although a complete solution of the dynamical problem is impracticable, much interesting information may be obtained from the principle of dynamical similarity. The argument has already been applied by Dupré (*Théorie Mécanique de la Chaleur*, Paris, 1869, p. 328), but his presentation of it is rather obscure. We will assume that when, as in most cases, viscosity may be neglected, the mass (M) of a drop depends only upon the density (σ), the capillary tension (T), the acceleration of gravity (g), and the linear dimension of the tube (a). In order to justify this assumption, the formation of the drop must be sufficiently slow, and certain restrictions must be imposed upon the shape of the tube. For example, in the case of water delivered from a glass tube, which is cut off square and held vertically, a will be the external radius; and it will be necessary to suppose that the ratio of the internal radius to a is constant, the cases of a ratio infinitely small, or infinitely near unity, being included. But if the fluid be mercury, the flat end of the tube remains unwetted, and the formation of the drop depends upon the internal diameter only.

The "dimensions" of the quantities on which M depends are :—

$$\sigma = (\text{Mass})^1 (\text{Length})^{-3},$$

$$T = (\text{Force})^1 (\text{Length})^{-1} = (\text{Mass})^1 (\text{Time})^{-2},$$

$$g = \text{Acceleration} = (\text{Length})^1 (\text{Time})^{-2},$$

of which M , a mass, is to be expressed as a function. If we assume

$$M \propto T^x \cdot g^y \cdot \sigma^z \cdot a^u,$$

we have, considering in turn length, time, and mass,

$$y - 3z + u = 0, \quad 2x + 2y = 0, \quad x + z = 1;$$

so that

$$y = -x, \quad z = 1 - x, \quad u = 3 - 2x.$$

Accordingly

$$M \propto \frac{Ta}{g} \left(\frac{T}{g\sigma a^2} \right)^{x-1}.$$

Since x is undetermined, all that we can conclude is that M is of the form

$$M = \frac{Ta}{g} \cdot F \left(\frac{T}{g\sigma a^2} \right), \quad . \quad . \quad . \quad . \quad (1)$$

where F denotes an arbitrary function.

Dynamical similarity requires that $T/g\sigma a^2$ be constant; or, if g be supposed to be so, that a^2 varies as T/σ . If this condition be satisfied, the mass (or weight) of the drop is proportional to T and to a .

If Tate's law be true, that *cæteris paribus* M varies as a , it follows from (1) that F is constant. For all fluids and for all similar tubes similarly wetted, the weight of a drop would then be proportional not only to the diameter of the tube but also to the superficial tension, and it would be independent of the density.

In order to examine how far Tate's law can be relied upon, I have thought it desirable, with the assistance of Mr. Gordon, to institute fresh experiments with water, in which necessary precautions were observed, especially against the presence of grease. Attention has been given principally to the two extreme cases, (i.) when the wall of the tube is thin, so that the external and internal diameters of the tube are nearly equal; (ii.) when the bore is small in comparison with the external diameter. The event showed that up to an external diameter of one centimetre or more, the size of the bore is of little consequence, but that for larger diameters the weight of the drop in (ii.) is sensibly less than in (i.). It scarcely needs to be pointed out that in (i.) the diameter can only be increased up to a certain limit, after which the tube would not remain full. In (ii.) the diameter can be increased to any extent, but the drop falling from it reaches a limit. The experiments of Tate extended also to case (ii.), but his results are, I believe, erroneous. For a diameter of one-half an inch (1.27 cm.) he found for the two cases drops in the ratio of 1.56 : 2.84.

In my experiments the thin-walled tubes were of glass, the

ends being ground to a plane, and carefully levelled. Ten drops, following one another at intervals of about 50 seconds, were usually weighed together. As to the interval, sufficient time must be allowed for the normal formation of the drop, but the fact that evaporation is usually in progress forbids too great a prolongation. The accuracy attained was not so great as had been hoped for. Successive collections, made without disturbance, gave indeed closely accordant weights (often to one-thousandth part), but repetitions after cleaning and remounting indicated discrepancies amounting to one-half per cent., or even to one per cent. The cause of these minor variations has not been fully traced; but the results recorded, being the mean of several experiments, must be free from serious error. Attention may be called to tubes 11 and 12 of nearly the same (external) diameter. Of these 11 was plugged so as to leave only a small bore, the end being carefully ground flat. It will be seen that the difference in the weights of the drops was but small.

Again, No. 10 was of barometer-tubing, having a comparatively small bore, which accounts for the slightly diminished weight of the drop. The other tubes were thin-walled. In all cases care was taken that the cylindrical part of the tube, though clean, should remain unwetted, a condition which precluded the use of diameters much less than those recorded.

Glass.			Metal.		
1	·088	·0375	15	·400	·1446
2	·134	·0526	16	·450	·1662
3	·191	·0712	17	·500	·1882
4	·200	·0755	18	·530	·2023
5	·256	·0923	19	·550	·2130
6	·354	·1151	20	·559	·2167
7	·383	·1362	21	·580	·2256
8	·406	·1461	22	·597	·2295
9	·459	·1703	23	·621	·2389
10	·465	·1698	24	·640	·2454
11	·521	·1969	25	·680	·2510
12	·523	·2023	26	·730	·2531
13	·566	·2210	27	·800	·2509
14	·584	·2339			

The numbers in the second column are the external diameters measured in inches (one inch=2·54 cm.), while the third column gives the weight in grams of a single drop, corrected for temperature to 15° C., upon the supposition

(corresponding to Tate's law) that the weight is proportional to surface-tension.

The entries under the heading "Metal" relate to experiments in which the glass tubes were replaced by metal disks, bored centrally and turned true in the lathe. The water was supplied from above through a metal tube soldered to the back (upper) face of the disk (fig. 1). At the time of use only the lower face was wetted.

Fig. 1.

A plot of both sets of numbers is shown in the figure (2). The two curves practically coincide up to diameters of about $\cdot 4$ inch, after which that corresponding to the disks falls below. The lower curve shows some irregularities, especially in the region of diameters equal to $\cdot 6$ inch. These appear to be genuine; they may originate in a sort of reflexion from the circumference of the disk of the disturbance caused by the breaking away of the drop. It is possible that at this stage the phenomenon is sensibly influenced by fluid viscosity.

Fig. 2.

That the size of the bore should be of secondary importance is easily understood. Up to the phase of instability, the phenomenon is merely a statical one, and the element of the size of the bore does not enter. It is only the rapid

motion which occurs during the separation of the drop that could be influenced. When the diameter is moderate, the most rapid motions occur at a level considerably below the tube, and the obstruction presented by the flat face of a thick-walled tube is unimportant.

The observations give materials for the determination of the function F in (1). In the following table, applicable to thin-walled tubes, the first column gives values of $T/g\sigma a^2$, and the second column those of gM/Ta , all the quantities concerned being in c.g.s. measure, or other consistent system.

$T/g\sigma a^2$.	gM/Ta .
2.58	4.13
1.16	3.97
.703	3.80
.441	3.73
.277	3.73
.220	3.60
.169	4.06

From this the weight of a drop of any liquid of which the density and the surface-tension are known can be calculated. For many purposes it may suffice to treat F as constant, say 3.8. The formula for the weight of a drop is then simply

$$Mg = 3.8Ta, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which 3.8 replaces the 2π of the faulty theory alluded to earlier.

The Liberation of Gas from Supersaturated Solutions.

The formation of bubbles upon the sides of a vessel containing "soda-water" or a gas-free liquid heated above its boiling-point, is a subject upon which there has been much difference of opinion. In one view, ably advocated by Gernez, the nucleus is invariably gaseous. That a small volume of gas, visible or invisible, provided that its dimensions exceed molecular distances, must act in this way is certain, and the activity of porous solids is thus naturally and easily explained. But Gernez goes much further, and holds that the activity of glass or metal rods, immersed in the liquid without precaution, is of the same nature, and to be attributed to the film of air which all bodies acquire when left for some time in contact

with the atmosphere. If a body is rendered inactive by prolonged standing in cold water; by treatment with alcohol, ether, &c., "qui dissolvent les gaz de l'air, plus abondamment que l'eau"*; or by heating in a flame; it is because by such processes the film of air is removed. One cannot but sympathise with Tomlinson† in his repugnance to such an explanation; but the position maintained by the latter that activity is due to contamination with grease is also not without its difficulties.

The question whether contact with air suffices to restore the activity of a piece of glass or metal that has been rendered inactive by heat or otherwise, appears to be amenable to experiment, and should not remain an open one. In 1892 I had a number of glass tubes prepared of about 1 cm. diameter for experiments in this direction. After a thorough heating in the blowpipe-flame, the ends of the tubes were hermetically sealed. At intervals since that date some of the tubes have been opened and compared with others which had undergone no preparation. Short lengths of rubber provided with pinch-cocks are fitted to the upper ends, by means of which aerated water is easily drawn in from a shallow vessel. Three tubes remaining over from the batch above mentioned were tried a few weeks ago, and establish the conclusion that *seven years contact with air fails to restore activity*. A similar experiment may be made with iron wires. If these be heated and sealed up in glass tubes, they remain inactive, but exposure to the air of the laboratory for a day or two restores activity.

In opposition to the contention that grease is the primary cause of activity, Gernez brings forward a striking experiment from which it appears that a drop of olive-oil itself liberates no gas when introduced with precaution. "Quant au rôle que jouent les corps gras, il est facile de s'en rendre compte: lorsqu'on frotte un corps quelconque entre les doigts légèrement graissés, on produit à sa surface une série d'éminences linéaires séparées par les sillons qui correspondent aux lignes de l'épiderme; les cavités forment un réseau de conduits qui contiennent de l'air, sont difficilement mouillés par l'eau et, par conséquent, constituent au sien du liquide une atmosphère, éminemment favorable au dégagement des gaz"‡.

It seems to me that Tomlinson was substantially correct in

* *Annales de l'Ecole Normale*, 1875, p. 319.

† *Phil. Mag.* vol. xlix. p. 305 (1875).

‡ *L. c.* p. 346.

attributing the activity of a non-porous surface to imperfect adhesion. We have to consider in detail the course of events when a surface, *e. g.* of glass, is introduced into the liquid. If the surface be clean, it is wetted by the water advancing over it, whether there be a film of air condensed upon it or not, and no gas is liberated from the liquid. But if the surface be greasy, even in a very slight degree, the behaviour is different. We know that a drop of water is reluctant to spread over a glass that is not scrupulously clean. If a large quantity of water be employed, some sort of spreading follows under the influence of gravity, but there is no proper adhesion, at least for a time, as appears at once on pouring the water off again. The precise character of the transition from glass to water when there is grease between is not well understood. It may be that there is something which can fairly be called a film of air. If so, its existence is a consequence of the presence of the grease. On the other hand, it appears at least equally probable that air is not concerned, and that the activity of the surface is directly due to the thin film of grease, whose properties, as in the case of greased water surfaces, are materially different from those of a thick layer.

On this principle, too, it is easier to understand the retention of a visible bubble when formed—a retention which often lasts for a long time. So soon as the gas is entirely surrounded by liquid of thickness exceeding the capillary limit, the bubble is bound to rise. It is difficult to see how the hypothetical film of air explains the failure of the liquid to penetrate between the bubble and the solid.

Colliding Jets.

In various papers (Proc. Roy. Soc. Feb. 1879, May 1879, June 1882) I have examined the behaviour of colliding drops and jets. Experiments with drops are very simply carried out by the observation of nearly vertical fountains, rising say to two feet from nozzles $\frac{1}{10}$ inch in diameter. The scattering of the drops, when the water is clean and not acted upon by electricity, shows that collision is followed by rebound. If the water is milky, or soapy with unclarified soap, or if the jet, though clean, is under the influence of feeble electricity, the apparent coherence and the heaviness of the patten made by the falling water are evidence that rebound no longer ensues, but that collision results in amalgamation. Eye observation, or photography, with the instantaneous illumination of electric sparks renders the course of events perfectly clear.

The form of the experiment in which are employed *jets*,

issuing at moderate velocities and meeting at high obliquities, is the more instructive; but it is liable to be troublesome in consequence of the tendency of the jets to unite spontaneously. It is important to avoid dust both in the water and in the atmosphere where the collision occurs. An electromotive force of one volt suffices to determine union; but so long as the jets rebound there is complete electrical insulation between them.

As to the manner in which electricity acts, two views were suggested. It was thought probable that union was the result of actual discharge across the thin layer of intervening insulation; but it was also pointed out that the result might be due to the augmented pressure to be expected from the electrical charges upon the opposed surfaces. From observations upon the colours of thin plates exhibited at the region of contact, which he found to be undisturbed by such electrical forces as would not produce union, Mr. Newall* concluded that the second of the above-mentioned explanations must be discarded.

On the other hand, as has been pointed out by Kaiser†, the progress of knowledge concerning electrical discharge has rendered the first explanation more difficult of acceptance. It would appear that some hundreds of volts are needed in order to start a spark, and that mere diminution of the interval to be crossed would not compensate for want of electromotive force.

A more attentive examination of the conditions of the experiment may perhaps remove some of the difficulties which seem to stand in the way of the second explanation. As the liquid masses approach one another, the intervening air has to be squeezed out. In the earlier stages of approximation the obstacle thus arising may not be important; but when the thickness of the layer of air is reduced to the point at which the colours of thin plates are visible, the approximation must be sensibly resisted by the viscosity of the air which still remains to be got rid of. No change in the capillary conditions can arise until the interval is reduced to a small fraction of a wave-length of light; but such a reduction, unless extremely local, is strongly opposed by the remaining air. It is of course true that this opposition is temporary. The question is whether the air can be anywhere squeezed out during the short time over which the collision extends.

* Phil. Mag. vol. xx. p. 33 (1885).

† Wied. Ann. liii. p. 667 (1894). Kaiser's own experiments were made upon the modification of the phenomenon observed by Boys, where the contact takes place between two soap-films.

It would seem that the electrical forces act with peculiar advantage. If we suppose that upon the whole the air cannot be removed, so that the *mean* distance between the opposed surfaces remains constant, the electric attractions tend to produce an instability whereby the smaller intervals are diminished while the larger are increased. Extremely local contacts of the liquids, while opposed by capillary tension which tends to keep the surfaces flat, are thus favoured by the electrical forces, which moreover at the small distances in question act with exaggerated power.

It is probably by promoting local approximations in opposition to capillary forces that dust, finding its way to the surfaces, brings about union.

A question remains as to the mode of action of milk or soapy turbidity. The observation, formerly recorded, that it is possible for soap to be in excess may here have significance. It would seem that the surfaces, coming into collision within a fraction of a second of their birth, would still be subject to further contamination from the interior. A particle of soap rising accidentally to the surface would spread itself with rapidity. Now such an outward movement of the liquid is just what is required to hasten the removal of the intervening air. It is obvious that this effect would fail if the contamination of the surface had proceeded too far previously to the collision.

In order to illustrate the importance of the part played by the intervening gas, I thought that it would be interesting to compare the behaviour of the jets when situated in atmospheres of different gases. It seemed that gases more freely soluble in water than the atmospheric gases would be more easily got rid of in the later stages of the collision, and that thus union might more readily be brought about. This expectation has been confirmed in trials made on several different occasions. It was found sufficient to allow a pretty strong stream of the gas under examination to play upon the jets at and above the place of collision. Jets of air, of oxygen, and of coal-gas were found to be without effect. On the other hand, carbonic acid, nitrous oxide, sulphurous anhydride, and steam at once caused union. Only in the case of hydrogen was there an ambiguity. On some occasions the hydrogen appeared to be without effect, but on others (when perhaps the pressure of collision was higher) union uniformly followed. Care was taken to verify that air blown through the same tube as had supplied the hydrogen was inactive, so that the effect of the hydrogen could not be attributed to dust. The action of hydrogen cannot be

explained by its solubility. Hydrogen is, however, much less viscous than other gases, and to this we may plausibly attribute its activity in promoting union. A layer of hydrogen may be effectively squeezed out in a time that would be insufficient in the case of air and oxygen.

The Tension of Contaminated Water-Surfaces.

In my experiments upon the superficial viscosity of water (Proc. Roy. Soc. June 1890) I had occasion to notice that the last traces of residual contamination had very little influence upon the surface-tension, but that they became apparent when compressed in front of the vibrating needle of Plateau's apparatus. Subsequently I showed (Phil. Mag. vol. xxxiii., p. 470, 1892) that according to Laplace's theory of Capillarity, in which matter is regarded as continuous, the effect of a thin surface-film in diminishing the tension of pure water should be as the *square* of the thickness of the film.

The tension of slightly contaminated surfaces was made the subject of special experiments by Miss Pockels ('Nature,' vol. xliii. p. 437, 1891), who concluded that a water-surface can "exist in two sharply contrasted conditions; the *normal* condition, in which the displacement of the partition [altering the density of the contamination] makes no impression upon the tension, and the *anomalous* condition, in which every increase or decrease alters the tension." It is only since I have myself made experiments upon the same lines that I have appreciated the full significance of Miss Pockels' statement. The conclusion that, judged by surface-tension, the effect of contamination comes on suddenly, seems to be of considerable importance, and I propose to illustrate it further by actual curves embodying results recently obtained.

The water is contained in a trough modelled after that of Miss Pockels. It is of tin-plate, 70 cm. long, 10 cm. broad, and 2 cm. deep, and it is filled nearly to the brim. The partitions, by which the oil is confined, are made of strips of glass resting upon the edge of the trough in such a manner that their lower surfaces are wetted while the upper surfaces remain dry. The strips may be $1\frac{1}{2}$ cm. wide, and for convenience of handling their length should exceed considerably the width of the trough. I have found advantage in cementing (with hard cement) slight webs of glass to the lower faces. The length of these is a rough fit with the width of the trough, enabling them to serve as guides preventing motion of the strips parallel to their length.

In order to observe the surface-tension Miss Pockels used

a small disk (6 mm. in diameter) in contact with the surface, measuring the force necessary to detach it. In my own experiments I have employed the method of Wilhelmy, which appears to be better adapted to the purpose. A thin blade is mounted in a balance, its plane being vertical and its lower horizontal edge dipping under the surface of the liquid. If absolute measures are required, the edge of the blade should lie at the general level of the surface when the pointer of the balance stands at zero. If m be the mass in the other pan needed to compensate the effect of the liquid, l the length of the blade, the surface-tension (T) may be deduced from the equation

$$2T = mg. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

When only differences of tension are concerned, the precise level of the strip is of no consequence. As regards material, glass is to be preferred and it should be thin in order not unduly to diminish the sensitiveness of the balance by the displacement of water. I have used a small frame carrying three parallel blades, the total length being 27 cm., while the thickness may be considered nearly negligible. Before use the glass is cleaned with strong sulphuric acid, and the angle of contact with the water when the balance is raised appears to be zero. The total value of m for a clean surface may then be calculated from (1), taking T at 74. We find $m = 4.1$ gms. The balance could be read without difficulty to .01 gm., giving abundant accuracy.

The position of the barrier, giving the length of the surface to which the grease is confined, is measured by a millimetre-scale, but is subject to a correction needed in order to take account of the additional surface operative when the suspended strip is raised. This amounts to about 3 cm., and is to be added to the measured length. In a set of experiments where the grease is successfully confined, the density is proportional to the reciprocal of the above corrected length. It sometimes happens that continuity is lost by the passage of grease across the barrier. This is of course most likely to happen when the tensions on the two sides differ considerably, and the danger may be mitigated by the use of a second barrier, so manipulated that the densities are nearly the same on the two sides of the principal barrier.

In commencing a set of observations the first step is to secure the cleanness of the surface. To this end the surface is *scraped*, if the expression may be allowed, along the whole length by one of the movable partitions, and, if thought necessary, the accumulated grease at the far end may be

removed with strips of paper. The operation should be repeated two or three times with intermediate insertion of the balanced strips until it is certain that no grease remains, competent to affect the tension even when concentrated. The weights now necessary to bring the pointer to zero give the standard with which the contaminated surfaces are to be compared.

If it be desired to begin with small contaminations, it is best to contract the area, say to about one-half the maximum, and then to apply the grease under examination with a previously ignited platinum wire until a small effect, such as $\cdot 02$ gm., is observed at the balance. If the surface be now extended to the maximum, the attenuated grease will have lost its power, and the original reading for clean surfaces will be recovered. The barrier may now be advanced, readings being taken at intervals as the grease is concentrated. It is often more convenient to make the final adjustment by moving the barrier rather than by correcting the weights.

An example will make manifest at once the character of the results obtained. On May 15, the weight for the clean surface being $1\cdot 65$ gm., the water was greased with castor-oil. With the barrier at 63 cm. this grease had no effect. The corrected length is 66, and the reciprocal of this, viz. 152, represents (for this series of observations) the density of the oil. With the barrier at 40, viz. at density 233, there was no change of the order of $\cdot 005$ gm. At 36 cm., or density 256, the oil had just begun to show itself distinctly, the weight being then $1\cdot 64$. At density 278 the weight became $1\cdot 62$. From this point onwards increase of density tells rapidly. At 308 the weight was $1\cdot 55$, and at 334 the weight was $1\cdot 40$. A plot of these results is given in fig. 3, and brings out more vividly than any description the striking character of the law discovered by Miss Pockels.

The effect of concentration beyond 571, giving $\cdot 70$ gm., could not be examined in the same series. It was necessary to add more oil, and then of course the reciprocals of the corrected lengths represent the densities on a different scale from before. Corresponding to 63 cm., of which the reciprocal is 159, the weight was now $1\cdot 20$ gm., falling to $1\cdot 00$ at 175, $\cdot 80$ at 204, $\cdot 70$ at 233, $\cdot 60$ at 351, $\cdot 55$ at 488, and finally $\cdot 52$ at 625. These values are plotted in fig. 4, and they show that from a certain density onwards the tension falls very slowly. This curve may be continued backwards by means of the results of fig. 3, for of course the densities corresponding to any particular weight, *e. g.* $1\cdot 20$ gm., are really the same in the two series.

It is of interest to inquire what point on these curves corresponds to the deadening of the movements of small particles

Figs. 3-6.

of camphor deposited upon the surface. On a former occasion I have shown (Phil. Mag. vol. xxxiii. p. 366, 1892) that whatever may be the character of the grease the cessation of the movements indicates that the tension falls short of a particular value. In the present method of experimenting there is no difficulty in determining what for brevity may be called the *camphor-point*. Two precautions should, however, be observed. It is desirable not to try the camphor until near the close of a set of experiments, and then to avoid too great a quantity. It would seem that the addition of camphor may sometimes lower the tension below the point due to the grease. The second precaution required is the raising of the balanced strip; otherwise when a weight is taken the density of the grease is altered. In several trials with castor and other oils the camphor-point was found to correspond with a drop of tension from that of clear water amounting to .9 gm. The points thus fixed are marked in figs. (3) and (4) with the letter C.

At this stage a certain discrepancy from former results should be remarked upon. Working by the method of ripples I had concluded that the camphor-point corresponded to a tension .72 of that of pure water, *i. e.* to a drop of 28 per cent. But the .9 gm. is only 22 per cent. of the calculated weight for pure water, *i. e.*, 4.1 gms. At this rate the

72 per cent. would become 78 per cent., and the difference seems larger than can well be explained as an alteration of standard in judging when the fragments are nearly dead.

One of the most striking conclusions to be drawn from an inspection of the curves is the slowness of the fall of tension which sets in soon after passing the camphor-point. On a rough view it would seem as if a second limit were being approached. But this idea is scarcely confirmed by actual further additions of oil, for the tension continues to fall slightly after each addition, even when large quantities are already present. But there is one peculiarity in the behaviour of the oil which suggests that the failure to reach a limit may be due to want of homogeneity. As is well known, the disk into which a drop deposited upon an already oiled surface at first spreads, soon breaks up, and the superfluous oil collects itself into little lenses. After this stage is reached it would be natural to suppose that the affinity of the surface for oil was fully satisfied, and that no further alteration in tension could occur. And in fact the balance usually indicated the absence of immediate effect. But if the surface were expanded so as to spread the added oil more effectively and then contracted again, a fall in tension was almost always observed. It would seem as if the surface still retained an affinity for some minor ingredient capable of being extracted, though satiated as regards the principal ingredient.

The comparison of the present with former results throws an interesting light upon molecular magnitudes. It has been shown (Proc. Roy. Soc. March 1890) that the thickness of the film of olive-oil, calculated as if continuous, which corresponds to the camphor-point, is about $2.0 \mu\mu^*$; while from the present curves it follows that the point at which the tension *begins* to fall is about half as much, or $1.0 \mu\mu$. Now this is only a moderate multiple of the supposed diameter of a gaseous molecule, and perhaps scarcely exceeds at all the diameter to be attributed to a molecule of oil. It is obvious therefore that the present phenomena lie entirely outside the scope of a theory such as Laplace's, in which matter is regarded as continuous, and that an explanation requires a direct consideration of molecules.

If we begin by supposing the number of molecules of oil upon a water surface to be small enough, not only will every molecule be able to approach the water as closely as it desires, but any repulsion between molecules will have exhausted itself. Under these conditions there is nothing to oppose the

$$\mu\mu = \text{micromillimetre} = 10^{-6} \text{ mm.}$$

Castor Oil. May 15. Fig. (3).		Castor Oil. May 15. Fig. (4).		Olive Oil. May 3. Fig. (5).		Cod Liver Oil. May 11. Fig. (6).	
Density.	Weight (in grams).	Density.	Weight (in grams).	Density.	Weight (in grams).	Density.	Weight (in grams).
0	1.65	0 obs.	1.65	0	8.45	0	8.28
152	1.65	98 calc.	1.65	159	8.45	77	8.27
213	1.65	108 "	1.64	324	8.30	113	8.25
233	1.65	117 "	1.62	350	8.20	125	8.20
256	1.64	122 "	1.60	376	8.10	137	8.10
278	1.62	130 "	1.55	405	8.00	147	8.00
290	1.60	136 "	1.55	430	7.90	154	7.90
308	1.55	141 "	1.40	461	7.80	171	7.70
323	1.50	148 calc.	1.30	483	7.70	213	7.60
334	1.40	159 obs.	1.20	518	7.60	303	7.50
351	1.30	175 "	1.00			392	7.45
377	1.30	204 "	.80			465	7.40
408	1.10	233 "	.70			526	7.35
435	1.00	351 "	.60			625	7.30
472	.90	488 "	.55				
510	.80	625 obs.	.52				
571	.70						

contraction of the surface—the tension is the same as that of pure water.

The next question for consideration is—at what point will an opposition to contraction arise? The answer must depend upon the forces supposed to be operative between the molecules of oil. If they behave like the smooth rigid spheres of gaseous theory, no forces will be called into play until they are closely packed. According to this view the tension would remain constant up to the point where a double layer commences to form. It would then suddenly change, to remain constant at the new value until the second layer is complete. The actual course of the curve of tension deviates somewhat widely from the above description, but perhaps not more than could be explained by heterogeneity of the oil, whereby some molecules would mount more easily than others, or by reference to the molecular motions which cannot be entirely ignored. If we accept this view as substantially true, we conclude that the first drop in tension corresponds to a complete layer one molecule thick, and that the diameter of a molecule of oil is about $1\cdot0\ \mu\mu$.

An attractive force between molecules extending to a distance of many diameters, such as is postulated in Laplace's theory, would not apparently interfere with the above reasoning. An essentially different result would seem to require a repulsive force between the molecules, resisting concentration long before the first layer is complete. In this case the tension would begin to fall as soon as the density is sufficient to bring the repulsion into play. On the whole this view appears less probable than the former, the more as it involves a molecular diameter much *exceeding* $1\cdot0\ \mu\mu$.

EXPLANATION OF FIGURES.

In the figures (and in the tables) there is no relation between the scales of the abscissæ representing the densities in the various cases. As regards the ordinates, representing weights or tensions, the scale is the same in all the cases, but the zero point is arbitrary. It may be supposed to be situated on the line of zero densities at a point $4\cdot1$ below the starting point of the curve.