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XL. *Experiments upon Surface-Films.**By* Lord RAYLEIGH, *Sec. R.S.**

THE experiments here described are rather miscellaneous in character, but seem of sufficient interest to be worthy of record. The greater number of them have been exhibited in the course of lectures at the Royal Institution.

The Behaviour of Clean Mercury.

According to Marangoni's rule, water, which has the lower surface-tension, should spread upon the surface of mercury; whereas the universal experience of the laboratory is that drops of water standing upon mercury retain their compact form without the least tendency to spread. To Quincke belongs the credit of dissipating the apparent exception. He found that mercury specially prepared behaves quite differently from ordinary mercury, and that a drop of water deposited thereon spreads over the whole surface. The ordinary behaviour is evidently the result of a film of grease, which adheres with great obstinacy.

The process described by Quincke is somewhat elaborate; but my experience with water suggested that success might not be so difficult, if only the mistake were avoided of pouring the liquid to be tried from an ordinary bottle. In the early experiments upon the camphor movements difficulty seems to have been experienced in securing sufficiently clean water surfaces. The explanation is probably to be found in the desire to use distilled water, and to the fact that the liquid would usually be simply poured from a stock bottle into the experimental vessel. No worse procedure could be devised; for the free surface in the bottle is almost sure to be dirty, and is transferred in great part to the vessel. In my experience water from the dirtiest cistern will exhibit the camphor movements, provided that it be drawn in the usual manner from a tap, and that the precaution be taken to give the vessel a preliminary rinsing.

In order to carry out the idea of drawing the liquid from underneath, an arrangement was provided like an ordinary wash-bottle, and was filled with tolerably clean mercury. As experimental vessels watch-glasses are convenient. They may be dipped into strong sulphuric acid, rinsed in distilled water, and dried over a Bunsen flame. When the glasses are cool they may be charged with mercury, of which the first

* Communicated by the Author.

portion is rejected. Operating in this way there was no difficulty in obtaining surfaces upon which a drop of water would spread, although, from causes that could not always be traced, a certain proportion of failures was met with.

Exposure of the glasses to the atmosphere soon tells upon the success of the experiment, although on one occasion spreading occurred after a glass had stood (with protection from dust) for 20 hours. Even so short an exposure as 10 minutes was found to prejudice the condition of the mercury surface. Although something here may have depended upon the special character of the sample of mercury, it will be advisable in repeating the experiment to pour the mercury at the last moment.

As might be expected, the grease which produces these effects is largely volatile. In many cases a very moderate preliminary warming of the watch-glass makes all the difference in the behaviour of the drop.

So far as I have observed, the spreading of the drop takes place always in a leisurely fashion. If a little powder of recently ignited magnesia be dusted over the mercury, there is no violent repulsion of the dust before the advancing water. But if a small drop of oil be substituted for the water, the powder is flashed away so quickly that the eye cannot follow the operation. The difference between the two cases appears to depend upon the atmospheric moisture. As soon as the mercury is poured, it coats itself with an aqueous film, and the subsequent spreading of the drop takes place upon a surface whose affinity for water is already largely satisfied. A drop of water that has spread and then partially gathered up again (as usually happens after a short interval) shows an interesting behaviour when breathed upon. The disk contracts somewhat, and then as the breath, which need hardly be visible, passes off, expands again; and thus a number of times. The temporary character of the effect indicates that it is due rather to the moisture of the breath than to any greasy contamination; a view confirmed by subsequent experiments, in which the breath was replaced by a current of pure air which had passed through warm water.

In the experiment with a powdered surface, the dust may be driven from the neighbourhood of a drop of petroleum by the action of vapour without actual contact of the liquids.

Drops of Bisulphide of Carbon upon Water.

The behaviour of a drop of CS_2 placed upon clean water is also at first sight an exception to Marangoni's rule. So far

from spreading over the surface, as according to its lower tension it ought to do, it remains suspended in the form of a lens. And dust which may be lying upon the surface is not driven away to the edge upon the deposit of the drop, as would happen in the case of oil. A simple modification of the experiment suffices, however, to clear up the difficulty. If *after* the deposit of the drop a little lycopodium be scattered over the surface, it is seen that a circular space surrounding the drop, of perhaps the size of a shilling, remains bare, and this however often the dusting be repeated, as long as any of the CS_2 remains. The interpretation can hardly be doubtful. The bisulphide is really spreading all the while, but on account of its volatility is unable to reach any considerable distance. Immediately surrounding the drop there is a film moving outwards at a high speed, and this carries away almost instantaneously any dust that may fall upon it. The phenomenon above described requires that the water surface be clean. If a very little grease be present there is no outward flow, and dust remains undisturbed in the immediate neighbourhood of the drop. With the aid of the vertical lantern, and a shallow dish whose bottom is formed of plate glass, these experiments are easily shown to an audience.

Movements of Dust.

When dust of sulphur or lycopodium is scattered upon the surface of water contained in a partially filled vessel, it is found that after a few seconds the dust leaves the edge and that a clear ring is formed of perhaps a centimetre in width. Two explanations suggest themselves. The action may be due to grease communicated to the surface from the edge of the vessel; or, secondly, it may be the effect of gravity upon those particles of the dust which lie within the limits of the capillary meniscus. The first explanation is rendered improbable by the non-progressive, or at least but very slowly progressive, character of the effect; and it is negatived by a repetition of the experiment in a varied form. It is found that if the vessel, whether of glass or metal, be filled *over the brim*, so that the capillary meniscus is convex, then, although as before a bare margin is formed, the effect is due to a motion of the dust outwards (instead of inwards, as in the former case), and therefore not to be attributed to grease.

A similar movement of dust was to be observed in the experiment above recorded, where magnesia was scattered upon a pool of mercury, and is undoubtedly due to gravity; but the full explanation is not so simple as might appear at first sight.

Even in the interior parts of the surface at a distance from the edge the sulphur particles do not retain their initial positions, but form aggregations into which continually increasing numbers are attracted. This is also due to gravity, neighbours tending, as it were, to fall into the depression by which every particle is surrounded.

Camphor Movements a Test of Surface-Tension.

The theory of these movements, due to Van der Mensbrugghe, implies that they will take place with greater or less vigour so long as the tension of the surface, which may be in some degree contaminated, is greater than that of a saturated solution of camphor. If, however, the contamination be so great that the tension falls below this point, the solution of camphor can no longer spread upon the surface, and the movements cease. Thus, according to this theory and to observations* upon a saturated solution of camphor, the movements are an indication that the actual tension does not fall below .71 of that of pure water.

Although there appeared to be no reason for distrusting this view, it was thought desirable to examine specially whether the cessation of the movements was really a question of surface-tension only, without regard to the character of the contamination. The readiest method of ensuring the equality of the tensions of two surfaces contaminated with different materials is to make the two surfaces parts of one surface, for two parts of the same surface cannot be at rest unless they have the same tension. The method of experiment was therefore to divide a surface of clean water contained in a large dish into two parts by a line of dust, and to communicate different kinds of grease to the surfaces on the two sides of the indicating line. If, for example, a small chip of wood, slightly greased with olive-oil, be allowed to touch one part of the surface, the line of dust is repelled by the expansion of that part, but the effect may be compensated by a slight greasing of the other part with oil of cassia. By careful alternate additions the line of dust may be kept central, while the two halves become increasingly greased with the two kinds of oil. At every stage of this process, so long as the surface is at rest, the tension of all parts is necessarily the same.

A large number of substances have thus been tried in pairs, of which may be mentioned oils of olive, cassia, turpentine, lavender, cinnamon, anise, petroleum, pseudocumene.

* Phil. Mag. November 1890.

In no case could any difference be detected in the behaviour of camphor fragments on the two sides. Whenever possible, the quantities of oil were adjusted to the point at which the movements were just ceasing. In case of overshooting the mark, the excess of oil could be easily removed by strips of paper, partially immersed and then withdrawn, the action being equivalent to an expansion of the surface. In several cases the volatility of the substance with which the surface was contaminated led to a subsequent retraction of the line of dust. Thus freshly distilled oil of turpentine, even at first barely capable of arresting the movements, soon passes off.

As was shown by Tomlinson, oil of anise is incapable of arresting the camphor movements. In the experiment with a partition of dust, olive-oil will drive oil of anise into a very small space, whose area is doubtless dependent upon the amount of other impurities present. In this case, as in all others, the behaviour of camphor is the same on the various parts of the surface.

It may thus be taken as established that the relation of a contaminated surface to the camphor movements is one of surface-tension only.

A similar method of experimenting may be applied to a rough determination of the degree of purity of cleansed surfaces. The whole of the surface under test is lightly dusted over, and olive-oil is applied at several places close to the circumference until camphor movements are nearly arrested. After each addition of oil the dusted area contracts, and at the close of operations it gives a measure of the extent to which the original contamination must be concentrated in order to stop camphor.

A few numbers may be given as examples, although in all probability the result is influenced by a variety of circumstances. A circular area of 10 inches diameter, occupied by tap water, and cleansed by the flexible hoop described in former papers, was tested on July 28, 1891. The application of oil, just sufficient to stop the camphor movements, drove the dust into a central circular patch of $2\frac{1}{2}$ inches diameter. When the surface was in its natural condition, unpurified by the action of the hoop, the central patch was of about 5 inches diameter. These numbers, approximately verified on repetition, show that the natural surface was about 4 times, and the purified about 16 times better than according to the camphor standard. The difference between the two cases is less than was expected, and would perhaps have been greater had distilled water been employed. It must be remembered also that contact with dust (sulphur) is unfavourable to the

purity of a water surface. In a very good light a special dusting might probably be dispensed with, the motion of the surface being evidenced by inevitable motes.

If the dust be applied in the first instance to a small central patch, which is then touched internally with a very small quantity of oil, the expansion of the dust in the form of a ring is followed by a slight but unmistakable rebound. The effect appears to take place when the surface is very clean to begin with, and is then somewhat difficult of explanation. I am disposed to think that it must be attributed in all cases to initial contamination. This is concentrated in front of the rapidly advancing ring, and has not time to diffuse itself equally over the whole external area. Under the influence of inertia the expansion of the central area may then proceed so far that its tension becomes greater than that of the parts immediately surrounding.

Influence of Heat.

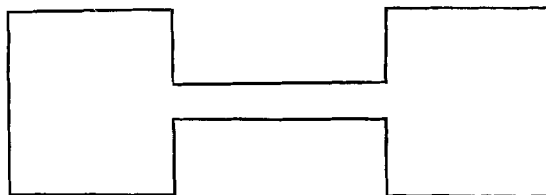
For a lecture experiment the effect of heat is best shown by holding a hot body near the surface of water contained in a shallow vessel with a glass bottom. The hot body may be the end of a glass rod heated by a flame, or more conveniently a small spiral of platinum wire, rendered incandescent at will by an electric current. The immediate effect of the heat is to lower the tension of the part of the surface affected; but the visible result depends entirely upon whether the surface be clean or otherwise. In the former case the heated surface expands, and an outward current is generated. This is rendered evident by the clearing away of dust. But if the original contamination exceed a very small quantity, a moderate expansion of the heated area brings the tension again up to equality with that of the surrounding surface, and there is no further action. In this case there is no visible clearing away of dust under the hot body.

Under favourable circumstances a very slight elevation of temperature suffices. On July 28 a shallow tin vessel 8×5 inches, the lid of a biscuit-box, was levelled and filled with tap-water from a rubber-hose, after a thorough preliminary rinsing *in situ*. A little dust (sulphur) was then scattered over, and the finger was brought underneath into contact with the bottom of the dish. After about 20 seconds the dust opened out, and a bare spot was formed over the finger of about $1\frac{1}{2}$ inch diameter. A spirit-flame, applied for a few seconds under one end of the dish, cleared away the dust from the larger part of the area. If when quiet was nearly restored, a little fresh dust was applied, and the experiment with the

finger repeated, the effect was more pronounced than before, and the bared space much larger, showing that the treatment with the spirit-flame had driven away most of the residual contamination.

The best effects were obtained with a dish somewhat larger than that above mentioned; and in subsequent experiments the difference of temperature between different parts was more readily maintained by the use of a vessel in which the main portions were connected by a comparatively narrow channel. In this way the tensions of surfaces, contaminated in different

Fig. 1.



degrees, may be equalized, the warmer purer surface in one compartment balancing the colder but greasier surface in the other. And the actual temperature difference necessary for equilibrium gives a measure of the small difference of tensions to be compensated*.

When the surface of the liquid in the tin vessel is but very slightly greased, a spot can no longer be cleared by the warmth of the finger held underneath. Indeed the spirit-flame itself soon becomes ineffective. And yet the greasing may be so slight that camphor fragments move with apparently unabated vigour.

It is of interest to compare the behaviour of saturated solution of camphor with that of greasy water. The former can scarcely be brought to rest, unless covered up. This is doubtless due to evaporation of camphor, aided by local draughts. A spirit-flame drives away dust in a manner impossible in the case of a merely greasy surface, whose tension may nevertheless be decidedly higher than that of the camphorated water.

It may here be mentioned that the lowering of tension by camphor follows a different law from the lowering caused by soap. In the latter case the fall of tension requires time, and at the first moment of its formation a free surface has almost the tension of pure water. Similar experiments to those

* The lowering of tension per degree Cent. is said to be $\cdot 0018$ of the total value.

formerly recorded* with soapy water have shown that the ratio of tensions for pure water and for solution of camphor are the same at the first moment of the formation of a free surface as when the measures are conducted statically.

Saponine and Soap.

A strong infusion of horse-chestnuts allowed excellent bubbles to be blown, up to 4 inches or more in diameter. When the interiors of equal bubbles of soap and of saponine were brought into communication, the latter contracted and the former expanded, showing that the tension of the saponine film was the greater. In order to obtain equilibrium, the diameter of the saponine bubble required to be about half as great again as that of the soap bubble. These saponine bubbles exhibited the characteristic wrinkling, when caused suddenly to contract by withdrawal of part of the contained air.

The foaming of Highland waterfalls is doubtless attributable to dissolved vegetable matter. In the autumn of 1890 I had an excellent opportunity of observing these effects in the case of the river Creed at Stornoway. By the coalescence of smaller ones hemispherical bubbles of remarkable size, up to a foot or more in diameter, were frequently formed, and endured for a few seconds; and yet not the smallest bubble could be blown from a tobacco-pipe. However, by collecting some of the foam and allowing it to subside, which took a good while, I obtained liquid from which bubbles could be blown with a pipe up to 4 inches diameter. But these bubbles behaved like soap, and not as had been rather expected, like saponine, remaining perfectly light and smooth when the included air was rapidly withdrawn.

Separation of Motes.

In the course of some experiments last year, in illustration of Sir G. Stokes's theory of ternary mixtures, I had prepared an association† of water, alcohol, and ether, in which the quantity of alcohol was so adjusted that the tendency to divide into two parts was almost lost. As it was, division took place after shaking into two nearly equal parts, and these parts were of almost identical composition. On placing the bottle containing the liquids in the concentrated light from an

* Proc. Roy. Soc. March 1890.

† *Association* is here employed as a general term denoting the juxtaposition of two or more fluids. Whether the result is a *mixture* depends upon circumstances.

arc lamp, I was struck with the contrast between the appearance of the two parts. The lower, more aqueous, layer was charged with motes, while the upper, more ethereal, layer was almost perfectly free from them. Some years ago I had attempted the elimination of motes by repeated distillation of liquid in vacuum, conducted without actual ebullition, but I had never witnessed as the result of this process anything so clear as the ethereal mixture above described.

The observation with the ternary association, which happened to be the first examined, is interesting, because the approximate equality of the liquids suggests that the explanation has nothing directly to do with gravitation. But the presence of alcohol is not necessary. Ether and water alone shaken together exhibit the same phenomenon. It would appear that when the two liquids are mixed together in a finely divided condition, the motes attach themselves by preference to the more aqueous one, and thus when separation into two distinct layers follows, the motes are all to be found below.

An obvious explanation, which, however, stands in need of confirmation, is that under the play of the capillary forces the energy is least when the motes, which may be presumed to be denser than either liquid, are in contact with the denser rather than with the rarer of the two. The density here referred to is that which occurs in Laplace's theory of capillarity, and may need to be distinguished from ordinary mechanical density.

I have lately endeavoured to obtain some confirmation of the views above expressed by the use of other liquids. It would evidently be satisfactory to exhibit the selection of motes by the upper, instead of by the lower, layer. Experiments with bisulphide of carbon and water, and also associations of these two bodies with alcohol, which acts as a solvent to both, gave no definite result, perhaps in consequence of a tendency to the formation of a solid pellicle at the common surfaces. But with chloroform and water, and with associations of chloroform, water, and acetic acid (acting as a common solvent), the experiment succeeded. The motes were always collected in the *upper*, more aqueous, layer, even when the composition of the two layers into which the liquid separated was so nearly the same that a few additional drops of acetic acid sufficed to prevent separation altogether.

In this and similar cases a marked tendency to foaming may be observed when the composition is such that separation just fails to take place.

The Lowering of Tension by the Condensation of Ether Vapour.

The suspension of water in an inverted tube of small bore is familiar to all. The limit of diameter was investigated some years ago by Duprez*. A glass tube, such as that shown in fig. 2, is ground true at the lower end, and at the upper end is connected to an india-rubber tube provided with a pinch-cock. Water is sucked up from a vessel of moderate size, the rubber is nipped, and by a *quick* motion the tube and the vessel are separated, preferably by a downward movement of the latter. In this way of working Duprez found that the liquid might remain suspended in tubes of diameter up to 16 millim., and with the aid of a sliding plate up to 19·85 millim. The theory is given in Maxwell's article in the *Encyclopædia Britannica* ("On Capillary Action"). For lecture purposes it is well not to attempt too much. The tube employed by me had an internal diameter of $14\frac{1}{2}$ millim., and there was no difficulty in obtaining suspension. The experiment on the effect of ether-vapour was then as follows:—The inverted tube, with its suspended water, being held in a clamp, a beaker containing a few drops of ether was brought up from below until the free surface of the water was in contact with ether vapour. The lowering of tension, which follows the condensation of vapour, is then strikingly shown by the sudden precipitation of the water.

Fig. 2.

*Breath Figures and their Projection.*

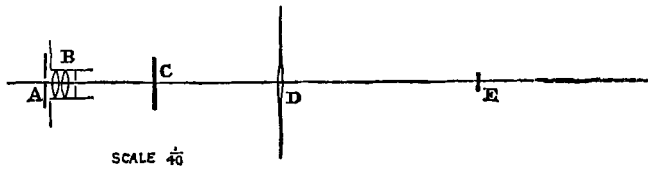
These figures are perhaps most readily prepared upon the plan described in Riess's 'Electricity.' The carefully cleaned glass plate upon which the image is to be received is placed upon a flat metallic slab, and upon it again rests the coin to be copied, for example, a shilling. The two conductors form the coatings of a Leyden jar, and are connected by wires to the discharging terminals of a large Wimshurst machine, the latter being set so as to give sparks about $\frac{1}{4}$ inch long. In my experiments about 20 turns of the handle were found sufficient to impress the latent image.

* "Sur un cas particulier de l'équilibre des liquides," *Bruxelles, Acad. Sci. Mém.* xxvi. 1851; xxviii. 1854.

The projection of the figures, developed upon the glass by breathing, requires a special arrangement, which it is the principal object of this note to describe. For this purpose the light simply transmitted by the undimmed parts of the plate must be intercepted, leaving the image to be formed by the light *diverted* from its path by the condensed breath. The arrangement was as follows:—

The ordinary condenser B (fig. 3) of the electric lantern was stopped down to an aperture of $\frac{3}{4}$ inch, and provided a

Fig. 3.



somewhat divergent beam of light of corresponding diameter. At a distance of $15\frac{1}{2}$ inches from the condenser was placed the slide C upon which a figure had been impressed. The focusing lens D was of plate-glass, 6 inches in diameter and 25 inches focus, and was of course distant from the breath figure by an amount slightly exceeding its own focal length. Any light that might pass outside was intercepted by a suitable mounting. So far there was nothing peculiar, except in respect to the dimensions of the focusing lens. But now between the latter and the screen was inserted a disk E of black card 2 inches in diameter, at such a distance (40 inches) from the lens as to receive a well-defined image of the hot carbons A. By this disk all regularly refracted light would be stopped, so that the screen would appear dark. If, however, any part of the prepared glass be dimmed by the breath, light is there diverted from its path, and thus escaping the stop proceeds to form an image of the part in question upon the screen. The dewed parts of the breath-figure are accordingly seen bright upon a dark ground; and with the arrangement described, in which the large diameter of the focusing lens is a leading feature, the projected images are very beautiful. A similar method would probably be adequate to the projection of smoke-jets.

In conclusion I may mention that the latent images can be developed in a more durable manner by a deposit of *silver*, the arrangements being such as are adopted for the silvering of mirrors, except that the action is stopped at an earlier stage. The washed and dried deposit may then be protected from mechanical injury by a coat of varnish.

March 4, 1892.