This article was downloaded by: [Cornell University]

On: 22 June 2012, At: 03:43

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number:
1072954 Registered office: Mortimer House, 37-41 Mortimer Street,
London W1T 3JH, UK

Philosophical Magazine Series 5

Publication details, including instructions for
authors and subscription information:

<http://www.tandfonline.com/loi/tphm16>

XLIII. On the tension of water surfaces, clean and contaminated, investigated by the method of ripples

Lord Rayleigh Sec. R.S.

Available online: 08 May 2009

To cite this article: Lord Rayleigh Sec. R.S. (1890): XLIII. On the tension of
water surfaces, clean and contaminated, investigated by the method of ripples ,
Philosophical Magazine Series 5, 30:186, 386-400

To link to this article: <http://dx.doi.org/10.1080/14786449008620040>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study
purposes. Any substantial or systematic reproduction, redistribution,
reselling, loan, sub-licensing, systematic supply, or distribution in any
form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any
representation that the contents will be complete or accurate or up to
date. The accuracy of any instructions, formulae, and drug doses should
be independently verified with primary sources. The publisher shall not
be liable for any loss, actions, claims, proceedings, demand, or costs or

damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

From these data the density of dry air at 747·97 millim., and at the temperature 15·70, is found to be 0·0012046. The last figure is doubtful, as being beyond the limit of accuracy with which the volume is known.

If, for confirmation of this result, reference is made to accepted results from the *Tabellen* of Landholt and Börnstein, the density of dry air under the same conditions of pressure and temperature is deduced as 0·0012033. From Biedermann's *Chemiker-Kalender* (1888) is deduced the number 0·0012052. The mean of these two closely agrees with the experimental result, absolutely indeed to the fourth significant figure, the last reliable one in the determination.

In conclusion, I may point out that this method leaves the gas finally in a vessel, which, by the addition of a small side way to the connexion *b*, may be made a most convenient one for the subsequent transference of the gas into any apparatus for its analysis.

The present method may, as in the case of Regnault's, be by obvious procedures applied to the determination of the variation of the density with change of temperature, or change of pressure. And its application to the determination of vapour densities suggests itself. In this case the temperature of the volumometer would, perhaps, best be adjusted by the use of a vapour in the jacket, and an arrangement for controlling its pressure.

XLIII. *On the Tension of Water Surfaces, Clean and Contaminated, investigated by the Method of Ripples.* By Lord RAYLEIGH, Sec. R.S.*

NUMEROUS and varied phenomena prove that the tension of a water surface is lowered by the presence of even a trace of grease. In the case of olive-oil, a film whose calculated thickness is as low as 2 micro-millimetres is sufficient to entirely alter the properties of the surface in relation to fragments of camphor floating thereupon. It seemed to me of importance for the theory of capillarity to ascertain with some approach to precision the tensions of greasy surfaces; and in a recent paper † I gave some results applicable to the comparison of a clean surface with one just greasy enough to stop the camphor movements and also with one saturated with olive-oil. The method employed was that depending upon the

* Read September 6 before Section A of the British Association at Leeds. Communicated by the Author.

† Proc. Roy. Soc. March 1890, vol. xlvii. p. 367.

rise of liquid between parallel plates of glass ; and I was not satisfied with it, not merely on account of the roughness of the measurement, but also because the interpretation of the result depends upon the assumption that the angle of contact with the glass is zero. In the opinion of Prof. Quincke, whose widely extended researches in this field give great weight to his authority, this assumption is incorrect even in the case of pure liquids, and, as it seemed to me, is still less to be trusted in its application to contaminated surfaces, the behaviour of which is still in many respects obscure. I was thus desirous of checking my results by a method independent of the presence of a solid body.

The solution of the problem was evidently to be found in the observation of ripples, as proposed by Prof. Tait, upon the basis of Sir W. Thomson's theory. Thomson has shown that when the wave-length is small, the vibration depends principally upon capillary tension ; so that a knowledge of corresponding wave-lengths and periods will lead to a tolerably accurate estimate of tension.

Besides some early observations of my own*, made for the most part for another purpose, I had before me the work of Matthiessen†, who has compared Thomson's formulæ with observation over a wide range of wave-length. The results are calculated on the basis of an assumed surface-tension, and are exhibited as a comparison of calculated and observed wave-lengths. On the whole the agreement is fair ; but the accuracy attained seemed to be insufficient for the purpose which I had in view. As will presently appear, an error in the wave-length is multiplied about three times in the tension deduced from it, so that, in a reversal of Matthiessen's calculations, the errors would appear much magnified.

Quite recently Mr. Michie Smith has published an account of experiments made by Thomson's method for the determination of the tension of mercury. Some anomalies were met with ; and it seems not improbable that the vibrations observed were in some cases an octave below those of the vibrating source‡.

When it is remembered that Thomson's theory is one of infinitely small vibrations, it will be seen that for my purpose it was necessary above all things that the amplitude of vibration should be very moderate. The sub-octave vibrations of

* "On the Crispations of Fluid resting upon a Vibrating Support," *Phil. Mag.* July 1883.

† *Wied. Ann.* xxxviii. p. 118 (1889).

‡ Faraday, *Phil. Trans.* 1831. See also Rayleigh, *Phil. Mag.* April and July 1883.

Faraday are especially to be avoided as almost necessarily of large amplitude. At the same time the limitation is not without its inconvenience. One of the great difficulties of the experiment is to see the waves properly, and this is much increased when the vibrations are extremely small.

In considering the problem thus presented, it occurred to me that it was essentially the same as that so successfully solved by Foucault in relation to the figuring of optical surfaces. The undisturbed surface of liquid is an accurate plane; the waves upon it may be regarded as deviations from optical truth, and may be made evident in the same way as any other deviations from truth in a reflecting surface. Guided by this idea, I was able to work with waves of which nothing whatever was to be seen by ordinary observation of the surface over which they were travelling.

In the application of Foucault's method it is necessary that light from a radiant point, after reflexion from the surface under test, should be brought to a focus, in the immediate neighbourhood of which is placed the eye of the observer. Any small irregularities in the surface then render themselves conspicuous to the eye focused upon it. In the present case the reflector is plane, and the formation of a real image of the radiant requires the aid of a lens. In my experiments this was usually a large single lens of 6 inches diameter and 34 inches focus. On one occasion an achromatic telescope-lens was substituted, but the aperture was too small to include the number of waves necessary for accuracy. Although the want of achromatism was prejudicial to the appearance of the image, it is not certain that the accuracy of the determinations was impaired, at least after experience in observation had been acquired. The lens was fixed horizontally near the floor, a few inches above the surface of the water under examination. The radiant point, a very small gas-flame, was situated in the principal focal plane, but a little on one side of the axis of symmetry, so that the image formed after reflexion from the water and a double passage through the lens might be a little separated from the source. For greater convenience reflecting strips of looking-glass were introduced at angles of 45° , or thereabouts, so that the initial and final directions of the rays were horizontal.

The smallness of the disturbance is not the only obstacle to its visibility. Even with Foucault's arrangement for viewing minute departures from planeness, nothing could usually be seen of the waves here employed without a further device necessary on account of the rapidity with which all phases are presented in succession. A clear view of the waves must be

an intermittent one, isoperiodic with the vibrations themselves, and may be obtained in the manner first described by Plateau. In the present case it was found simplest to render the light itself intermittent. Close in front of the small gas-flame was placed a vibrating blade of tin-plate rigidly attached to the extremity of the prong of a large tuning-fork, and so situated that once during each vibration the light was intercepted by the interposition of the blade. The vibrations of the fork were maintained electromagnetically in the usual manner, and the intermittent current furnished by the interrupter fork was utilized, as in Helmholtz's vowel-sound experiments, to excite a second, in unison with itself. The second fork generated waves in the dish of water by means of a dipper attached to its lower prong.

When the action is regular, the vibrations of the two forks are strictly isochronous, even though the natural periods may differ somewhat*. The view presented to the observer is then perfectly steady, and corresponds to one particular phase of the vibration, or rather, since the illumination is not instantaneous, to an average of phases in the neighbourhood of a particular one.

Even in the case of a perfectly regular train of waves, the appearance will depend upon the precise position occupied by the eye. It is evident that the light most diverted from its course is that reflected from the shoulders of the waves—the points midway between the troughs and crests, for it is here that the slope of the surface is greatest. Thus if the eye be moved laterally outwards from the focal point, until all light has nearly disappeared, the residual illumination will mark out the instantaneous positions of one set of shoulders, all other parts of the complete wave remaining dark. This is one of the most favourable positions for observation. If the deviation from the focal point be in the opposite direction, the other set of shoulders will be seen bright.

The aspect of the waves was not always equally pleasing. Sometimes the formation of stationary waves, due to reflexions, interfered with regularity. A readjustment of the walls of the vessel relatively to the dipper would then often effect an improvement. The essential thing is that there should be no

* A dirty condition of the mercury sometimes leads to the failure of several successive contacts. During the interval the vibrations of the second fork, being unconstrained, take place in their natural period. In this way a phase-discrepancy may set in, to be subsequently corrected when the regular contacts are reestablished. Such a state of things is to be avoided as distracting to the eye, and unfavourable to accurate observation.

ambiguity in the wave pattern over the measured part of the field. It would occasionally happen that in certain positions of the eye a change of phase would occur in the middle of the field, so that the bright bands in one part were the continuation of the dark bands of another part. Near the transition the bands would appear confused, a sufficient indication that no measurement must be attempted. On the other hand, it is not necessary that the contrast between the dark and bright parts should be very great. Indeed the measuring marks were better seen when no part of the field was very dark.

Fig. 1 gives a general idea of the appearance of the field. On the right is seen a paper with a notched edge, the use of

Fig. 1.

which was to facilitate the counting. The measuring arrangement was something like a beam compass. Stout brass wires, attached to a bar of iron, were shaped at their ends like brad-awls, and the edges were placed parallel to the crests of the waves. In order to avoid residual parallax, the rod was so supported that the edges were in close proximity to the water surface.

In many of the experiments the distance between the edges was set beforehand, *e.g.* to 10 centim., and was not altered when the wave-lengths varied with the deposition of grease. The number of wave-lengths included was determined by

counting, and estimation of tenths. Usually the discrepancy between Mr. Gordon's estimation and my own did not exceed a single tenth, and in a large proportion of cases there was no difference. Probably the mean of our readings would rarely be wrong by more than $\frac{1}{20}$ of a wave-length, when the pattern was well seen. In the experiments specially directed to the determination of the tension of a clean surface, it was found advisable to work with an unknown distance; otherwise the recollection of previous results interfered with the independence of the estimates.

It is probable that somewhat greater accuracy in single measurements might have been attained had the distance been adjustable by a smooth motion within reach of the observer. Each measuring edge might then have been set to the most favourable position, that is, to the centre of a bright band. The frequent removal of the apparatus for comparison with a scale would, however, be rather objectionable; and it was thought doubtful whether any final gain would accrue in the mean of several observations.

Some trouble was experienced from the communication of vibrations through unintended channels. In order to prevent the direct influence of the interrupter fork upon the liquid surface, it was found advantageous to isolate it from the floor by supporting it upon a shelf carried upon the walls across a corner of the laboratory. On one occasion it was noticed that the waves were visible without the aid of the arrangement for making the light intermittent. This was traced to a tremor of one of the mirrors, supported upon the same shelf as the interrupter fork. Such a method of rendering the waves visible is objectionable, since it destroys the definition of the measuring points. The tremor was eliminated by the introduction of rubber tubing under the stand of the interrupter.

During the experiments on greasy surfaces one pair of forks only was employed. The frequency of the interrupter was about 42 per second, so that the intermittent current could be used to excite a fork of about 126. The beats between this and a standard Koenig fork of 128 were counted at intervals, and found to be sufficiently constant. The pitch of the standard has been verified by myself*, and at the temperature of the laboratory may be taken with sufficient accuracy to be 128. If we take the number of beats per minute at 98, we have for the frequency of the interrupter

$$f = \frac{1}{3} \left(128 - \frac{98}{60} \right) = 42.12.$$

* Phil. Trans. 1883, p. 316.

In the case of clean water another pair of forks of about 128 was employed as a check. The number of beats was 184 per minute, and

$$f = 128 - \frac{184}{60} = 124.9.$$

The water was contained in a shallow 12'' × 10'' porcelain dish; and before commencing observations its surface was purified with the aid of an expansible hoop of thin sheet brass. The width of the hoop is greater than the depth of water, and it is deposited in the dish so as to include the dipper, but otherwise in as contracted a condition as possible. It is then opened out to its maximum area with the effect of attenuating many times the thickness of the greasy film, which no amount of preliminary cleaning seems able to obviate. It not unfrequently happened that the first attempt to get a clean surface was a partial failure, but a repetition of the operation was usually successful. It seems as if impurity attaches itself to the brass so obstinately that only contact with a clean water surface will remove it.

In the earlier experiments the waves were generated by a dipper of circular section, a closed tube of glass, somewhat like a test-tube. The measurements were quite satisfactory, but I felt doubts as to a possible influence of curvature upon wave-length. In order to avoid any risk of this kind, and to render the waves straight from the commencement, a straight horizontal edge of glass plate, about 2½ inches long, was afterwards substituted, and worked very satisfactorily. It is not necessary or desirable that the dipper should pass in and out of the water. In most cases the vibrations employed were very small, and the edge of the dipper was immersed throughout.

The purity of the water surface could be judged by the result of the observation of the number of wave-lengths; the smallest number corresponding to the purest surface. But it soon became apparent that a more delicate test was to be found in the general appearance of the wave pattern. Upon a clean surface there is a strong tendency to irregularity, dependent no doubt upon reflexions, which become more important when the propagation is very free. In order to meet this, it was often found necessary to weaken the vibrations of the secondary fork, either by putting it more out of tune with the primary, or by shifting its magnet to a less favourable position, or, finally, by shunting the current across. A slight trace of grease would then render itself evident by a damping down of the waves before any change

could be observed in the wave-length. After a little experience with the forks in a given state of adjustment, a momentary glance at the pattern was sufficient to enable one to recognize the condition of the surface.

The interpretation of the observations depends upon the following formula, due to Thomson :—

Let U = velocity of propagation,
 λ = wave-length,
 τ = periodic time,
 ρ = density,
 T = superficial tension,
 h = depth of water,

then (Bassett's 'Hydrodynamics,' vol. ii. p. 177)

$$U^2 = \frac{\lambda^2}{\tau^2} = \left(\frac{g\lambda}{2\pi} + \frac{2\pi T}{\rho\lambda} \right) \tanh \frac{2\pi h}{\lambda};$$

so that to find T we have

$$T = \frac{\rho\lambda^3}{2\pi\tau^2} \coth \frac{2\pi h}{\lambda} - \frac{g\lambda^2\rho}{4\pi^2}.$$

In the present experiments the effect of the limitation of depth is negligible. We have $h = 1.8$ centim., and for the greatest value of λ about .7 centim. Now

$$\coth \frac{2\pi h}{\lambda} = \frac{1 + e^{-4\pi h/\lambda}}{1 - e^{-4\pi h/\lambda}} = 1 + 2e^{-4\pi h/\lambda},$$

approximately, when h is relatively large; so that

$$\coth (2\pi h/\lambda) = 1 + 2e^{-30} = 1,$$

with abundant accuracy. Again, in the case of water we have $\rho = 1$; and thus

$$T = \frac{\lambda^3}{2\pi\tau^2} - \frac{g\lambda^2}{4\pi^2},$$

which is the formula by which the calculation of T is to be made. The second term will be found to be small in comparison with the first, so that approximately T varies as λ^3 . A one per cent. error in the estimation of λ will therefore involve one of three per cent. in the deduced value of T . In many of the experiments about 15 waves were included between the marks. An error of $\frac{1}{10}$ of a wave is thus 1 in 150, leading to a two per cent. error in T . We may expect the final mean value to be correct to less than one per cent., but we must not be surprised if individual results show discrepancies of two per cent.

An example (August 2) will now be given in which the surface of clean water was greased with oleic acid. The dish

after rinsing was filled with water drawn from a tap in connexion with a cistern supplied mainly by rain water, and placed in position. On expansion of the brass hoop the number of waves included between the measuring points was estimated to be 13·7, 13·8 by the two observers. A piece of paper was then greased with oleic acid, and with this a platinum wire, previously cleaned by ignition, was wiped. On introduction of part of the wire into the water contained within the hoop, the number of waves rose to 15·4, 15·3. Upon this surface camphor scrapings were found to be quite dead, so that the mark had been overshot.

The dish was then refilled. Upon expansion the number of waves upon the clean surface was 13·7, 13·7. On contamination with a little oleic acid, 14·8, 14·8. Camphor was now moderately active. More oleic was added. Readings were now 15·4, 15·4, and camphor was quite dead.

The point to be fixed evidently lay between 14·8 and 15·4. A fresh surface was taken, and on addition of a little oleic the readings were 14·8, 14·8. Camphor was then tried and found moderately active. Reading still 14·8. A little more oleic added; readings 15·1, 15·1; camphor scrapings were now "nearly dead." More oleic; 15·2, 15·2; camphor "very nearly dead." More oleic; 15·4, 15·4; "not absolutely dead." More oleic; 15·5, 15·5; camphor "absolutely dead." The temperature of the water was 63° F.

On a previous occasion (July 29) accordant results had been obtained. Clean water 13·7, 13·7. Oleic added; 15·0, 15·0; camphor nearly dead. More oleic; 15·2, 15·25; camphor very nearly dead. Oleic; 15·55, 15·6; camphor dead. On both days the distance over which the waves were measured was 9·20 centim.

It may be well to exhibit in full the calculation for the clean water:—

log 9·2 =	·9638	log g =	2·9917
log 13·7 =	1·1367	log λ =	1·8271
log λ =	1·8271		1·8271
	3		2·6459
log λ ³ =	1·4813	log 4π ² =	1·5962
log 42·12 =	1·6245	log 11·2 =	1·0497
	1·6245		
	2·7303		
log 2π =	·7981		
log 85·5 =	1·9322		

$$\text{Finally, } T = 85·5 - 11·2 = 74·3.$$

If we take as the reading when the camphor is nearly dead 15.2, we find in like manner

$$T = 62.7 - 9.1 = 53.6.$$

After this example a summary of results may suffice. The interest attaching to the determination of the tension of a clean surface led me to strive after a higher degree of accuracy than perhaps would otherwise have been necessary. The following table contains the results obtained with both forks:—

Date.	Distance.	Frequency.	Tension.	Water.	Temp. F.	Remarks.
1890.						
June 23...	9.05	40.9	72.3	Tap		Telescope lens.
25...	4.12	40.9	74.5	"	73	
26...	11.70	40.9	73.7	"	66	
30...	11.27	40.12	74.0	"	61	
July 1...	9.96	42.12	73.2	"	61	Strip dipper introduced.
2...	9.96	42.12	74.7	"	62	
4...	9.96	42.12	74.7	Distilled	64	
8...	9.96	42.12	74.7	"	60	
25...	10.00	42.12	74.2	Tap	65	
25...	9.20	42.12	75.2	"	65	
28...	9.20	42.12	74.3	"	68	
28...	9.20	42.12	74.3	Distilled	68	
29...	9.20	42.12	74.3	"		
Aug. 2...	9.20	42.12	74.3	Tap	63	
July 23...	10.00	124.9	74.1	Tap	65	
23...	9.49	124.9	73.2	"	66	
23...	8.13	124.9	73.5	Distilled	66	

The mean result with the graver fork is $T = 74.2$; and with the quicker one $T = 73.6$. The discrepancy of nearly one per cent. marks the limit of accuracy. It should be remarked that some of the consecutive results where no variation occurred in the distance between the points cannot be regarded as quite independent.

On several occasions distilled water proved a less satisfactory subject than tap water. The surface seemed more unwilling to become and remain clean. Sometimes after expansion a notable increase of readings would occur in the course of a few minutes without assignable cause.

I was very anxious to satisfy myself that in the surfaces experimented upon by the wave method a high degree of purity was really attained. In the experiments of July 28 a Plateau needle vibrating upon a portable stand was introduced. After the examination by the method of waves the dish was brought out into a good light, and the quality of the surface tested by observation of the motion of motes when the needle

lying upon it was caused to vibrate by an external magnet*. In making the necessary arrangements there was some risk of introducing contamination, so that the discovery of an unclean surface would prove nothing definite. If, however, the behaviour of the surface under the needle test was good, it could be inferred with confidence that the measured waves were not affected by impurity. On two occasions the test succeeded fairly well.

The observations with the 128 fork were rather difficult, the waves being about twice as close as in the other case. In the calculation of results it appears, as was to be expected, that the importance of the second term, due to gravity, is diminished. Thus for July 22,

$$T = 76.5 - 2.4 = 74.1.$$

The general result that at temperatures such as 65° (18° C.) the tension of clean water surfaces is about 74.0 C.G.S. absolute units of force per centimetre seems entitled to considerable confidence. It agrees with some former observations † of my own upon the transverse vibrations of jets, as has been remarked by Mr. Worthington ‡. Some interesting experiments upon the vibrations of falling drops by Lenard § point also in the same direction. On the other hand it deviates largely from the higher value, about 81, which Prof. Quincke thinks the most probable. The deviation from 81 is certainly not due to contamination. It has been explained that great care was taken in this respect during the present experiments; and in the jet method the surfaces are probably the purest attainable. The method favoured by Quincke depends upon the measurement of large flat bubbles confined under the horizontal surface of a solid body. In default of experience I must leave it to others to judge whether a systematic error due to optical or other causes could enter here. Mr. Worthington contends that some of Quincke's deductions from his measurements require correction for curvature perpendicular to the meridional plane. To this and other criticisms Prof. Quincke has replied ||.

Experimenters upon capillary tubes have generally been led to adopt the lower value, but here the interpretation involves an assumption that the angle of contact θ is zero. What these measurements give in the first instance is $T \cos \theta$; so that if $\theta = 30^{\circ}$, or thereabouts, the higher value of T is the one really

* "On the Superficial Viscosity of Water," Proc. Roy. Soc. June 1890, vol. xlviii. p. 139.

† Proc. Roy. Soc. 1879, vol. xxix. p. 71.

‡ Phil. Mag. 1885, vol. xx. p. 51.

§ Wied. Ann. Bd. xxx. (1887).

|| *Ibid.* xxvii. p. 219 (1886).

indicated. This is the view adopted by Quincke, who in an important series of observations* has shown that the edge angle between water and glass has frequently a considerable value dependent upon the impurity of glass surfaces, even when carefully cleaned by ordinary methods. But I confess that the argument does not appear to me conclusive. The angles recorded are maximum angles. If after a drop has been deposited some of the liquid is drawn off, the angle may be diminished almost to zero. Observations upon capillary heights correspond surely to the latter condition of things, for no experimenter measures the gradual rise of liquid in a dry tube. I am disposed to think that the assumption $\theta=0$ is legitimate, and thus that the lower value of T is really supported by experiments of this class.

Leaving now the results for pure surfaces, let us pass on to those found for water contaminated with grease up to the point where the camphor scrapings were judged to be "very nearly dead." It must be remembered that the additions of oil were discontinuous, and that the point could not always be hit with precision. On any one day it is possible to set up a fairly precise standard of what one means by "very nearly dead;" but the standard is liable to vary in one's own mind, and is of course impossible to communicate to another. Too much importance therefore must not be ascribed to exact agreement or the failure of it. On one day experiments were made by varying the areas enclosed within the hoop. Thus, if the motions were a little too lively, they could be deadened to the required point by contraction of the area and consequent concentration of grease. This procedure was not so convenient as had been hoped, in consequence of the mechanical disturbance attending a motion of the hoop. In all cases an observation, for the most part recorded in the previous table, was made first upon a clean surface, so as to ensure that the contamination was all of the kind intended. The results are collected in the annexed table:—

Date.	Water.	Oil.	Tension.	Remarks.
June 30.....	Tap	Olive-oil	53.7	
July 1.....	"	"	51.1	
2.....	"	"	52.1	
4.....	Distilled	"	53.0	
7.....	"	"	53.0	Not quite independent.
11.....	"	"	53.0	" "
29.....	Tap	Oleic Acid	53.6	
Aug. 2.....	"	"	53.6	
2.....	"	Olive-oil	52.4	
2.....	"	"	52.4	Another sample.

* Wied. *Ann.* 1877, vol. ii. p. 145.

The tension of the surface when the camphor movements are just stopping may thus be reckoned at 53·0 C.G.S., or about 72 per cent. of that of a clean surface. There is some reason to infer that the tension is the same whatever kind of grease be used. In the last experiment the sample of oil was one of which it was necessary to take decidedly more than usual (in the ratio of about 3 : 2) in order to stop the motions. This was proved by the balance in the manner described in a former paper. I have other grounds for thinking it probable that the tension does not depend upon the kind of oil, and hope to investigate the matter further by a more appropriate method.

On several occasions the effect of large additions of oil was tried. The limit did not appear to be very definite; for a second and even a third drop gave a sensible indication. The results were June 30, 38·8; July 1, 40·3; July 7, 41·0; July 8, 41·7; July 26, 38·9; mean 40·1. They relate to olive-oil; and it is possible that the largeness of the quantity required to approach the limit depends upon the heterogeneous character of the substance.

Two observations were made of the effect of additions of oleate of soda to distilled water. When the limit seemed nearly attained final readings were taken with the results: July 8, 25·3; July 11, 24·6; mean 25·0. It will be seen that the tension is lowered very much further by soap than by oil.

The principal results of the present experiments may be thus summarized. The tension of a water surface, reckoned in C.G.S. measure, is in the various cases :—

Clean	74·0	100
Greasy to the point where the camphor motions nearly cease	53·0	72
Saturated with olive-oil	41·0	54
Saturated with oleate of soda	25·0	34

In the last column the tensions are exhibited as fractions of that of a clean surface.

POSTSCRIPT, Sept. 19.

It appeared probable that the tension of otherwise pure water saturated with camphor would be the same as that of greasy water upon which camphor fragments were just dead ;

and before the above paper was written I had already attempted to examine this point. The experiment, however, did not succeed. The camphorated water had decidedly too much tension (wave-number 14·7 instead of 15·5), but on the other hand the liquid was clearly not saturated, inasmuch as fresh camphor scrapings were lively upon an expanded surface. I have recently returned to the subject with water which has stood in contact with excess of camphor for more than a month.

Sept. 15. Fresh clean water. Expanded 13·7, 13·7. Motes still. Olive-oil added, 15·2, 15·2; camphor fragments moderately active. More oil, 15·3, 15·3; camphor nearly dead. More oil, 15·5, 15·5; camphor dead. Fragments of camphor and motes quite still.

The saturated solution of camphor was now substituted. Surface expanded; 15·5, 15·5. Expanded, 15·5. This number could not be reduced by any number of expansions of the surface.

It was observed that the surface was usually in motion, as evidenced by an irregular drift of motes and camphor fragments. The latter had no individual motion, all neighbouring particles moving together. The effect is probably due to local evaporation of camphor and accompanying increase of tension. Associated with this was a fluctuation backwards and forwards of the number of waves, such as was never observed with pure or simply greasy water.

We are thus justified in the conclusion that saturated solution of camphor has the same tension as is found for greasy water when camphor fragments are just dead. When the saturated solution was diluted with about an equal volume of water, the wave-number was reduced to 14·7. In these experiments the distance between the points was 9·20 centim., and the frequency was 42·12, so that the observations are directly comparable with those in the example calculated at length.

The comparison of tensions for clean and camphorated water may also be effected by the method of capillary heights. Some observations by Mr. Gordon gave the following:—

Clean water	7·94,	7·91,	7·92
Water changed	7·92,	7·90,	7·90
Saturated camphor	5·63,	5·68,	5·65
Clean water	7·97,	7·90,	7·92
Water changed	7·94,	7·96,	7·93
Saturated camphor	5·62,	5·63,	5·66

Thus, as a mean, capillary height for clean water is 7.93 centim., and for water saturated with camphor 5.64. The ratio of these is .71.

Observations by myself upon the same tube, but read in a somewhat different manner, gave

Clean water..... 8.04, 8.03, 8.04, 8.05.

Water changed ... 8.02, 8.02.

Camphorated water 5.77, 5.80, 5.79, 5.80, 5.80, 5.83.

As means we may take 8.03 centim. and 5.80 centim., giving for the ratio .71, as before.

The ratio of tensions thus found agrees remarkably well with that deduced from the observations upon ripples, viz. .72. It will be remembered that the latter might be expected to be somewhat higher, as corresponding with a condition of things where camphor fragments were *nearly*, but not quite dead.

October 8.—I take this opportunity of recording that a film of grease, insufficient to check the motion of camphor fragments, exercises a marked influence upon the reflexion of light from the surface of water in the neighbourhood of the polarizing angle. In the case of a clean surface and at the Brewsterian angle the reflexion of light polarized perpendicularly to the plane of incidence appears to vanish in accordance with the formula of Fresnel.

XLIV. *The Expansion of Water and other Liquids.*
By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.*

[Plates VII. & VIII.]

MY investigation of various properties of sulphuric acid (Journ. Chem. Soc. 1890, pp. 65, 331, and Phil. Mag. 1890, xxix. p. 427) showed that the curved figures representing these properties, or the figures representing the rate of change of these properties with change in percentage composition—the first differential coefficient, obtained by dividing the difference between the values obtained for two different solutions by the difference in their percentage strength—indicated the existence of more or less sudden changes of curvature at certain points corresponding to the composition of definite hydrates. The method adopted in examining any curved figure, to ascertain whether it was a single continuous curve

* Communicated by the Author.