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E.S. Johonnott Jun. Ph.D. ^a

^a Rose Polytechnic Institute , Terre Haute, Indiana
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LXVIII. *The Black Spot in Thin Liquid Films.*By E. S. JOHONNOTT, JUN., *Ph.D.**

IN some previous work† on this subject it was found that, in general, the black film consisted of two portions. That first formed varied in thickness between $40\ \mu\mu$ and $12\ \mu\mu$. The first black was found to break naturally into the second when the atmosphere was incompletely saturated. With a thoroughly enclosed film it was necessary to heat the system in order to form the second black film; which had, apparently, a constant thickness of $6\ \mu\mu$ in all cases.

Effect of Change in Pressure.—Recently it was discovered that great changes in the character of these films could be produced by changing the pressure on the atmosphere surrounding the films. A sudden increase in the pressure was accompanied by a rapid thinning of the film; while, on the other hand, a sudden diminution of the pressure was accompanied by a correspondingly rapid increase in the thickness. On subjecting the first black film to sudden increase in pressure it was possible to convert it quickly into a second black; if then the pressure was suddenly diminished, the second black became a first black. In many cases it was possible to continue this thickening until the film showed the yellow of the first order.

The evident explanation of these effects is that the heating due to adiabatic compression is accompanied by an increased vapour-pressure and, consequently, evaporation from the surface of the film. While, on the other hand, adiabatic expansion causes cooling and condensation on the film.

Fig. 1 represents a simple arrangement for producing these effects. The film is formed on a rectangular frame of glass-fibre, F, mounted on a rubber stopper. This stopper fits firmly into the mouth of an inverted beaker containing the solution‡. Blowing or sucking in a rubber tube, attached at P, the pressure in the upper vessel is varied without contaminating the solution. If the upper vessel is carefully chosen the films may be observed quite advantageously with a low-power microscope. A simple gas-jet makes an

* Communicated by the Author.

† Phil. Mag. vol. xlvii. p. 501 (June 1899).

‡ The solution was made in the following manner:—7 grams of oleic acid (refined) and 2 grams of caustic soda are thoroughly boiled in about 100 c.c. of distilled water. This gives about 7.5 grams of oleate of soda which is diluted to about 50 of water to 1 of soda and again boiled. An excess of acid is not harmful, while an excess of soda is decidedly so.

excellent illuminant, and at the same time may be used to heat the film.

Fig. 1.

Let the temperature be adjusted with the flame and the pressure with the mouth until the first black film is about to break into the second. Then pinching the tube with the fingers will cause the second black to appear as small perfectly round spots in the first black film; releasing the pressure, after the film has become the second black, will cause the first black to appear, in a similar manner, as spots in the second black.

Thickness of the Black Film.—In view of these circumstances, it was thought advisable to repeat the measurements on the thickness of the black film. The work was begun in the Ryerson Physical Laboratory of the University of Chicago, and through the courtesy of the officers of instruction, in kindly lending the necessary apparatus, was carried to completion elsewhere.

In order to vary the thickness, by changing the pressure, and at the same time to measure the thickness, a different form of the interferometer was required. In fig. 2 is shown a familiar form of the Michelson interferometer that was used. The object that was to be gained was simply that both

optical paths should lie alike in the atmosphere of the films. The long brass box in which the films were formed is shown at B. The films were 221 in number and formed on frames of glass-fibre as in the former work. The box was sealed,

Fig. 2.

and connected to a manometer and suitable apparatus for varying the pressure. The fringes were viewed with a telescope. All other details were much the same as in the earlier work, and may be found described therein.

At the first trial it was apparent that the reading of the number of fringes displacement could not be made as promptly as the thickness could be altered by varying the pressure. This was due to the distortion produced in the fringes by quickly changing the pressure. It was very difficult to obtain trustworthy data when working with rapid changes in the pressure, and, on the whole, this part of the work was somewhat disappointing. Nevertheless, with less rapid alterations in the pressure, it was possible to pass the black film through all its phases with little if any distortion in the fringes.

A large portion of the time was spent in working with no variation in the pressure. The method usually employed was to form the films in the morning and take readings of the thickness throughout the day, with a more or less rapidly rising temperature. The box was surrounded with a large water-jacket to maintain a uniform temperature. It was found that this outer box filled with air served the purpose quite as well.

The following table was taken with no variation in pressure. The box containing the films was firmly sealed. The temperature recorded was the mean of the readings of two thermometers, placed within the box, B.

TABLE I.

Age of Film.	Fringes Deflect.	No. Films.	Mean Thickness.	Mean. Temp.	Remarks.
hr. min.			$\mu\mu$.	$^{\circ}$ C.	
1 18	4.0	221	16.0	25.5	All first black.
4 33	4.1	221	16.4	25.0	" "
7 58	6.0	221	24.0	23.5	" "
21 33	3.8	221	15.2	25.3	" "
26 23	3.0	217	12.2	26.5	Two second black.
26 51	2.5	217	10.15	28.0	
27 3	1.5	215	6.16	28.7	All second black.

In the light of the results recorded in the former paper, this table requires little comment. The increase in the thickness with falling temperature; the limiting thickness of the first black film at about $12\mu\mu$; and the mean thickness of the second black at about $6\mu\mu$, were therein illustrated a number of times.

In the above table, however, since the number of films was over four times as great, the number of fringes displacement was correspondingly greater.

In the former paper it was remarked that, "a number of observations indicated that the thickness of the second black film was not constant." With the number of films there employed the deflexion was only about .35 fringes, when all of the frames held second black films. In the present case the corresponding deflexion was 1.5 fringes. With this greater sensibility it was at once apparent that the second black film was of variable thickness. While the limiting thickness of the second black was approximately $6\mu\mu$, the upper limit, in many cases, was at least 50 per cent. greater.

In fact, in behaviour, the black films were found to be quite similar; *i.e.*, with a sealed atmosphere and a rising temperature, a rapid thinning immediately after birth was characteristic of both types. This rate of thinning became smaller and smaller as the limiting thickness was approached. The rate of thinning of the second black was so great, at first, that usually the limiting thickness was reached before observations could be made. The persistence of the black films at the limiting thickness, together with the tendency to reach this condition quickly, seems to indicate that the films were of quite uniform thickness, at the limit.

The data in Table II. were taken from a number of tables similar to Table I. The thickness is given in micro-millimetres ($\mu\mu$).

TABLE II.

A.	B.
Limiting Thickness of First Black Film.	Mean Thickness of the Second Black Film.
11.05, 12.20, 12.20, 13.15, 11.10, 12.30 11.75, 12.60, 13.30.	6.03, 6.24, *9.25, 5.52, 6.17, 5.05, 6.28, *7.30, *9.50, 5.40, 6.40, *8.0.
Mean 12.18.	Mean 6.76.

It would be difficult, in section B, to distinguish between the values corresponding to the unstable condition and the condition of limiting thickness. The larger values, marked with the asterisk, were, however, in all cases followed by smaller values included in the table. If we take the mean of the values, not including these larger values, to determine the limiting thickness of the second black, we obtain 5.88 $\mu\mu$. This would indicate that the limiting thickness of the second black is, approximately, half that of the first. No very great thickness was measured in the first black, since it was impossible to count the coloured fringes for such large deflexions.

Variable Atmospheric Pressure.—The following readings were obtained when changing the pressure on the atmosphere surrounding the films.

TABLE III.

Time.	Fringes defect.	No. films.	Mean thick.	Temp. ° C.	Pressure change.	Remarks.
A.M.			$\mu\mu$		cms. Hg	
9.08	films	formed.		17.8		
9.32	3.0	101	26.8	20.0	none.	All first black.
9.50	2.3	100	20.3	20.0	"	" "
10.20	2.0	98	18.0	21.0	"	" "
	3.4	98	30.6	...	-4.6	
					...	
					+9.2	All second black.
10.23	.9	98	8.1	21.6	...	" "
	System	allowed	to come	to normal	pressure.	
10.40	2.0	97	18.2	...	none.	All first black.
	4.2	96	38.5	...	-6.4	
					...	" "
					+12.8	
10.44	.9	95	8.4	21.2	...	All second black.

A large bottle, containing some of the solution, was connected to the film-box by a long rubber tube. The pressure was altered by changing the elevation of this bottle.

As shown in the table, the films were allowed to thin to the first black, then the pressure was diminished by 4.6 cms. of mercury. This caused the films to thicken from $18\ \mu\mu$ to $30.6\ \mu\mu$. The pressure was then increased by 9.2 cms., and the films were quickly thinned to the second black at a mean thickness of $8.1\ \mu\mu$.

Surface-tension in the Black Film.—In this connexion it may be of some interest to describe some work that was undertaken to determine the surface-tension in the black film. The method of Sondhaus* was employed.

A ring, 15 centimetres in diameter, was made of glass-fibre. This was attached to one arm of a sensitive Oertling balance and lifted from the surface of the solution. The film formed, although a catenoid, was quite approximately a cylinder.

The following table is a typical record of the observations made.

TABLE IV.

Age of film.	Supporting force.	Surface-tension.	Temp. ° C.	Remarks.
min.	mgs.	mgs. per cm.		
0	2495	26.5	24.0	No colour.
2	2475	26.35	...	Coloured quickly.
8	2465	26.20	...	5 per cent. first black.
18	2455	26.07	...	All " "
25	2450	26.00	...	10 per cent. second black.
37	2445	25.95	25	All " "
44	2440	25.90	...	" " "
56	2435	25.83	26	" " "

With these results plotted in a curve, it is quite evident that to the discontinuity in the thickness, there, apparently, corresponds no discontinuity in the tension. Otherwise, however, the varying rate with which the tension falls is quite similar to the manner in which the film thins. And it should be observed that these phenomena point to a variable condition in the second black film, both with respect to tension and thickness.

The Five Black Films.—Viewing the films with a micro-

* Sondhaus, Pogg. Ann. Ergbd. viii. p. 266.

scope, in the arrangement shown in fig. 1, it is oftentimes possible to distinguish as many as five black films. These break, one into another, in the same manner in which the black film is ordinarily formed, each succeeding film being, apparently, the thinner. The first three formed are, however, quite evanescent and seldom extend over an elevation greater than two or three millimetres. The fourth and fifth are identical with those which have been termed the first and second black films, respectively. Oftentimes all five films are in the field of view at once.

Speculations.—The apparent continuity of the surface-tension in passing from one black film to the other has been observed by Professors Reinold and Rücker. Based on what may be termed Lord Kelvin's* minimum surface-tension principle, they suppose the tension to remain constant as the films thin to the limiting thickness of the coloured film. Then the tension is supposed to fall as the film continues to thin until a minimum tension is reached, after which the tension rises. Now it is evident that, for these thinner films, equilibrium could not be reached unless the thinning continues so far that the tension again rises to that of the coloured film.

On this theory it should be possible to have the black film in equilibrium with the coloured film of various thicknesses. Their experimental observations substantiate this theory in a very interesting manner. If a discontinuity occurs in the thickness between the successive black films, it is reasonable to suppose, as Poynting and Thomson† have remarked, that a variation in the tension, similar to that which has been described, takes place.

Laplace's theory of capillarity shows that the inference to be drawn is that we have alternate molecular forces of attraction and repulsion as we pass from one black film to the next. Or according to the minimum surface-tension principle, there should be as many undulations in the curve representing thickness and tension as there are black films.

Another theory of these discontinuities might be proposed, which may be little more than an analogy.

Long ago, Professor James Thomson‡, in discussing the unstable condition supposed to exist between the super-

* Phil. Trans. 1886, Part ii. p. 679.

† 'Properties of Matter,' p. 166.

‡ Maxwell, 'Theory of Heat,' p. 127.

saturated vapour and superattenuated liquid states, says :—
“ We cannot expect experimental evidence on this part of the curve unless this state of things may exist in some part of the thin superficial stratum of transition from the liquid to its own gas, in which the phenomena of capillarity take place.”

Suppose that we imagine a liquid film in equilibrium with its surrounding saturated atmosphere. Let heat be applied to the system. Then may it not be that the film will become coated with a thin stratum of superattenuated liquid which will continue to thicken until, possibly, its outer portion passes over into the unstable condition, causing the attenuated layer quickly to evaporate? If, on the other hand, heat taken from the system should produce a corresponding layer of supersaturated vapour next to the film, it should be expected that a thickening of the film would result from condensation.

Observations made with the apparatus shown in fig. 1 accord with this theory. For example, suppose that we obtain a first black film near its limiting thickness, so that a slight increase in the pressure will cause the second black film to appear. This second black at first appears as small, perfectly round, black spots in the first black film, which expand to replace the first black as the pressure is increased. If then the pressure be slightly lessened, perfectly round spots of the first black will appear in the field of the second black film. This latter effect is more difficult to obtain than the former, indicating that the supersaturated vapour condition is more difficult to realize than the superattenuated liquid. In fact, the thickening process ordinarily is so rapid that a second black film will appear to pass, as has already been remarked, continuously, to even the yellow of the first order.

Of course this is merely speculation. Possibly the best excuse for making such is contained in the following words of Maxwell :—“ The surface which forms the boundary between a liquid and its vapour is the seat of phenomena, on the careful study of which depends much of our future progress in the knowledge of the constitution of matter.”

Rose Polytechnic Institute,
Terre Haute, Indiana, Feb. 14, 1906.