Properties of Thin Films.[1]

By Sir WILLIAM B. HARDY, F.R.S.

EVERY one knows of the three states in which matter can exist—solid, fluid, and gas or vapour. Thin films of matter, familiar to all in the form of soap bubbles or lubricating films of oil, are no less than a fourth state, because, choose what physical constant we may, it will have a different value for any particular kind of matter in this state from what it has in any of those other states which are more easily apprehended by the senses.

Life itself depends upon this fourth state of matter. There is a film spread over the surface of each living cell which seems to control the passage of substances into or out of the cell. This film is actively maintained by the expenditure of energy on the part of the cell. The new technique of microdissection, by which living cells so small as to be almost or quite invisible can be dissected, has increased our knowledge of this surface film. If it be punctured at one place the living matter in the neighbourhood of the puncture becomes curdled in appearance and dies, but the membrane grows in at the back of this dead substance, cutting it off from the rest of the cell. This is the fundamental surgery of living matter.

I cannot hope to do more now than deal in haphazard fashion with this vast subject. I propose to begin with an experiment which, in spite of its simplicity, shows how ubiquitous films are, and how our most elementary impressions of the external world depend upon them.

Take, for example, smoothness. It is not a property of solid matter in mass, but of this fourth state of matter. A tea-cup has the delicate velvety feel of a polished surface; but neither porcelain nor ware is really smooth in that sense. Their surface, like that of all other naturally occurring surfaces, is covered by a film of greasy matter, which may come from the atmosphere or from the 'clean' cloth with which the object has been dried. If that film be removed the surface feels harsh and rough because, to use the engineer's phrase, one's finger-tips, if they are freshly washed, seize to it.

It is not possible quickly to remove the film. The necessary procedure would take too long, and in any case the film would quickly re-form in the atmosphere of a room. I can, however, destroy its effectiveness by taking advantage of a curious property of water. That substance is not only not a lubricant for vitreous surfaces, but it is also an anti-lubricant in that it destroys the effect of the natural lubricating film. All I have to do, therefore, is thoroughly to wet the surfaces of the tea-cup and saucer, and the tea-cup ceases to slide in the saucer.

A tea-cup suggests a storm, and that suggests the curious power which oil has of smoothing the sea. The oil spreads over the surface of the water until the layer is only about the five-millionth of a millimetre in thickness. A figure of that kind is apt to mean little; I will therefore try to give an impression of the minute quantity of oil needed in another way. In 1919 an oil ship was wrecked inside the Lizard. The oil-tanks were burst open and the oil rapidly escaped. There has been no sensible quantity of oil in the wreck for the last six years, yet sufficient still escapes to the surface of the sea to produce an obvious 'smooth' for a mile or more to leeward. The effect of a film of oil of quite invisible thickness upon the sea is very real. A vessel labouring in a sea-way or running before a gale can, and does, find some measure of safety by streaming bags filled with oil to windward, and Pliny records how the oyster-fishers used oil to calm the surface of the sea so that they were more easily able to work.

It is obvious that the presence of this oil film cannot seriously modify the energy of great seas, say, a quarter of a mile from crest to crest; but when seas enter a 'smooth' they change their character with dramatic suddenness. They lose their viciousness, and the moment they are in the 'smooth' take the character of those relatively harmless undulations which do not break on to a vessel, but merely make her roll and pitch. The question how the oil film, so tenuous as to be of invisible thickness, curbs the sea is an interesting one, and the attempt to answer it will inevitably introduce us to the chief properties of films on water.

In the late 'nineties a most ingenious method of demonstrating the existence of films on water, and of controlling them for experimental purposes, was devised by a German lady, Fräulein Pockels. I think I may say without exaggeration that the immense advances in the knowledge of the structure and properties of this fourth state of matter which have been made during this century are based upon the simple experimental principle introduced by Miss Pockels. Take an oblong trough of metal filled with water. On the surface of the water, quite invisible because it is even thinner than the invisible dead black portion of a soap film, there is a layer of greasy contamination. If I lay upon the trough a strip of glass or metal so that it touches and is wetted by the water, and move it along, I can compress the superficial film in front and expand it behind. Both processes are easily rendered visible by scattering lycopodium dust on the surface.

The capacity which these films have of expansion is easily shown by sweeping the natural film to one end, thus leaving a tolerably clean surface of water behind. Some lycopodium dust is now placed at one end and the surface touched with a platinum wire, the extreme tip of which has just been dipped into an oil. The dust particles are swept away swiftly in front of the advancing film of oil, although the film itself is absolutely invisible.

The film tends to spread, but the surface of the water in virtue of its surface tension tends to contract. It is this same surface tension which rounds up drops of fluid to spheres, or as near an approach to the spherical shape as other forces which may be operating, such as gravity, permit. There are therefore opposing influences: the tendency of the water to contract, opposed by the tendency of the film to expand, with

[1] Discourse entitled "Films," delivered at the Royal Institution on January 29.

the result that composite surfaces of oil and water have a surface tension less than that of pure water. Composite fluid surfaces have also an enhanced mechanical stability. When a ring of wire a few centimetres in diameter is withdrawn from clean water no film is formed across it, but when the surface of the water is coated with oil it acquires the property of forming free films, which may have an endurance comparable even with that of a soap bubble. In Fig. 1 the curve E F G H gives the surface tension plotted against the quantity of oleic acid per unit area of surface, and the curve A B C D gives the duration of bubbles which have been formed on the surface by allowing air to escape slowly and regularly from an orifice within the trough. It will be noticed that the bubbles are most stable when the film of contamination is just dense enough to begin to alter the surface tension, and that the bubbles have no stability when contamination is either vanishingly small or very great.

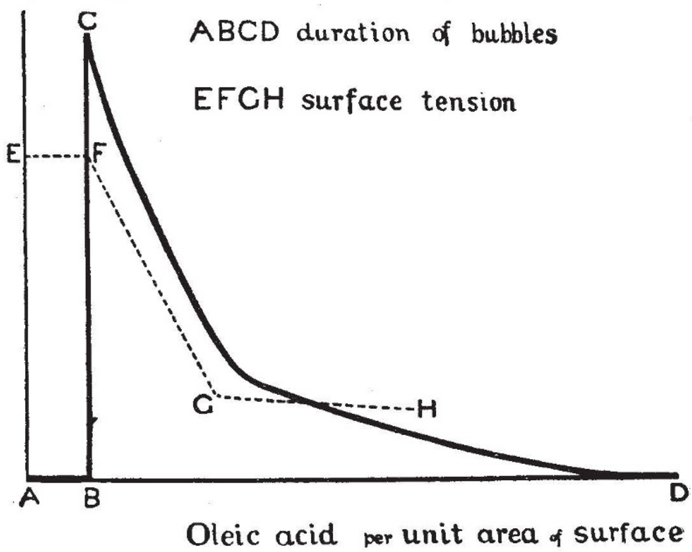

FIG. 1.

Do these properties of composite surfaces, namely, the lowered surface tension and the increased mechanical stability, explain the calming of the sea? In my opinion the answer is 'No,' but current doctrine would perhaps say 'Yes.' It has been pointed out that the special capacity of composite surfaces to resist extension and their mechanical stability, which is only another special aspect of the same thing, tends to prevent the inevitable expansion of the surface which occurs when a wave is formed. This has been held to be a sufficient explanation. I do not think it is, and for two reasons. The first is that the surface of the sea is always contaminated by something which lowers its surface tension and gives to it a remarkable measure of mechanical stability. One of the most striking aspects of a heavy gale is the 'windrows,' which are due to the foam formed when a sea breaks being blown by the wind in long lines over the surface. Foam after all is no more than a collection of bubbles; obviously therefore these naturally formed bubbles have great stability.

The nature of the film which covers the surface of the sea must remain uncertain. Sometimes it is composed of substances like saponin, of vegetable origin, derived from the masses of seaweed flung upon the coast. Foam of this kind is remarkably stable. I have seen it on the day following an on-shore gale knee-deep in the hollows above Flamborough Head. The bruising and shattering of seaweed is, however, a coastal happening and 'windrows' are deep-sea phenomena.

The true explanation of the 'smooth' produced by a film of oil was, I think, furnished by Benjamin Franklin in 1773. His discussion is worth reading. It has the spacious dignity and charm which the hurry and specialisation of to-day have of necessity banished from scientific papers. He tells how he was at sea in 1757 with a convoy of ninety-six sail, the wind being very fresh, and how he noticed a 'smooth' in the wake of two of the vessels. He inquired the cause of one of the officers and was told with some degree of contempt, it being a thing which every fool should know, that the 'smooth' was due to the fact that the cook had just thrown greasy water over the side. In those days tallow was used to coat the bottoms of vessels to keep them clear of growth, and Franklin also notes the 'smoothness' in the wake of vessels which had been freshly tallowed.

Franklin's explanation is based entirely upon friction. The oil makes the sea so very smooth that the wind cannot 'catch upon it.' I confess Franklin's explanation did not appeal to me at first, but I believe he is right. The comparative safety of a 'smooth' is due, not to the fact that the seas in it are sensibly smaller than those outside of it, but to the fact that they have been deprived of their viciousness. Now the viciousness of a sea, the degree of danger it carries to the mariner, is measured by its instability. It is when the head of the sea topples over and becomes a mass of water moving with a high velocity that it is dangerous. Within the limits of a 'smooth' produced by oil the seas cease to break, or to 'crack,' as Cornish fishermen say. The wind not only drives a sea forward by its horizontal pressure, but also draws the crest upwards by friction against the surface of the wave.

If the friction between the air and the water be greatly reduced, the wind fails to lift the crest of a wave to the point at which it is blown bodily over by the horizontal pressure. The wave then sinks down to a relatively harmless 'swell.'

The 'catch' of the wind upon the waves is not, however, confined simply to a direct frictional pull, and here it is that the surface tension perhaps comes in. It is easy to convince oneself that an oil film prevents the formation of ripples—that is, of the very smallest kind of wave. When there is no oil film, a great wave carries countless ripples and wavelets each of which gives the wind a direct thrust on the surface. It is to the suppression of ripples and wavelets that the characteristic smooth appearance is due, and when they cease to be formed, the chief 'catch' of the wind upon the sea is lost.