reference frame

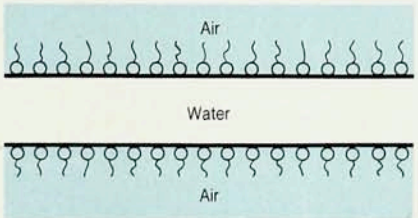
Bubbles

Pierre-Gilles de Gennes

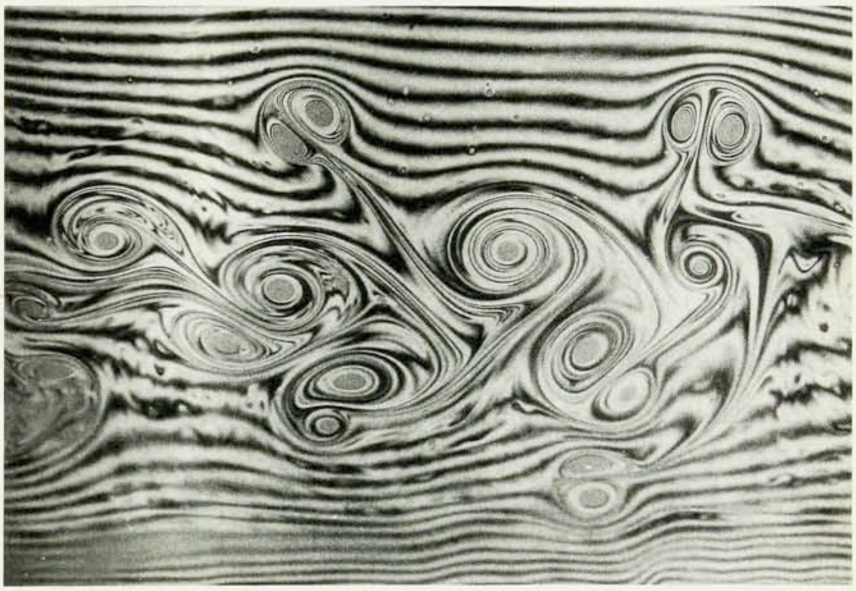
Soap films have fascinated people for many centuries. The films actually come in two kinds: young films, which are relatively thick and give beautiful interference colors, and old films, which have thinned out to about 100 Å and appear black. The black films have reached a local minimum in free energy. The long-range van der Waals forces, which tend to thin out the films, are balanced in the "black" state by short-range repulsions between the two surfactant layers (figure 1).

Many of us believed that the first observations on black films were due to Robert Hooke and Isaac Newton. But a few years ago we learned through David Tabor that the true discoverers were the Assyrians, who practiced divination by setting up films with oil and water in a bowl; the erratic motions in the film could be suitably interpreted in terms of future events. They noticed the formation of black spots—the first reference on thin films was written on clay tablets more than 3000 years ago.

The fascination has not decreased. In fact, Americans entered the game very early. The first quantitative study on monolayers of fatty acids at the surface of water was by Benjamin Franklin: Measuring the volume of oil required to cover a pond of known area, he determined the size of the oil molecule. Later came Josiah Willard Gibbs, who observed many soap films and established interfacial thermodynamics. Still later Irving Langmuir studied monolayers. The peak of classical art on soap films was reached with Karol Mysels, Kozo Shinoda and their colleague, the theorist Stanley Frankel.[1]



A soap film is a thin slab of water protected by two monolayers of surfactant. Each surfactant molecule has a polar head facing the water and an aliphatic tail directed toward the air. In classical soaps the polar head is an acid group, $(CO_2)^-$. Figure 1



Unstable vortex street seen in a soap film behind a moving cylinder. (Photograph courtesy of Yves Couder.) Figure 2

They performed a series of textbook studies on films pulled on a vertical frame. Among other behavior, they noticed remarkable flow patterns in the films provided that the surfactant monolayers are two-dimensional liquids (not solids) and can be sheared. These flows have nearly zero viscosity and show a rich variety of behavior. For instance, a thick region is heavy and falls down, while a piece of black (thin) film climbs up; near the vertical edges of the frame this leads to strange patterns. More recently, Yves Couder used a large, horizontal film to study two-dimensional turbulence (figure 2).

We know many things about soap films. For instance, they exhibit fluctuations in thickness ("peristaltic" modes). A group in Utrecht has studied these using photon beat techniques. The peristaltic modes of black films are sensitive to the long-range (electrostatic and van der Waals) forces in the films. The resulting plots of force versus thickness are not quite perfect,

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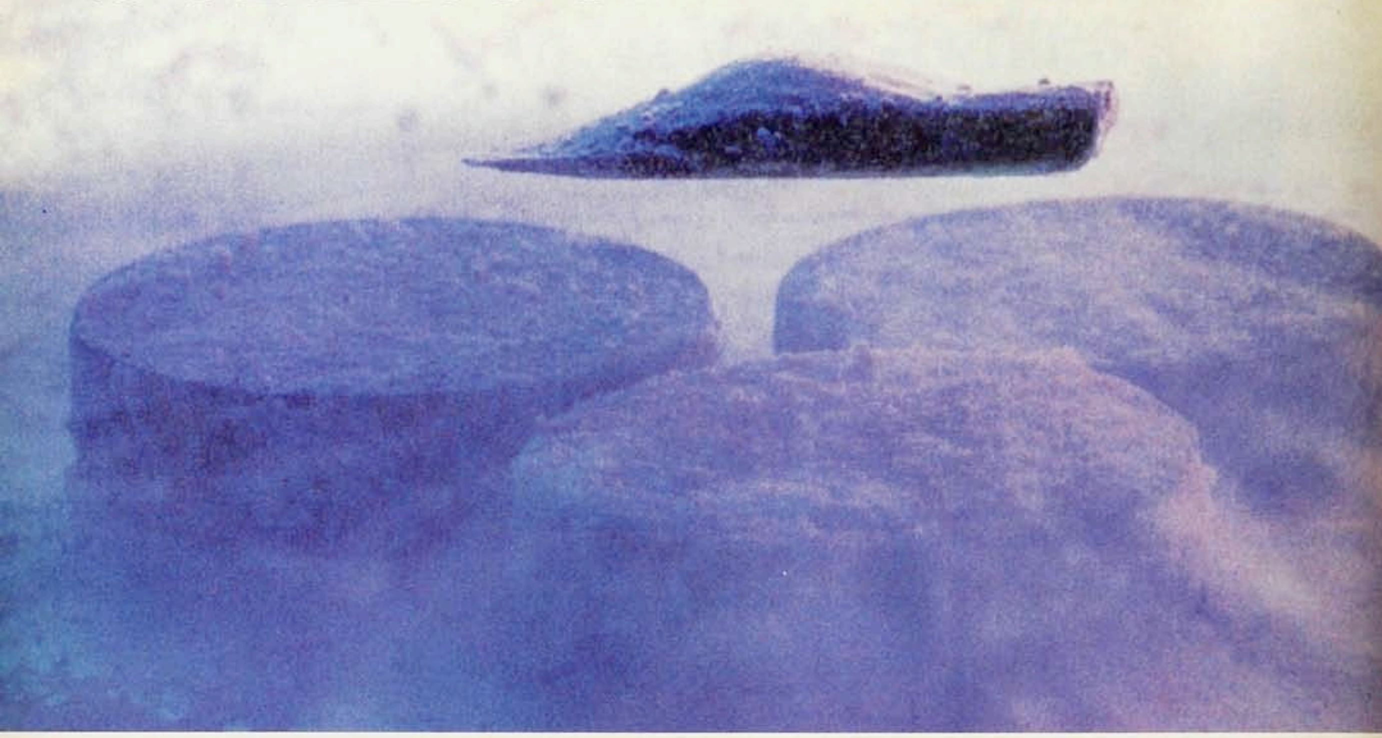

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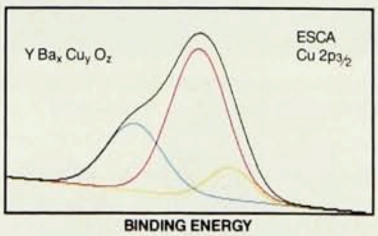

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however. One source of discrepancy may be charge fluctuations inside the electrostatic double layers, which can give spectacular (attractive) corrections to the classical (mean field) analysis of Lev Landau, B. V. Deryagin, E. J. W. Vervey and J. T. Y. Overbeek. Another possible source of discrepancy is a rounding off of the film free energy versus thickness, due to capillary fluctuations: The local thickness of the film may differ from the mean. Capillary fluctuations are now a fashionable subject, and we should soon get an answer here.

Possibly more significant in practice is the nonlinear process by which a thick (metastable) film can transform into a thin black film. There is now a theory for this, and a few measurements were taken long ago by Mysels, but we need more.

The fragility of soap bubbles is well known. Mysels and his coworkers provoked bursting at the center of a film (with a spark) and showed that the film expands at acoustic velocities, often emitting an "aureole" (shock wave) ahead of the growing hole.

We know a lot about soap films, and thus at first sight the situation might appear idyllic. In fact, we are left with many mysteries. In particular, we do not fully understand what controls the stability of bubbles. Gibbs noticed one important point, for the case where the surfactant, the surface active substance, is strictly insoluble (confined to monolayers). If a film is extended locally, the extended portion has less surfactant, and thus a higher surface tension; the perturbed region tends to shrink, and this provides stability. Gibbs also noticed that this effect is reduced if the surfactant is soluble in water—in the extended region, some surfactant may move from the water to the monolayers, and restore nearly the same surface tension everywhere. One would thus predict that insoluble monolayers are an excellent choice for stable films, and that sufficiently concentrated surfactant solutions are not as good. But, as Jacob Lucassen has emphasized, the reality is rather different.[2] Film stability remains a challenge for scientists, and a source of perplexity for engineers. Foams are important in practical applications—and not yet fully understood. Bubbles are still a challenge to our imagination.

References

1. K. Mysels, K. Shinoda, S. Frankel, *Soap Films*, Pergamon (1959).
2. J. Lucassen, in *Anionic Surfactants*, E. H. Lucassen-Reynders, ed., Marcel Dekker, New York (1981), ch. 6. □