Soap Films and Some Fundamentals of Thin-Liquid Films

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Abstract

A brief summary of recent results of research on the thinning, equilibria, and bursting of soap films is given along with a proposal for the nomenclature of systems involving adsorption.

Introduction

The original presentation of this paper at the Symposium on Lipid, Monolayer, and Bilayer Models and Cellular Membranes was based on color movies, photographs, and diagrams. Hence it is not suitable for the printed page, nor can the same arguments be conveyed without these visual aids in an article of reasonable length. However, most of the ideas have been reported earlier, and it may be worthwhile now to survey the main points with key references to the original publications.

All thin-liquid systems, soap films, lipid membranes, concentrated emulsions, or foams are derived from adsorbed layers of molecules at an interface, be it water-air, oil-air, or water-oil. Two parts of such an interface can approach through either phase and then give a thin layer which may or may not be sufficiently stable for further study. Depending on which of the two phases becomes the thin one, there can be aqueous films in oil or in air, or oil films in water or in air. The symposium was mainly concerned with the oil-in-water films whereas my own interests have been and are in the water-in-air (or soap film) systems, more especially those stabilized with anionic surfactants. Many problems are however common to both systems, and some may be studied more easily in one and some in the other.

Nomenclature

The existence of many structures involving adsorbed layers introduces difficulties of nomenclature, which are compounded by the fact that researchers concerned with various aspects of adsorption, from catalysis to membranes and from electrochemistry to enzymology, have only limited channels of communications with each other. The only novel contribution of my paper was a nomenclature proposal summarized in Fig. 1. It is based on the use of "layer" (mono-, di-, symmetrical, and unsymmetrical) to describe the relation of the film to the neighboring phases and of "molecular" (mono-, poly-, complete, or incomplete) to describe the amount and arrangement of the significant molecules involved. It was also suggested that the oil-in-water films be called "invert" films by analogy with invert (water-in-oil) emulsions. The term "lipid" membrane for this system may be somewhat misleading since all films involve adsorbed lipid molecules or ions, and thin soap films may consist mainly of lipids.

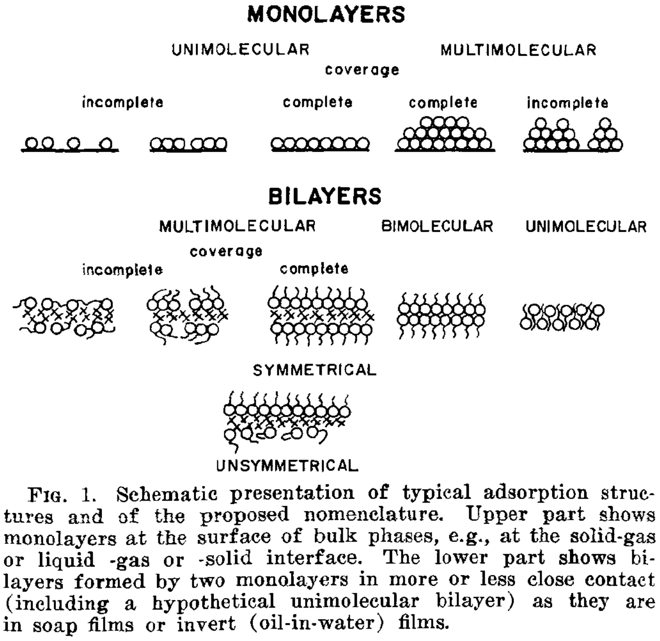

Fig. 1. Schematic presentation of typical adsorption structures and of the proposed nomenclature. Upper part shows monolayers at the surface of bulk phases, e.g., at the solid-gas or liquid -gas or -solid interface. The lower part shows bilayers formed by two monolayers in more or less close contact (including a hypothetical unimolecular bilayer) as they are in soap films or invert (oil-in-water) films.

Soap Films

In a soap film the approach of two air-water interfaces involves easily observable kinetics, which lead to a (metastable) equilibrium, followed by an extremely rapid kinetic step, namely, bursting and true equilibrium. For films thicker than about 800Å, the kinetics involve gravity as the main driving-force. The predominant mechanisms may be gravitational convection in which thicker and thinner film elements exchange positions in the film, marginal regeneration in which thinner film elements replace thicker ones at the boundaries of the film, and viscous flow of the intralamellar fluid between the two surface layers (1,2).

For films thinner than about 800Å the effect of van der Waals forces may become predominant and lead to a disproportion of the film into a thicker welt and the thinner equilibrium film (3). The latter then grows by gradual displacement of the welt along the boundary between the two thicknesses. Nucleation of this abrupt transition, like the nucleation of other sudden changes in thickness, including bursting, is likely to be by the growth of spontaneous fluctuations in film thickness under the influence of van der Waals forces opposed by surface tension (4).

The fact that the film reaches a metastable equilibrium and does not burst immediately under the influence of the thinning forces is due to the presence of repulsions which increase rapidly at small thicknesses. The most important of these for ionic systems is the diffuse, electric, double-layer repulsion (5,2). As the range of this repulsion changes greatly with ionic strength, the equilibrium thickness also varies with electrolyte content in good agreement with the theory (6).

At high NaCl (but not LiCl) concentrations, another abrupt transition to a film with a thickness of about 45Å, the so-called second black film, is observed (7). The forces governing this structure are not yet accounted for.

The free-energy difference between the surface of bulk solution and the thin film in metastable equilibrium with it is the depth of the minimum in a free-energy vs. thickness diagram. It can be measured by determining the contact angle between film and solution, and a method for doing this has been recently described (8). In unpublished work (9) contact angles as high as 16° have been observed, and those below 10′ minutes of arc have been measured.

An additional thinning factor, the hydrostatic pressure upon the film, can be varied if the film is formed in a properly constructed porous support (2). Under proper conditions this permits the direct measurement of the force of double-layer repulsion as a function of distance and has resulted in good agreement with theory (10).

The bursting of a soap film is a rapid process; once started, it is completed in about 1/1000 of a second. Modern high-speed flash techniques permit however the taking of sharp photographs and give a clear view of what happens during this time. The receding rim of the hole in a film can reach the speed of 150 miles per hour and can be surrounded by an aureole propagating at least twice as fast. This behavior gives some information about surface kinetics on the microsecond scale (11).

The optical thickness of these films can be measured quite precisely by comparing the amount of monochromatic light reflected by a given film with the maximum amount which it reflects when the optical thickness is equal to a quarter wavelength of the light. The determination of the material thickness involves, in addition, information about the refractive index of the film and especially of the various layers which form it (12). A simple way of treating this problem for any number of layers and for any medium surrounding the film has now been given (13). The experimental determination of the refractive indices is difficult however (14). Fortunately, good guesses can be made from independent information about the structure of the films, based on what is known about adsorption on bulk surfaces (15) and films (16) and from radiotracer studies of films (17).

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Discussion

DR. KENNETH S. COLE (National Institutes of Health, Bethesda, Md.): I would certainly like to compliment you on the beautiful effects and the extraordinarily ingenious experiments and equally ingenious interpretations. I am very hesitant to ask this question, but in some of the simpler of the films, is there a relatively simple kinetics for the growth of the black area increase as a function of time?

DR. K. J. MYSELS: Miss W. R. McEntee has made some unpublished measurements which answer this question directly. She studied circular almost horizontal films in which the spontaneous growth of the black film at the expense of the thicker film surrounding it can be seen with a minimum of disturbances. To the extent that other factors can be controlled, especially evaporation to which the rate is quite sensitive, she found that the area of black film increased with the square of time, i.e. that the radius increased at a constant rate. This rate was somewhat dependent on the thickness of the thicker film and very dependent on the ionic strength which controls the double layer repulsion. This makes good sense since the change of thickness should be strictly local process occurring over the distance of a few microns or less separating the two thicknesses. The driving force is always the same, due primarily to van der Waals attraction and is to some extent counteracted by the double layer repulsion which limits the thickness of the black film. A greater thickness of the thick film means that the resultant force has to displace a larger volume of liquid for a given linear progress and hence the rate becomes slower.

In other words, the linear displacement of the boundary between the two films proceeds at a constant rate as long as the driving forces and the resistances operating at that boundary are constant.

DR. W. P. GIBBLE (Hunt-Wesson Foods, Inc., Fullerton, Calif. Would not the region of the "Plateau border" surrounding the film be micelle-like, with water layers separating the oriented molecules of surfactant?

DR. K. J. MYSELS. The Plateau border is essentially a portion of the bulk solution—a meniscus surrounding the film whose shape is determined by the surface tension, the hydrostatic suction, and the boundary conditions (including the one that it meet the surfaces of the film). Its structure is therefore that of the bulk liquid with micelles present if the concentration is high enough but certainly—if anything—more disorganized than the film.