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LIGHT SCATTERING BY SOAP FILMS

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Abstract

A theory is constructed describing the scattering from a liquid film (e.g., a soap film) of a light beam polarized normal to the plane of incidence. This scattering is due to the small irregular corrugations caused by thermal motion. The interference of the reflected incident beam with its multiple reflections (and refractions) and similarly the interference produced from the scattered beam have been taken into account. The corrugations of the two surfaces may be correlated depending on the forces holding the film in equilibrium. Where weak forces are operative, the corrugations of the two surfaces are not correlated. An estimation of the correlation between the corrugations of the two film surfaces was made from current theories of film stability in which the principal forces are attributed to an electrostatic repulsion between soap ions on the two surfaces of the film and van der Waals' attraction among the molecules in the film.

Preliminary measurements on soap films formed from ionic and nonionic soap solutions with glycerol are reported. It was found that the dependence of the light scattering on wavelength and angle of observation was in agreement with theory. Light scattering from very thin (black) films gave data about interaction which could be interpreted in terms of electrical forces and van der Waals' forces and led to values of the surface potential $\psi_0 = 40$ mv. and a van der Waals' constant $A = 1.3 \times 10^{-12}$ erg. However, the value of the reciprocal Debye-Hückel thickness, κ, found in this manner was three times larger than could be expected from the concentration of the electrolytes present in the soap solution.

Introduction

The light scattering by liquids and by solutions, in particular colloidal solutions, has provided a large amount of information concerning the weight, size, and interaction of the molecules involved. This bulk light scattering is caused by fluctuations in density and in concentration. It was pointed out by Von Smoluchowski (1) that besides "bulk" scattering there may occur a scattering from the *surface* of a liquid, owing to the small irregular corrugations caused by thermal motion. Mandelstam (2) has been able to calculate this light scattering in the plane of incidence of the primary light beam. He found that the main contribution to the scattering is inversely proportional to λ^2 (λ is wave length of light used) and due to the mean square of the gradient of the corrugations.

This situation is quite different from that in bulk scattering, where the main contribution to the light scattering is proportional to the mean square of the fluctuations, and the intensity of the scattered light proportional to λ^4. Only near the critical point does a term proportional to the mean square of the gradient become important in bulk light scattering, as was pointed out recently by Debye (3).

As an illustration of the order of magnitude of surface light scattering one calculates from Mandelstam's equations that for an index of refraction, $n = 1.36$; an angle of incidence, $\theta_0 = 60°$; an angle of observation of the scattered beam, $\theta = 45°$; a surface tension, $\gamma = 30$ dynes/cm.; a wave length, $\lambda = 546$ mμ the light scattered from 1 cm.^{2} of the surface is of the order of $S = 7.5 \times 10^{-7}$ (see Eqs. [12] and [12*a*] for a definition of S), which is somewhat less than the bulk scattering of 1 cm.^{3} of clean water.

The scattering outside of the plane of incidence was calculated by Gans (4) and by Andronow and Leontowicz (5); these authors included the case of a total reflecting surface.

Probably owing to the experimental difficulty caused by the simultaneous occurrence of bulk light scattering, the phenomenon of surface light scattering has not been investigated thoroughly.

Some qualitative experiments were done by Mandelstam on the liquid boundary between methanol and CS_2 near the critical mixture temperature, where the scattering is rather strong.

Quantitative experimental work was done by Raman and Ramdas (6) on some 60 organic liquids and on mercury. They observed a semiquantitative correspondence of the dependence of the light scattering on γ and n as predicted by Mandelstam. Similar experiments were performed by Jagannathan (7) and Hariharan (8). Ramdas (9) also reported some qualitative experiments on monomolecular films.

The λ^2-law was confirmed by Barichanskaia (10) experimenting with the phenol/water and isobutyric-acid/water boundaries near the critical mixing temperatures.

In all this experimental work the comparison of intensities was done by visual or photographic means.

This paper deals with the light scattering of thin liquid films (e.g., soap bubbles). As the amount of bulk phase present in thin films is small, we may expect the light scattering from the surfaces to predominate, particularly in a medium having a small turbidity like air.

We will extend the light scattering theory of single surfaces to the case of thin films. Some complications which have to be dealt with are:

1. Interference of the waves reflected (and refracted) by both surfaces, as well in the incident as in the scattered light.

2. The presence of a component (soap) necessary to stabilize the film.

3. Internal forces, e.g., Coulombic and van der Waals' forces (11, 12),

between the two surfaces of the film. These forces not only influence the corrugations of the surfaces but also give rise to phase correlations between corrugations on the two surfaces.

Theory

In the theory of light scattering as given by Mandelstam (2) and Andronow and Leontowicz (5), the surface corrugations are represented by a Fourier series. Each term of the series gives rise to a pair of diffracted light waves: one at each side of the surface. The intensities of the diffracted waves, which are obtained making use of Maxwell's equations with the appropriate boundary conditions, are proportional to the square of the respective Fourier coefficients.

In the case of a liquid the Fourier coefficients will fluctuate independently and the mean intensity of the diffracted scattered light will be proportional to the mean square of the Fourier coefficients. This mean square of the Fourier coefficients was obtained with the aid of a fluctuation theorem due to Einstein (13).

We will develop a theory of the light scattering by a liquid film along the same lines. However, the evaluation of the intensity of the diffracted light using Maxwell's equations would be quite lengthy. We propose a simpler method, leading to the same result, using the scattering equations for a single boundary and well-known interference formulas.

The discussion is restricted to primary light polarized normal to the plane of incidence, and scattered light observed in the plane of incidence.

Diffraction of Light by a Single Corrugated Boundary

Two transparent media 1 and 2 with refractive indices n_1 and n_2, respectively, are separated by a flat boundary lying in the X-Y plane. The interface corrugates with amplitudes z that are small compared to the wavelength of the light (λ). As did Rayleigh (14), Mandelstam, and Andronow and Leontowicz, we assume that these corrugations in an area extending from $x = -\frac{1}{2}a$, $y = -\frac{1}{2}a$ to $x = +\frac{1}{2}a$, $y = +\frac{1}{2}a$, can be expressed by a Fourier series:

$$z = \sum_{\rho=-\infty}^{+\infty} \sum_{\sigma=-\infty}^{+\infty} \zeta_{\rho\sigma} e^{ip(\rho x+\sigma y)}. \qquad [1]$$

Here $p = 2\pi/a$; a, satisfying the condition $a \gg \lambda$, is the period of the series and $\zeta_{\rho\sigma}$ are the complex Fourier coefficients. Since z is real, the coefficients are connected in pairs by the relations:

$$\zeta_{-\rho,-\sigma} = \zeta^*_{\rho,\sigma}\,; \qquad \zeta_{\rho,-\sigma} = \zeta^*_{-\rho,\sigma}\,; \qquad \zeta_{-\rho,\sigma} = \zeta^*_{\rho,-\sigma}\,,$$

where $\zeta^*_{\rho\sigma}$ is the complex conjugate of $\zeta_{\rho\sigma}$, etc.

A plane incident light wave traveling from medium 1 into medium 2

will give rise to a series of plane diffracted waves. In fact each term of the Fourier series will give two diffracted waves, one into medium 1 and one into medium 2, the directions of which are given by elementary diffraction theory:

$$\text{for medium 1: } \begin{aligned} \sin\theta\cos\varphi - \sin\theta_0 &= \rho p/k_1 \\ \sin\theta\sin\varphi &= \sigma p/k_1 \end{aligned} \qquad [2a]$$

$$\text{and for medium 2: } \begin{aligned} \sin\theta'\cos\varphi' - \sin\theta_0' &= \rho p/k_2 \\ \sin\theta'\sin\varphi' &= \sigma p/k_2 \end{aligned} \qquad [2b]$$

Here $k_1 = 2\pi/\lambda_1$ and $k_2 = 2\pi/\lambda_2$; λ_1 and λ_2 are the wave lengths of the light in medium 1 and 2, respectively; θ_0 and θ_0' are the angles of incidence and refraction of the primary beam (lying in the X-Z plane), whereas θ, φ and θ', φ' define the altitude and azimuth of the diffracted waves in medium 1 and 2, respectively (see Fig. 1).

It follows from Eqs. [2a] and [2b] that the directions of the diffracted waves in medium 1 and 2 are connected by Snellius' law:

$$\varphi = \varphi', \quad \text{and} \quad \sin\theta/\sin\theta' = k_2/k_1 = n_2/n_1 = n. \qquad [2c]$$

The relations between ρ, σ, θ_0 , θ, and φ are illustrated in Fig. 2. A circle of unit radius is centered at a distance $\sin\theta_0$ from the crossing of two axes

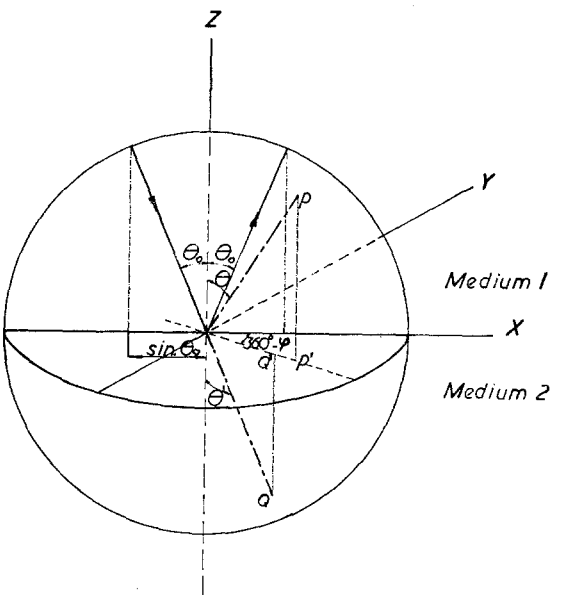

FIG. 1. Diffraction of light at corrugated boundary in the X-Y plane. Diffracted light beam (—·—·—) and incident and reflected light beam (——). The refracted beam has not been drawn for clarity.

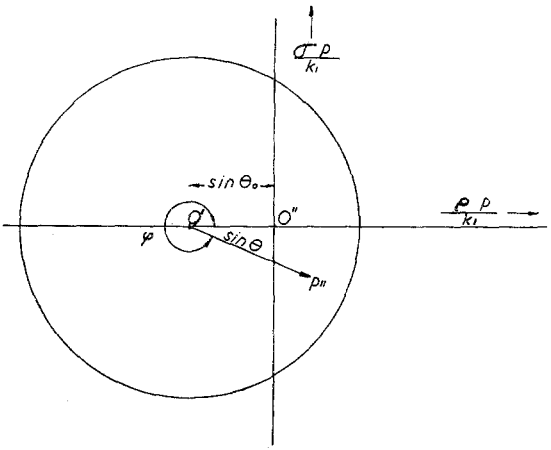

FIG. 2. Relation between the Fourier indices, ρ, σ and the angles of incidence θ_0 and observation, θ; φ.

on which ρ and σ (in units k_1/p) are plotted. For a given pair of whole numbers ρ and σ represented by the point P'', the line $O'P''$ represents $\sin\theta$, whereas the angle $O''O'P''$ equals φ.

Fourier terms corresponding with points (ρ, σ) outside the unit circle in Fig. 2 give no diffracted waves; this means that corrugations with small wavelengths (smaller than about λ) will not contribute to light scattering (14).

If the height z of the corrugation is small with respect to the wavelength of the light, the amplitude of the diffracted waves is proportional to $\zeta_{\rho\sigma}/\lambda$.

We assume that the incident wave with unit amplitude is polarized with the electrical vector normal to the plane of incidence. For a diffracted wave outside the plane of incidence, the amplitude of the component parallel to the boundary surface is (15)

$$A_{\rho\sigma} = 2ik_1\,\zeta_{\rho\sigma}\,\frac{\sin(\theta_0 - \theta_0')\cot\theta_0\sin\theta\cos\varphi}{\sin(\theta + \theta')}. \qquad [3]$$

This applies to the diffracted wave in medium 1 as well as to the one in medium 2.

For diffracted waves observed near the plane of incidence ($\varphi = 0$) this becomes equal to:

$$A_{\rho\sigma} = 2ik_1\,\zeta_{\rho\sigma}\,\frac{\sin(\theta_0 - \theta_0')\cot\theta_0\sin\theta}{\sin(\theta + \theta')}. \qquad [3a]$$

Equation [3a] may be transformed into:

$$A_{\rho\sigma} = \frac{ik_1\,\zeta_{\rho\sigma}}{2\cos\theta}(n^2 - 1)tt_0, \qquad [3b]$$

where t and t_0 are Fresnel coefficients and n is defined in Eq. [2c].

$$t_0 = \frac{2 \cos \theta_0}{\cos\theta_0 + n \cos\theta_0'}; \qquad [4a]$$

$$t = \frac{2 \cos \theta}{\cos \theta + n \cos \theta'}. \qquad [4b]$$

In the case of an incident wave traveling with angle θ_0' from medium 2 into medium 1 the amplitude may be obtained from the Eqs. [3*b*], [4*a*], and [4*b*] with the substitutions $k_1 \rightarrow k_2$; $\zeta_{\rho\sigma} \rightarrow (-\zeta_{\rho\sigma})$; $n \rightarrow 1/n$; $\theta \rightleftarrows \theta'$; and $\theta_0 \rightleftarrows \theta_0'$. Thus

$$A'_{\rho\sigma} = \frac{ik_2(-\zeta_{\rho\sigma})}{2\cos\theta'} \left[\frac{1}{n^2} - 1\right] t't_0', \qquad [3c]$$

where

$$t_0' = \frac{2 \cos \theta_0'}{\cos \theta_0' + (1/n) \cos \theta_0} = \frac{2n \cos \theta_0'}{\cos \theta_0 + n \cos \theta_0'} \qquad [4c]$$

and

$$t' = \frac{2 \cos \theta'}{\cos \theta' + (1/n) \cos \theta} = \frac{2n \cos \theta'}{\cos \theta + n \cos \theta_0'}. \qquad [4d]$$

And obviously Eq. [3*c*] may be written as:

$$A'_{\rho\sigma} = \frac{ik_1 \zeta_{\rho\sigma}}{2 \cos \theta} (n^2 - 1) t t_0'. \qquad [3d]$$

With the help of the above equations we are now able to obtain a solution for the more complicated case of a film.

As we mentioned above these equations are valid only if the incident light is polarized normal to the plane of incidence, and if the scattering is observed in the plane of incidence.

The coefficients, $\zeta_{\rho\sigma}$, were not specified except for their order of magnitude; $(\zeta_{\rho\sigma}/\lambda) \ll 1$; in the case of a liquid surface $\overline{\zeta_{\rho\sigma}^2}$ may be obtained from fluctuation theory.

Diffraction of Light from a Corrugated Film Bounded by Two Identical Media

We consider a film (medium 2) with refractive index n_2 and thickness h between two identical media 1 and 3 with refractive index n_1. We take the upper boundary (1–2) to be in the X-Y plane and the lower boundary (2–3) to be in a plane at a distance h beneath it. Similar to the case of a single boundary (Eq. [1]) we now represent the corrugations of the boundaries (1–2) and (2–3) by:

$$z_{12} = \sum_{\rho=-\infty}^{+\infty} \sum_{\sigma=-\infty}^{+\infty} \zeta_{\rho\sigma} e^{ip(\rho x + \sigma y)};$$

$$z_{23} = \sum_{\rho=-\infty}^{+\infty} \sum_{\sigma=-\infty}^{+\infty} \eta_{\rho\sigma} e^{ip(\rho x + \sigma y)}. \qquad [5]$$

Both boundaries will contribute to the diffracted light, but the situation is complicated by the multiple reflections of regular and diffracted waves. As in the one boundary case the diffracted waves obey Snellius' law and hence interference will occur.

We will first consider the interference of the regular waves. The incident wave with amplitude ψ^0 traveling in medium 1 undergoes multiple reflection and refraction at the upper and lower boundaries of the film (see Fig. 3).

As a result of interference four waves are obtained; the amplitudes ψ may be obtained by a well-known procedure (16): the phases of ψ^0, ψ^A, and ψ^C are compared at the origin O in the boundary (1–2), whereas those of ψ^B and ψ^D are compared at the origin O' in the boundary (2–3)

$$\psi^0 = 1; \tag{6a}$$

$$\psi^A = r_0\left(1 - \frac{t_0 t_0' e^{-2i\beta}}{1 - r_0^2 e^{-2i\beta}}\right); \tag{6b}$$

$$\psi^B = \frac{t_0 e^{-i\beta}}{1 - r_0^2 e^{-2i\beta}}; \tag{6c}$$

$$\psi^C = -\frac{t_0 r_0 e^{-2i\beta}}{1 - r_0^2 e^{-2i\beta}}; \tag{6d}$$

$$\psi^D = \frac{t_0 t_0' e^{-i\beta}}{1 - r_0^2 e^{-2i\beta}}; \tag{6e}$$

where

$$\beta = (2\pi/\lambda_2)h \cos \theta_0', \tag{6f}$$

h is the thickness of the film, and

$$r_0 = \frac{\cos \theta_0 - n \cos \theta_0'}{\cos \theta_0 + n \cos \theta_0'}. \tag{6g}$$

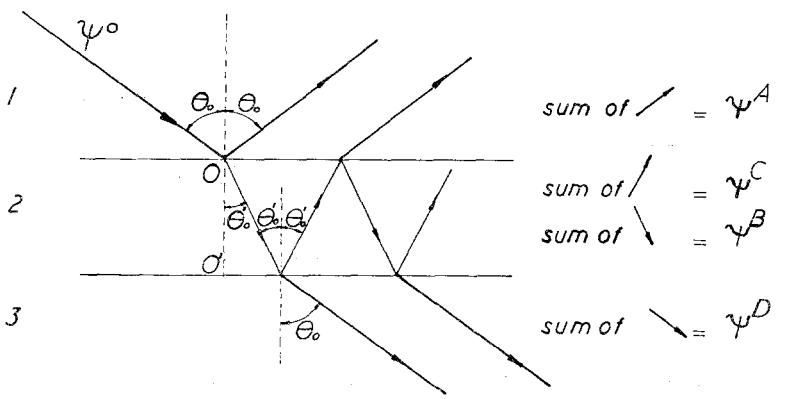

FIG. 3. Interference after multiple reflection and refraction of the incident light beam.

From [4a] and [4c] follows:

$$t_0 = 1 + r_0\,; \qquad t_0' = 1 - r_0\,. \tag{6h}$$

For a film ψ^0 will give rise to a diffracted wave as in the case of a single boundary, and so also will ψ^B and ψ^C. More precisely, ψ^0 will give rise to diffraction at the boundary (1–2); ψ^C at the boundary (2–1); and ψ^B at the boundary (2–3).

The waves diffracted into the film will undergo multiple reflection, refraction, and diffraction at the film boundaries. Multiple diffraction will be neglected, however, as the amplitudes are of higher order in ζ/λ.

The amplitudes of the diffracted waves after interference may be obtained as follows. The wave ψ^0 gives rise to one diffracted wave in medium 1 and another one in medium 2 (see Fig. 4, dashed lines). The amplitudes are:

$$\psi^0 A^{12}_{\rho\sigma}, \tag{7a}$$

where $A^{12}_{\rho\sigma}$ is given by Eq. [3b]. As indicated by the full lines in Fig. 4, the diffracted wave in medium 2 undergoes multiple reflection and refraction giving rise to a number of interfering waves. The resulting amplitudes in medium 1 and 3 are given by

$$-\psi^0 A^{12}_{\rho\sigma} \frac{rt' e^{-2i\alpha}}{1 - r^2 e^{-2i\alpha}} \tag{7b}$$

$$\psi^0 A^{12}_{\rho\sigma} \frac{t' e^{-i\alpha}}{1 - r^2 e^{-2i\alpha}} \tag{7c}$$

with

$$\alpha = (2\pi/\lambda_2) h \cos\theta'; \tag{7d}$$

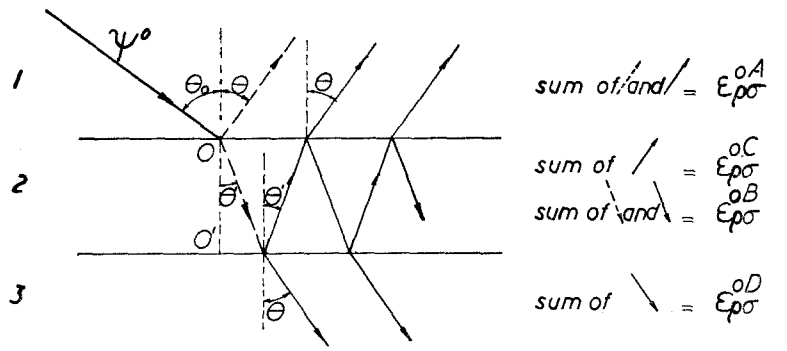

FIG. 4. Interference after multiple reflection and refraction of diffracted light beam.

$$r = \frac{\cos\theta - n\cos\theta'}{\cos\theta + n\cos\theta'}; \qquad [7e]$$

and, as follows directly from [4b] and [4d],

$$\begin{aligned} t &= 1 + r; \\ t' &= 1 - r. \end{aligned} \qquad [7f]$$

The total amplitude $\epsilon_{\rho\sigma}^{0A}$ of the diffracted wave in medium 1, produced by ψ^0, is the sum of [7a] and [7b], whereas the amplitude $\epsilon_{\rho\sigma}^{0D}$ of the corresponding diffracted wave in medium 3 is given by [7c]:

$$\epsilon_{\rho\sigma}^{0A} = \psi^0 A_{\rho\sigma}^{12}\left[1 - \frac{rt'e^{-2i\alpha}}{1 - r^2e^{-2i\alpha}}\right]; \qquad [8a]$$

$$\epsilon_{\rho\sigma}^{0D} = \psi^0 A_{\rho\sigma}^{12}\frac{t'e^{-i\alpha}}{1 - r^2e^{-2i\alpha}}. \qquad [8b]$$

Analogously the amplitudes of the diffracted waves after the interference produced by ψ^B and ψ^C are given by

$$\epsilon_{\rho\sigma}^{BA} = \psi^B A_{\rho\sigma}^{23}\frac{t'e^{-i\alpha}}{1 - r^2e^{-2i\alpha}}; \qquad [8c]$$

$$\epsilon_{\rho\sigma}^{BD} = \psi^B A_{\rho\sigma}^{23}\left[1 - \frac{rt'e^{-2i\alpha}}{1 - r^2e^{-2i\alpha}}\right]; \qquad [8d]$$

$$\epsilon_{\rho\sigma}^{CA} = \psi^C A_{\rho\sigma}^{21}\left[1 - \frac{rt'e^{-2i\alpha}}{1 - r^2e^{-2i\alpha}}\right]; \qquad [8e]$$

$$\epsilon_{\rho\sigma}^{CD} = \psi^C A_{\rho\sigma}^{21}\frac{t'e^{-i\alpha}}{1 - r^2e^{-2i\alpha}}. \qquad [8f]$$

The coefficients $A_{\rho\sigma}^{21}$ and $A_{\rho\sigma}^{23}$ are similar to $A_{\rho\sigma}^{12}$ and can be obtained from Eqs. [3b] and [3d]:

$$\begin{aligned} A_{\rho\sigma}^{12} &= Lt_0 t\zeta_{\rho\sigma} \\ A_{\rho\sigma}^{21} &= Lt_0' t\zeta_{\rho\sigma} \\ A_{\rho\sigma}^{23} &= -Lt_0' t\eta_{\rho\sigma} \end{aligned} \qquad [9a]$$

where

$$L = \frac{ik_1(n^2 - 1)}{2\cos\theta}. \qquad [9b]$$

The *total* amplitudes of the waves diffracted into medium 1 and medium 3 are given by

$$\epsilon_{\rho\sigma}^{A} = \epsilon_{\rho\sigma}^{0A} + \epsilon_{\rho\sigma}^{BA} + \epsilon_{\rho\sigma}^{CA} \equiv A_{\rho\sigma}^{R}; \qquad [10a]$$

$$\epsilon_{\rho\sigma}^{D} = \epsilon_{\rho\sigma}^{0D} + \epsilon_{\rho\sigma}^{BD} + \epsilon_{\rho\sigma}^{CD} \equiv A_{\rho\sigma}^{T}. \qquad [10b]$$

We will refer to $A^R_{\rho\sigma}$ and $A^T_{\rho\sigma}$ as the amplitudes of "reflected" and "transmitted" diffracted waves. We observe that the phase of $A^R_{\rho\sigma}$ was compared at the origin in boundary (1–2) and the phase of $A^T_{\rho\sigma}$ at the origin in boundary (2–3).

With the help of Eqs. [6], [8], [9*a*, *b*], and [10*a*, *b*] we obtain ultimately:

$$A^R_{\rho\sigma} = Lt_0 t \frac{(1 - r_0 e^{-2i\beta})(1 - re^{-2i\alpha})\zeta_{\rho\sigma} - t_0' t' e^{-i\beta} e^{-i\alpha} \eta_{\rho\sigma}}{(1 - r_0^2 e^{-2i\beta})(1 - r^2 e^{-2i\alpha})} \qquad [10c]$$

and

$$A^T_{\rho\sigma} = Lt_0 t \frac{t' e^{-i\alpha}(1 - r_0 e^{-2i\beta})\zeta_{\rho\sigma} - t_0' e^{-i\beta}(1 - re^{-2i\alpha})\eta_{\rho\sigma}}{(1 - r_0^2 e^{-2i\beta})(1 - r^2 e^{-2i\alpha})}. \qquad [10d]$$

We must now obtain equations for the intensity of the scattered light.

Intensity of the Scattered Light

In the Fourier series (1) and (5) the period a is large with respect to λ. Consequently the waves diffracted by successive Fourier terms will have only minor differences in their directions (see Eqs. [2]) which means that the diffracted light, called scattered light here, will be diffuse.

Mandelstam (2) obtained for the relative intensity of the scattered light seen from the point of observation in a solid angle $d\Omega$

$$\frac{I}{I_0} = |A_{\rho\sigma}|^2 \Delta\rho\Delta\sigma. \qquad [11]$$

The number of waves, $\Delta\rho\Delta\sigma$, falling into $d\Omega$ in medium 1 may be obtained from Eqs. [2*a*, *b*], which connect ρ and σ with θ and φ (remember that φ is about zero).

$$\Delta\rho\Delta\sigma = \left(\frac{a}{\lambda_1}\right)^2 \sin\theta \cos\theta \, d\theta \, d\varphi = \left(\frac{a}{\lambda_1}\right)^2 \cos\theta \, d\Omega.$$

Making this substitution Eq. [11] becomes

$$\frac{I}{I_0} = |A_{\rho\sigma}|^2 \left(\frac{a}{\lambda_1}\right)^2 \cos\theta \, d\Omega. \qquad [11a]$$

For convenience we introduce a dimensionless quantity S, the "surface scattering ratio" defined as

$$S = \frac{I \cos\theta}{I_0 \, d\Omega}. \qquad [12]$$

As $d\Omega = d\omega \cos\theta/r^2$, where $d\omega$ is the area of the surface enclosed by $d\Omega$ at a distance r, we may write

$$S = \frac{Ir^2}{I_0 \, d\omega}; \qquad [12a]$$

thus S is the intensity relative to the intensity of the incident light, of the light scattered by 1 cm.^{2} of the interface and observed at a distance of 1 cm.

Substitution of Eq. [12] into Eq. [11a] gives:

$$S(\theta_0, \theta, \varphi) = |A_{\rho\sigma}|^2 \left(\frac{a}{\lambda_1}\right)^2 \cos^2\theta. \qquad [13]$$

For a single boundary $A_{\rho\sigma}$ may be obtained from Eq. [3*b*], whereas for a film $A_{\rho\sigma}$ has to be substituted by $A^R_{\rho\sigma}$ and $A^T_{\rho\sigma}$ defined in Eqs. [10*c*] and [10*d*].

Thus far we have not specified the corrugations of the boundary; the Fourier coefficients $\zeta_{\rho\sigma}$ and $\eta_{\rho\sigma}$ which are needed in Eqs. [9] and [10] are still unknown. In the next section we will calculate the corrugations of a film of liquid.

Corrugations of a Liquid Film

The surface of a liquid will corrugate irregularly owing to the Brownian motion of the molecules. The Fourier coefficients (given in Eq. [5]) will fluctuate independently (2) and we need to find the mean square value of these coefficients.

The calculation is based on an equipartition theorem due to Einstein (13, 2): when the state of a system near equilibrium may be described by a set of parameters α_i and the work which has to be performed to bring the system by a "thermodynamical" path from equilibrium to that state may be written as

$$W = \sum_i \beta_i \alpha_i^2, \qquad [14]$$

then the mean value of each term in the series equals $kT/2$; hence

$$\overline{\alpha_i^2} = \frac{kT}{2\beta_i}. \qquad [14a]$$

The β_i's are constants of the system considered. In our case the Fourier coefficients $\zeta_{\rho\sigma}$, $\eta_{\rho\sigma}$ take the place of the α_i's.

The expression for the work, W, needed to create a corrugation in a liquid surface consists of several terms. First there is the work needed to extend the surface area

$$W_1 = \gamma \Delta\omega, \qquad [15]$$

where γ is the surface tension. The change in interface area, $\Delta\omega$, may be closely approximated by the following integral which is valid for small corrugations.

$$\Delta\omega = \frac{1}{2} \iint_{-\frac{1}{2}a}^{+\frac{1}{2}a} \left[\left(\frac{\partial z_{12}}{\partial x}\right)^2 + \left(\frac{\partial z_{12}}{\partial y}\right)^2 + \left(\frac{\partial z_{23}}{\partial x}\right)^2 + \left(\frac{\partial z_{23}}{\partial y}\right)^2\right] dx\, dy. \qquad [16]$$

A soap film, however, is at least a two-component system and since the ratio of surface area to volume may be quite large we might expect that γ depends on $\Delta\omega$ (surface elasticity) as pointed out by Gibbs. In this case Eq. [15] may be approximated to second order by a power series development giving

$$W_1 = \gamma_0 \Delta\omega + \frac{1}{2}\frac{\partial\gamma}{\partial\omega}(\Delta\omega)^2 = \left(\gamma_0 + \frac{\Delta\gamma}{2}\right)\Delta\omega. \qquad [15a]$$

Reflection (with the aid of the Gibbs isotherm equation) on the magnitude of $\Delta\gamma$ under the extremely small dilatation $\Delta\omega$ implies that $\gamma_0 \gg \Delta\gamma/2$, where γ_0 is the static surface tension of the system. We therefore neglect the $\Delta\gamma$ term from W_1.

Further, work is needed to displace material against gravity. The amount of work, however, is negligible for horizontal films and even zero for vertical films.

By making use of Eqs. [5], W_1 becomes

$$W_1 = \tfrac{1}{2}\gamma a^2 p^2 \sum [\zeta_{\rho\sigma}\zeta^*_{\rho\sigma} + \eta_{\rho\sigma}\eta^*_{\rho\sigma}](\rho^2 + \sigma^2). \qquad [17]$$

In the third place there is an extra energy contribution, not found in the case of a single boundary, due to correlation of the corrugations of the upper and lower boundaries of the film (due to molecular forces, to be specified later on).

If the free energy of interaction per unit area is given by $V(h)$, as a function of the thickness of the film, then the work dissipated in performing a small corrugation is to the second order:

$$V(h + z_{12} - z_{23}) - V(h) = \frac{dV}{dh}(z_{12} - z_{23}) + \frac{1}{2}\frac{d^2V}{dh^2}(z_{12} - z_{23})^2 \qquad [18]$$

and, integrated over the film area:

$$W_2 = \frac{dV}{dh}\iint_{-\frac{1}{2}a}^{+\frac{1}{2}a}(z_{12} - z_{23})\,dxdy + \frac{1}{2}\frac{d^2V}{dh^2}\iint_{-\frac{1}{2}a}^{+\frac{1}{2}a}(z_{12} - z_{23})^2\,dxdy. \qquad [19]$$

Using Eq. [5] we see that the first term vanishes, whereas the second term becomes:

$$W_2 = \frac{1}{2}\frac{d^2V}{dh^2}\sum(\zeta_{\rho\sigma} - \eta_{\rho\sigma})(\zeta^*_{\rho\sigma} - \eta^*_{\rho\sigma}). \qquad [19a]$$

In order to apply Eqs. [14] and [14a] the total amount of work $W = W_1 + W_2$ must now be written as a sum of squares. The values of the squares $|\zeta_{\rho\sigma}|^2$, $|\eta_{\rho\sigma}|^2$, and $|\zeta_{\rho\sigma} - \eta_{\rho\sigma}|^2$ are not independent, however. To overcome this difficulty we introduce a new variable

$$\phi_{\rho\sigma} = \eta_{\rho\sigma} - c_{\rho\sigma}\zeta_{\rho\sigma} \qquad [20]$$

with

$$c_{\rho\sigma} = \frac{b}{a_{\rho\sigma} + b}, \qquad [20a]$$

$$a_{\rho\sigma} = \tfrac{1}{2}\gamma a^2 p^2(\rho^2 + \sigma^2), \qquad [20b]$$

and

$$b = \frac{1}{2}\frac{d^2V}{dh^2}. \qquad [20c]$$

Equation [20*b*] may be transformed according to Eq. [2]. In medium 1 we obtain

$$a_{\rho\sigma} = \tfrac{1}{2}\gamma a^2 k_1^2(\sin^2\theta - 2\sin\theta_0 \sin\theta\cos\varphi + \sin^2\theta_0); \qquad [20d]$$

and for $\varphi = 0$

$$a_{\rho\sigma} = \tfrac{1}{2}\gamma a^2 k_1^2(\sin\theta - \sin\theta_0)^2. \qquad [20e]$$

For the total work we can now write:

$$W = W_1 + W_2 = \sum (a_{\rho\sigma} + b)\phi_{\rho\sigma}\phi^*_{\rho\sigma} + \sum (a_{\rho\sigma} + b)(1 - c^2_{\rho\sigma})\zeta_{\rho\sigma}\zeta^*_{\rho\sigma}. \qquad [21]$$

From Eq. [14*a*] we obtain:

$$\overline{\phi_{\rho\sigma}\phi^*_{\rho\sigma}} = \frac{kT}{2(a_{\rho\sigma} + b)}; \qquad [21a]$$

$$\overline{\zeta_{\rho\sigma}\zeta^*_{\rho\sigma}} = \frac{kT}{2(a_{\rho\sigma} + b)}\,\frac{1}{1 - c^2_{\rho\sigma}}. \qquad [21b]$$

For reasons of symmetry $\overline{\eta_{\rho\sigma}\eta^*_{\rho\sigma}} = \overline{\zeta_{\rho\sigma}\zeta^*_{\rho\sigma}}$ and $\overline{\zeta_{\rho\sigma}\eta^*_{\rho\sigma}} = \overline{\zeta^*_{\rho\sigma}\eta_{\rho\sigma}} =$ real,[1] whereas the value of this quantity may be obtained from Eqs. [20], [21], and [21*a*]:

$$\overline{\phi_{\rho\sigma}\phi^*_{\rho\sigma}} = (1 + c^2_{\rho\sigma})\overline{\zeta_{\rho\sigma}\zeta^*_{\rho\sigma}} - 2c_{\rho\sigma}\overline{\zeta_{\rho\sigma}\eta^*_{\rho\sigma}}. \qquad [21c]$$

Thus we obtain ultimately:

$$\overline{\zeta_{\rho\sigma}\zeta^*_{\rho\sigma}} = \overline{\eta_{\rho\sigma}\eta^*_{\rho\sigma}} = \frac{\tfrac{1}{2}kT}{a_{\rho\sigma} + 2b}\left[1 + \frac{b}{a_{\rho\sigma}}\right]; \qquad [21d]$$

$$\overline{\zeta_{\rho\sigma}\eta^*_{\rho\sigma}} = \frac{\tfrac{1}{2}kT}{a_{\rho\sigma} + 2b}\left[\frac{b}{a_{\rho\sigma}}\right]. \qquad [21e]$$

These equations show that for $b \ll a_{\rho\sigma}$ the cross coefficient $\overline{\zeta_{\rho\sigma}\eta^*_{\rho\sigma}}$ is

[1] When $\zeta_{\rho\sigma} = a + bi$, and $\eta_{\rho\sigma} = c + di$, then

$$\overline{\zeta_{\rho\sigma}\eta^*_{\rho\sigma}} = \overline{ac} + \overline{bd} - i(\overline{ad} - \overline{bc}), \quad \text{and} \quad \overline{\zeta^*_{\rho\sigma}\eta_{\rho\sigma}} = \overline{ac} + \overline{bd} + i(\overline{ad} - \overline{bc}).$$

For reasons of symmetry, $\overline{ad} = \overline{bc}$.

small and the correlation will be weak. For $b \gg a_{\rho\sigma}$ the cross coefficient is equal to the main coefficients: $\overline{\zeta_{\rho\sigma}\eta^*_{\rho\sigma}} = \overline{\zeta_{\rho\sigma}\zeta^*_{\rho\sigma}} = \overline{\eta_{\rho\sigma}\eta^*_{\rho\sigma}}$ and the correlation will be strong. Hence in the first case the corrugations of the two boundaries will fluctuate randomly whereas in the last case the film corrugates as a whole: $(\zeta_{\rho\sigma} = \eta_{\rho\sigma})$.

The intensity of the scattered light may be calculated from these equations and the Eqs. [10*c*], [10*d*], and [13].

Light-Scattering Equations and Discussion

The light scattering of a liquid film (observed in the plane of incidence with the incident electrical wave polarized normal to the plane of incidence) may now be obtained by combining the Eqs. [13], [10*c*, 10*d*], and [21*d*, 21*e*]. The "reflected" scattering is

$$S^R = \frac{\frac{1}{4}(n^2 - 1)^2(kT/\lambda_1^2)}{\gamma\,(\sin\theta - \sin\theta_0)^2 + 2Q}\left[G_0 G_1 + \frac{QG_0 G_3}{\gamma\,(\sin\theta - \sin\theta_0)^2}\right], \qquad [22]$$

and the "transmitted" scattering

$$S^T = \frac{\frac{1}{4}(n^2 - 1)^2(kT/\lambda_1^2)}{\gamma(\sin\theta - \sin\theta_0)^2 + 2Q}\left[G_0\, G_2 + \frac{QG_0\, G_4}{\gamma(\sin\theta - \sin\theta_0)^2}\right]. \qquad [23]$$

Here

$$G_0 = \frac{t^2 t_0^{\,2}}{R(r^2, \alpha)R(r_0^2, \beta)}. \qquad [24a]$$

$$G_1 = R(r, \alpha)R(r_0, \beta) + t'^2 t_0'^2. \qquad [24b]$$

$$G_2 = t'^2 R(r_0, \beta) + t_0'^2 R(r, \alpha). \qquad [24c]$$

$$G_3 = G_1 - 2t'^2 t_0'^2 \cos\alpha\cos\beta + 2tt't_0t_0' \sin\alpha\sin\beta. \qquad [24d]$$

$$G_4 = G_2 - 2t'^2 t_0'^2 \cos\alpha\cos\beta - 2tt't_0t_0' \sin\alpha\sin\beta. \qquad [24e]$$

$$R(r, \alpha) = 1 + r^2 - 2r\cos 2\alpha. \qquad [25a]$$

$$R(r_0, \beta) = 1 + r_0^2 - 2r_0\cos 2\beta. \qquad [25b]$$

$$R(r^2, \alpha) = 1 + r^4 - 2r^2\cos 2\alpha. \qquad [25c]$$

$$R(r_0^2, \beta) = 1 + r_0^4 - 2r_0^2\cos 2\beta. \qquad [25d]$$

$$Q = \frac{\lambda_1^2}{4\pi^2}\frac{d^2V}{dh^2}. \qquad [26]$$

We may recall here that β was defined by Eq. [6*f*]; α by Eq. [7*d*]; r_0, t_0, t_0' by the Eqs. [6*g*, 6*h*]; and r, t, t' by the Eqs. [7*e*, 7*f*]; r_0 and r are *negative*.

Equation [22] may be compared with the equation derived by Mandelstam (2) for the scattering by a single surface. Using our symbols and neglecting, as was done for the film, the very small contribution to the

work of corrugation by gravity this equation reads:

$$S^R = \frac{\frac{1}{4}(n^2 - 1)^2(kT/\lambda_1^2)t_0^2t^2}{\gamma(\sin\theta - \sin\theta_0)^2} . \qquad [27]$$

It appears that in the case of a film $t_0^2t^2$ is replaced by G_0G_1 and terms describing the interaction between the film surfaces are added.

The expressions defined in [24] and [25] are complicated functions of the angles of incidence θ_0 and of observation θ, and of the refractive index and thickness of the film. Further Q is an unknown function of the thickness of the film.

In the limiting case $\alpha/\beta = 1$ (thus $\theta = \theta_0$; $r = r_0$) the G_i's are periodic functions of h (through β); G_0 , G_1 , and G_2 are maximal at $\beta = 0, \pi$, etc., and minimal at $\beta = \pi/2, 3\pi/2$, etc., whereas G_3 has maxima at $\beta = \pi/2, 3\pi/2$, etc., and minima at $\beta = 0, \pi$, etc.; G_4 is zero.

The values of the extrema are

$$\max\ (G_0) = 1/t_0'^4 \qquad \min\ (G_0) = t_0^4/(t_0^2 - t_0 + t_0')^4$$

$$\max\ (G_1) = 2t_0'^4 \qquad \min\ (G_1) = t_0^4 + t_0'^4$$

$$\max\ (G_2) = 2t_0'^4 \qquad \min\ (G_2) = 2t_0^2t_0'^2$$

$$\max\ (G_3) = 4(t_0^2 - t_0 + t_0')^2 \qquad \min\ (G_3) = 0$$

$$\max\ (G_4) = 0 \qquad \min\ (G_4) = 0$$

When $\alpha/\beta \neq 1$, the strict periodicity disappears. But since $\alpha/\beta (= \cos\theta'/\cos\theta_0')$ does not deviate much from unity, we may expect a shift of the extrema and an increasing smoothening of the functions only when β does not exceed a few periods.

We next consider two limiting cases: *i.e.*, very small and very large values of Q.

Weak Interaction between Corrugations: $Q \ll \gamma(\sin\theta - \sin\theta_0)^2$

When the free energy of deformation of two opposite boundary elements of the film depends largely upon the increase of surface area and far less on the distance of separation the two boundaries will corrugate independently. This is expressed by the condition $Q \ll \gamma(\sin\theta - \sin\theta_0)^2$.

Equations [22] and [23] are now transformed into:

$$S^R = \frac{\frac{1}{4}(n^2 - 1)^2(kT/\lambda_1^2)}{\gamma(\sin\theta - \sin\theta_0)^2} G_0 G_1 \qquad [28]$$

$$S^T = \frac{\frac{1}{4}(n^2 - 1)^2(kT/\lambda_1^2)}{\gamma(\sin\theta - \sin\theta_0)^2} G_0 G_2 . \qquad [29]$$

In this limiting case the scattering does not depend on Q. The products G_0G_1 and G_0G_2 may be obtained from Eq. [24]. From the discussion of

these G-functions, given above, it will be apparent that these products have their first maximum at $h \to 0\,(\alpha \simeq \beta \to 0)$ and their first minimum at $\beta = \pi/2$ approximately. This is illustrated for G_0G_1 in Fig. 5.

Strong Interaction between Corrugations: $Q \gg (\sin\theta - \sin\theta_0)^2$

In this case the film will corrugate as a whole and the light scattering is:

$$S^R = \frac{\frac{1}{8}(n^2-1)^2(kT/\lambda_1^2)}{\gamma(\sin\theta - \sin\theta_0)^2}\, G_0\, G_3\,; \qquad [30]$$

$$S^T = \frac{\frac{1}{8}(n^2-1)^2(kT/\lambda_1^2)}{\gamma(\sin\theta - \sin\theta_0)^2}\, G_0\, G_4\,. \qquad [31]$$

Similar to the former case the scattering does not depend explicitly on Q. The dependence on h, however, is just the opposite: G_0G_3 and G_0G_4 are minimal for $h \to 0$, and their first maximum is approximately at $\alpha \simeq \beta = \pi/2$. A graph of G_0G_3 is also given in Fig. 5.

At intermediate values of Q the full Eqs. [22] and [23] must be used.

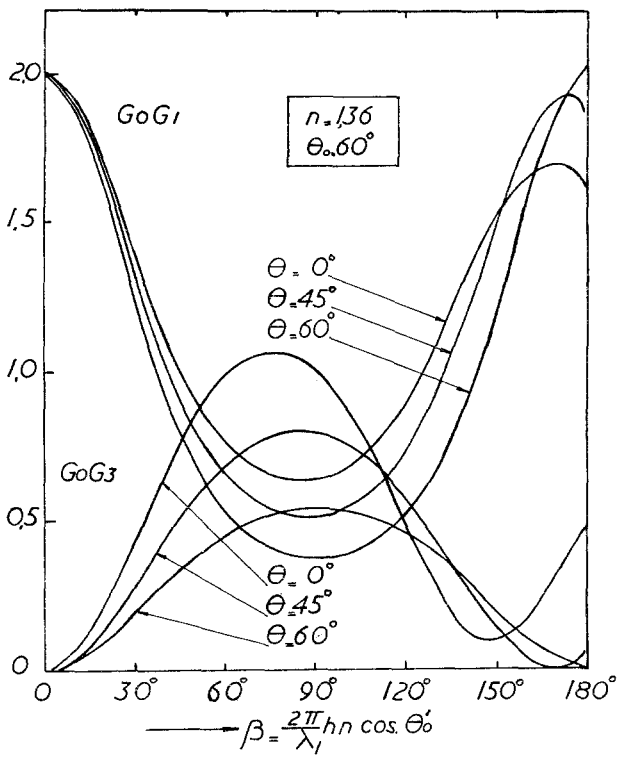

FIG. 5. Intensity of the scattered light for uncorrelated (G_0G_1) and fully correlated corrugations (G_0G_3) of film surfaces as a function of film thickness at different angles of observation.

Comparison of Scattering with Reflection and Transmission

The fractions of light which are reflected and transmitted by the film can be obtained easily from Eqs. [6*b*, *e*]:

$$R = |\psi^A|^2 = \frac{4r_0^2 \sin^2\beta}{1 + r_0^4 - 2r_0^2 \cos 2\beta}; \qquad [32]$$

$$T = |\psi^D|^2 = \frac{(1 - r_0^2)^2}{1 + r_0^4 - 2r_0^2 \cos 2\beta}; \qquad [33]$$

$$R + T = 1.$$

Here R and T are the reflection and transmission coefficients of the film.

From these equations it follows that R is minimal for $\beta = 0, \pi$, etc., and maximal for $\beta = \pi/2, 3\pi/2$, etc.; the opposite applies to T.

From the discussion of light scattering for small Q and large Q, given above, one may conclude that for small Q the light scattering (both S^R and S^T) is minimal if R is maximal, whereas for large Q the opposite is true.

Since films showing maxima and minima in their reflection are rather thick, we may expect Q to be small, and that reflection and scattering will have opposite extrema. This was indeed observed experimentally.

Extrapolation Formulas

In order to obtain the values of γ and Q from experimental data it will be advantageous to write the Eqs. [22] and [23] in a form suitable for extrapolation, which is possible if Q is not too large. At the same time we will take into account some residual volume scattering of the film and that part of its surroundings seen by the light detector. The volume scattering of the film depends on its constitution and will be considered more closely in the following section. The volume scattering of the surroundings depends on the scattering power of the media 1 and 3 (e.g., air). At present it will be sufficient to know that the residual volume scattering, which will be denoted by A, is small and for the polarization state of the light used, independent of θ.

For convenience we make the following substitutions:

$$K = \tfrac{1}{4}(n^2 - 1)^2 (kT/\lambda_1^2); \qquad [35]$$

$$\Theta = (\sin\theta - \sin\theta_0)^{-2}; \qquad [36]$$

$$\chi = G_3/G_1 < 2; \qquad [37]$$

then Eq. [22] may be transformed into:

$$S^R = A + \frac{KG_0 G_1}{\gamma}\Theta\left[1 + \frac{\chi Q}{\gamma}\Theta\right]\left[1 + \frac{2Q}{\gamma}\Theta\right]^{-1}, \qquad [38]$$

or, neglecting powers of Θ higher than the second,

$$S^R = A + \frac{KG_0 G_1}{\gamma}\Theta\left[1 - \frac{(2 - \chi)Q}{\gamma}\Theta\right]. \qquad [39]$$

One must keep in mind here that this expansion is valid only if

$$(2Q\Theta/\gamma) \ll 1.$$

If, for example, at $\theta_0 = 60°$ the scattering is measured between approximately 45° and 0°, then $4/3 \leqq \Theta \leqq 40$, so in that case $2Q/\gamma$ must be small compared to 0.025.

The value of A may be obtained from a plot of S^R against Θ. The slope at small Θ is equal to KG_0G_1/γ and will decrease with increasing Θ by an amount depending on Q. The values of γ and Q may be obtained from intercept and slope of $(S_R - A)/(KG_0G_1\Theta)$ against Θ. It is, however, advantageous to plot the reciprocal: $(KG_0G_1\Theta)/(S_R - A)$ as a function of Θ.

The factor χ, which is (much) smaller than 2, allows the expansion of $[1 + (\chi Q\Theta/\gamma)]^{-1}$ to converge more rapidly than that of $[1 + (2Q\Theta/\gamma)]^{-1}$ (see Fig. 5 remembering that $\chi = G_3/G_1$). This implies that the graph is linear over a longer range.

Doing so, we obtain

$$\frac{KG_0\,G_1}{S_R - A}\,\Theta = \gamma + (2 - \chi)Q\Theta + \cdots; \qquad [40]$$

γ and $(2 - \chi)Q$ may now be obtained from a plot of Eq. [40] against Θ.

Light Scattering by A Soap Film

We will consider three points: the contribution of the bulk scattering of the film; the influence of the adsorbed layer on the optical properties of the film; and the magnitude of the interaction parameter Q.

Bulk Scattering

Besides surface scattering, a soap film will also give bulk scattering; the total scattering per cm.^{2} of soap film is:

$$S(\text{total}) = S(\text{surface}) + R_\theta h. \qquad [41]$$

Here R_θ is the volume scattering per cm.^{3} (known as Rayleigh's ratio) and h is the thickness of the film. Let us calculate the order of magnitude of the volume scattering and compare this with the surface scattering, which has the order of magnitude 7.5×10^{-7} (see introduction). A 10% solution of sodium lauryl-sulfate, for example, has per cm.^{3} a volume scattering close to 25×10^{-5} cm.$^{-1}$. The volume scattering per cm.^{2} soap film is $25 \times 10^{-5}\ h$; this is less than 1% of the surface scattering if $25\ h \times 10^{-5} < 7.5 \times 10^{-9}$, *i.e.*, if $h < 3000\ A$. Hence in most cases the volume scattering may be neglected.

Adsorbed Layers

In the light-scattering theory given above, the film was considered to be homogeneous. A soap film, however, is a three-layer system and the

theory should be extended to a system of three homogeneous layers: an aqueous layer sided by two "oil" layers (hydrophobic tails of the soap ions). The adsorbed soap layers, however, are very thin (20 A.). As a first approximation, we assume that these "oil" layers corrugate as a whole (with constant thickness) with the surfaces of the aqueous soap layer. Then their contribution to the light scattering will be negligible.

The Interaction between the Surfaces

The most interesting point of the discussion is the investigation of the magnitude of molecular interactions in the soap film by means of their effect on light scattering.

In order to proceed we must adopt a model for the structure of a soap film. We will use here a picture composed from suggestions made by several authors and discussed recently by Overbeek (11). The film consists of a bulk layer of soap solution between two layers of adsorbed soap ions. The ionic heads face the soap solution and the hydrophobic tails the surrounding atmosphere (air).

For the free energy of interaction per cm.^{2} soap film we write after Duyvis (17)

$$V = \frac{64nkT}{\kappa}\Phi^2 e^{-\kappa(h-2\delta)} - \frac{A}{12\pi h^2} + Ph. \qquad [42]$$

Here

n = concentration of 1-1 electrolyte in molecules/cm.^{3}
k = Boltzmann's constant.
T = absolute temperature.
$1/\kappa = \sqrt{\epsilon kT/8\pi e^2 n}$ = double layer thickness.
Φ = $\tanh(e\psi_0/4kT)$.
ψ_0 = surface potential (= potential in the plane of the ionic heads).
h = total thickness of the soap film.
δ = thickness of the adsorbed soap layer (hydrocarbon tails).
A = van der Waals' constant.
P = pressure difference between inside of the film and the surrounding atmosphere.

A stable equilibrium will occur when V is minimal, i.e., when $dV/dh = 0$ and d^2V/dh^2 is positive.

The interaction parameter Q defined in Eq. [26] can be calculated from d^2V/dh^2.

By introducing

$$B = \frac{8\epsilon k^2T^2}{\pi e^2}\Phi^2 e^{2\kappa\delta} = 1.47 \times 10^{-6}\Phi^2 e^{2\kappa\delta}, \qquad [43]$$

Equation [42] can be somewhat condensed to

$$V = B\kappa e^{-\kappa h} - \frac{A}{12\pi h^2} + Ph. \qquad [44]$$

At sufficiently small thickness of the film the interaction parameter Q defined in Eq. [26] can be found from light scattering and from it the value of d^2V/dh^2 can be calculated.

Differentiation of Eq. [44] shows that

$$\frac{d^2V}{dh^2} = B\kappa^3 e^{-\kappa h} - \frac{A}{2\pi h^4} \qquad [45]$$

and that d^2V/dh^2 can be considered as a function of h with parameters A, B, and κ.

After a sufficiently long drainage period the film will reach an equilibrium thickness for which $dV/dh = 0$ or

$$dV/dh = 0 = -B\kappa^2 e^{-\kappa h} + \frac{A}{6\pi h^3} + P. \qquad [46]$$

This gives another relation between A, B, and κ. These relations can be used to determine A, B, and κ from measurable properties of the film.

Experimental

To test the above theory some preliminary experiments were performed.

Apparatus

An apparatus was constructed similar to that of Brice-Phoenix and described by Brice, Halwer, and Speiser (18). The light source was a super high pressure mercury lamp (Philips SP500) from which the green (546 mμ) and blue (436 mμ) lines were selected by interference filters. The closed light-scattering cell was made of black *perspex* (I.C.I. acrylic sheet) and had a cylindrical window to observe the scattering (see Fig. 6). The atmosphere within the closed cell was always saturated with respect to the soap solution. The vertically polarized primary light beam (10 × 3 mm.) was focused on the center of the cell via a tube provided with appropriate diaphragms and disappeared into a Rayleigh horn. The soap film was suspended on a rectangular glass frame (24 × 40 mm.) which could be rotated around the vertical axis. The primary beam reflected by the soap film was intercepted by a mirror of polished absorption

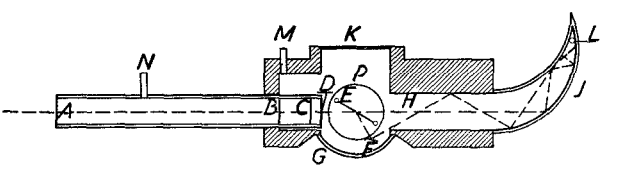

FIG. 6. Top view of light scattering cell. A, entrance window; B, C, and D, slits; E, glass frame with soap film; F, black mirror; G, window; H, polished walls; J, Rayleigh horn; K, extra window; L, M, and N, in and outlets for vapor; P, cylindrical vessel for soap solution.

glass and reflected into the Rayleigh horn. A cylindrical vessel containing the soap solution was located in the cell below the glass frame. This vessel was moved up and down in order to draw the film. A light detector, supplied with a photomultiplier tube (R.C.A. 1P28), was moved around the center of the cell. The entire light spot on the soap film was "seen" by the photo tube. The light scattering could be measured to within 15° of the reflected beam.

Calibration

The photometer was calibrated with a "standard" diffusing reflector. Magnesium oxide from burning magnesium ribbon was smoked into a copper surface to a depth of *ca.* 1 mm. The MgO layer obtained in this way was smooth and probably had a reflectance of 96%–99% (19). The incident beam was attenuated with neutral filters. The scattering from the MgO surface measured at different angles followed the cosine law of Lambert.[2] The accuracy of the calibration was presumably not higher than 10%.

Qualitative Experiments

Some observations were made with soap films drawn from solutions of *Teepol* (a commercial product consisting of a mixture of petroleum sulfonates) in a concentration of a few per cent with glycerol content up to 80%. After a fresh film was drawn in the light-scattering cell a very weak diffuse light spot could be seen on the surface. The intensity of the spot varied with the angle of observation, being greatest near the reflected and transmitted primary light beam. The intensity also depended upon the angle of incidence, being greatest at grazing incidence ($\theta_0 \approx 90°$).

Although no special care was taken to remove dust from the solution, only a few dust particles could be seen on freshly drawn films. Draining appeared to eliminate these dust particles and the light spot then became entirely diffuse. The angular dependence observed was in qualitative agreement with the predominant angularly dependent factor $(\sin \theta_0 - \sin \theta)^{-2}$.

As the film drained weakly colored fringes appeared with white incident light, and dark and light fringes with monochromatic light. On bringing the eye very near to the reflected beam, the scattered light could be seen together with a small part of the reflected beam, clearly revealing that the dark fringes of the scattered light met the light fringes of the reflected light. This phenomenon is in accordance with the theory given above. The fringes became sharper when the refractive index of the solutions was higher (higher glycerol content) and when the angles of incidence and observation were larger. This was to be expected because in both cases the maxima and minima of the function G_0G_1 become sharper.

[2] In our notation, Lambert's law is S^R (ideal diffusor) $= \cos \theta_0 \cos \theta/\pi$.

On further draining the light reflected from the film took on a silvery grey appearance, and later a sharp border appeared at the top of the frame separating the grey film from the (much thinner) black film. The light scattering remained diffuse up to a region near the boundary of the grey and black portions of the film where the intensity of the scattered light brightened up appreciably owing to irregular streaming in the film. Scattering of the black film itself could not be observed, even with white light. This can be explained if it is assumed that in a black film the interaction parameter Q is very large giving rise to a very small scattering (see Eq. [30]).

Similar results were obtained with nonionic detergents (higher alcohols condensed with polyethyleneoxide).

A quite different behavior was observed, however, when a small percentage of an ionic detergent (*i.e.*, sodium lauryl sulfate, or sodium dodecyl benzene sulfate) was added to the nonionic detergent. The sudden appearance of the black film region was not observed, but the grey film drained continuously until it remained stable for at least six weeks at what was presumably the equilibrium position (*cf.* reference 11, 17). The reflection and therefore the thickness of this "equilibrium" film was greater than those of the formerly described black film.

This continuously draining film was a good system for the quantitative experiments which will now be described.

Quantitative Experiments

The films were drawn from a solution of 640 mg. of a nonionic detergent in which octylphenol was condensed with about 7 oxyethylene groups (*Servo*, Delden, the Netherlands) with 8.7 mg. purified sodium lauryl sulfate and 20 ml. glycerol (*Analar*) in 100 ml. distilled water. The surface tension of this solution (determined using the ring method) was 33 dynes/cm. and the refractive indices at 546 mμ and 436 mμ were 1.360 and 1.365, respectively.

The light scattering was measured at $\theta_0 = 60°$ and the angle of observation, θ, was varied between 0° and 45° at different draining times.

Immediately after formation of a new film, the draining was rather fast and the scattering drifted during the measurement. Therefore only experiments in which identical results were obtained in going from 0° to 45° and back from 45° to 0° will be reported.

The thickness of the film was determined from the intensity of the reflected light compared with its maximum value at $h = \lambda_2/4 \cos \theta_0'$ (see Eqs. [32] and [6*f*]). For n the refractive index of the solution was used.

The results are shown in Fig. 7 where the light scattering ratio S^R is plotted against $\Theta = (\sin \theta_0 - \sin \theta)^{-2}$ (see Eq. [39]).

From $h = 530$ A. to $h = 320$ A. the plots are linear in Θ indicating that

the second term containing the interaction parameter Q is small. The slope is equal to KG_0G_1/γ, and its increase with decreasing thickness may be expected from the increase of G_0G_1 (see Fig. 5).

The curve deviates from linearity in the range from $h = 320$ A. to $h = 130$ A. and this can be explained by an increase of Q. It is further apparent that the bulk scattering, A, is negligible here.

The values of γ and Q may be obtained from a plot of the form suggested by Eq. [40]. Since several lines drawn according to Eq. [40] nearly coincide, the function $K\Theta/(S_R - A)$ is plotted instead of $KG_1G_0\Theta/(S_R - A)$. This is permissible because G_0G_1 is nearly independent of θ and thus of Θ (see Fig. 5) so that to a good approximation

$$\frac{K\Theta}{S_R - A} = \frac{\gamma}{G_0\,G_1} + \frac{(2-\chi)Q\Theta}{G_0\,G_1} \qquad [47]$$

will linearly relate $K\Theta/(S_R - A)$ to Θ.

The results for two wave lengths, $\lambda_1 = 546$ mμ and 436 mμ, respectively, are presented in Figs. 8 and 9. In the calculation of K, from Eq. [35], the refractive index of the solution was used. The linearity of the plots indicates that the pronounced angular dependence is adequately described by the function $\Theta = (\sin\theta_0 - \sin\theta)^{-2}$ and that the higher order

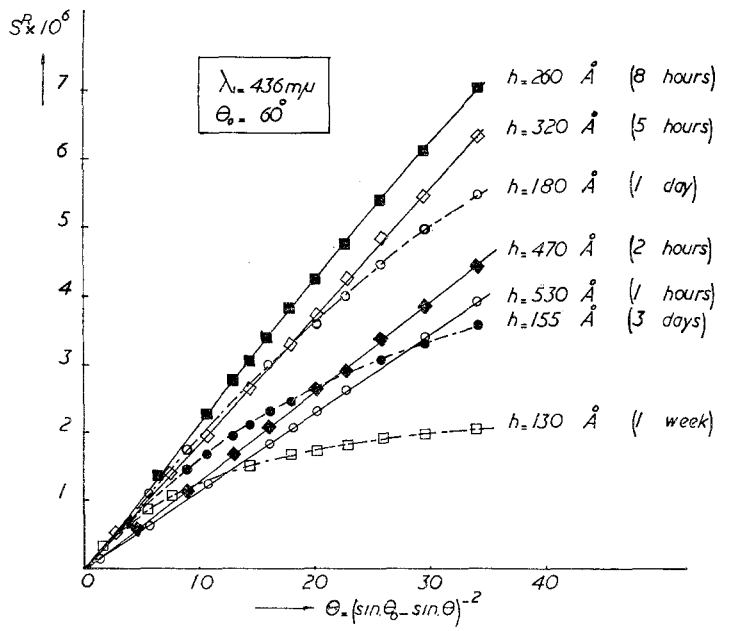

FIG. 7. Light scattering of a soap film as a function of $(\sin\theta_0\text{-}\sin\theta)^{-2}$ at different thicknesses and draining times. Several points near the origin are omitted for clarity.

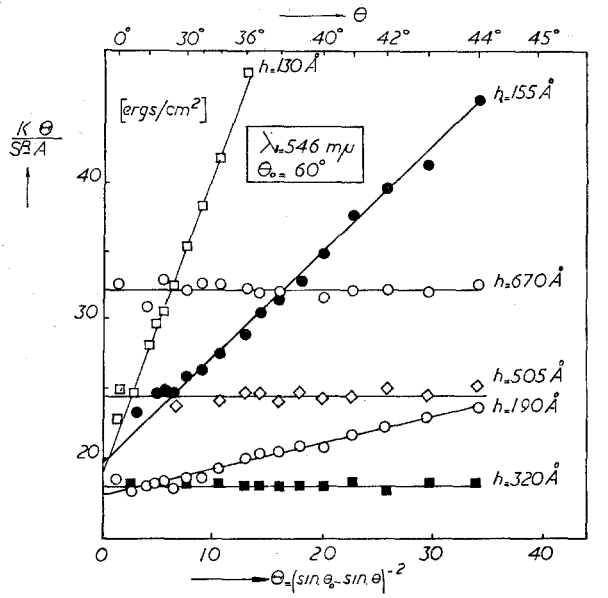

FIG. 8. Reduced light scattering of a soap film as a function of $(\sin \theta_0 - \sin \theta)^{-2}$ at different thicknesses and at $\lambda = 546$ mμ. The line for $h = 130$ A. remains linear up to $\Theta = 35$.

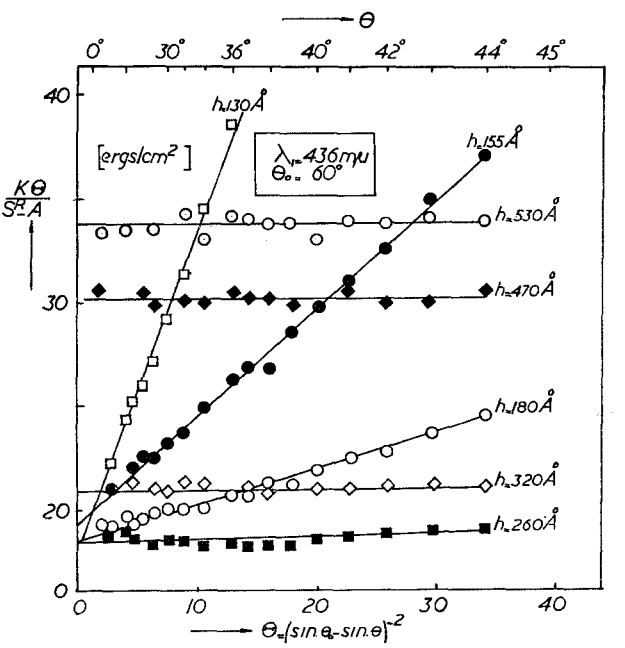

FIG. 9. The same as Fig. 8 but at $\lambda = 436$ mμ.

terms of the power series expansion can indeed be ignored. From the intercepts and slopes in the Figs. 8 and 9 and from the functions G_0G_1 and χ calculated from Eqs. [24*a*, *b*] and [24*b*, *d*] γ, Q, and d^2V/dh^2 may be obtained (see Tables I and II).

The values of γ found are scattered but the agreement between the mean value 32.6 ergs/cm.^{2} at $\lambda = 546$ mμ and 32.8 ergs/cm.^{2} at $\lambda = 436$ mμ supports the λ^2 dependence of surface scattering. The results are also in good accord with the value of the surface tension of the soap solution of 33 dynes/cm. found by the ring method.

The values of d^2V/dh^2 for both wave lengths are in satisfactory agreement, confirming the λ^2 dependence of Q. In Fig. 10 log (d^2V/dh^2) is plotted as a function of h.

There are two terms in d^2V/dh^2: one due to double layer repulsion and the other to van der Waals'-London attraction; the former contains the

TABLE I

Calculation of the Interaction Parameter Q and of d^2V/dh^2 from the Data of Fig. 8

$\lambda = 546$ mμ

h [A.]	$\frac{\gamma}{G_0G_1}$	G_0G_1	γ [ergs. cm^{-2}]	$\frac{(2-\chi)Q}{G_0G_1}$	$\frac{2-\chi}{G_0G_1}$	Q	$\frac{d^2V}{dh^2} \times 10^{-10}$ [ergs. cm^{-4}]
130	19	1.93	36.5	2.20	1.02	2.15	2.85
155	19.5	1.90	37	0.76	1.03	0.74	0.98
190	17.5	1.84	32	0.19	1.05	0.18	0.24
320	18	1.60	29				
505	24.5	1.25	30.5				
670	32	0.97	31				

TABLE II

Calculation of the Interaction Parameter Q and of d^2V/dh^2 from the Data of Fig. 9

$\lambda = 436$ mμ

h [A.]	$\frac{\gamma}{G_0G_1}$	G_0G_1	γ [ergs. cm.$^{-2}$]	$\frac{(2-\chi)Q}{G_0G_1}$	$\frac{2-\chi}{G_0G_1}$	Q	$\frac{d^2V}{dh^2} \times 10^{-10}$ [ergs. cm.$^{-4}$]
130	18.5	1.89	35	1.50	1.03	1.45	3.00
155	19.5	1.84	36	0.52	1.05	0.49	1.02
180	18.5	1.80	33.5	0.17	1.07	0.16	0.33
260	18.5	1.60	29.5	0.02	1.14	0.015	0.03
320	21	1.44	30				
470	30	1.08	32.5				
530	34	0.97	33				

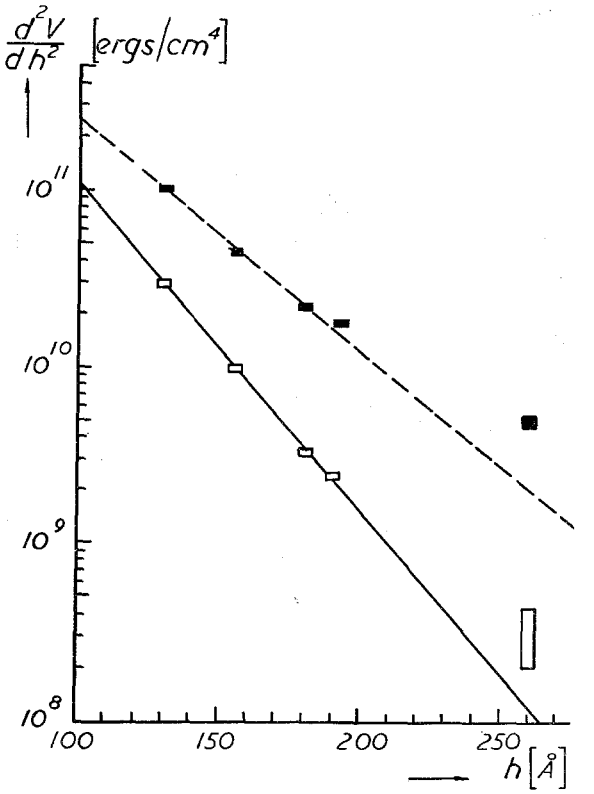

FIG. 10. Interaction between film surfaces as a function of thickness d^2V/dh^2(⊡); $d^2V/dh^2 + 21 \times 10^{-14}/h^4$(■).

parameters κ and B and the latter A. To find κ, B, and A the following procedure was used. A reasonable value for A was selected and resulting values of the function log $(d^2V/dh^2 + A/2\pi h^4)$ plotted against h. Then according to Eq. [45], κ and B are obtained from the slope and the intercept of this plot. However, κ and B should also conform to the equilibrium condition given by Eq. [46] for $h = h$ equilibrium. Values of A which did not lead to fulfillment of this latter condition were rejected, and thus best values of all three parameters were eventually obtained.

In our case the best fit was found for a van der Waals' constant $A = 1.3 \times 10^{-12}$ erg, $\kappa = 3.0 \times 10^6$cm.$^{-1}$, and $B = 0.185 \times 10^{-6}$. In our case the pressure P was 2300 dynes/cm.^{2} and the equilibrium thickness was taken to be equal to the lowest value of h obtained (130 A.).

The van der Waals-London constant A is 2 to 3 times higher than found previously by other methods (20). Using Eq. [43] the value of B leads to $\psi_0 \approx 40$ mv. for $\delta = 0$ or $\psi_0 \approx 20$ mv. for $\delta = 20$ A., which is not un-

reasonable. The value found for κ is about 5 times higher than is to be expected from the concentration of sodium lauryl sulfate in the bulk solution. From the electrical conductance of the solution it could be concluded that a small amount of other electrolyte is present, which would reduce the discrepancy to a factor of three. A further part of this discrepancy may perhaps be due to some evaporation in the film.

There is, however, another consideration which renders the values of κ, A, and B less trustworthy. In Fig. 10 a straight line has been drawn through values of both log (d^2V/dh^2) and log $(d^2V/dh^2 + A/2\pi h^4)$ to conform to the theoretical interpretation. However, the latter function is less well represented by a straight line than is the former. This is contrary to expectation from theoretical predictions (Eq. [45]). More systematic experiments are required in order to understand more fully the reason underlying the deviations from theory.

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