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Two-dimensional rheology of soap films

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Abstract. We present an entirely new experimental device dedicated to the study of the mechanical behaviour of freely suspended soap films. We find that the measured surface viscosity is comparable to the surface viscosity of Gibbs monolayers, but surprisingly, we found that soap films have a small shear modulus.

1. Introduction

The understanding of foam drainage provides fascinating fields of study as regards both theory [1] and experiments [2–4]. Theory might for instance find some interest in the study of the flow in a branched (statistical) network formed by Plateau borders. The thinning process of the single films (soap films) enclosing an air cell is also quite interesting; indeed, the liquid contained in a film is sucked into the Plateau borders where the pressure is smaller than that inside the film because of the negative curvature of the border. Nevertheless, the thinning is generally not uniform along the Plateau border; the border absorbs the thicker parts and generates very thin parts that do not reflect the light since their thickness is much smaller than the wavelength of light. These thin parts appear as black spots whose diameter is about 1 mm. The process of thinning of the film (and hence of a foam) is then due to this generation of these thin parts (the whole process was termed marginal regeneration by Mysels *et al* [5]) that move upward inside a film (because of buoyancy) to form an extended area of metastable black films. There is thus a need to characterize the motion of these 2D bubbles and to then determine the role that thickening agents (such as polymers) might have in the foam drainage. This was the motivation for us to build a new apparatus entirely devoted to the study of the viscoelastic properties of freely suspended soap films.

2. Experiment

The principle of the new set-up is quite simple and is sketched in figure 1. A soap film is formed on a porous ring (of radius $R = 16$ mm) made of sintered glass. On this film, we gently deposit a magnetic disc of magnetic moment μ (a Mylar disc carrying a small magnet or a circular piece of magnetic recording tape). This disc (of radius $r = 12$ mm) is suspended because of the surface tension of the soap film (the soap solution does not wet the disc) and is centred by an accurate horizontal levelling of the film. An oscillating magnetic field ($H(t) = H_0 \cos \omega t$) is then applied through a pair of Helmholtz coils and exerts a torque on the magnetic disc. We study the response (i.e. the amplitude of the rotation of the disc) by following the displacement of a laser beam reflecting from a tiny mirror glued

2D RHEOMETER

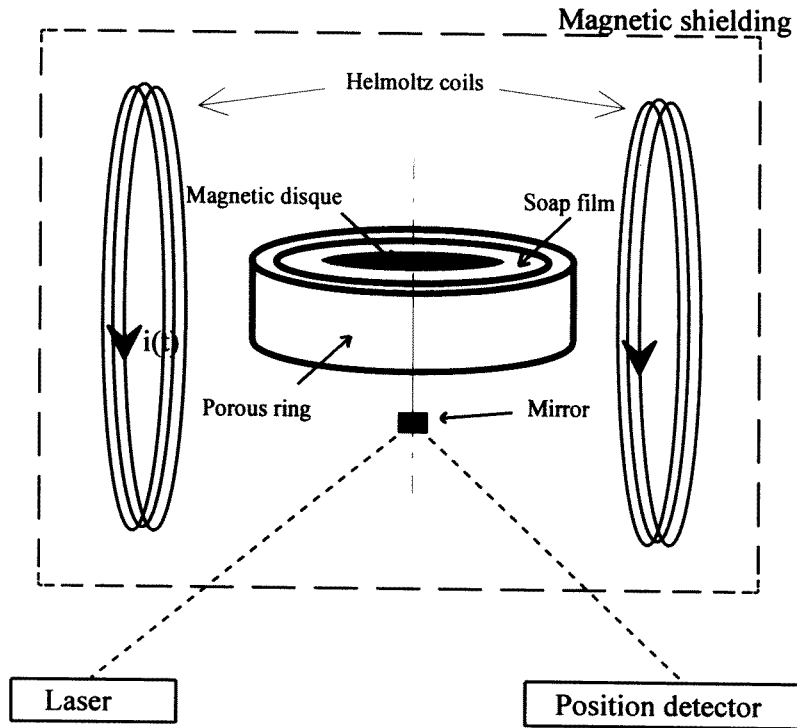


Figure 1. A schematic representation of the experimental set-up.

onto the disc. The total weight of the disc is about 13 mg. The system (i.e. ring, soap film and disc) is kept in a closed chamber to avoid evaporation, and the entire set-up is shielded from the Earth's magnetic field using a sheet of μ -metal.

The rotation θ of the disc is determined by the following torques. The driving torque reads

$$\mu H(t) \sin \theta. \quad (1)$$

The inertial torque of the disc is

$$I \frac{d^2 \theta}{dt^2} \quad (2)$$

with I the moment of inertia of the disc. Assuming that the film has 2D viscoelastic properties, we can define E^{2D} , the 2D shear modulus, and η^{2D} , the surface viscosity. We have thus two additional torques, an elastic torque:

$$2\pi E^{2D} \frac{r^3}{R-r} \theta \quad (3)$$

and a friction torque:

$$2\pi\eta^{2D} \frac{r^3}{R-r} \frac{d\theta}{dt}. \quad (4)$$

We assume in this very first analysis that E^{2D} and η^{2D} are frequency independent. The solution of the complete equation determining the motion of the disc is not obvious in general (we have to deal with a Mathieu equation) but can be greatly simplified if we study small-amplitude rotations $\theta \ll 1$ and if we are careful to set the magnetic momentum of the disc at rest perpendicular to the axis defined by the Helmholtz coils. The equation for the rotation θ of the disc then reads

$$\frac{d^2\theta}{dt^2} + \alpha \frac{d\theta}{dt} + \beta\theta = \left(\frac{\mu H_0}{I}\right) \cos \omega t \quad (5)$$

with

$$\alpha = \frac{2\pi\eta^{2D}}{I} \frac{r^3}{R-r} \quad \text{and} \quad \beta = \frac{2\pi E^{2D}}{I} \frac{r^3}{R-r}. \quad (6)$$

Equation (5) has a permanent solution $\theta(t) = \theta_0 \cos(\omega t + \phi)$ with

$$\theta_0 = \frac{(\mu H_0/I)}{(\alpha^2\omega^2 + (\beta - \omega^2)^2)^{1/2}} \quad (7)$$

and

$$\phi = \tan^{-1}\left(\frac{-\alpha\omega}{(\beta - \omega^2)}\right). \quad (8)$$

The study of the response of the disc as a function of the exciting frequency ω should allow via a simple fit to access the viscoelastic constants E and η .

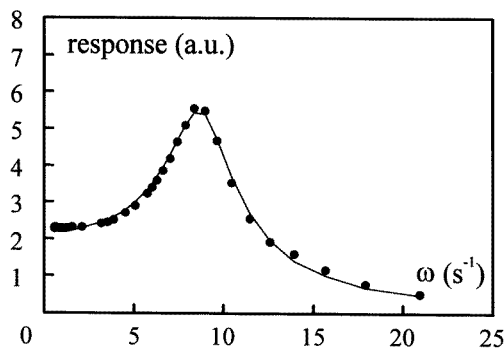


Figure 2. The rotational response of the disc versus the magnetic field angular frequency for a soap film made with a fluorinated surfactant; the bulk surfactant concentration is 1 g l^{-1} (well above the cmc) and the data were taken six hours after the formation of the film on the ring.

3. Results

Figure 2 and figure 3 represent the response of the disc (i.e. the amplitude of the rotation normalized by the exciting field) with respect to frequency. Full lines represents fits of the data to equation (5) and are used to extract E^{2D} and η^{2D} (table 1). The results of figure 2 have been obtained with a fluorinated surfactant (a betaine with a grafted perfluorinated tail

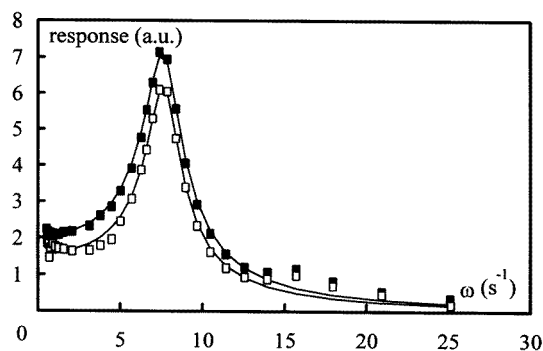


Figure 3. The rotational response of the disc versus the magnetic field angular frequency for a soap film made with SDS; the bulk surfactant concentration is about equal to the cmc (2.4 g l^{-1}) and the data were taken after 6 hours (■) or 20 hours (□) after the formation of the film on the ring.

Table 1. 2D viscoelastic constants.

	E^{2D} (mdyn cm^{-1})	η^{2D} ($\mu\text{dyn cm}^{-1} \text{ s}$)
BF (6 hours old)	11	525
SDS (6 hours old)	8.6	320
SDS (20 hours old)	8.6	280

of six carbon atoms) while SDS (sodium dodecyl sulphate) was used to obtain the results of figure 3.

Notice in figure 3 the onset of a second peak revealing a harmonic generation because of too large amplitudes of rotation.

4. Discussion and conclusion

4.1. Surface viscosities

The systems studied exhibit surface viscosities—equal to a few hundreds of $\mu\text{dyn cm}^{-1} \text{ s}$ —comparable to those of monolayers. It is interesting to obtain the corresponding bulk value η^{3D} through $\eta^{3D} = \eta^{2D}/e$ where e is the film thickness; e is about 20 nm for the soap films studied (common black films) and thus we get a bulk value η^{3D} of a few hundreds of poise (i.e., the viscosity of a standard motor lubricant); this has to be compared to the bulk value obtained using the same derivation for compressed monolayers, which is usually in the 10^4 – 10^7 P range [6], more characteristic of butter. This might reflect a lower packing of the surfactant molecules in soap films, characteristic of a 2D liquid state.

4.2. Surface elasticity

The fact that we find a shear modulus for soap films, even if it is very low, is surprising. Many experiments suggest that surfactant molecules gather into a 2D liquid state and thus that no shear modulus should exist (at least in the limit of zero frequency). Some experiments have nevertheless shown non-zero shear modulus values for monolayers of egg albumin for instance (E^{2D} of the order of 0.1 dyn cm^{-1}) [6] that seem natural if we think

about the likely presence of entanglements of the protein chains at the interface. Our values might have several origins:

- (i) the motion of the magnetic disc on the film induces compression as well as shearing (mode transformation): this should be avoided by studying very small rotations;
- (ii) the shielding from the Earth's magnetic field is not efficient enough: different experiments, with different systems, but with the same experimental geometry (the same orientation, the same disc) have given different resonance frequencies, so we think that the magnetic field of the Earth should not be a problem;
- (iii) the film really has a faint shear modulus.

4.3. Conclusion

We are developing a set-up to measure the viscoelastic constants of soap films based on a new design. This should allow us to determine the mechanical behaviour of assemblies of surfactants in states different from the lyotropic liquid-crystalline states or the monolayer state. The effect of incorporation of polymer molecules inside the films is currently under study.

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