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Theoretical stability diagram of solvent-containing black lipid films

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Abstract. Recently, we have developed an analytical, semi-microscopic theory for the macroscopic behavior of a solvent-containing black lipid film subjected to an electric cross film voltage, Δ. Here we employ the theoretical expressions derived for the disjoining pressure, Π_D, the film elasticity, ε_F, and the film tension, γ_F, to construct the stability diagram of the film, in the Π_D-Δ-plane. Depending on its state (Π_D, Δ), the film is stable or is prone to squeezing or bending deformations. For a monooleate film we show how the destruction of the plane film due to a periodic thickness fluctuation (squeezing) is facilitated by two mechanisms: *i)* lowering of Π_D at fixed Δ; *ii)* lowering of Δ at fixed Π_D, provided that the film is in a stable state characterized by $\Pi_D < -7.03 \times 10^3$ dyne/cm^2 and $\Delta > 0$ mV. Bending of a low tension film (single interface tension $\gamma_s \sim 0.025$ dyne/cm^1) can be achieved only for $\Delta > 170$ mV and $\Pi_D > -8.7 \times 10^4$ dyne/cm^2. Finally, we demonstrate the existence of a marginal state (Π_D^0, Δ^0) where the film is predicted to exhibit strong fluctuations both in the squeezing and in the bending mode.

Key words: Black lipid membranes, disjoining pressure, film tension, film elasticity, film stability

In biophysics, hydrocarbon films – composed of phospholipids and proteins – have been much appreciated for their ability in simulating the properties of natural membranes as, for example, in cross membrane transport (Miller 1978; Schindler and Quast 1980; Boheim et al. 1981). The preparation of such films has, however, been largely empiric (Mueller et al. 1963; Montal and Mueller 1972) and the precise parameters which affect the film stability are still open to question.

In order to shed some (theoretical) light on these problems, we have recently developed a theory on the large scale and long time dynamics (hydrodynamics) of solvent-saturated lipid films (LF) (Wendel et al. 1982; Wendel and Bisch 1983, 1984; Bisch and Wendel 1985). Here we want to report its predictions for the large scale stability of LF.

In our theory, we considered a LF set up similar to the Sheludko arrangement for soap films (Sheludko 1967; Fettiplace et al. 1974): LF was in thermal, chemical, and mechanical equilibrium with its Plateau border and it was surrounded by two aqueous, bulk electrolytes (cf. Fig. 1). The latter were biased at different potentials in order to simulate the electric field applied across the LF in the capacity measurements e.g., by Haydon et al. (Andrews et al. 1970; Fettiplace et al. 1974).

The forces acting in this system arise from van der Waals interactions, from electrostatics, and from

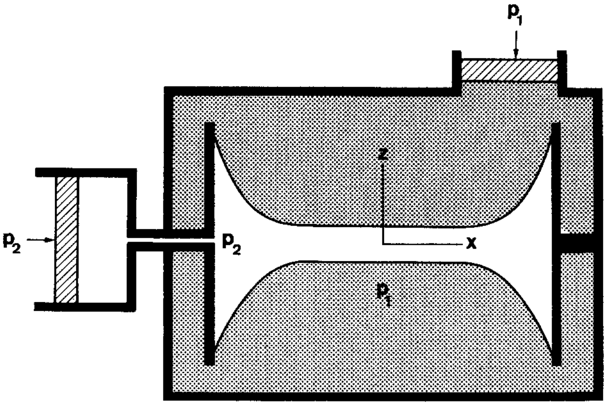

Fig. 1. Schematic film set up. The plane film in the interior of the chamber is in equilibrium with its meniscus and with its Plateau border, i.e., with the bulk phase of the film forming material. The isotropic pressure p_2 in this phase in general differs from the pressure p_1 in the bulk electrolyte. This difference is called the disjoining pressure and it has been assumed to be positive in the figure

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"sterics". The model for the latter force is novel and employs the following intuitive picture. Apart from other properties, each of the lipid "surfactant" layers is characterized by an order parameter field, $\eta(\mathrm{r})$, which mimics the orientation of the hydrocarbon segments present in the bulk film with respect to the normal to the flat film surface (Seelig and Seelig 1980). As the film surfaces approach each other (film thinning) we found that the two interfaces start coupling to each other so as to raise the order close to the film centre.

This effect finds its immediate expression in the macroscopic properties of the LF. For example, for a mechanically equilibrated film the disjoining pressure, i.e., the pressure difference between bulk electrolyte and film forming bulk phase, was shown (Wendel and Bisch 1983) to be given by (1) ($\beta h \gg 1$):

$$\Pi_D = -\frac{H}{6\pi h^3} - \frac{\varepsilon \Delta^2}{8\pi h^2} + 2A[\eta_b]\ \beta^2 \eta_s^2 \exp(-\beta h)\,, \tag{1}$$

where now we have accounted for the drop of the electric potential, Δ, across the film with uncharged surfaces. The first term on the RHS is the van der Waals pressure which arises at the interface between electrolyte and film, h is the film thickness and H the Hamaker constant. The second term represents the compressional electrostatic pressure which arises between Plateau border and film phase; ε (~ 2.1; Andrews et al. 1970) is the dielectric constant of the film. The "steric" pressure involves the second moment, $A[\eta_b]$, of the Ornstein-Zernike direct correlation function of the bulk hydrocarbon phase, with order η_b. β is the inverse decay length of the interfacial order and η_s represents the surface order on the hydrocarbon side of the film surface.

On the macroscopic scale, film stability is determined by the response of the film to bending (BE) and squeezing (SQ) type deformations (Bisch et al. 1981). This response depends in turn, on the sign of the film tension, γ_F, and of the film elasticity, ε_F. $\gamma_F < 0$ implies instability against bending, $\varepsilon_F < 0$, instability against squeezing; $\gamma_F > 0$ together with $\varepsilon_F > 0$ indicate general film stability.

The film elasticity is related to the variation of the disjoining pressure with film thickness. It is defined by (Bisch and Wendel 1985)

$$\begin{aligned}\varepsilon_F &= -\left(\frac{\partial}{\partial h}\Pi_D\right)\cdot h^2\\ &= -\frac{H}{2\pi h^2} - \frac{\varepsilon}{4\pi h}\Delta^2\\ &\quad + 2A[\eta_b](\eta_s)^2(\beta h)^2\beta \exp(-\beta h)\,.\end{aligned} \tag{2}$$

The second equality results upon inserting the expression for Π_D from (1). Within the framework of her heuristic model, Gallez (1983) is lead to an equation similar to (2).

For an incompressible film in thermodynamic equilibrium, the film tension is defined by (De Feijter et al. 1978; Bisch and Wendel 1985)

$$\begin{aligned}\gamma_F &= 2\gamma_s + \Pi_D \cdot h + \int_h^\infty \Pi_D(h)\,\mathrm{d}h\\ &= 2\gamma_s - \frac{H}{4\pi h^2} - \frac{\varepsilon}{4\pi h}\Delta^2\\ &\quad + 2A[\eta_b](\beta\eta_s)^2 h \exp(-\beta h)\,,\end{aligned} \tag{3}$$

where the second equality is due to substitution of (1).

γ_s is the (positive) interfacial tension of a single, i.e., non-interacting interface, between two semi-infinite phases of water and hydrocarbon. γ_s also contains the contribution of the steric interaction between the lipids within the single interface layer.

Before choosing an appropriate presentation of our theoretical predictions for the stability of LF we recall: *i*) In experiments on the physical chemistry of soap films it is common to control the difference p_1-p_2 of the external pressures (Fig. 1) (Sheludko 1967); *ii*) for mechanically equilibrated films, p_1-$\mathrm{p}_2 = \Pi_D$; *iii*) homogenization of solvent containing LF and thus variation of the equilibrium film thickness is effected by application of electric fields across the film (Fettiplace et al. 1974); *iv*) the marginal states which separate stable from unstable states are given by $\gamma_F = 0$ (for single interfaces this criterion was derived, for example, by Sanfeld et al. 1979) and by $\varepsilon_F = 0$.

We are thus lead to the presentation of Fig. 2. There we have drawn the marginal disjoining pressures, i.e., $\Pi_D(\gamma_F = 0)$ and $\Pi_D(\varepsilon_F = 0)$ as a function of the voltage Δ applied across the film. For Fig. 2 we assumed $\mathrm{H} = 3.48 \times 10^{-14}$ erg (Andrews et al. 1970), $2A[\eta_b](\beta\eta_s)^2 = 1.29 \times 10^8\ \mathrm{Nmm}^{-2}$, and $\beta = 4.55\ \mathrm{nm}^{-1}$. The values of the last two quantities were obtained from a fit to the experimental data on the thickness dependence of the "steric" disjoining pressure of monooleate films (Andrews et al. 1970; Bisch and Wendel 1985).

Film instabilities have to be looked for at $\Pi_D < 0$ or $(\mathrm{p}_1$-$\mathrm{p}_2) < 0$. Generally, for $\Pi_D < 0$, the overlap of the interfacial order fields, i.e., its disjoining action, is not sufficiently developed to compensate the van der Waals and electrostatic compression. Thus, the film tended to drain if Π_D were not compensated for by the hydrostatic pressure difference, p_2-p_1. Hydrostatic compensation down to arbitrarily small values of Π_D is limited, however, by film instability. There are two unstable domains (hatched areas in Fig. 2) due to the potential instability of the film against periodic thickness fluctuations (SQ) and against film bending (BE). The domain of SQ instability is bounded from above, at $\Delta = 0$ mV. From (1) and (2) the threshold is found to be $\Pi_D{}^{\mathrm{up}} = -7.03 \times 10^3$ dyne/cm^2. This means: Plane LF at $\Pi_D > \Pi_D{}^{\mathrm{up}}$ is stable with respect to any periodic thickness profile.

For BE film instability there is no upper limit to Π_D, though the marginal states with $\Pi_D \geqq 0$ (continuation of lower Π_D ($\gamma_F = 0$) branch) show up for high voltages, Δ. There is, however, a minimum Π_D, $\Pi_D{}^{\mathrm{low}}$, below which bending does not occur. There is also a threshold voltage Δ^{low} (~ 170 mV in Fig. 2) below which LF cannot be made to bend by electrostatic means. From (3) we see that Δ^{low} and thus $\Pi_D{}^{\mathrm{low}}$ are essentially determined by the single interface tension γ_s (~ 0.025 dyne/cm^1 in Fig. 2; this value was chosen in view of the low tension interfaces with biological relevance [Harvey and Danielli 1938; van Oss 1979]).

From (1)–(3) one can see that there is a voltage Δ^0 such that Π_D (Δ^0, $\gamma_F = 0$) $=$ Π_D (Δ^0, $\varepsilon_F = 0$) $\equiv$ $\Pi_D{}^0$. From Fig. 2 we obtain $\Pi_D{}^0 \sim -8.7 \times 10^4$ dyne/cm^2, $\Delta^0 = \Delta^{\mathrm{low}} \sim 170$ mV. Experimentally this point is interesting because LF in a stable state (Π_D, Δ) close to ($\Pi_D{}^0$, Δ^0) will exhibit strong fluctuations of both BE and SQ type; their relative weight can be fixed by manipulating Π_D or Δ.

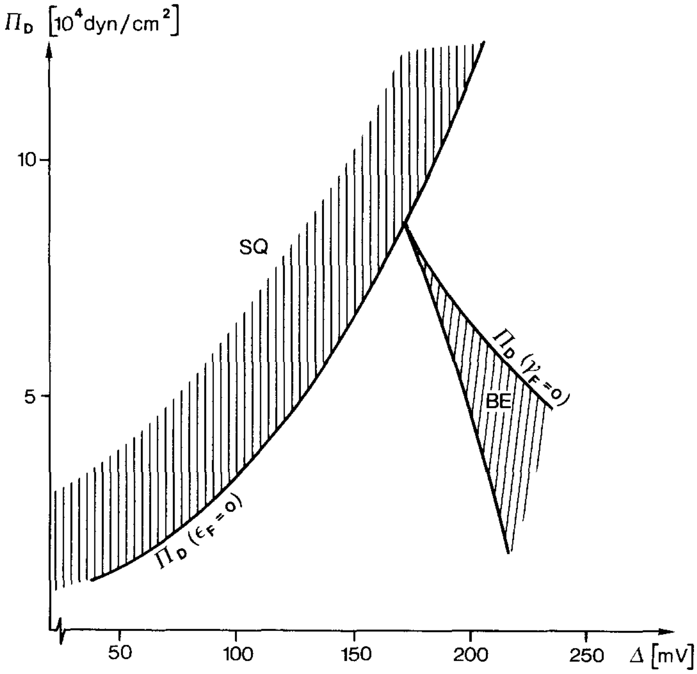

Fig. 2. Stability diagram of a plane film as a function of the experimentally controllable parameters, disjoining pressure, p_1-p_2 $= \Pi_D$, and cross film voltage Δ. Depending on the state (Π_D, Δ), the plane film is stable or unstable (hatched areas). Unstable films are unstable against periodic thickness fluctuations (SQ) or against "muffin-tin" like deformations (BE)

In fact, the stability diagram (Fig. 2) suggests possibilities for deliberately triggering one of the two types of film instability: In a Gedanken-experiment we choose a stable film state (Π_D, Δ) sufficiently far, but not too far, from ($\Pi_D{}^0$, Δ^0). Then the increase of Δ at fixed Π_D eventually triggers a BE instability of the film. In contrast, a decrease in Δ eventually causes LF to yield to a periodic thickness fluctuation. A similar SQ instability is triggered by lowering the disjoining pressure Π_D at fixed cross film voltage, Δ.

In view of the geometric patterns involved (Wendel et al. 1981), one is tempted to consider bending as the linear precursor of "vesiculation"; and squeezing as the linear precursor of the decay of LF into oil droplets in water ("micellization").

In conclusion, we hope to have encouraged experimentalists to carry out detailed experiments along the lines proposed here. Besides the manipulation of the disjoining pressure and cross film voltage it would be especially interesting to pin down the influence of the surface order, η_s, or the packing density of the surfactant; in our theory η_s was assumed to be independent of the film thickness. Finally, we note that the study of films in equilibrium with a Plateau border is important with respect to foams (Lucassen 1981).

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