SUPPLEMENT I:

A. Microinterferometry of foam films

A computerized version of the microinterferometric set up of Scheludko and Exerova (see e.g. Scheludko A (1967) Adv. Colloid Interface Sci. 1:391; Exerova D, Kruglyakov P Foam and foam films (1998) Elsevier, Amsterdam; Platikanov D, Exerowa D (2005) Thin Liquid Films. In: Lyklema H (ed): Fundamentals of Interface and Colloid Science, Elsevier, Amsterdam Vol. 5.; Izmailova VN, Yampolskaya GP, Summ BD (1988) Surface Phenomena in Protein Systems, Khimia, Moscow) for studying thin foam films was used.

In the established experimental procedure the registered time trace of the intensity of mono-chromatic light reflected from the lower and the upper film surfaces is governed by light interference from an optically denser film of diminishing thickness; the interferograms are used to obtain the time trace of the film thickness. The same phenomenon is responsible for the colorful appearance of soap bubbles in polychromatic light.

Depending on surfactant type and concentration thin microscopic foam film kinetics exhibit qualitatively different pattern.

Plane parallel film thinning

With soluble low molecular weight surfactants initially the foam film drains irregularly; at lower thickness (below ca 130 nm and sufficiently small radii) an almost plane-parallel film is observed, followed by black spots and black film formation or film rupture.

A typical inteferogram for a low molecular weight soluble surfactant is shown in Fig S1A.

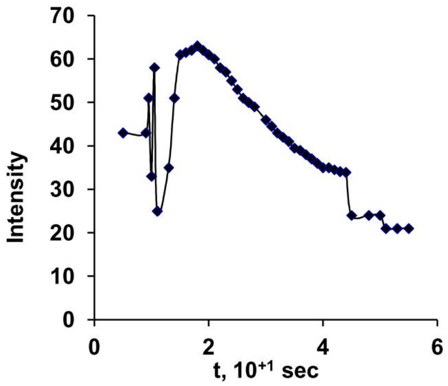

Fig. S1A. Dependence of reflected light intensity on time for plane parallel film thinning.

Film thickness is calculated from the ratio between the intensities measured of the reflected monochromatic light **I**, corresponding to a certain thickness, and **I$_{max}$**, corresponding to the interference maximum, according to the formula:

$$h_w = \frac{\lambda}{2\pi n}\left(k\pi \pm \arcsin\sqrt{\frac{I/I_{max}}{1+\left[\left(n^2-1\right)/2n\right]^2\left(1-I/I_{max}\right)}}\right) \qquad \text{(S1)}$$

where **h$_w$** is the so-called equivalent film thickness, i.e . the thickness of a foam film with refractive index of the solution **n**; **k** is the interference order

In the cases studied in this paper only with the samples containing Curosurf a relatively regular film thinning was observed after the last interference minimum, but with a significant decrease of the velocity of thinning shortly after the last interference maximum: an interferogram is depicted in Fig S1B. After that the thickness abruptly diminishes to that of a black film.

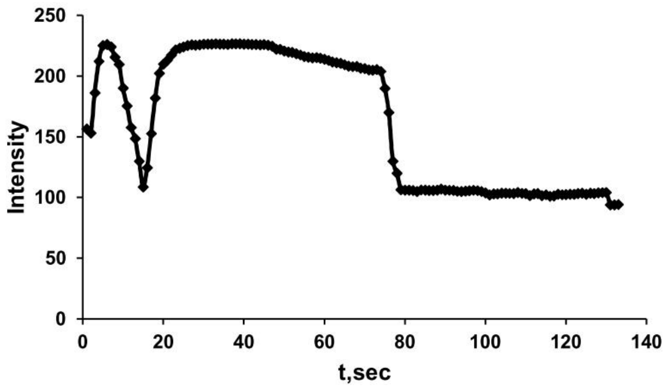

Fig. S1B. Dependence of reflected light intensity on time for Curosurf films.

Lenses and dimple formation

In many cases (especially with natural surfactants and their multicomponent mixtures, as in the cases studied here) almost plane parallel film thinning is never observed (see e.g. Lalchev ZI (1997) Surface Properties of Lipids and Proteins at Bio-Interfaces, In: Birdi, K.S. (ed.): Handbook of Surface and Colloid Chemistry. CRC Press, Boca Raton; Z. Lalchev, Monograph: Phospholipid Foam Films - Types, Properties and Applications, Chapter 15 in: Colloid Stability – The role of Surface Forces (vol.1), Wiley-VCH Verlag GmbH (T. Tadros Ed.), 2006, p. 383-408.; Vassilieff CS, Panaiotov I, Manev ED, Proust JE, Ivanova Tz (1996) Biophys. Chem. 58:97; C.S.Vassilieff, E.D.Manev. Evolution of White Spots in Lipid Foam Black Films of DMPC, Colloid & Polymer Sci. **273**, 512 (1995). and references therein).

An observation of almost axisymmetric dimple flattening in lipid foam films is described in ref (Mitev DJ, Tsekov R, Vassilieff CS (1997) Colloid Surfaces B: Biointerfaces 10:67). In some of the cases studied here after irregular thinning a stable (in the experimental time scale) dimple is formed (see figures 3-5 in the main text). In that case the positions of the interference maxima and minima (called Newton fringes or Newton rings) can be used to obtain the dimple profile. This is a straightforward extension of the so called topographical method to obtain the shape of a thicker lens in a black foam film (D.A. Haydon, J.L. Taylor, Nature 217 (1968) 739) or the contact angle between the foam film and the meniscus surrounding it (A. Sheludko, B. Radoev, T. Kolarov, Trans. Faraday Soc. 64 (1968) 2213).

The procedure is illustrated in the next Fig S2:

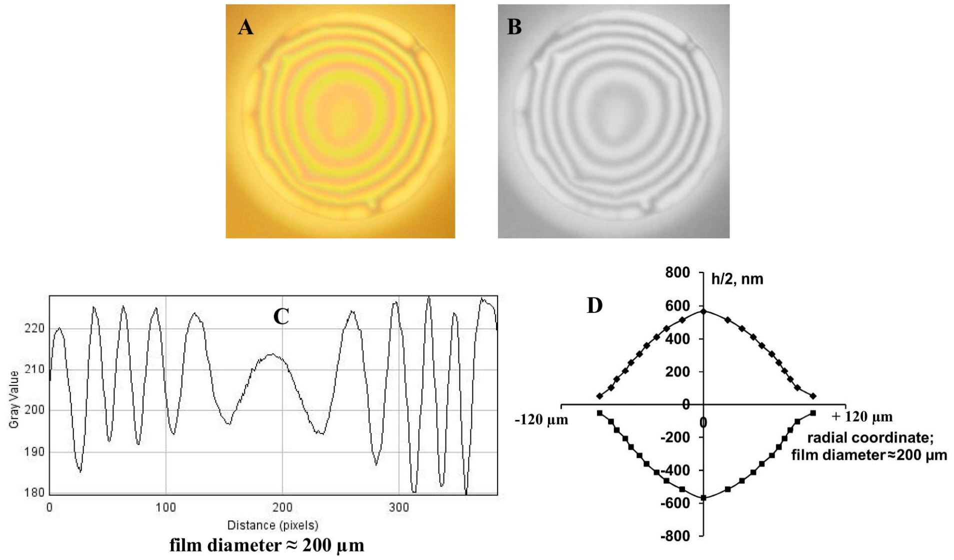

Fig S2. Legend:

A) picture in white reflected light;

B) in green monochromatic light;

C) intensity profile at the equatorial diameter;

D) dimple profile constructed from the positions of the interference maxima and minima (the respective thickness is a multiple of $\lambda/4n$); the refractive index of pure water is used (equivalent water thickness) and it is assumed that the dimple is symmetric with respect to the plane at $h = 0$.

B. Disjoining pressure from kinetic measurements of foam film thinning (dynamic method of Sheludko and Exerova)

The idea underlining this method is that knowing the hydrodynamic law, which governs the thinning of a liquid film, one can get information about the driving force, and hence about the disjoining pressure, from the experimentally measured velocity of thinning (A. Scheludko, *Adv. Colloid Interface Sci.*, 1967, **1**, 391-464.; D.Exerova and P. Kruglyakov, Foam and Foam Films, Elsevier, Amsterdam, 1998.; S. Nir and C. S.Vassilieff, in Thin Liquid Films, ed. I. B. Ivanov, M. Dekker, New York, 1988, pp. 207–274.; D. Platikanov and D. Exerowa, in Fundamentals of Interface and Colloid Science, ed. H. Lyklema , Vol. 5, Chapter 6, Elsevier, Amsterdam, 2005, pp. 1-91.). The method has been mainly applied to microscopic horizontal foam films assuming that the hydrodynamic law is given by Reynolds' equation, which is valid for a plane-parallel film with tangentially immobile surfaces (cylindrical gap between two solid plates filled by a viscous fluid; A. Scheludko, G. Dessimirov and K. Nikolov, Annuaire Univ. Sofia. Fac. Chim., 1955, 49, 127-141.;O. Reynolds, Phil. Trans. R. Soc. Lond., 1886, 177, 157-234.).

$$\left(\frac{dh}{dt}\right)_{\mathrm{Re}} = -\frac{2h^3(P_c - \Pi)}{3\eta r^2} \qquad \text{(S2)}$$

where t is time, h is film thickness, P_c is capillary pressure, Π is disjoining pressure, η is dynamic viscosity and r is film radius. It is convenient to express the velocity of thinning as

$$\left(\frac{dh^{-2}}{dt}\right)_{\mathrm{Re}} = \frac{4(P_c - \Pi)}{3\eta r^2} \qquad \text{(S3)}$$

The velocity of thinning is measured in the microinterferometric set up (A. Scheludko and D. Exerova, Izv. khim. inst. BAN, 1959, 7, 123-132.; A. Scheludko and D. Exerowa, Kolloid-Z., 1959, 165, 148-151.; A. Scheludko and D. Exerowa, Kolloid-Z., 1960, 168, 24-35.). The experimental film thinning data are used to determine the disjoining pressure from Eq (A3), obtained from (A2)

$$\Pi^* = \frac{\Pi}{P_c} = 1 - \frac{(dh^{-2}/dt)_h}{(dh^{-2}/dt)_0} \qquad \text{(S4)}$$

The derivatives of h^{-2} with respect to time t are taken at higher thicknesses where Π is insignificant ($\Pi \ll P_c$; initial linear slope denoted by subscript 0) and at lower thicknesses where Π(h) contributes to the driving force of film thinning.

The trends are illustrated in Fig. S3 for the cases of attractive ($\Pi < 0$) and repulsive ($\Pi > 0$) disjoining pressures. The initial linear slope can be used to determine the viscosity of the film liquid.

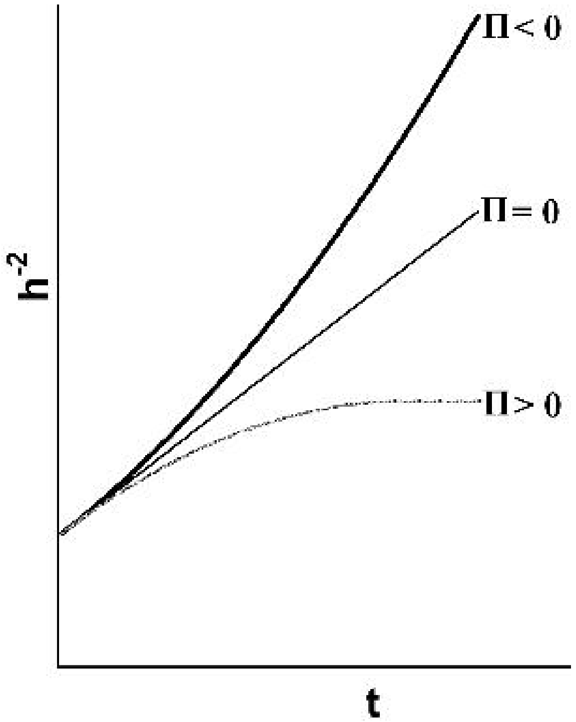

Fig. S3. Various type of foam film thinning represented in Reynolds coordinates (arbitrary scales).

There are many limitations in the applicability of the "dynamic method" (C. Vassilieff, A. Michailova and E. Basheva, Annuaire Univ. Sofia. Fac. Chim., 1981, 75, 184-188.; C. S. Vassilieff, B. N. Nickolova and E. D. Manev, Colloid Polymer Sci., 2008, 286, 475-480.):

- tangentially immobile film surfaces,
- negligible corrugations of planar film surfaces (small enough film radius ~ 10^{-2} cm),
- constant film radius and viscosity during the film thinning,
- negligible evaporation from the film.

But this method has an important advantage: it gives the possibility to estimate repulsive and attractive contributions to the disjoining (($\Pi > 0$) or "joining" ($\Pi < 0$) pressure under conditions when they are not compensated and an equilibrium liquid film is not formed .