

## Comment on “Stability of Soap Films: Hysteresis and Nucleation of Black Films”

Castelletto *et al.* addressed in a Letter [1] the very interesting question of how the transition from electrostatically stabilized common black films (CBF) to sterically stabilized Newton black films (NBF) and vice versa takes place. However, some points are not in line with our current knowledge.

(1) The fact that the transition from CBF to NBF is a first-order phase transition has been known for years. It has often been observed experimentally that the NBF arises through formation of NBF nuclei in the thicker CBF which then grow until the whole CBF becomes an NBF—a process known as “black spot formation” (reviewed in [2]). Contrary to what is stated in the Letter [1], a hysteresis of the transition was already observed in 1987 (Fig. 3.57 of [2], and [3]) using the thin film pressure balance technique with the porous plate film holder of Exerowa and Scheludko [2]. Metastable CBFs in the transition region have been described, including the time for the CBF-NBF transition (lifetime of the metastable CBF); see p. 210 in [2]. The authors of [1] have used exactly the same experimental method; hence the results can be well compared.

(2) For the evaluation of the electrostatic part of the disjoining pressure  $\Pi$  a simple exponential is used [Eq. (1) of Ref. [1]]. This is questionable as this approximation is based on two assumptions. First, a low surface charge density is required (as mentioned by the authors), and, second, the film thickness  $h$  has to be larger than twice the Debye length [4]. The latter assumption, however, is not fulfilled. Indeed, a very poor agreement between the experimental data and the theoretical curves is actually seen in Fig. 2, which is usually not the case for nonionic surfactants (reviewed in [5]). Moreover, it is mentioned on p. 048302-3 that a surface charge density of  $0.9 \text{ mC m}^{-1}$  was obtained. As the surface charge density strongly depends on the electrolyte concentration (reviewed in [5]), we are wondering to which composition this number refers. In any case, a fitting procedure using the exact equations of the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory and an appropriate model for the determination of the most reliable water core thickness [2] have to be used in order to get reliable information from the experimental  $\Pi$ - $h$  curves.

(3) The results presented in Figs. 1 and 2 are not in line with the general observation that the surface charge density decreases significantly with increasing surfactant concentration at concentrations already far below the critical micellar concentration (CMC) (reviewed in [6]). In other words, the conditions reported in Ref. [1] (low salt concentration, surfactant concentration of 2 times the CMC, and pressures above 100 Pa) are not expected to lead to the formation of a CBF. Indeed, in a disjoining pressure study with the same surfactant ( $\text{C}_{12}\text{E}_6$ ) published only recently [6], it is shown that no CBF is formed if (a) the surfactant concentration slightly exceeds the CMC ( $10^{-4}M$ , i.e.,

1.25 CMC), (b) the electrolyte content is  $10^{-4}M$ , and (c) pressures higher than 300 Pa are applied. These conditions are very similar to those reported in connection with Fig. 2(a), where a CBF is seen nevertheless up to 2000 Pa.

(4) It seems questionable to us to use a nucleation theory and assume that hydrodynamic contributions are negligible. The authors say that they started the measurements when the film thickness had reached equilibrium. However, they do not show any precise criterion for the time at which the film thinning ends and the count of delay time begins. Their procedure is obviously possible only if the thinning time is much shorter than the delay time for nucleation of the thinner film. It is, however, easy to show that typical values of thinning times for this type of films are comparable to delay times. One can use the following expression to obtain the velocity of thinning [7]:  $V = -dh/dt = 2h^3[\Delta P - \Pi(h)]/(3\eta R^2)$ , where  $\Delta P$  is the applied pressure,  $\eta$  the liquid viscosity, and  $R$  the film radius. We will take  $R = 100 \text{ }\mu\text{m}$  (it cannot be much smaller in the system used),  $\eta = 10^{-3} \text{ kg s m}^{-1}$ ,  $\Delta P = 900 \text{ Pa}$  (as quoted for the delay time data of Fig. 3), and for the metastable film thickness  $h_f \sim 20 \text{ nm}$  [Fig. 2(a), samples with the same salt content, ( $2 \times 10^{-4}M$ )]. A numerical calculation [8] leads to thinning times of 55 s to reach  $h/h_f = 0.9$ , 79 s for  $h/h_f = 0.95$ , and more than 140 s for  $h/h_f = 0.99$ . These thinning times are longer than the average delay time at this  $\Delta P$  (less than 30 s; see Fig. 4).

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