LETTER TO THE EDITOR

Reply to the Letter by Derjaguin and Churaev

Derjaguin and Churaev (1) have severely criticized our work (2) where measurements of the film and line tensions were carried out with a film formed between a planar fluid interface and a bubble which shrinks with time. We analyze below the points raised by Derjaguin and Churaev in the order they appear in their letter. We also analyze those arguments of Platikanov *et al.* (3) which were used in the letter (1).

(i) Derjaguin and Churaev (1) noted that the dependence of the film tension γ on the disjoining pressure Π (or the capillary pressure P_c) should be rather weak. We agree with this statement which is true for *equilibrium systems*. In fact we made the same comment in Ref. (2), where we argued also that the variation of γ with P_c "is not a simple effect like the dependence of the film tension . . . on the capillary pressure." Moreover, we hypothesized then, and our latest data indicate the same, that this and other observed effects could have, at least in part, a nonequilibrium origin. Thus, the experiments in Ref. (3), cited in (1), which were carried out with a film formed on the tip of a capillary cannot be directly compared to ours.

(ii) Derjaguin and Churaev (1) claim that "the erroneousness of the experiments [in Ref. (2)] . . . has amply been proved in the paper by Platikanov *et al.*" (Ref. (3)). One of the criticisms in Ref. (3) is directed against our procedure for checking the reliability of our data by finding the limiting values γ_∞ of the film tension γ for large bubbles and comparing them with the data of de Feijter and Vrij (4). To do that "we attempted an *extrapolation* . . . and connected the *last few* experimental points with the zero of the coordinate system" (see Fig. 8 and the text on p. 137 and Ref. (2)). According to Platikanov *et al.* (3) in our work "the *end* of the curve has been connected with the zero." Based on their understanding of our procedure they proposed another method for calculation of γ_∞ (see their Fig. 4), by connecting *only the end* of the curve, i.e., the *last point* with the zero (see the dashed lines in their Fig. 4) and found our value of γ_∞. They considered this as proof of the failure of our procedure. In fact, if one *extrapolates* correctly the last portion of their (broken) curve, the calculated value of γ_∞ corresponds to a contact angle 40.6° instead of our value 8.8°. Therefore, this procedure does not prove the point.

(iii) According to Derjaguin and Churaev (1) we tried "to support [the] erroneous experiments . . . by referring to allegedly existing agreement with the theory [from Ref. (5)] of line tension, κ." In fact, we compared our results not with the theory from Ref. (5), but with the more general equation of Starov and Churaev (6) for the line tension κ of a sessile drop:

$$\kappa/r_c = P_c t_1 - (P_c - \Pi_2)^2/2a + \sigma\{1 - [1 + (P_c - \Pi_2)^2/a\sigma]^{-1/2}\}, \quad [1]$$

where r_c is the radius of the contact line, σ is surface tension, and Π_2, t_1, and $a = (\Pi_1 - \Pi_2)/t_1$ are the parameters of the disjoining pressure isotherm. In Ref. (5) Churaev *et al.* kept only the first term in [1] and analyzed the approximate expression,

$$\kappa/r_c = P_c t_1, \quad [2]$$

which is valid only for very small drops (see below). For *larger drops* (small P_c) we expanded [1] in series to obtain (2)

$$\kappa/r_c = (t_1 + 3\Pi_2^3/2a^2\sigma)\, P_c - 3\Pi_2^4/8a^2\sigma. \quad [3]$$

As is evident from Fig. 1, the general Eq. [1] and our approximation [3] are practically identical, i.e., $\kappa/\kappa_\alpha = 1$ (curve 3).[1] All experiments with bubbles, both those of Platikanov *et al.* (3, 7, 8, 11) and ours (2), were performed at contact radii greater than $r_c = 5$ μm. In this size range (on the right hand side of the dashed line in Fig. 1) Eq. [2] and the theory from Ref. (5) do not hold (see curves 1 and 2 in Fig. 1), contrary to the statement of Platikanov *et al.* that Eq. [2] "is valid for bigger drops up to the limiting case of $P_c \to 0$ and $r_c \to \infty$" (p. 104 in Ref. (3)). We cited, however, Ref. (5) because it is closely connected with (6) and investigates in more detail some of the equations derived in (6). We apologize if this not very appropriate citation has led to some misunderstandings.

(iv) We found in our paper (2) that "the line tension κ strongly depends on the geometrical parameters of the system." Such a dependence follows also from the theory of Starov and Churaev (6). Indeed, for relatively *large* drops (i.e., $P_c \to 0$), both Eqs. [1] and [3] yield

$$\kappa/r_c = -N\Pi_2^4/a^2\sigma, \quad [4]$$

with $N = \frac{3}{8}$. The same equation with $N = \frac{1}{16}$ follows also from Eq. [52] of another paper of Churaev and Starov (9), where they considered the case of two attached bub-

[1] Platikanov *et al.* (3) argued that our Eq. [3] "is physically meaningless: for large drops at $P_c \to 0$, $r_c \to \infty$, κ/r_c should be zero but according to [this equation] $\kappa/r_c = -3\Pi_2^4/8a^2\sigma$ = const!." However, the general Eq. [1] also gives κ/r_c = const. at $P_c \to 0$; i.e., this is due to limitations of the theory of Starov and Churaev (6) rather than to our approximation.

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bles. By applying the approach of Ref. (9) to a bubble at an interface, we obtained $N = \frac{5}{8}$ (unpublished results). In Fig. 2 we have plotted our experimental data for κ (from Ref. (2)) as a function of r_c. One sees that the linear portions of the experimental curves 1 and 2 have slopes very close to that of the theoretical curve 3, calculated from Eq. [4] with $N = \frac{5}{8}$ and values of Π_2, t_1, and a from Ref. (6). However, just as in Ref. (2), "we [again] deem . . . this numerical coincidence fortuitous" (cf. p. 139 in (2)) and do not claim anything more than *qualitative* agreement with the theory of Starov and Churaev (6, 9). This curvature dependence of κ ensuing from Eq. [4] is quite different from "the dependence of κ on r_c, similar to the dependence of the surface tension of liquids on the curvature of their surface," meant by Derjaguin and Churaev in their letter (1). Indeed, they analyzed in (5) the curvature dependence of κ using an equation which follows directly from Eq. [2] and is therefore valid only for very small bubbles ($r_c < 5$ μm), whereas Eq. [4] is valid for large bubbles. This is probably why our experimental results, obtained with large bubbles, are in contradiction with their theory for small bubbles.

(v) At the end of their letter Derjaguin and Churaev concluded that "the absolute values of κ, obtained in (2), exceed by two orders of magnitude those that are theoretically possible, as well as those, determined in other experiments made on foamy films." In fact, they could have addressed the same critical remark to the experimental results of Platikanov *et al.* Indeed, for Newton black films, de Feijter and Vrij (10) calculated $\kappa = -5.2 \times 10^{-12}$ N which is by absolute value two orders of magnitude lower than the values of κ determined by Platikanov *et al.* in Refs. (3, 7, 8, 11). As to the experimental works cited by Derjaguin and Churaev (besides those from Refs. (2, 3)), no one deals with the *dynamic* system studied by us—a shrinking bubble. Finally, it should be noted that Gaydos and Neumann (12) measured for *sessile* drops *positive* line tensions of the order of 2.5×10^{-6} N which are by absolute value much higher than our largest value (-10^{-7} N) and more than four orders of magnitude higher than the value (-1×10^{-10} N) calculated for the same system by Churaev *et al.* in (5). Such a variety of theoretical and experimental values for the line tension is hardly an argument in favor of the above categoric conclusion of Derjaguin and Churaev.

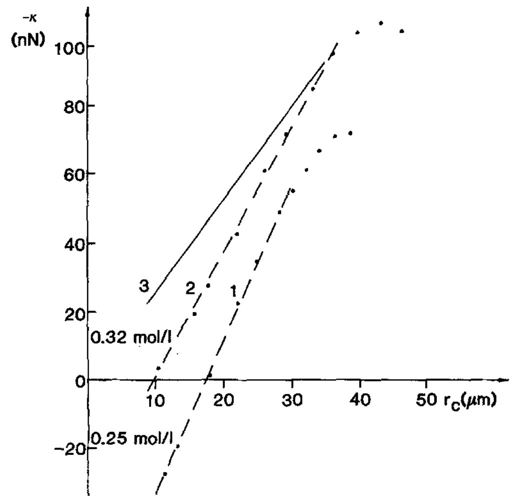

FIG. 2. Our data from (2) for κ vs r_c at two different electrolyte concentrations (curves 1 and 2). Curve 3 is calculated from Eq. [4] with $N = \frac{5}{8}$ and values of Π_2, t_1 and a from Ref. (6).

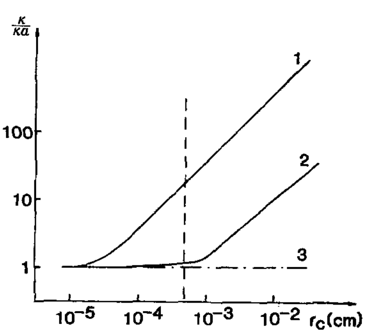

FIG. 1. Comparison of the values of the line tension κ_α, calculated from the approximated Eqs. [2] (curves 1 and 2) and [3] (curve 3), with κ calculated from the general Eq. [1] for different r_c. Curves 1 and 3 are with the values of Π_2, t_1, and a from (6), and curve 2 is with the respective values from (5).

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