

# Comment on “Faceting and Flattening of Emulsion Droplets: A Mechanical Model”

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García-Aguilar *et al.* [1] have shown that the deformations of “shape-shifting droplets”, reported in a series of experimental papers spawned by Refs. [2, 3], are consistent with an elastic model. Here we show that the interplay between surface tension and intrinsic curvature in this model is mathematically equivalent to a physically very different phase-transition mechanism of the same process described previously [4, 5]. Hence, the models cannot distinguish between the two mechanisms, and it is not possible to claim that one mechanism underlies the observed phenomena without a more detailed comparison of the predictions of both mechanisms with experiments. We suggest that the increasing number of seemingly contradictory experimental results indicates that the two systems [2, 3] are different. The observed “shape-shifting” processes are therefore likely to be similar outcomes of two very different physical mechanisms.

Using the notation of Ref. [1], we consider a faceted droplet deforming under the interplay of surface tension and bending elasticity, with energy

$$E = \iint [\gamma_0 + 2\kappa(H - H_0)^2] dA; \quad (1)$$

we shall justify neglect of the stretching and gravity terms in Eq. (1) of Ref. [1] presently. If the droplet radius  $R$  is much larger than  $H_0^{-1}$ , then  $(H - H_0)^2 \approx H_0^2$  everywhere except in a neighborhood of characteristic extent  $f(\delta)H_0^{-1}$  near the facet edges, in which  $H \approx H_0$ , as in Fig. 1(d) of Ref. [1]. The dimensionless  $f(\delta)$  depends on the edge geometry, for example through the dihedral angle  $\delta$ . With these approximations,

$$E = \gamma \iint dA - 2\kappa H_0 \int f(\delta) d\ell, \quad (2a)$$

where  $\gamma = \gamma_0 + 2\kappa H_0^2$ , as in Ref. [1], and the line integral is along the facet edges. Rescaling lengths with  $R$ , the scaled energy  $\hat{E} = E/\gamma R^2$  is

$$\hat{E} = \iint d\hat{A} - \alpha \int f(\delta) d\hat{\ell}, \quad (2b)$$

with dimensionless tension  $\alpha = 2\kappa H_0/\gamma R$ . In Ref. [5] we obtained the same functional form (2b) for a phase transition model in which deformations are driven by formation of a metastable rotator phase [2, 4, 5] near the

droplet edges. In that case,  $\alpha = A\Delta\mu/\gamma R$ , where  $A$  is a characteristic cross-sectional area of rotator phase and  $\Delta\mu$  is a difference of chemical potentials.

To justify neglect of stretching and buoyancy energies, we consider a typical droplet radius  $R = 10 \mu\text{m}$  [2], so  $R \gg H_0^{-1} \approx 60 \text{ nm}$  [1] and  $r \equiv RH_0 \approx 170$ . The relative importance of stretching, buoyancy, and intrinsic curvature depends on  $r$ , the non-dimensional parameters  $\Upsilon$ ,  $\Pi$  defined in Ref. [1], and the non-dimensional energy differences  $\Delta\mathcal{E}_S$ ,  $\Delta\mathcal{E}_G$ ,  $\Delta\mathcal{E}_H$  computed from its Table I. With  $\Upsilon \approx 4$ ,  $\Pi \approx 10^{-8}$  [1], for the icosahedron-platelet transition,

$$|\Delta\mathcal{E}_H| r \approx 9400, \quad \Upsilon |\Delta\mathcal{E}_S| r^2 \approx 35, \quad \Pi |\Delta\mathcal{E}_G| r^4 \approx 29. \quad (3)$$

Hence  $|\Delta\mathcal{E}_H| r \gg \Upsilon |\Delta\mathcal{E}_S| r^2, \Pi |\Delta\mathcal{E}_G| r^4$ ; the same separation holds at the sphere-icosahedron transition. Thus, from Eq. (3) of Ref. [1], intrinsic curvature swamps stretching and buoyancy, justifying (1).

Estimating  $\alpha$  reinforces the equivalence: for the elastic mechanism, using Fig. 2(d) of Ref. [1] to estimate  $\Gamma \approx 0.02$  at the icosahedron-platelet transition, we find  $\alpha = 2(\Gamma r)^{-1} \approx 0.6$ ; for the phase transition mechanism,  $A \approx 0.3 \mu\text{m}^2$  [6],  $\Delta\mu \approx 6 \cdot 10^5 \text{ N/m}^2$  [4],  $\gamma \approx 5 \text{ mN/m}$  [7], so  $\alpha \approx 4$ .

The calculations of García-Aguilar *et al.* consider static shapes [1], and cannot show, for example, that an icosahedral droplet would flatten dynamically into a hexagonal platelet rather than a different, lower energy shape. Because of the model equivalence, the results of Ref. [5] showing that an icosahedral droplet can flatten dynamically into a hexagonal platelet under the phase-transition mechanism also show it is possible under the elastic mechanism of Ref. [1].

Experimental studies of “shape-shifting” droplets have obtained seemingly contradictory results: surface tension measurements [7, 8] differed by orders of magnitude; cryoTEM experiments showed monolayers at the droplet surface [9], while differential scanning calorimetry detected multilayers [6]. However, the cationic surfactant C<sub>18</sub>TAB used in Refs. [3, 8, 9] has a relatively high surface freezing temperature, while Refs. [2, 5–7] used different surfactants covering a range of freezing temperatures. These real differences of the experimental

systems [6, 7, 10] and the corresponding and mathematically equivalent phase-transition and elastic mechanisms are therefore physically different realizations of a more general “shape-shifting” mechanism based on the interplay of positive surface tension and negative edge tension in faceted droplets.

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