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

$$E = \iint \left[\gamma_0 + 2\kappa(H - H_0)^2\right] \mathrm{d}A; \tag{1}$$

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 δ. With these approximations,

$$E = \gamma \iint \mathrm{d}A - 2\kappa H_0 \int f(\delta)\,\mathrm{d}\ell, \tag{2a}$$

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

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

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 $R = 10\,\mu$m [2], so $R \gg H_0^{-1} \approx 60\,$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 Υ, Π 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,

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

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 α 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, $A \approx 0.3\,\mu\mathrm{m}^2$ [6], $\Delta\mu \approx 6 \cdot 10^5\,\mathrm{N/m}^2$ [4], $\gamma \approx 5\,\mathrm{mN/m}$ [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_{18}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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