Comment on "Faceting and Flattening of Emulsion Droplets: A Mechanical Model"

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. Therefore, the observed shape-shifting processes are 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

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

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,

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

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

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

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 nondimensional parameters Υ, Π defined in Ref. [1], and the nondimensional 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,

$$|\Delta\mathcal{E}_H| r \approx 9400, \quad \Upsilon|\Delta\mathcal{E}_S| r^2 \approx 33, \quad \Pi|\Delta\mathcal{E}_G| r^4 \approx 27. \tag{3}$$

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 Eq. (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, $A \approx 0.3\ \mu m^2$ [6], $\Delta\mu \approx 6 \times 10^5\ N/m^2$ [4], $\gamma \approx 5$ 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 dynamically flatten 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; cryo-TEM 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.

We thank L. Giomi for discussions. This work was supported in part by the Max Planck Society (P. A. H.) and Fellowships No. EP/M017982/1 (R. E. G.) and No. EP/

R028915/1 (S. K. S.) from the Engineering and Physical Sciences Research Council.

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Received 5 February 2021; accepted 11 May 2021; published 25 June 2021

DOI: 10.1103/PhysRevLett.126.259801

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