

García-Aguilar *et al.* Reply: In their Comment [1], Haas *et al.* advance two hypotheses on the nature of the shape transformations observed in surfactant-stabilized emulsion droplets [2–9], as well as the theoretical models that us [10] and others [11,12] have introduced to account for these observations. (1) Because of the different surfactants used in Refs. [2–4] and [5–8], the physical mechanisms underpinning the shape transformations may, in fact, differ in spite of the extraordinary resemblance in the experimental output. (2) The theoretical models introduced in Refs. [10] and [11,12] are mathematically equivalent by virtue of the small magnitude of the stretching and gravitational energies considered in Ref. [10]. In this Reply, we argue that neither of these hypotheses is well justified.

To test the first hypothesis, we have performed direct cryo-TEM imaging of Brij 78 nonionic surfactant-stabilized emulsions, as those used in Refs. [5,6]. The interface of a faceted alkane $[\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3]$, denoted as C_{16} droplet, suspended in a 1.5% (by weight) aqueous Brij solution [inset to Fig. 1(a)], clearly demonstrates the absence of any surface-adjacent structure, such as the rotator crystals hypothesized in Refs. [5,11]. The only detectable feature is a clearly defined interfacial layer, as that observed in C_{18}TAB -stabilized emulsions discussed in Ref. [10]. To extract the interfacial layer's thickness, we fit the intensity profiles across the interfaces with a tilted Gaussian function [Fig. 1(b)]. The full width at half maximum (FWHM) varies with the magnification M , averaging to $t = 2.9 \pm 0.2$ nm at the highest accessible magnification. This t value matches the previously estimated thickness of a monolayer [4]. Furthermore, as in our previous studies [4], we linearly extrapolate the experimental FWHM values to $M^{-1} \rightarrow 0$ [Fig. 1(a)]. The corresponding interfacial thickness of the Brij-stabilized system, 2.3 ± 0.2 nm, perfectly agrees with the 2.2 ± 0.9 nm value previously reported for interfacially frozen C_{18}TAB -stabilized C_{16} emulsions [4], indicating that only one crystalline monolayer is present at the interface of these faceted droplets, for either of the surfactants. Our analysis is further validated by the much smaller $t = 0.7 \pm 0.1$ nm of the C_{18}TAB -stabilized cyclohexane (C_6H_{12}) emulsion, where no interfacial freezing takes place and the droplets are rounded [open circles in Fig. 1(a)].

With respect to the second hypothesis, we notice that the numbers $\Delta\mathcal{E}_S$ and $\Delta\mathcal{E}_G$, used by Haas *et al.* to conclude that stretching and gravity are unimportant, correspond to energy minima and are not representative of the entire energy landscape, hence, cannot be used to support the

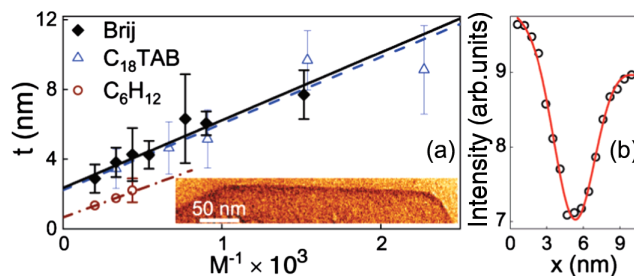


FIG. 1. (a) The cryo-TEM interfacial widths t of the faceted C_{16} emulsion droplets, stabilized with C_{18}TAB [4] or with Brij 78 surfactant (see legend), perfectly coincide. A much thinner interfacial width is obtained for a C_6H_{12} emulsion, where no interfacial freezing takes place. Inset: The cryo-TEM image of the edge of a Brij-stabilized faceted droplet. The “glow” lookup table is employed. (b) Cryo-TEM intensity profile across an interface of a faceted Brij-stabilized droplet. The average fitted FWHM are shown in (a).

authors’ conclusions. Specifically, the stretching energy of a spherical crystal depends on the configuration of the topological defects and ranges from the numbers \mathcal{E}_S in Table I of Ref. [10] to infinity (as any two of the twelve seed disclinations approach each other). Thus, stretching cannot be excluded *a priori*, and its effect is, in fact, pivotal for the emergence of the icosahedral structure, where the twelve seed disclinations are maximally spaced. Similarly, because of the quartic dependence on $r = RH_0$, where R is the droplet radius and H_0 the spontaneous curvature, the gravitational energy \mathcal{E}_G is a rapidly increasing function of R . In the example considered by Haas *et al.*, $R = 10 \mu\text{m}$ [1], which, using $H_0^{-1} \approx 60$ nm and $\Pi \approx 10^{-8}$ [10], gives $r \approx 167$ and $\Pi\Delta\mathcal{E}_G r^4 \approx 27$. Thus, $\Pi\Delta\mathcal{E}_G r^4$ is much smaller than the dimensionless bending energy difference $\Delta\mathcal{E}_{Hr} \approx 9 \times 10^3$ [1]. Yet, it is sufficient to take a droplet of radius $R = 45 \mu\text{m}$ ($r = 750$), thus, well within the experimental range, i.e., 1–150 μm [Fig. 1(f) in Ref. [10]], for $\Pi\Delta\mathcal{E}_G r^4$ to have the same order of magnitude of $\Delta\mathcal{E}_{Hr}$. For the largest droplets ($R = 150 \mu\text{m}$, $r = 2500$), $\Pi\Delta\mathcal{E}_G r^4$ is 1 order of magnitude larger than $\Delta\mathcal{E}_{Hr}$, emphasizing the importance of gravity in the system.

We are grateful to Moshe Deutsch, and Ray Goldstein for discussion. This work is partially supported by the Netherlands Organisation for Scientific Research (NWO/OCW), as part of the D-ITP program (I. G. A. and L. G.), the Vidi scheme (P. F. and L. G.), the Frontiers of Nanoscience program (L. G.), and the Israel Science Foundation, Grant No. 1779/17 (E. S.).


Published by the American Physical Society under the terms of the Creative Commons Attribution 4.0 International license. Further distribution of this work must maintain attribution to the author(s) and the published article’s title, journal citation, and DOI.

Ireth García-Aguilar,¹ Ayelet Atkins,² Piermarco Fonda,^{1,3} Eli Sloutskin^{4,2} and Luca Giomi^{1,*}
¹Instituut-Lorentz, Universiteit Leiden
 P.O. Box 9506, 2300 RA Leiden, Netherlands

²Bar-Ilan Institute of Nanotechnology
and Advanced Materials, Bar-Ilan University
Ramat-Gan 5290002, Israel

³Theory and Bio-Systems
Max Planck Institute of Colloids and Interfaces
Am Mhlenberg 1, 14476 Potsdam, Germany

⁴Physics Department, Bar-Ilan University
Ramat-Gan 5290002, Israel

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

DOI: [10.1103/PhysRevLett.126.259802](https://doi.org/10.1103/PhysRevLett.126.259802)

* giomi@lorentz.leidenuniv.nl

- [1] P. A. Haas, R. E. Goldstein, D. Cholakova, N. Denkov, and S. K. Smoukov, preceding Comment, *Phys. Rev. Lett.* **126**, 259801 (2021).
- [2] S. Guttman, Z. Sapir, M. Schultz, A. V. Butenko, B. M. Ocko, M. Deutsch, and E. Sloutskin, *Proc. Natl. Acad. Sci. U.S.A.* **113**, 493 (2016).
- [3] S. Guttman, Z. Sapir, B. M. Ocko, M. Deutsch, and E. Sloutskin, *Langmuir* **33**, 1305 (2017).
- [4] S. Guttman, E. Kesselman, A. Jacob, O. Marin, D. Danino, M. Deutsch, and E. Sloutskin, *Nano Lett.* **19**, 3161 (2019).
- [5] N. Denkov, S. Tcholakova, I. Lesov, D. Cholakova, and S. K. Smoukov, *Nature (London)* **528**, 392 (2015).
- [6] D. Cholakova, N. Denkov, S. Tcholakova, I. Lesov, and S. K. Smoukov, *Adv. Colloid Interface Sci.* **235**, 90 (2016).
- [7] N. Denkov, D. Cholakova, S. Tcholakova, and S. K. Smoukov, *Langmuir* **32**, 7985 (2016).
- [8] D. Cholakova, N. Denkov, S. Tcholakova, Z. Valkova, and S. K. Smoukov, *Langmuir* **35**, 5484 (2019).
- [9] O. Marin, M. Tkachev, E. Sloutskin, and M. Deutsch, *Curr. Opin. Colloid Interface Sci.* **49**, 107 (2020).
- [10] I. García-Aguilar, P. Fonda, E. Sloutskin, and L. Giomi, *Phys. Rev. Lett.* **126**, 038001 (2021).
- [11] P. A. Haas, R. E. Goldstein, S. K. Smoukov, D. Cholakova, and N. Denkov, *Phys. Rev. Lett.* **118**, 088001 (2017).
- [12] P. A. Haas, D. Cholakova, N. Denkov, R. E. Goldstein, and S. K. Smoukov, *Phys. Rev. Research* **1**, 023017 (2019).