PNAS LETTER

Reply to Buttersack et al.: Challenges in contactless temperature determination of supercooled aqueous droplets

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Buttersack et al. (1) have commented on the temperature probing methods and proposed mechanism of droplet freezing in our findings (2). A high-speed infrared camera with pixel resolution of 15 μm was utilized to determine emissivity-corrected temperature changes through an infrared-transparent zinc selenide optical window. The infrared camera was calibrated with a silicon diode sensor at the pressure node, the latter was also exploited to monitor the simulated atmospheric temperature with errors up to ±0.5 K (SI Appendix) (2). The levitating sample was selected within the customizable region-of-interest of the camera for precise temperature reading (3) with errors up to ±0.9 K originating from radiative fluctuations which become prominent for μm-sized droplets. However, this approach is suitable for relatively larger droplets (d ≈ 1.0 mm) and accounts for the protruded ice crystals formed (4, 5). Evaporative cooling effects are negligible as confirmed by the gas phase Fourier-transform infrared spectroscopy data and unchanged droplet size, also inhibiting greater extent of supercooling (2).

Freezing of larger droplets (~10 μL, S/V = 2.2 mm^{-1}) was found to show a volume dependence (2) while surface nucleation was remarkably pronounced for atmospherically significant smaller droplets (~1 μL, S/V = 4.8 mm^{-1}) with rapid temperature increase during dendritic shell formation followed by complete freezing (figure 2B). For droplets larger than 2.4 ± 0.5 μL (figure 2D), volume-dependent cooling become apparent.

At the dynamic buffer gas–water droplet interface, the microliter-sized levitating supercooled droplet experiences acoustic radiation pressure (6) influencing the surface energy (4). A crystalline nucleus at the droplet surface when exposed to water–air interface undergoes lowering of surface energy, further triggering surface nucleation—proposed as "pseudoheterogenous" (7, 8). This interfacial activation at much lower extent of supercooling by some 5 K is a critical "additional" actor as opposed to homogenous bulk nucleation. Conversely, it does not belong to typical heterogenous nucleation as foreign substances are absent. Prior studies (9, 10) reveal supercooling by more than 20 K compared to our observation of 5 K plausibly originating due to differences in the essential experimental conditions that influence the droplet freezing process, e.g., chamber pressure, surrounding medium, relative humidity, etc., among which the exact pressure and composition inside the chamber are not known. In our case, negligible evaporative cooling at the atmospheric pressure likely results in the observed lower supercooling (2, 11). Nevertheless, as some parameters are not well-defined, a quantitative comparison deemed inaccurate (2, 9, 10).

Here, temporal resolution of Raman spectra is 10 s, and the dynamical features including the fast events are cumulative during the acquisition (2). Droplet cooling occurs in the initial 30 s followed by formation of supercooled water (30 to 50 s) as perceived by the altered O–H stretch pattern. Afterward, the rapidly generated thin ice shell (50 to 60 s) is corroborated by the emergence of the ice band at 3,144 cm^{-1}—also represents the inflection point of the phase transition (figure 2G) and further develops until the typical hexagonal ice formation via complete freezing (2). These observations outline the distinct freezing steps as mentioned—contrary to the claim by Buttersack et al. To the best of our knowledge, no prior droplet freezing studies combining acoustic levitation and Raman spectroscopy have been reported unfolding key freezing steps with molecular structure evolution.

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The authors declare no competing interest.

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