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MORPHOLOGICAL TRANSITIONS IN FROZEN COLLOIDAL DROPLETS

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ABSTRACT

The use of thermal gradients to self-assemble colloidal particles into ordered structures, also known as ice templating, is well understood. Freezing colloidal droplets leads to complex shapes which is of both scientific and technological significance. While frozen pure water droplets show a sharp tip at their apex, colloidal droplets show a flat top morphology. Preliminary experiments with colloidal suspensions of alumina show an array of morphological features, based on initial particle concentration. The present work attempts a parametric investigation with implications in droplet based ice templating.

INTRODUCTION

Sub-cooled slurries or aqueous suspensions when subjected to directional temperature gradient lead to precise structures. Given the freezing conditions, suspended particles are segregated from the ice crystals. Subsequently, ice is sublimated to create complex composites of exceptional strength and toughness[1]. This is of great significance to nanoscale fabrication, cryopreservation and water treatment in extremely cold regions[2]. Although, the phenomenon is well understood during bulk solidification, it has not been thoroughly investigated in the context of "container-less solidification" or droplet freezing. Pure water expands upon freezing. This combined with the contact line dynamics at the liquid-air-solid trijunction leads to a sharp tip in frozen droplets of pure water[3]. Several groups have demonstrated that freezing droplets of aqueous suspension[4] leads to a flat top instead of the "pointy tip". The flattening effect is attributed to a Marangoni circulation due to ice-particle segregation at the contact-line. Our preliminary experiments with wider parametric window (particle size and freezing conditions) show diverse range of morphological transformations, indicating some gaps in scientific understanding. The present work attempts to unearth this nexus and may have implications for bottom up manufacturing using ice templating, hitherto unexplored in droplets.

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METHDOLOGY

Materials

Aqueous colloidal suspensions of alumina (primary particle size 13 nm, Sigma Aldrich) were dispersed in de-ionized water in the volume fraction (φ) ~10^{-4} to 10^{-3}. They were sonicated for 60 minutes at 100 W and then stirred for another 60 minutes before being used for experiments. The use of surfactants to stabilize suspension was avoided to prevent alterations to the surface tension of the suspension. Anodized aluminium coupons were used as substrates. The initial contact angle on these substrates is > 130°. See Grizen et al[5] for more details on substrate preparation.

Freezing experiments

Air cooled thermoelectric cooler (TE-Technology), housed inside a double walled, plexiglass chamber was used for all experiments. A micropipette was used to dispense 10 µl droplets on the substrate, initially at room temperature. Subsequently, the chamber was closed and the cooler was ramped down to -25°C. The substrates' underside was monitored during freezing. Droplets froze between 15 °C to 18 °C. A high frame rate camera (v411, Phantom) fitted with a 1X telecentric lens was used to image droplet freezing events at 1000 frames per second (fps). A halogen light source (OSL2, Thorlabs) with a flexible optical fibre illuminated the droplet from the top and behind.

4. RESULTS

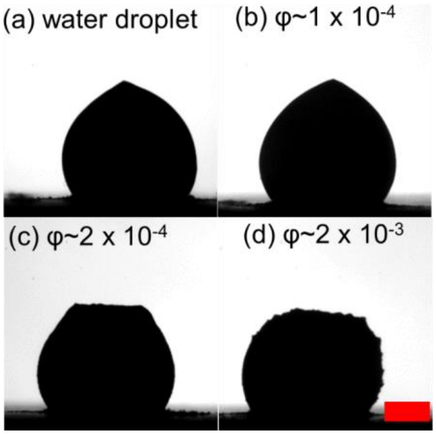

Fig. 1 *Tip to plateau transition in frozen droplets for (a) pure water droplet (b) φ~1 x 10^{-4} (c) φ~2 x 10^{-4} (d) φ~1 x 10^{-3} .The scale bar (bottom right) equals 2 mm.*

Fig.1 summarizes the morphological alterations in the final frozen shape. It is evident that as the initial particle concentration is increased, the frozen tip (Fig. 1b) disappears and the top is truncated (Fig 1c). At much higher concentration, the droplet develops a lumpy appearance with zagged edges. To understand this, we used top illumination to observe the internal motion of the freezing front as shown in Fig. 2. It shows the sequence of events during droplet freezing at the end of the recalescence stage, when the freezing front is first observed (t=0 s). At t=10 s, it is observed that freezing front is at a lower height for pure water droplet (Fig. 2a) than for φ~2 x 10^{-3} (Fig. 2d). It is well known that particles are segregated by the moving solidification front. However, as the initial particle concentration increases, the segregated particles form a denser network, hindering mass transport from the liquid side to the frozen side. This evident from the smaller value of frozen front 'h' at similar stage of the freezing process.

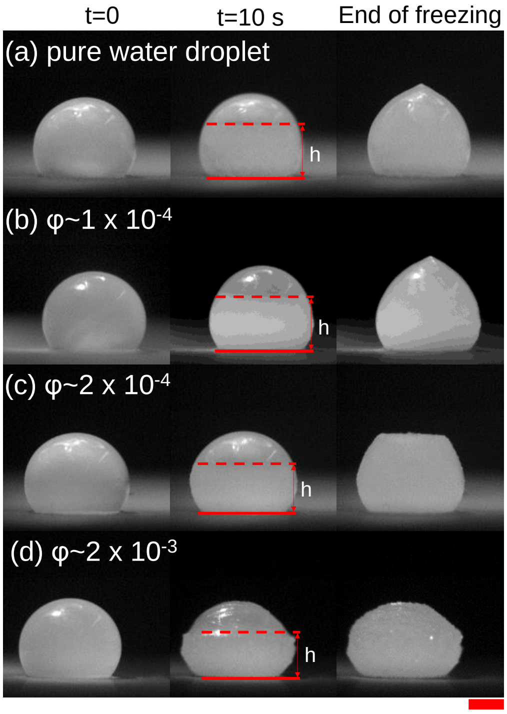

Fig. 2 *Sequence of droplet freezing at t=0 s (post-recalescence stage), t=10 s (freezing front height is shown as h) and end of freezing. This sequence is shown for (a) pure water droplet (b) φ~1 x 10^{-4} (c) φ~2 x 10^{-4} (d) φ~1 x 10^{-3}. The scale bar (bottom right) equals 2 mm.*

5. CONCLUSIONS

Freezing experiments with different colloidal suspension of alumina at different particle concentrations. Morphological transformation from pointy tips to truncated cylinders to lumpy shapes were observed. The transition is attributed to the hindered liquid transport across an increasingly denser particle network, based on the initial particle concentration. The effect of initial contact angles and substrate temperatures needs to be explored further.

ACKNOWLEDGMENT

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