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In situ observation of the unstable lens growth in freezing colloidal suspensions

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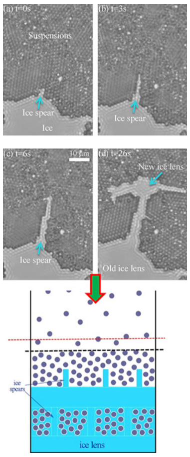
GRAPHICAL ABSTRACT

Freezing polystyrene microsphere (PS) suspensions.



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ABSTRACT

There is a lack of knowledge on the growth dynamics of the formation of a new ice lens without frozen fringe in freezing colloidal suspensions. With experimental observations, we revealed that a new ice lens can be induced by a single ice spear rather than frozen fringe. This ice spear is possibly from the particle-induced undercooled region in front of the freezing interface and the consequent morphological instability. After the appearance of the new ice lens, its growth dynamics are quantitatively analyzed. The growth speed of ice decreases with time, which can be attributed to the premelted film flow-controlled interface movement.

1. Introduction

Lens growth of ice plays a central role in colloidal science [1], materials processing [2,3], and frost heaving etc. [4–8]. In particular, frost heave induces road damage after winter cold spells, and the heaving forces are capable of damaging infrastructure such as pipelines, railways, and buildings [9]. The characteristic of frost heaving is the segregation between ice and particles, where segregated lenses of ice align perpendicular to the direction of the thermal gradient [10].

Since 1929, Taber [11,12] did some experiments to investigate the

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mechanisms of frost heaving. People thought the volume expansion of water/ice transformation (9%) should be the essential reason of frost heaving. However, when water is replaced by benzene or nitrobenzene liquid, frost heaving still exists [13]. Thus, the volume expansion of phase transformation cannot be the major reason, which in turn was later revealed to be the segregated lenses of ice. The growth of ice lens is related to the interfacial energy differences among soil particles, ice and water [14]. The growth speed of a single lens has been solved by the force balance between the thermo-molecular force (or disjoining force) and the viscous force [15].

However, the common situation is multi-lens growth in experiments [16]. How a new ice lens appears in front of the freezing interface is the question of interest. The most widely accepted theory for multiple ice lenses formation is frozen fringe, i.e. the coexistence of particles and pore ices, which is similar to the eutectic phase in alloy solidification [17]. Frozen fringe is a bridge connecting neighbor ice lenses. However, using Raman spectroscopy analysis, Watanabe et al. [16,18] could not detect a pore-ice-bearing fringe in front of ice lenses and thus suspected that the frozen fringe may not be universally valid. Recently, some research groups have confirmed the frozen fringe in different systems of experiments [10,19]. It seems that frozen fringe is one of the ways to form a new ice lens. Moreover, researchers [20] proposed a theory of ice-filled crack propagation based on the particle-induced undercooling [21,22], without the requirement of a frozen fringe. However, there are no growth details of the crack-like segregated ice. By means of experiments with directional freezing colloidal dispersions, Worster et al. [10] discovered speed-dependent ice lenses. At low speeds, they found frozen fringe. At high speeds, the frozen fringe vanished and another pattern formed. Therefore, it is important to investigate the formation and growth details of multiple ice lenses when frozen fringe vanishes.

In this paper, we investigate the growth of multiple ice lenses by in-situ observation of the formation of a new ice lens. A single ice spear is found to stimulate the emergence of a new ice lens. This ice spear is possibly caused by the particle-induced undercooling and the consequent morphological instability. Meanwhile, quantitative characteristics of growth dynamics are obtained after the appearance of a new ice lens. These growth details of ice interface can be explained as the premelted film flow-controlled interface movement.

2. Experimental methods

In our experiments, two suspensions were provided, i.e. alumina suspensions and polystyrene microsphere (PS) suspensions. Alumina suspensions were prepared by $\alpha-$alumina powder (Wanjing New Material, Hangzhou, China, $\geq$99.95% purity) with a documented average diameter of $\sim$80 nm (with 95% particles ranging from 40 to 120 nm in size and a density of 3.97 g cm^{-3}). The preparation strictly followed Ref. [10], in order to suppress the solute effects and highlight the particle effects on the freezing behavior of water. The particles were charge stabilized by a solution of analytical-grade HCl. The final pH of suspensions we used was approximately 4 and thus the suspensions had a zeta potential of around 80 mV according to Fig. 1 of Ref. [10], which was in the region of stable dispersions. PS suspensions were from the company Bangslab, USA. The mean diameter is 1.73 μm with a polydispersity smaller than 5%. The prepared alumina suspensions were added into rectangular glass capillary sample cells (with a cross-section of 1 mm × 0.05 mm) and the commercial PS suspensions were added into monolayer sample cells [4] before freezing. The initial volume fraction of particles φ_0 = 9.74%, 15.97% (wt% = 30, 43) were provided. The Bridgman freezing setup and experimental procedure have been described in Ref. [23]. In the setup, the thermal gradient is produced by two heating and cooling zones separated by a gap. Sample translation across the thermal gradient is provided by a servo-drives motor. Observation is achieved through an optical microscope stage with a charge-coupled device (CCD) camera.

During directional freezing, the thermal gradient was controlled as G = 7.23 K/cm. Images were recorded via a CCD camera with 2580 × 1944 sensitive elements on a time-lapse video recorder and further analyzed by the software image processing (Image Pro plus 6.0). In all images presented, segregated ice is bright and the particle suspension is dark.

3. Results and discussions

3.1. Observation of an ice spear

The panorama of forming new ice lenses with the help of ice spears is presented in Fig. 1(a). The continuous dynamic process is shown in the Supplementary Movie S1. Fig. 1(b) shows growth details of a new ice lens at the pulling speed V = 0.8 μm/s. In the experiment, the ice interface rejected all particles into the liquid with low pulling velocity. Particles were accumulated in front of the interface and built a concentrated particle layer according to the mass conservation of particles. At t = 0 s, a formed ice lens grew. And then its growth became unstable and an ice spear sprouted from the formed ice lens. The tip of the ice spear grew much faster than that of the ice lens. Accordingly, the ice spear penetrated into the close-packed particle layer in dense suspensions at t = 40 s. At t = 100 s, the ice spear laterally grew perpendicular to the direction of thermal gradient. The growth morphology of the ice spear is similar to crack propagation across the close-packed particle layer. At t = 200 s, a new ice lens formed and kept growing. The ice spear connected two adjacent ice lenses. From the experimental observations, the ice spear played a central role in the formation of multiple ice lenses. Some other experiments report similar results of ice spear growth, as presented in Supplementary Figure S1.

In freezing PS suspensions, the ice spear was also observed to form a new ice lens as shown in the Fig. 2. The growth of the ice spear in PS suspensions was much faster than that in alumina suspensions. This observed ice-filled crack propagation confirms the theory proposed in Ref. [20]. Ice spears in these two different systems prove that ice spear-induced ice lenses can be a general mode of periodic ice lenses.

3.2. Origin of the ice spear

The emergence of the ice spear requires undercooling. Through interfacial position comparison between the suspension and its supernatant in Fig. 3(a), we exclude the effect of solutes on the interface undercooling. In Fig. 3(a), the left cell is the freezing supernatant. The right cell is freezing suspensions. The red dotted line is the interface position of supernatant. The pink line is the initial tip position of an ice spear. The position discrepancy Δy between the red dotted line and the pink line is around 165.97 ± 27.66 μm in a linear thermal gradient G (= 7.23 K/cm). The undercooling to form an ice spear can be calculated as $\Delta T = G\Delta y = 0.12 \pm 0.02$ K. The ice spear is from an undercooled region ahead of the freezing interface and the consequent morphological instability. Through analyzing the undercooled state of the concentrated particle layer, we explain the appearance of ice spears. The interface of ice pushes all particles away due to the interface energy difference Δγ between ice, water and particles. On the other hand, viscous flow of water drags the moving particles. These push force and drag force provide an effective pressure to consolidate particles, forming a close-packed particle layer. For the concentrated particle layer, the balance of the external pressure p_s, the hydrodynamic pressure p_l and the osmotic pressure Π inside is

$$p_s = p_l + \Pi \tag{1}$$

where p_l can be calculated by Darcy's law. The osmotic pressure Π changes the freezing point of water T_L in front of ice interface. The Darcy's pressure increases linearly from the freezing interface which leads to the linear decrease of osmotic pressure. Therefore, the freezing point T_L linearly increases according to