Can secondary nucleation exist in ice banding of freezing colloidal suspensions?*

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The formation mechanism of ice banding in the system of freezing colloidal suspensions, which is of significance in frost heaving, ice-templating porous materials and biological materials, is still a mystery. Recently, the theory of secondary nucleation and growth of ice has been proposed to explain the emergence of a new ice lens. However, this theory has not been quantitatively examined. Here, we quantitatively measure the initial interfacial undercooling of a new ice lens and the nucleation undercoolings of suspensions. We find that the interfacial undercooling cannot satisfy the nucleation undercooling of ice and hence disprove the secondary nucleation mechanism for ice banding.

Keywords: colloidal suspensions, freezing, nucleation, ice banding

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1. Introduction

Ice banding (or ice lens) is a familiar pattern of ice segregation in a concentrated colloidal suspensions system, which features alternating macroscopic layers of ice and colloids transverse to the temperature gradient.[1,2] These transverse segregated ice lenses (shown in Fig. 1) are of importance, because they are closely related to the formation of frost heaving,[3] mechanical properties of ice-templating porous materials,[4,5] and tissues of biological materials.[6]

The microscopic patterns of ice bandings have been extensively investigated since Taber's experiments on frozen soils in 1929.[7,8] The most widely accepted theory for ice lens formation is the "rigid ice" model, which treats the suspensions as a rigid or elastic porous matrix.[9,10] This model suggests that ice lensing in rigid-ice formulations requires the existence of a "frozen fringe". The frozen fringe is a region of partially frozen suspensions beyond the warmest ice lens and the succeeding ice lens is initiated from the frozen fringe.[2,11] However, using Raman spectroscopy analysis, Watanabe *et al.*[11] could not detect a pore-ice-bearing fringe in front of ice lenses and thus suspected the "rigid ice" model. Afterwards, a disequilibrium mechanism based on particle trapping was presented to explain the ice banding in rapid solidification of colloidal suspensions[12] (i.e., > 100 μm/s), drawing on an analogy with solute banding in rapid alloy solidification.[13] However, this model ignores the effects of the concentrated particle layer ahead of the interface.

Recently, the theory of secondary nucleation of ice has been proposed to explain the emergence of a new ice lens, corresponding to the engulfment of a layer of particles. A new ice nucleus will appear, with the help of a nucleator, in front of the undercooled freezing interface. This theory is based on the particulate constitutional supercooling (PCS) caused by concentrated particles in front of the advancing freezing interface and without the requirement of a frozen fringe.[14,15] This theory seems to be a correct way to clarify the formation of ice banding in the system of freezing concentrated colloidal suspensions. Nevertheless, we currently find that the PCS is usually too small and has little effect in thermodynamics on pattern formation if the effect of solutes is dominant.[16,17] On the other hand, nucleation requires a relatively large undercooling because of the fierce competitions between Gibbs free energy of bulk and interfacial free energy at the initial stage of phase transformation.[18–23] Moreover, the temperature at the growth surface of the ice lens was estimated to be -0.06 °C, which may be insufficient to provide enough nucleation undercooling.[11] These imply that the theoretical model of secondary nucleation may not be correct.

Currently, the mechanisms of frozen fringe and secondary nucleation are two popular viewpoints for how the new ice lens forms. However, both of them still have imperfections. The frozen fringe, just a hypothesis, has never been observed in the precise experiments.[11,24] The secondary nucleation, even with the help of nucleator, is difficult. A "geometrical super-

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cooling" (i.e., PCS) was proposed to supply the undercooling of secondary heterogeneous nucleation.[15] However, the magnitude of geometrical supercooling is extremely small,[16] which implies the secondary heterogeneous nucleation may not exist. Here we focus on the latter, and a quantitative examination for the secondary nucleation theory is needed, which will present an insight into ice lensing.

In this paper, we carry out a careful examination on the secondary nucleation theory via directly measuring the interfacial undercooling of a new ice lens and the nucleation undercooling of freezing colloidal suspensions. By comparing the nucleation undercooling with the interfacial undercooling, the reasonability of secondary nucleation theory in freezing colloidal suspensions is revealed.

2. Experiment

In the experiments, the α-alumina powder with a mean diameter $d = 50$ nm and a density of 3.97 g·cm^{-3} was utilized (Wanjing New Material, Hangzhou, China, $\geq 99.95\%$ purity, monodispersity). The alumina suspensions were prepared by using HCl (hydrogen chloride) and deionized water as the solvent following Ref. [2]. Also the stable dispersity of alumina suspensions has been confirmed in Ref. [2]. The initial volume fraction of particles was $\phi_0 = 9.74\%$ (30 wt%). The Bridgman freezing setup and experimental procedure have been described in Ref. [25]. During directional freezing, the temperature gradient was kept at $G = 7.23$ K/cm and the pulling speed was $V = 16$ μm/s.

3. Results and analyses

Figure 1 shows the ice banding formed as the particles are engulfed periodically by the advancing freezing interface. The dynamic formation process of this periodical ice banding is also presented in the Movie S1 (Supplementary Information).

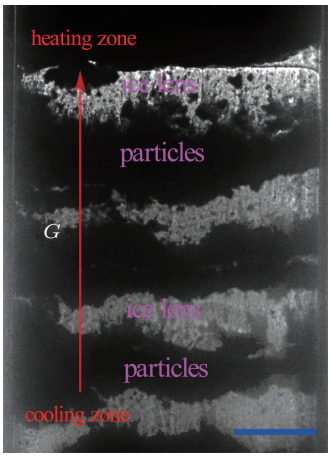


Fig. 1. (color online) Ice banding during freezing alumina suspensions with mean diameter $d = 50$ nm, initial volume fraction $\phi_0 = 9.74\%$, temperature gradient $G = 7.23$ K/cm and pulling speed $V = 16$ μm/s. The scale bar is 200 μm.

As to the formation mechanism of ice banding, the emergence temperature of a new ice lens is the essential feature. So far, the interface undercooling that a new ice lens initially emerges has been conjectured theoretically and no unanimous conclusion has been obtained.[9,26] Although some experimental facilities have been used to investigate the formation about ice banding and ice lens,[2] the interface temperature of a new ice lens can hardly be captured in previous experimental investigations of ice lenses, due to the big size of the Hele–Shaw cell (380 mm×100 mm×3 mm) and the large gap between the heating and cooling zones (60 mm).[2] The experimental apparatus used here is exquisite and can be used to in situ observe the formation of ice banding and accurately determine the interfacial temperature at which a new ice lens initially emerges.[25]

Figure 2 shows the measured temperature of a new ice lens through the interface position difference between the supernatant (left cell of Fig. 2) and the suspensions (right cell of Fig. 2) within a microscopy. A linear thermal gradient is built across the upper and the bottom ends of the cell, which are the heating zone and the cooling zone respectively (indicated in Fig. 1). Accordingly, the temperature measurement is converted into distance measurement in the thermal gradient platform. The position of solid/liquid interface in the supernatant cell (red dotted line in Fig. 2) is slightly higher than that of emergence of a new ice lens (blue dotted line in Fig. 2). The discrepancy of the solid/liquid interface positions between the supernatant and the new ice lens is 13.83 μm, corresponding to an undercooling of 0.01 °C under $G = 7.23$ K/cm. This indicates that the interfacial temperature of the supernatant is only slightly higher than that of the newly formed ice lens. The interfacial temperature of the supernatant is calibrated to −0.03 °C, by comparing with freezing deionized water (0 °C), under $G = 7.23$ K/cm and $V = 16$ μm/s. Based on the interfacial temperature of the supernatant, the measured temperature of a new ice lens is around −0.04 °C. This measurement is consistent with the theoretical prediction (around 0 °C) in Refs. [27] and [28] and experimental data (−0.06 °C) in Ref. [11]. In addition, Movie S1 also clearly shows that the interface position at which a new ice lens initially emerges is very close to the interface position of the supernatant (−0.03°C).

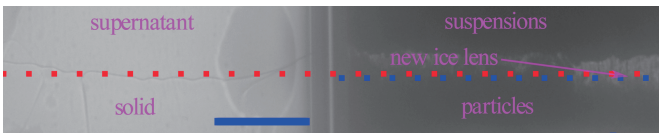


Fig. 2. (color online) Interface positions of supernatant (red dotted line) and suspensions (blue dotted line). Blue dotted line is the position at which a new ice lens initially emerges. The scale bar is 200 μm.

Since the undercooling (−0.01 °C) at which a new ice lens emerges is very small, it might not afford the heterogeneous nucleation undercooling in the secondary nucleation

theory. The nucleation undercooling for the alumina suspensions is an important factor determining the success or failure of the mechanism of secondary nucleation. In the literature reviewed, the nucleation undercooling of suspensions has rarely been gauged in the fields of freezing colloidal suspensions. Nevertheless, there are many experiences about the measurements of nucleation undercooling in alloy solidification.[18,19] In the homogeneous refrigeration of the liquid suspensions, the nucleation undercooling corresponds to the temperature at which the solidification begins and the released latent heat of solidification will suddenly raise the temperature of suspensions. The temperature initially leading to liquid/solid transformation, i.e., the nucleation undercooling, can be recorded by calorimeter.[29] Here, the time–temperature curves are recorded by a Yokogawa LR 4110 temperature recorder. The temperature of the recorder is calibrated by a standard platinum resistance thermometer with an uncertainty of ± 0.1 °C.[25,30] The suspensions are placed into a 1-ml hydrophobic plastic tube in which inserted is the probe of the temperature recorder. The hydrophobic plastic tube can inhibit heterogeneous nucleation of ice on its surface.

Figure 3 shows the cooling curve of initial suspensions with the volume fraction of ϕ_0, under the average cooling rate of $R_c = 5.29 \times 10^{-2}$ K/s which is in the same order of magnitude as $G \times V (= 1.16 \times 10^{-2}$ K/s). With the decrease of ambient temperature, the temperature of initial suspensions decreases until the nucleation occurs. A characteristic temperature of -8.4 °C is measured, which also reflects nucleation undercooling of ice (-8.4 °C) as shown in Fig. 3. Since nucleation is random and has a probability in a limited range of temperature, multiple measurements of nucleation undercoolings are applied to the identical system. After eight measurements of nucleation undercooling, the average nucleation undercooling for the initial suspension is -6.9 ± 1.8 °C. Moreover, considering the fact that the volume fraction of particles in the concentrated layer ahead of the interface during freezing is much higher than ϕ_0s we also measure the nucleation undercoolings in dense suspensions with $\phi = 55\%$ (83 wt%). Typically, the maximum particle random packing is usually $\phi = 55\%$.[14] The average undercooling of nucleation for the dense suspensions is gauged to be -6.77 ± 1.4 °C for three measurements. The nucleation undercoolings of both initial diluter (-6.9 °C) and denser (-6.77 °C) suspensions are in the same order of magnitude as the datum (around -12 °C) in Ref. [31].

The inserted metallic probe of the recorder may also affect the measured ice nucleation in the colloidal suspension. Through measuring the nucleation undercooling of the supernatant centrifuged from the initial suspensions, the effect of the metallic probe on ice nucleation is assessed. The nucleation undercooling of the supernatant is measured to be -9.1 ± 1.2 °C, the result which is averaged over seven measurements. The measured nucleation undercoolings of the supernatant (-9.1 °C) and the suspensions (-6.77 °C or -6.9 °C), indicate that the wetting angle of alumina nanoparticles is smaller than that of the metallic probe. Therefore, the nucleation gives priority to the help of alumina nanoparticles, when the alumina nano-particles and the metallic probe coexist.

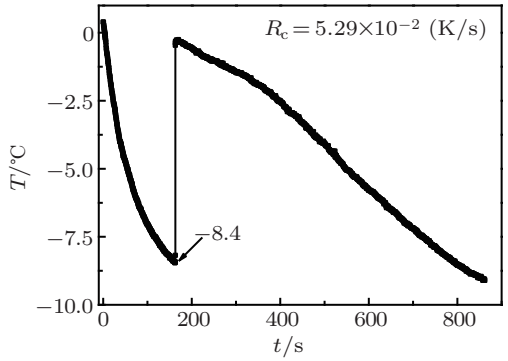


Fig. 3. (color online) Cooling curve of suspensions, under the average cooling rate of $R_c = 5.29 \times 10^{-2}$ K/s. The saltation of temperature indicates the beginning of solidification.

Although both the nucleation undercooling and interfacial undercooling were separately tested in previous work,[16,29] the rationality of secondary nucleation has never been judged by the connections between the nucleation undercooling and the interfacial undercooling. Therefore, comparisons between the nucleation undercooling and the interfacial undercooling of a new ice lens are performed and the results are shown in Fig. 4. The reliability of all experimental data in the present paper are clarified as mentioned above. Both of the nucleation undercoolings of initial diluter (-6.9 °C) and denser (-6.77 °C) suspensions are two orders of magnitude larger than the interfacial undercooling (-0.01 °C) at which a new ice lens initially emerges. It reveals that the interfacial undercooling is much smaller than the nucleation undercooling of generating a new ice lens. Accordingly, secondary nucleation mechanism for ice banding and ice lens can hardly exist.

Furthermore, the definition of nucleation must be clarified, and it is ambiguously used in the previous work.[15,26] The meanings of homogeneous nucleation, heterogeneous nucleation and epitaxial growth are different. Homogeneous nucleation is induced by thermodynamic fluctuations occurring randomly throughout the liquid, and uninfluenced by the presence of any extrinsic surfaces, such as internal interfaces provided by dispersed colloidal particles, or contact with crucible or mold walls needed to support the liquid. Homogeneous nucleation occurs strictly by thermodynamic fluctuations unaided by other effects.[32,33] The temperature of homogeneous nucleation of water/ice transformation is about -40 °C. In the freezing colloidal suspensions, discussion of homogeneous nucleation is useless in the presence of many particles. Heterogeneous nucleation is influenced by the presence of extrinsic

surface of particles. However, undercooling of heterogeneous nucleation is also much larger than the interfacial undercooling as mentioned above. Therefore, the heterogeneous nucleation can hardly exist, i.e., the ice-filled flaw (secondary nucleation), a key part of the theory, can hardly exist ahead of the warmest ice lens. In Ref. [15], new ice lenses can then nucleate from the shrinkage cracks in a region where sufficient geometrical supercooling exists. However, this case is epitaxial growth but not nucleation. The major difference is the crystal orientation. Epitaxial growth does not need nucleation but continuously grows from its existing crystalline structure. Meanwhile, epitaxial growth requires almost no supercooling, rather than sufficient geometrical supercooling.

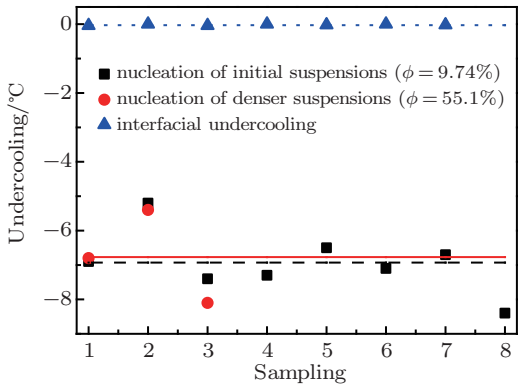


Fig. 4. (color online) Comparison between nucleation undercooling and interfacial undercooling at which a new ice lens emerges. The points are experimental data and the lines are average values.

Finally, the magnitude of "geometrical supercooling" proposed in Ref. [15] is largely controversial, which means that it cannot satisfy the undercooling of secondary nucleation as mentioned above. The small interfacial undercooling for a new ice banding presented here requires a new forming mechanism for ice banding, and should be an essential indicator of the future proposed model. It seems that the frozen fringe mechanism may be the possible choice to explain the ice banding mechanism. However, there is no experimental evidence nor argument. We will try to re-examine the frozen fringe mechanism in the future work.

4. Conclusions

In the present work, we quantitatively measure the interfacial undercooling at which a new ice lens initially emerges and the nucleation undercoolings of initial diluter and denser suspensions. The reliabilities of all experimental data in the present paper are clarified. The nucleation undercoolings of both initial diluter (−6.9 °C) and denser (−6.77 °C) suspensions are both two orders of magnitude larger than the interfacial undercooling (−0.01 °C) at which a new ice lens initially emerges. The interfacial undercooling cannot match with the nucleation undercooling of a new ice lens. Therefore, the secondary nucleation mechanism for ice banding and ice lens can hardly appear. In the future, a new formation mechanism of ice banding should be proposed to explain how a new ice lens forms.

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