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ABSTRACT
Investigating the nucleation and freezing behavior of supercooled water under temperature gradients is of significance for theoretical research and practical application. This paper focuses on the freezing temperature of bulk supercooled water in a rectangular container for which the temperature at two sides can be controlled to present a temperature difference. The experimental results show that the nucleation temperature under temperature differences will be lower than that under isothermal conditions. In addition, an increase in the temperature difference is shown to linearly increase the supercooling needed for ice nucleation. The temperature gradient is capable of suppressing heterogeneous ice nucleation. Based on the classical nucleation theory, the free energy barrier for heterogeneous nucleation is attributed to the main factor to affect the nucleation rate. By comparing theoretical evaluations with experimental results, correction on the free energy barrier was conducted to predict the nucleation rate in the temperature gradient. Our experimental research and theoretical correction reveal the nucleation behavior of supercooled water under nonequilibrium conditions.

Freezing and supercooling of water generally occur in our daily lives and have a significant impact on many areas such as climate, aircrafts, food and biological sample preservation, and wind turbines. 1–7 Whether water freezes under a subcooled state is determined by ice nucleation. 8,9 The water remains as liquid up to about −38 °C and homogeneously freezes at slightly colder temperatures, where only ice is found.10 Any ice formation must start with heterogeneous ice nucleation at higher temperatures.1 However, heterogeneous ice nucleation is commonly related to impurities and surface contact.11–13 Ice nucleation can also be triggered by a variety of perturbations14 including mechanical vibrations,15,16 electric fields,17 optical breakdown,18 negative pressure,19,20 and ultrasonic waves.21 These research studies were conducted almost under thermodynamic equilibrium conditions. However, there is a temperature difference in some practical applications, for example, quickly preparing supercooled droplets from room temperature water,22 exposing warm water to cold environment,23 or putting supercooled preservation of biological samples in a warm environment.24

In the case of temperature-gradient effects on nucleation, Reguera and Rubi have analyzed homogeneous nucleation in inhomogeneous media.25 Their analytical results suggested that the nucleation process can be strongly affected by the presence of a large temperature gradient. Motooka and Munetoh found that the plane of recrystallized thin Si films can be controlled by adjusting the temperature gradients through molecular-dynamics simulations of nucleation and crystallization.29 Das et al. have proposed a temperature gradient field theory of nucleation, which indicates that the nucleation rate is higher at the thermal gradient field interstitial than that at the liquid-particle interface.30 These studies based on theoretical and numerical analysis qualitatively imply that temperature gradients can affect nucleation.

Huang et al. have experimentally studied the stability of deep-supercooled water under thermal disturbances induced by plunging the samples into a 37 °C water bath or putting them into a 37 °C incubator. However, the frozen samples are very few under these thermal disturbances.31 Okawa et al. have investigated the effect of the cooling rate on freezing of supercooled water under linear temperature distribution.32 Although there is a temperature difference, the effects of temperature gradients on nucleation from supercooled water have not been demonstrated.
In order to understand the influence of temperature gradients on the release of supercooling from bulk water, we carried out water freezing experiments to measure median nucleation temperatures under different temperature differences. In our experiments, a rectangular acrylic container filled with ultrapure water is placed tightly between the two Peltier elements, which can control temperature via current supply, as shown in Fig. 1(a). The details of the experimental methods can be found in the supplementary material, and the schematic diagram of the experimental setup is shown in Fig. S1 of the supplementary material. In the process of phase transition from water to ice, the latent heat will be released. Hence, there is a sudden increase in the measured temperature when water starts to freeze.

Figure 1(b) shows the detection of icing formation, and the lowest temperature is defined as the nucleation temperature. The locations of temperature measurement are schematically illustrated in Fig. S2 of the supplementary material.

In this work, four experiments were carried out and the conditions are given in Table I. Case 1 is conducted as the isothermal cooling experiment to determine the natural nucleation temperature of bulk supercooled water. Other three cases are implemented to examine the effect of the temperature gradient on the nucleation process. During the unilateral cooling experiments, the temperature of the other side will decrease gradually because of heat transfer, as shown in Fig. 1(b), which shows the cooling curves in case 3. The cooling curves of other cases are provided in Fig. S3 of the supplementary material, and the corresponding average cooling rates 1 min before nucleation occurs are provided in Table SI of the supplementary material. "Although there is a difference in the cooling rate among the cases, it is worth mentioning that the freezing temperature in each case is not affected by the difference." The thermal resistance of the bulk water in the container can be characterized as \( x/\lambda_w (\sim 10^{-2} \text{ m}^2 \text{ K/W}) \), where \( x = 5.4 \text{ mm} \) is the width of the container and \( \lambda_w \approx 0.6 \text{ W/(m K)} \) is the thermal conductivity of water, which is almost negligible relative to the equivalent surface convective heat transfer resistance during slow cooling causing the Biot number to approach zero. Therefore, for the temperature distribution in the container, we can assume that it is isothermal in case 1 and linear in cases 2–4.

Figure 2(a) shows the box plot of the measured nucleation temperatures (repeat 20 times for each case). The sequence number of nucleation events is shown in Fig. S4 of the supplementary material, and the distribution of nucleation temperature is correspondingly shown in Fig. S5 of the supplementary material. The median nucleation temperature \( T_N \) is \(-16.3 \pm 5.0 \text{ °C} \) in case 1, i.e., isothermal cooling tests, and they are \(-20.1 \pm 5.0 \text{ °C} \), \(-21.7 \pm 5.0 \text{ °C} \), and \(-23.5 \pm 5.0 \text{ °C} \) in tests under three temperature differences, respectively. While nucleation starts in the experimental processes of cases 2, 3 and 4, the average measured temperatures of the other side \( T_a \) are \(-6.8 \pm 5.0 \text{ °C} \), \(1.8 \pm 5.0 \text{ °C} \), and \(10.1 \pm 5.0 \text{ °C} \), respectively. Figure 2(b) shows the temperature of both sides of the container when ice forms and the corresponding fitting curve as a function of temperature gradient \( k \). It can be seen that nucleation occurs at a lower temperature as long as there is a temperature difference. When supercooled water is contacted with the cooled substrate, ice usually forms via a heterogeneous nucleation process at the water-substrate interface and starts at the lower-temperature region. According to the temperature

| Cases | \( T_1 \) and \( T_2 \) (°C) | Cooling methods |
|-------|-----------------|-----------------|
| 1     | 5               | Isothermal     |
| 2     | -5              | Unilateral     |
| 3     | 5               | Unilateral     |
| 4     | 15              | Unilateral     |

TABLE I. Initial temperatures and cooling methods.
A random freezing with changing nucleation rates in the continuously cooling experiments can be described as a nonhomogeneous Poisson process, and the nucleation probability $P_N(T)$ is quantified as

$$P_N(T) = 1 - e^{-\int_{T_m}^{T} \frac{N}{k_BT} dt},$$  \hspace{1cm} (1)$$

when the water temperature at the water-solid interface $T$ is below the ice melting temperature $T_m$ (273.15 K). $R(t)$ is the cooling rate at the water-solid interface and set to a constant 2.5 $^\circ$C/min in our calculation. Here, $J$ is the rate of formation at which the critical ice embryo performs phase transformation at a fixed temperature $T$ and can be predicted as

$$J(T) = AK(T)e^{-\frac{\Delta G_{hete}}{k_BT}},$$  \hspace{1cm} (2)$$

where $A$ is the contact area between water and the substrate with temperatures below $T_m$. $K$ is a kinetic prefactor accounting for the diffusive flux of water molecules to cross the ice surface, $k_b$ is the Boltzmann constant, and $\Delta G_{hete}$, the heterogeneous free energy barrier to form the critical ice embryo which can be given as

$$\Delta G_{hete}(T) = \frac{16\pi \gamma_{iw}^3}{3(\Delta G_e(T))} f(m,a),$$  \hspace{1cm} (3)$$

where $\gamma_{iw} = 28 + 0.29(T-T_m)$ (erg/cm²), 237.15 $\leq T \leq 273.15$ K $\Delta G_e(T) = \Delta H_e(T_m-T)/T_m$ is the ice-water interfacial energy and $\Delta G_{hete}(T) = \Delta H_e(T_m-T)/T_m$ is the volumetric free energy difference per unit volume between ice and water. Here, $\Delta H_e = 287$ MJ/m³ is the water volumetric enthalpy of fusion.\cite{37,41} The function $f(m,a) = \frac{1}{2} + \frac{1}{2} \left( \frac{1-ma}{w} \right)^{3} \left( \frac{1+wa}{w} \right) - \frac{1}{w} \left( \frac{wa}{w} \right)$, which varies between 0 and 1 and depends on the Young’s contact angle $\theta$ of the ice embryo (cluster) on the foreign particle (underlying surface) in supercooled water and the relative size $a$ of foreign particles with respect to the ice embryo. In the function, $m = \cos(\theta)$, $a = R_p/\rho$, and $w = \sqrt{1 + a^2 - 2ma}$. $R_p$ is the radius of the foreign particle and is also considered as surface roughness $R_a$ for the substrate\cite{32,40} (the average $R_a$ is 0.007 $\mu$m in this work). $\rho = 2y_{iw}/\Delta G_v$ is the radius of the critical ice embryo.

The kinetic prefactor can be gained as

$$K(T) = N_c \frac{k_BT}{h} \exp \left( \frac{\Delta F_diff}{k_BT_a} \right),$$  \hspace{1cm} (4)$$

where $N_c$ ($\approx 10^{19}$ m⁻²) is the number of monomers of water in contact with the unit area of the ice surface, $h$ is Planck’s constant, and $\Delta F_diff(T) = k_BT_a/2k_BT_a$ is the activation energy for diffusion of a water molecule to cross the ice-water boundary with the constant values of $E = 892$ K and $T_b = 118$ K in the temperature range from 150 K to 273 K for liquid water.\cite{43}

Until now, we could not predict the nucleation rate due to the unknown contact angle $\theta$, which can be regarded as surface material dependent and commonly utilized as an empirical parameter at constant.\cite{37,41,44} In the current work, $\theta$ is determined with experimental results by setting $P_N = 0.5$ in Eq. (1) at the specific temperature $T_N = -16.3$ $^\circ$C in case 1. Finally, $\theta$ is taken as 58.3° here. Figure 3 shows the nucleation rate as a function of temperature and the influence of changes in the contact area. According to the evaluation of the nucleation rate, the median nucleation temperature will just only decrease about 0.2 $^\circ$C due to the area reduction in experiments with temperature differences.

FIG. 2. (a) Measured nucleation temperatures in four cases. The dashed lines show the mean nucleation temperatures, the solid lines inside the boxes represent the median $T_{n}$, and the bottom and top lines of the boxes represent the first and third quartile. Upper and lower whiskers connected with the box using solid lines show the measured highest and lowest nucleation temperatures, respectively. (b) The temperature of the two sides of the container when nucleation occurs as a function of temperature gradient $k = \frac{T_{n}-T_{b}}{w}$, where $w = 5.4$ mm is the width of the container.
How does the temperature gradient affect the nucleation rate? To seek the possible nucleation mechanism, we search breakthroughs in the composition of the nucleation rate in Eq. (2). Due to an exponential growth of the nucleation rate as the temperature decreases, the variation of the coefficient $\frac{AN_e k_B T}{k_BT}$ before the natural exponential $e$ will not obviously change the nucleation rate. Thus, the index $-\frac{\Delta G_{het} + \Delta F_{diff}}{k_BT}$ is decisive for the nucleation rate. It consists of two parts: the free energy barrier $\frac{\Delta G_{het}}{k_BT}$ and the diffusion activation energy $\frac{\Delta F_{diff}}{k_BT}$. Figure 4 shows their change as a function of temperature. It can be seen that the variation of the free energy barrier with temperature is striking compared to that of diffusion activation energy. Hence, we infer that an increase in the heterogeneous nucleation energy barrier in a temperature gradient leads to nucleation rate reduction.

To explore the correlation between the temperature gradient and the variation of the heterogeneous nucleation energy barrier, we correct the evaluation of the nucleation rate in Eq. (2) to agree with our experimental results as $J''(T) = AN_e k_B T C e^{-\frac{\Delta G_{het}}{k_BT}} e^{-\frac{\Delta F_{diff}}{k_BT}}$, where $C$ is a modified function speculated to be related to temperature gradient $k$. For isothermal cooling in case 1, i.e., for $k=0$, it is known that $C=1$. For the case of $k \neq 0$, $C$ can be determined by making the adjusted nucleation rate evaluated through changing the value of $C$ achieve $P_N$ as equal to 0.5 at the corresponding median nucleation temperature. The fitted value of $C$ and the corrected nucleation rate are given in Table II, and it is surprising that the modified function $C$ is in linear correlation with the temperature gradient, as shown in Fig. 5(a), which may testify that our inference is correct. Figure 5(b) shows the evaluation of the nucleation rate as a function of temperature under different gradients. For a given temperature gradient, the order of magnitude of the reduction in the nucleation rate will gradually decrease as the temperature decreases. This is why the rate of change in median nucleation temperature with the temperature gradient is lower than that of average temperature of the other side in Fig. 2(b).

In conclusion, we carry out water freezing experiments for bulk supercooled water in an acrylic container under various temperature differences. Our results show that a larger degree of supercooling is needed for the initiation of nucleation under temperature gradients. Theoretical analysis is based on the CNT, the free energy barrier for heterogeneous nucleation is conjectured as the main factor, and we correct it by using a prefactor accounting for the temperature gradient to make the evaluation of the nucleation rate consistent with the experimental results. The results indicate that the temperature gradient enhances the free energy barrier for heterogeneous nucleation to reduce the nucleation rate, and the modified function is in linear correlation with the temperature gradient under our experimental conditions. Our observation can be helpful to control ice nucleation in practical applications by adjusting the temperature gradients and can give an understanding of ice nucleation under the thermodynamic nonequilibrium state. The underlying mechanism as to why the heterogeneous free energy barrier enhanced under temperature gradients cannot be revealed in this paper remains unknown, which may be related to the wall heat flux similar to bubble nucleation with the wall temperature gradient or microscopic mechanism of heat transfer in water under temperature gradients. Further work is needed to develop a thermodynamic model to shed light on the exact mechanism.

![FIG. 3. Evaluation of the nucleation rate J as a function of temperature and the effect of the contact area. The contact angle $\theta = 58.3^\circ$ is determined by using the median nucleation temperature $T_N = -16.3^\circ$C in case 1 and setting the corresponding nucleation probability $P_N = 0.5$.](image)

![FIG. 4. The free energy barrier and the diffusion activation energy as a function of temperature under isothermal conditions.](image)

### Table II. The values of the correction function and the corresponding nucleation rates and probabilities at the median nucleation temperature in cases 2–4 ($A = 100 \text{ mm}^2$).

| $T_N$ (°C) | $C$     | $J''$ (s$^{-1}$) | $P$   |
|-----------|---------|-----------------|-------|
| 20.1      | 1.86    | 0.158           | 0.49  |
| 21.7      | 2.35    | 0.161           | 0.51  |
| 23.5      | 3.01    | 0.143           | 0.49  |
See the supplementary material for details of the experimental method and data.

The authors declare no competing financial interest.

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