Ice-water interfacial energy between 235.35 and 237.15 K deduced from homogeneous nucleation rate

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Abstract

Stan's experimental data of ice nucleation are re-analyzed in this paper. The ice-water interfacial energy is calculated from available data by classical nucleation models. Linear regression is employed to model the relation between the nucleation rate and temperature. A linear equation is suggested to calculate the ice-water interfacial energy between 235.35 and 237.15 K. The equation indicates that the ice-water interfacial energy decreases with temperature quicker than what is suggested by recent studies. This implies that, according to Stan's experiment, the structure of water molecular cluster is more similar to that of ice nucleus. A hybrid ice-water model with the ratio of cubic ice to hexagonal ice being 2:1 is utilized. Linear average is performed on the hybrid ice-water interfacial energy by the ratio. The result fits well with the ice-water interfacial energy given by the suggested equation.

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1. INTRODUCTION

Liquid water is supercooled as its temperature goes below 0 °C. Small water droplets can remain in liquid state while being cooled well below 0 °C. Water molecular cluster with hexagonal structure may occur because of thermal fluctuation. The cluster is the origin of ice nucleus which has the possibility to grow into ice crystal. Critical size of the ice nucleus is defined such that if some more molecules join the nucleus and in turn the radius increases, then the growth of the nucleus is more probable than its decay. In the opposite case, the nucleus reveals a tendency to decay. If the ice nucleus is formed without being subjected to any foreign particles or substrate, it is formed by homogeneous nucleation. The formation energy supplied to the nucleus under isothermal nucleation is

$$\Delta F = V(f_i - f_w) + S\sigma_{i/w} \quad (1)$$

where ΔF is the formation energy in J, V and S are the volume and surface area of the ice nucleus in m^3 and m^2 , respectively; f_i and f_w are the free energy of ice and water in Jm^{-3} , $\sigma_{i/w}$ is the ice-water interfacial energy in Jm^{-2} .

The energy needed to form a critical nucleus is defined as energy barrier. Eq. (1) suggests that the interfacial energy increases the formation energy of the ice-water system, which is energetically unfavorable for nucleation.

The ice-water interfacial energy is the energy required to form a unit area of ice surface out of water. Though the interfacial energy is crucial for ice nucleation, understanding of it is still rather primitive, especially when homogeneous nucleation rises.

The ice-water interfacial energy can be obtained by theoretical analysis or experimental work [1,2]. It has been revealed that the ice-water interfacial energy obtained by some nucleation experiments shows considerable spread [3, 4]. Turnbull [5] noted that the solid-liquid interfacial energy of a number of metals and metalloids were closely related to their melting latent heat and solid density. Jeffery and Austin [3] modified this relation for the ice-water interfacial energy to compensate for its significant decrease with temperature. Luo et al. [6] presented a general method to determine the solid-liquid interfacial energy by the maximum degree of supercooling and applied it to the ice-water system.

Nucleation rate is defined as the number of critical nuclei arising in the liquid phase per unit volume and per unit time. Many solid-liquid interfacial physicochemical properties, such as interfacial energy, can be derived from nucleation rate by use of classical nucleation models.

Gránásy et al. [7] used the Cahn-Hilliard approach to evaluate the ice-water interfacial properties obtained by ice nucleation experiments between 235 and 240 K. The ice-water interfacial energy obtained from these experiments was consistent with that given by classical thermodynamic theory. Murray et al. [8] demonstrated the difference between the interfacial energy of hexagonal ice-water system and cubic ice-water system. If cubic ice nuclei were exclusively formed, the interfacial energy was between 20 and 24 mJm⁻², which was 78 percent of hexagonal ice-water interfacial energy.

In this paper, models of classical nucleation theory are discussed and utilized to

calculate the ice-water interfacial energy. Some homogeneous ice nucleation experimental systems are investigated. The ice-water interfacial energy is derived from Stan's experimental data. The rest of the paper is organized as follows: In Sec. 2, the classical nucleation models are discussed. Some homogeneous ice nucleation experimental systems are reviewed in Sec. 3. The ice-water interfacial energy are discussed in Sec. 4. Finally, the results are summarized in Sec. 5.

2. MODELS OF HOMOGENEOUS NUCLEATION

The number of critical ice nuclei formed per unit volume of water is given by the Boltzmann's expression

$$n(r_c) = 2 \frac{\rho_w}{\rho_i} \left(\frac{\sigma_{i/w}}{kT} \right)^{1/2} \exp\left(-\frac{\Delta F_g}{kT}\right) \quad (2)$$

where k is the Boltzmann constant in JK^{-1} , T is the equilibrium temperature in K, ρ_w and ρ_i are the density of water and ice in kgm^{-3} , ΔF_g is the free energy barrier in J.

If we apply the Kelvin Law to formation energy defined by Eq. (1), the free energy barrier can be derived as

$$\Delta F_g = \frac{4\pi r_c^2 \sigma_{i/w}}{3} \quad (3)$$

where r_c is the critical radius in m.

The critical radius can be found by integrating the equilibrium condition for an ice nucleus in the water. Substituting for r_c in Eq. (3) using the integrating results yields [3]

$$\Delta F_g = \frac{16\pi\sigma_{i/w}^3}{3[\bar{L}_m\bar{\rho}_i \ln(T_0/T)]^2} \quad (4)$$

where T_0 is the ice melting temperature at standard pressure in K, $\bar{L}_m$ is the average ice latent heat of melting between T_0 and T in Jkg^{-1} , $\bar{\rho}_i$ is the average ice density between T_0 and T in kgm^{-3} .

It can be found from Eq. (4) that $\sigma_{i/w}$ enters as a third power in the exponential expression in Eq. (2). So $\sigma_{i/w}$ has a significant influence on the number of critical ice nuclei. A ten per cent change in the value of $\sigma_{i/w}$ can cause the number to change by a factor of 10^6 [9].

Water molecules diffuse across the ice-water interface to form ice nuclei. Using the absolute reaction rate theory, Turnbull and Fisher [10] achieved the flux density of water molecules diffusing across the interface

$$n(d) = \frac{N_c kT}{h} \exp\left(-\frac{\Delta g^\#}{RT}\right) \quad (5)$$

where N_c is the number of monomers of water in contact with unit area of the ice surface, h is the Planck's constant in Js, R is the Molar gas constant in $Jmol^{-1}K^{-1}$, $\Delta g^\#$ is the activation energy of the diffusion of water molecule across the interface in $Jmol^{-1}$.

Multiplying Eq. (2) by Eq. (5) yields ice nucleation rate

$$J = 2N_c \left(\frac{\rho_w kT}{\rho_i h}\right) \left(\frac{\sigma_{i/w}}{kT}\right)^{1/2} \exp\left(-\frac{\Delta g^\#}{RT}\right) \exp\left(-\frac{\Delta F_g}{kT}\right) \quad (6)$$

where J is ice nucleation rate in $m^{-3}s^{-1}$.

The density and activation energy in Eq. (6), the average density and latent heat of melting in Eq. (4), can be expressed as functions of the equilibrium temperature.

These functions are listed in the Appendix.

The ice-water interfacial energy can be obtained from Eq. (6) if the ice nucleation rate is given by data from ice nucleation experiments.

3. EXPERIMENTAL METHODS

Nanoscale or microscale water droplets are employed to perform homogeneous nucleation experiment for the following reasons. Firstly, water used in the experiment cannot be absolutely pure and a fine water droplet has a lower probability being nucleated by foreign particles. Secondly, tiny water droplets can levitate in gas or water-insoluble liquid, so the impact of substrate on homogeneous nucleation can be eliminated. Finally, the number of frozen droplets is regarded as the number of ice nuclei formed in the experiment, which means that forming of an ice nucleus is the result of only one nucleation event per droplet. This requires not only the ice nucleus grows very quickly, which is true under homogeneous nucleation condition, but also the size of the droplet is very small.

The homogeneous nucleation of water droplet is a first-order phase transition. If water droplets have the same temperature and volume, the decay of the number of unfrozen water droplets can be regarded as a first-order kinetic reaction

$$N_u = N_0 \exp(-V_d J \tau) \quad (7)$$

where N_u is the number of unfrozen water droplets, N_0 is the initial number of water droplets, τ is the nucleation time in s.

If the number of unfrozen water droplets and initial water droplets are given, the ice nucleation rate can be obtained from Eq. (7).

Some experimental systems are designed to study homogeneous ice nucleation. In

the expansion cloud chamber system, water droplets are generated simultaneously by condensing vapor in a gas [11]. The pressure and temperature of the mixture of vapor and the carrier gas decrease sharply as it expands in the chamber and ice nuclei arise in water droplets. The size and the number of initial water droplets are measured by the small angle X-ray scattering technique. The number of unfrozen droplets is measured by the Fourier transform infrared spectroscopy.

Though the cloud chamber is a classical method to perform homogeneous ice nucleation, it has some intrinsic disadvantages. The number of initial and unfrozen droplets measured by the X-ray scattering and Fourier transform infrared spectroscopy is just at the statistical level. So is the size of the droplets. Each water droplet condensed from vapor doesn't have the same size, which is inconsistent with the requirement of Eq. (7). The most serious disadvantage is that the equilibrium temperature is derived from solving supersonic flow equation of the mixture. This introduces great uncertainty to the temperature. Because the temperature has strong impact on ice nucleation, it is important to detect the temperature accurately.

An experimental system with an electrodynamic trap is designed to levitate an electrically charged water droplet in the center of the trap [12]. The water droplet nucleates while being cooled in the trap. The size and nucleation of the droplet are detected by a CCD camera. There is no way to measure the temperature at the center of the trap where the droplet is located. So the temperature is measured at the periphery of the trap and regarded as the temperature of the droplet. It takes several minutes for the droplet to be cooled down to the equilibrium temperature. The

evaporation of water causes considerable temperature difference between the center and the periphery of the trap. So it is inappropriate to equal the measured temperature to the equilibrium temperature of the water droplet. The size is different from droplet to droplet because of the evaporation process, though the uniformity of droplet size was much better than that obtained in cloud chamber.

To control the size and temperature of the water droplet with considerable precision, Stan et al. [13] developed an ice nucleation experimental system within a microfluidic channel. Liquid fluorocarbon flowed through the channel with water droplets suspending in it. Water droplets were generated from a nozzle one after another. The droplet size could be adjusted by changing the flow rate of fluorocarbon or water. The flow and nucleation of the droplets were visualized by a high-speed camera combined with a microscope. The size of the droplets could be controlled within a relative standard deviation of $\pm 1.2\%$.

Much effort was paid to control and measure the temperature of the droplets flowing through the channel. A plate having separated temperature-controlling zones was attached to the channel. Five zones located at the middle of the plate were cooled down to different temperatures by thermoelectric modules. The droplets were cooled down when they flowed through these zones. The temperature gradient vertical to the axis of the channel was controlled by blowing cold nitrogen gas to the top surface of the channel. The temperature of these zones could be stabilized to desired values with the fluctuation smaller than $\pm 0.1^\circ\text{C}$.

Linear arrays of thin-film thermocouples were embedded in the inner wall of the

channel. The distance between the thermocouples and the droplets was less than 0.1 mm. There were 19 thermocouples located within a distance of 2.2 mm along the channel. A two-step numerical model was employed to convert the measured temperature to that of the droplets. The maximum error of the droplet temperature was estimated less than $\pm 0.41^{\circ}\text{C}$.

Because great effort is made to control and measure the size and temperature of the droplets in Stan's system, it is reasonable to conclude that Stan's experimental data is reliable and valuable to be analyzed for more information about ice nucleation.

4. RESULTS AND DISCUSSION

1) Nucleation Rate

37211 water droplets with the diameter of $79\ \mu\text{m}$ were generated within 700 seconds in the Stan's experiment. 34267 out of these droplets were effectively nucleated. The temperature of these droplets and their cooling rate are available at a website [14]. These data are utilized to calculate the ice nucleation rate by Eq. (7). The results are shown in Fig. 1.

In Fig. 1, the relation between ice nucleation rate and temperature is plotted in both linear and logarithmic coordinates. The diamonds plotted in linear coordinates show that the nucleation rate increases sharply with decreasing temperature. The nucleation rate at -37°C is 137 times the rate at -36°C . The ice-water interfacial energy dominates ice nucleation, so a faster nucleation rate implies a lower ice-water interfacial energy.

Fig. 1 Relation between ice nucleation rate and temperature derived from Stan's experiment

The squares plotted in logarithmic coordinates indicate that homogeneous ice nucleation can be regarded as a first-order reaction. The nucleation rate is analogous to reaction rate constant while increasing steeply with decreasing temperature.

The nucleation rate shown in Fig. 1 exhibits lower noise than that given by recent experiments [8,12]. This is in part a result of high datum throughput by Stan's experiment. The datum ensemble presented by Stan is the largest among what is reported for ice nucleation up to now. The real-time temperature measurement and uniformity of droplet size also contribute to the low noise of the data.

Linear regression analysis is utilized to fit the nucleation rate with temperature.

Within the experimental temperature range (235.35-237.15 K), the ice nucleation rate can be expressed as

$$\ln J = -4.48t - 149.25 \quad (8)$$

where t is the equilibrium temperature in $^{\circ}\text{C}$.

A straight line corresponding to Eq. (8) is plotted in Fig. 2. The other two straight lines suggested by recent studies are also shown in Fig. 2. These lines are plotted only within their experimental temperature range. It can be found from Fig. 2 that the nucleation rate given by Stan's experiment is in agreement with results given by the other experiments. The line corresponding to Eq. (8) shows a steeper slope than the other two, which indicates that a closer relation between ice nucleation rate and temperature is suggested by Stan's experiment. It also implies that the ice-water interfacial energy decreases quicker with temperature according to Stan's experiment.

Fig. 2 Relation between ice nucleation rate and temperature given by different experiments

2) Ice-water Interfacial Energy

A numerical program is designed based on the models discussed in section 2 to calculate the ice-water interfacial energy. Ice nucleation rate derived from Stan's

experiment is used in the calculation. The relation between the ice-water interfacial energy and temperature is obtained by linear regression

$$\sigma_{i/w} = 7.15 \times 10^{-4} t + 0.05 \quad (9)$$

Eq. (9) is plotted in Fig. 3. The lines suggested by Jeffery and Austin [3] and Gránásy et al. [7] are also shown in Fig. 3. Fig. 3 shows that the ice-water interfacial energy calculated by Eq. (9) is less than that given by the other two lines.

Hexagonal ice is assumed to be formed during homogeneous nucleation in previous studies. Recent X-ray diffraction experiment confirms that cubic ice is first formed as a metastable phase and part of cubic ice re-crystallizes to the stable hexagonal ice [15]. Murray et al. [8] estimate the ice-water interfacial energy at 235.8K with two ice nucleation models. Hexagonal ice is the only crystal phase formed in one model, and cubic ice is exclusively formed in the other. The hexagonal ice-forming model yields the ice-water interfacial energy as 26.8 mJm^{-2} , while the cubic ice-forming model gives the value as 20.8 mJm^{-2} .

As part of cubic ice transforms to hexagonal ice, a hybrid ice phase exists in the ice-water system during nucleation. Johnston and Molinero [16] performed a molecular dynamic simulation on the homogeneous ice nucleation. The ratio of cubic ice to hexagonal ice was found to be 2:1 in the hybrid ice-water system. The hybrid ice-water interfacial energy can be obtained by linear combination of the interfacial energy of cubic ice-water and hexagonal ice-water with the ratio

$$\frac{2 \times 20.8 + 1 \times 26.8}{3} = 22.8 \text{ mJm}^{-2}$$

The ice-water interfacial energy is 23.3 mJm^{-2} at 235.8 K by Eq. (9), which fits

well with the value given above.

Fig. 3 Relation between the ice-water interfacial energy and temperature

Fig. 3 shows that all of the three lines agree on the fact that the ice-water interfacial energy decreases with temperature. The line corresponding to Eq. (9) decreases quicker than the other two lines. This indicates that, according to the Stan's experiment, the structure of water molecular cluster becomes more similar to that of ice nucleus as temperature decreases.

5. CONCLUSIONS

The classical nucleation models are discussed. Some ice nucleation experimental systems are evaluated. The ice nucleation rate is calculated by the models using Stan's experimental data and fitted with temperature by linear regression. The ice-water interfacial energy is derived from the nucleation rate. A linear equation is provided to calculate the ice-water interfacial energy in the temperature range between 235.35 and 237.15 K. The ice-water interfacial energy calculated from the

equation is consonant with that given by linear averaging of the interfacial energy of cubic ice-water and hexagonal ice-water at 235.8 K. The ice-water interfacial energy derived from Stan's experimental data decreases quicker with temperature than what is suggested by recent studies. This is interpreted as, according to Stan's experiment, that the structure of water molecular cluster is more similar to that of ice nucleus as the temperature decreases.

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APPENDIX

PHYSICAL PROPERTIES OF SUPERCOOLED WATER AND ICE

Expressions of the density of supercooled water and ice are taken from Bogdan [4].

The expression for water is

$$\rho_w = \sum_{n=0}^6 a_n t^n$$

where $a_0 = 0.99986$, $a_1 = 6.69 \times 10^{-5}$, $a_2 = -8.486 \times 10^{-6}$, $a_3 = 1.518 \times 10^{-7}$,

$a_4 = -6.9484 \times 10^{-9}$, $a_5 = -3.6449 \times 10^{-10}$, $a_6 = -7.497 \times 10^{-12}$, ρ_w is in gcm^{-3} , and

for ice

$$\rho_i = \sum_{n=0}^2 b_n t^n$$

where $b_0 = 0.9167$, $b_1 = -1.75 \times 10^{-4}$, $b_2 = -5 \times 10^{-7}$, ρ_i is in gcm^{-3} .

Expression of the latent heat of melting of ice is taken from Tabazadeh et al. [17]

$$L_m = \sum_{n=0}^2 c_n t^n$$

where $c_0 = 6005.2356$, $c_1 = 18.2718$, $c_2 = -6.354$, L_m is in $Jmol^{-1}$.

The average value of the latent heat of melting and the density of ice is defined as

integral average from 0 °C to equilibrium temperature t

$$\bar{L}_m = \frac{1}{\Delta t} \int_t^0 L_m dt \quad \text{and} \quad \bar{\rho}_i = \frac{1}{\Delta t} \int_t^0 \rho_i dt$$

where $\Delta t = 0 - t$ is the supercooling degree of the equilibrium system in °C.

The expression of activation energy is taken from Pruppacher and Klett [1]

$$\Delta g^\# = 0.023 \exp(-1.13 \times 10^{-2} t + 2.74 \times 10^{-4} t^2 + 1.085 \times 10^{-6} t^3)$$

where $\Delta g^\#$ is in $Jmol^{-1}$.

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