A Dendritic Growth Model for Icing of Supercooled Water

Tianbao Wang, Min Chen*

Department of Engineering Mechanics, Center for Nano and Micro Mechanics
Tsinghua University, Beijing 100084, China

wtb14@mails.tsinghua.edu.cn, *mchen@tsinghua.edu.cn

Abstract— **Dendritic growth of ice in supercooled water droplets is studied theoretically and experimentally. The measured dendritic growth velocity of ice shows a good agreement with the prediction of the Langer and Müller-Krumbharr (LM-K) growth model at supercoolings less than 7 K, whereas an increasing overestimation in the latter is observed as the droplets are further supercooled. We modify the LM-K dendritic growth model with the consideration of the influence of interface kinetics. In the present model, a dendrite grows in the limit of marginal stability coupled with the diffusion process at the liquid-solid interface, and the interface kinetics supercooling is introduced in solving the dendritic growth problem. Our modification to the LM-K model well describes the dendritic growth of ice in water supercooled up to 25 K. This work provides a solution to the dendritic growth of ice in the high supercooling regime and can serve as a reliable input for the studies of icing problems in engineering fields.**

Keywords— ***Dendritic growth; Icing; Interface kinetics; Supercooling; Water droplet***

I. INTRODUCTION

The growth velocities of dendritic ice in the bulk of supercooled water has been experimentally and theoretically studied by various researchers. However, a dendritic growth model that is applicable for supercooled water in a large supercooling regime is still lacked. In principle, given the thermal diffusion equations in liquid and solid phases combining specific initial and boundary conditions, the dendritic growth in pure supercooled liquids can be solved. However, a number of approximations have to be made to simplify the theoretical model. First, the dendrite tip shape was approximated as a rotating paraboloid in a supercooled pure melt [1]. Then, Ivantsov gave the relationship between the growth velocity and the dendrite tip radius by solving the diffusion process in front of the paraboloid tip [2]. Langer and Müller-Krumbharr (LM-K) argued that the dendrite grew with a tip having a size at the marginal stability limit and developed the constrained growth model [3-6]. The LM-K model well predicts the slow dendritic growth at small supercoolings irrespective of the chemical nature of systems. In the case of supercooled water, Shibkov et al. reported a good agreement between the measured two-dimensional growth velocity of an ice crystal and the prediction of the LM-K model at the supercoolings less than 5 K [7, 8]. However, a more reasonable interpretation of the dendritic growth of ice, in particular in higher supercooling regime, should consider the interface kinetics [9-10]. The Wilson-Frenkel model [11-12] gives a microscopic picture of interface kinetics. If the rapid dendritic growth is supposed to obey the limit of stability still, we can model the rapid dendritic growth by coupling the LM-K model with the Wilson-Frenkel model. In this work, we show that the coupled models can well describe the dendritic growth of ice at deep supercooling.

II. THEORETICAL BASIS

A. LM-K Model for Dendritic Growth

The classical approach to describe the dendritic growth of a crystal from a pure melt is formulated in terms of a free boundary problem. The temperature fields in solid and liquid phase satisfy a heat diffusion equation with two boundary conditions. The first is the conservation of energy. The second is the relationship between the interface temperature and the thermodynamic melting point, considering the effect of capillarity and interface kinetics. The solution of the free boundary problem was first derived by Ivantsov [2]. He neglected the capillarity and interface kinetics effects and assumed a paraboloid shape of the dendritic tip. The tip moves at constant velocity, which is inversely proportional to the tip radius. In Ivantsov's solution, the dimensionless supercooling $\Delta = c_p \Delta T / L$ is related to the Peclet number p as [2]:

$$\Delta = p e^{p} E_1\left(p\right) \tag{1}$$

where $E_1\left(p\right) = \int_p^{\infty} \frac{\exp\left(-y\right)}{y} dy$; $p = \frac{vR}{2\alpha}$.

$\Delta T = T_m - T_\infty$ is the initial bulk supercooling of the melt, T_m is the equilibrium melting temperature, T_∞ is the liquid temperature far away from the liquid-solid interface, L is the latent heat per volume, and c_p is the specific heat per unit volume, α is the thermal diffusivity. Ivantsov's solution gives a coupling of v and R , whereas their single-valued dependence of supercooling is unavailable.

The dendritic tip has a size at marginal stability, which was introduced by Langer and Muller-Krumbhaar in their model of dendritic growth (LM-K model) [3-4]. They analyzed the stability of the Ivantsov's paraboloidal dendrites by treating the effect of surface tension as a linear perturbation, and divided the continuum family of Ivantsov's solutions into stable and unstable regions. They assumed that the selected dendrite corresponds to the point of marginal stability separating the stable and unstable regions. This conjecture leads to the prediction of a universal selection parameter defined as $\sigma = \alpha d_0 / vR^2 \approx 0.025$ which provides an additional relation between the growth velocity and the tip radius. Here d_0 is a capillarity length given by $d_0 = T_m \gamma c_p / L^2$, where γ is the solid-liquid surface tension. The growth velocity as a single-valued function of bulk supercooling is calculated on the basis of the marginal stability hypothesis. The dendritic growth velocity related to dimensionless supercooling Δ and dimensionless velocity $V = vd_0/2\alpha$ is given as follows:

$$V = \sigma p^2 \tag{2}$$

B. Wilson-Frenkel Model for Interface Kinetics

To consider the effect of interface kinetics during dendritic growth of a supercooled melt, we can use the kinetics supercooling term ΔT_k in the boundary condition at the interface, that is, the interface temperature is modified as $T_i = T_m - \Delta T_k$. Mostly, ΔT_k is related to the growth velocity v by a constant interface kinetics coefficient μ as $\Delta T_k = v/\mu$. However, this assumption may not be suitable for some substances. For instance, the MD simulations of the crystal growth of Lennard-Jones liquid [13] and silicon [14] have shown that the growth velocities are in good agreement with Wilson-Frenkel model. Rozmanov *et al.* [15] performed a MD simulation of ice crystal growth and found that temperature dependent growth velocities can be fitted by a functional form similar to the Wilson-Frenkel expression. Thus for the present dendritic growth model, we choose the Wilson-Frenkel model to take into account the effect of interface kinetics.

The Wilson-Frenkel model proposes the growth velocity of a pure material as follows [16]:

$$v = \frac{6aD(T_i)}{\Lambda^2}\left[\exp\left(-\frac{L}{kT_m}\right) - \exp\left(-\frac{L}{kT_i}\right)\right] f \tag{3}$$

where a is the cube root of the atomic volume, D is the mass diffusion coefficient in front of the interface, Λ is an average diffusion jump distance in the liquid, T_i is the interface temperature, k is the Boltzmann constant, and f is the fraction of repeatable growth sites at the interface. Assuming that $\beta = \Lambda^2/af$, we can rewrite equation (3) as follows:

$$v = \frac{6D(T_i)}{\beta}\left[\exp\left(-\frac{L}{kT_m}\right) - \exp\left(-\frac{L}{kT_i}\right)\right] \tag{4}$$

The chosen parameters for water are chosen as $L = 6.0\times10^3\ \mathrm{J\cdot mol^{-1}}$, $T_m = 273.15\ \mathrm{K}$. For convenience, β is assumed constant [16], and the mass diffusion coefficient $D(T_i)$ in front of the interface is approximated by bulk mass diffusion coefficient which can be obtained from experiments. The value of the unknown interface kinetics factor β can be determined on the basis of the experiment results. For instance, Xu *et al.* [17] measured the growth velocity of crystalline ice from 180 K to 262 K by using a pulse-laser-heating technique. They calculated the interface kinetics factor by fitting the Wilson-Frenkel model. However, the maximum growth velocity of ice they measured was approximately 10 cm/s, which is much less than the measured maximum dendritic ice growth velocity (60 cm/s) [7]. We tend to use the experimental results of dendritic ice growth velocity to determine the interface kinetics factor β by applying the coupled model.

C. Model of Dendritic Growth Involving Interface Kinetics

In LM-K model, the interface temperature is assumed to be the melting point without considering the interface kinetics effect. Here we introduce the interface temperature in LM-K model, and the solution of dendrite growth problem is written as：

$$\frac{T_i - T_\infty}{L/c_p} = \Delta - \frac{T_m - T_i}{L/c_p} = pe^p E_1(p) \tag{5}$$

In the coupled dendritic growth model, as shown in Figure 1, the interface temperature is considered as a supercooled temperature instead of the equilibrium melting point. By applying the Wilson-Frenkel model, the interface temperature is directly related to the growth velocity involving the kinetics effect. Therefore, we reasonably use the Wilson-Frenkel description of the interface temperature (equation 4) in our model. The final growth velocity of ice dendrites can be calculated by solving the equations (1), (2), (4) and (5) simultaneously. Before the solving, the interface kinetics factor β can be fitted by using the experimental dendritic ice growth velocity results.

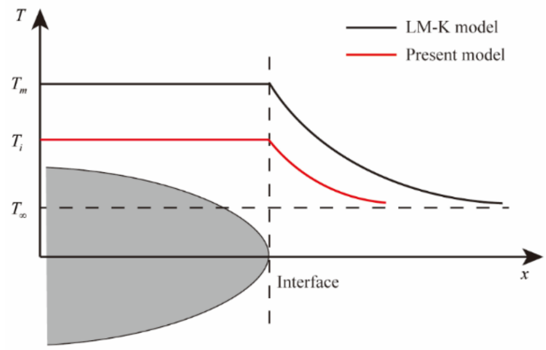

Fig. 1 The schematic diagram of the coupled dendritic growth model.

III. Experimental Method

The dendritic growth of ice in a single supercooled water droplet on a cold plate was investigated by high-speed CCD. The schematic diagram of the experimental apparatus is given in Figure 2.

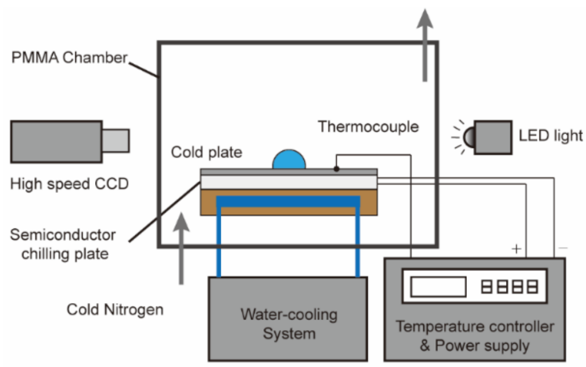

Fig. 2 Schematic of the experimental apparatus.

The main component of the apparatus was a thermally controlled PMMA chamber. The chamber was cooled by the supply of cold nitrogen gas. The water droplet was dispensed from a glass syringe connected to a micropump and deposited on the superhydrophobic surface. The environmental humidity was kept low by dry nitrogen flow, to avoid frost formation on the substrate. The substrate was cooled by a thermoelectric cooler and controlled by a temperature controller module to maintain a constant supercooling. The superhydrophobic surface was fabricated by coating the silicon substrate by silanized silica nanobeads with diameter 30 nm dispersed in isopropanol (Glaco, Soft99) [18].

Ultrapure water with a resistivity of 18.2 MΩ·cm was used in the experiments. First, a droplet was placed on the superhydrophobic surface, and the surface was cooled to the target temperature. After the temperature was kept for 2-3 min, the water droplet was cooled to the target temperature. This method could ensure the active control of supercooling from 5 K to 13 K for the droplets with a volume of 125 μL. The crystallization of ice was triggered by a needle attached an ice crystallite. To achieve larger supercoolings, we reduced the droplet volume to 5−15 μL, in which crystallization occured spontaneously from the liquid-substrate interface due to heterogeneous nucleation. The maximum supercooling in the present experiments reached 21 K. The growth process was recorded with a high-speed CCD at a rate of 2,000 fps.

IV. Results and Discussion

Figure 3(a) shows the dendritic growth process triggered by a fine needle. The growth velocity of a single three-dimensional dendrite is measured by analyzing the variation of dendrite length with time. Figure 3(b) shows the spontaneous dendritic growth of ice after heterogeneous nucleation at high supercoolings. The crystal growth in Fig. 3b consists of two distinct stages: the initial rapid growth and the subsequent slow growth. During the first process, high supercooling drives rapid crystal growth, leading to the dendritic morphology of interface due to thermal instability. This stage is accompanied by the rapid release of latent heat, which depresses the supercooling in front of the interface until reaching the equilibrium melting point. After the initial rapid growth, a mushy zone representing the mixing of dendrites and liquids between dendritic arms forms. The dendritic growth velocity is approximated by the front velocity of the envelope of the mushy region, as shown in Figure 3(b).

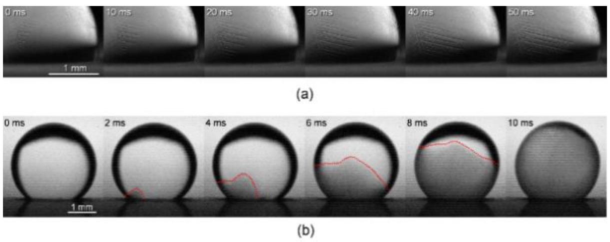

Fig. 3 The schematic diagram of the coupled dendritic growth model. Dendritic ice growth in a supercooled water droplet. (a) Dendritic ice growth triggered by a fine needle attached an ice crystallite; temperature of the water droplet is −5 ºC. (b) Spontaneous dendritic ice growth after nucleation; the temperature of the water droplet is −21 ºC.

The dendritic growth velocity of ice as a function of bulk supercooling is presented in Figure 4. For the sake of comparison, the growth velocity of two-dimensional single dendrite reported by Shibkov *et al.* [7] and the prediction of the LM-K model are provided. Our experimental data well agree with the results obtained by Shibkov *et al.* and also the prediction of the LM-K model at supercoolings less than 7 K. As the supercooling exceeds 7 K, the LM-K model shows an overestimation of the growth velocity, more distinctive with increasing supercooling. The overestimation is largely attributed to the absence of the interface kinetics effect in the LM-K model, as mentioned above.

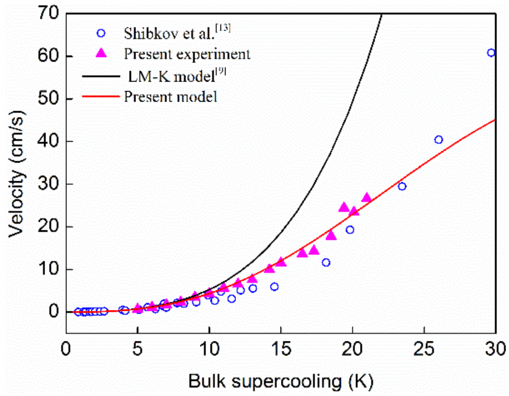

Fig. 4 Dendritic growth velocity under different supercoolings: comparison of the experimental and literature data with LM-K model and the coupled model.

The interface kinetics effect in the present dendritic growth model depends on two parameters, the diffusion coefficient $D(T_i)$ and the interface kinetics factor β. We use the bulk diffusion coefficients that are taken from the NMR experiments by Price *et al.* [19] to approximate $D(T_i)$. The interface kinetics factor β is related to microscopic quantities including the atomic jump distance from liquid to interface and the repeatable growth sites at the interface. In fact, it is difficult to be determined directly by experiments, and the reported estimations of β vary in the order of magnitude. Therefore, the accurate prediction of the dendritic growth velocity without any priori knowledge is very tough. However, if the present model faithfully reflects the physical nature of dendritic growth, a good fit to the experimental data is expected. It means that a well-worked dendritic growth model of ice used in the high-supercooling environment can be available for the studies of the icing problem in macroscopic levels. Figure 4 shows the fit to the experimental data up to the supercooling of 21 K, and the good consistent between our model and the experimental measurements can be set up with $\beta = 7.1\times10^{-11}$ m.

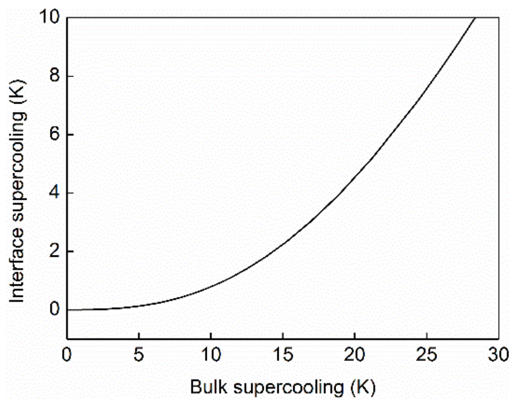

Fig. 5 The interface supercoolings at different bulk supercoolings in the coupled model.

However, our model predicts that the supercooling dependence of the dendritic growth of ice decreases as the supercooling is further increased in contrast to experiments reported by Shibkov *et al.* [7]. It suggests that the dendritic growth prematurely steps into the interface-kinetics-dominated regime in our model compared to the experimental results. This deviation may be introduced by the knowledge of β and $D(T_i)$. First, the definition of $D(T_i)$ refers to the diffusion coefficient in front of the liquid-solid interface [20], whereas in our calculation the bulk diffusion coefficient of water is used instead. The underlying ordered clusters and the density fluctuation close to the interface may cause a difference between them. Second, the assumption that β is independent on supercooling is taken in the calculation. It is possible that the value of β varies with supercooling considering that the fraction of repeatable growth sites at the interface depends on temperature [16, 21]. The clarification of these potential factors requires further investigations of the dynamic process of dendritic growth at an atomic level, for instance, by MD simulations. In a word, the present model with its parameter set can well describe the dendritic growth of ice up to ΔT~25 K. This supercooling range covers most icing processes in engineering applications. Thus the model is beneficial for the relevant research of preventing icing.

Figure 5 shows the interface supercoolings versus different bulk supercoolings in the present model. The interface supercooling can be neglected when the bulk supercooling is lower than ~7 K. Actually, the interface supercooling is about 0.31 K at 7 K bulk supercooling. The neglect causes an error of 7.6% in the dendritic velocity. Thus we recommend the present model for the prediction of dendritic growth velocities in supercooled water at supercoolings larger than 7 K.

V. Conclusions

The dendritic growth velocity of ice in water droplets has been measured in a supercooling range of $\Delta T \le 21$ K, and the maximum of 26.6 cm/s is obtained. Based on the experimental results, we focus on the theoretical description of the dendritic growth of ice over a wide supercooling range. The classical LM-K model accurately predicts the growth velocity of ice at small supercoolings ($\Delta T < 7$ K), whereas yields a significant overestimation with further increasing supercooling. We modify the LM-K model by introducing the interface kinetics effect following the Wilson-Frenkel model. The interface is no longer regarded as the thermodynamic equilibrium but deserves an interface supercooling. The bulk supercooling in the Ivantsov's solution of the dendritic growth with the paraboloid shape is rewritten as the interface supercooling accordingly. The latter drives the interface moving via coupling the atomic diffusion in front of the interface. For the dendritic growth of ice, our model shows good consistency with the experimental results up to the supercooling of 25 K.

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