Mesoscopic Dynamical Model of Ice Crystal Nucleation Leading to Droplet Freezing

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ABSTRACT: We present a numerical model to study the dynamic behaviors and heat conduction of freezing liquid droplets based on the MDPDE method (many-body dissipative particle dynamics with energy conservation configurations). In this model, the freezing processes involved in cooling, recalescence, and nucleation are considered. A new scaling method was developed to connect the mesoscopic MDPDE coefficients and macrothermal conductivity. The freezing of water droplets on cold surfaces with different wettabilities was simulated. Both the evolution of temperature and ice−liquid interface movement showed close agreement with the experimental data. We discuss the formation of a pointy tip on the top of an ice-drop and nucleation and growth during the recalescence stage. The rapid expansion of the recalescence region and the growth of the solid-phase region were calculated numerically, and this showed that the nuclei distribution of the two processes were completely different. The MDPDE model can not only predict the freezing time and shape deformation of ice-drops but also the nuclei formation and crystal growth during solidification. This study provides a useful tool for deicing material design.

INTRODUCTION

Ice formation on material surfaces plays an important role in refrigeration, air conditioning, aerospace, agriculture, and applications in many other fields.1−3 In particular, in aircraft applications, mainly anti-icing and deicing methods have been developed to prevent or weaken frosting.4−6 It is widely agreed that the freezing process of a droplet can be described in four distinct stages:5−7 (1) Precooling stage: a droplet is cooled by a cold source. During this stage, the temperature of the droplet can be cooled below the equilibrium freezing temperature but crystal nucleation does not occur. (2) Recalescence stage: supercooling-induced kinetic crystal grows rapidly from crystal nuclei. In this stage, supercooling is exhausted, and the droplet retains its equilibrium temperature. (3) Solidification stage: the crystal grows until the droplet is completely frozen. During this stage, the crystal growth rate is governed by the heat transfer rate. (4) Cooling stage: the temperature of a frozen droplet is cooled close to the temperature of the cold source. In our previous droplet freezing studies,8−10 we found that the crystal growth was delayed when the contact area between an ice-drop and a cold surface was artificially reduced by roughness, wettability, and microstructures. However, the design of deicing surfaces still requires an accurate numerical method to predict both the temperature transition and dynamic movement of freezing liquid.11−12

In 2003, Hindmarsh et al.13 provided the first simple heat balance numerical model to predict the temperature transition of a suspended freezing droplet. In 2014, Chaudhary et al.14 further studied the freezing of a droplet on a cold surface, with the solid/liquid interface position predicted by the temperature method expressed on deforming grids. They developed a well-accepted theory to simulate all four stages of freezing. In 2007, Zhang et al.15 created a smoothed particle hydrodynamics (SPH) model to study the spreading and solidification that occurs during the impact of a droplet. In 2019, Gong et al.16 developed a lattice-Boltzmann method (LBM) model to predict crystal nucleus deformation. In both the SPH and LBM models, the stages of freezing were ignored, and phase change was considered to occur as soon as the droplet temperature reached the equilibrium temperature. Therefore, the temperature evolution and freezing time did not match previous experimental studies.5−8

The many-body dissipative particle dynamics (MDPD) method has been widely utilized to study the dynamic behaviors of liquid droplets.17−21 Based on our previous...
study, the MDPD method has advantages in simulating droplet with severe deformation (like droplet impacting, spreading, and splashing). Due to its high stability, the MDPD method can simulate splashed secondary droplets, which are challenging to simulate by other mesoscopic methods (including LBM, because of mesh deformation). Besides, the DPD method has been famous for its calculation efficiency. In 2016, Yamada et al. integrated an equation of the internal energy state into the MDPD method to develop the MDPDE method (the MDPD method with energy conservation configurations), which made the simulation of temperature transition possible. As a result, except for phase change, the temperature transition and dynamic behaviors of liquid droplets can be predicted by the MDPDE method. Therefore, it is meaningful to develop the MDPDE method to simulate the phase change phenomenon. As a result, except for phase change, the temperature transition and dynamic behaviors of liquid droplets can be predicted by the MDPDE method.

Combining previous theoretical studies of the liquid phase change and numerical studies of the dynamical methods, a simple heat balance model can only predict the temperature fluctuation. Dynamical methods (like LBM and SPH) were good at simulating the deformation of the droplet, but solidification progress was thought to begin as soon as the droplet temperature reached the equilibrium value. However, the real physical process of freezing was far more complex than this, which led to a much shorter freezing time in previous dynamical methods than the experiment results. The ice nucleation model in this study considered the whole four stages (precooling, recalescence, solidification, and cooling) during droplet freezing, which made the simulation of all physical progress (the formation of a recalescence region, the development of a solidification structure, etc.) possible. Therefore, the simulation results using this model will be more precise than previous dynamic methods. In this study, the temperature transition, ice crystal nucleation, and dynamic behaviors of droplets that occur during the liquid phase change were investigated. First, we develop a simple equation to connect mesoscopic MDPDE parameters to macrothermal conductivity, which is then verified by the classical one-dimensional heat conduction. Next, the freezing process of a liquid on cold surfaces with different wettabilities is simulated. The temperature evolution during the four stages of freezing and interphase movement are in good agreement with the experimental data. Finally, we discuss ice shape deformation and crystal nucleus growth during droplet freezing.

**METHOD**

**MDPDE Governing Equations. Interactions between Liquid Particles.** In the MDPD method, each particle represents a cluster of real molecules moving in a Lagrangian fashion. Both fluids and solids were modeled by a group of DPD particles. In each time step $\Delta t$, all particles were defined by mass $m_i$, temperature $T_i$, position $x_i$, velocity $v_i$, and interaction force $F_{ij}$. The interaction force usually consisted of conservative force $F_{ij}^C$, dissipative force $F_{ij}^D$, and random force $F_{ij}^R$.

$$F_{ij} = F_{ij}^C + F_{ij}^D + F_{ij}^R$$

$$F_{ij}^C = A_{ij} \omega (r_{ij}) \vec{c}_i \cdot \vec{c}_j + B_{ij} (\vec{p}_i + \vec{p}_j) \omega (r_{ij}) \vec{c}_j$$

$$\omega_d (r_{ij}) = 1 - r_{ij}/r_{c,d} \quad (r_{ij} < r_{c,d}) \quad \text{or} \quad 0$$

$$\overline{p}_i = \sum_{ij} F_{ij} (1 - r_{ij}/r_{c,d})^2$$

$$F_{ij}^D = -\gamma \omega_d (r_{ij}) (\vec{c}_i \cdot \vec{c}_j)$$

$$F_{ij}^R = \zeta \omega_d (r_{ij}) \phi (\Delta t)^{-1/2}$$

$$\zeta^2 = 4TT_k \rho / (T_i + T_j)$$

$$\vec{c}_j = r_{ij}/|r_{ij}|$$

where $r_{ij}$ is the relative position of particles $i$ and $j$; $r_c$ is the cut-off range for the interaction of two particles and was usually chosen to be 1.1$r_{c,d}$; $A_{ij}$ and $B_{ij}$ are the amplitudes of attractive and repulsive forces, respectively; $\gamma$ and $\zeta$ are the amplitudes of the dissipation and random force, respectively; $\overline{p}_i$ is the number density of particle $i$; $\omega$ and $\omega_d$ are weight functions; $k_B$ is the Boltzmann constant; $\phi (\Delta t)$ is a random distribution function with zero mean unit variance; and the cut-off for attractive force $r_{c,d} = 0.75r_c$.

**Internal Energy Equation.** The total internal energy, expressed as heat capacity $C$, and temperature $T_i$ is composed of mechanical energy-caused viscous heating $q_{ij}^D$, temperature difference-caused heat transport $q_{ij}^L$, and thermal fluctuation-caused random heat flux $q_{ij}^R$. The governing equations can be expressed as follows:

$$C_i \frac{dT_i}{dt} = \sum_{j \neq i} \left( q_{ij}^V + q_{ij}^C + q_{ij}^R \right)$$

$$q_{ij}^V = \frac{1}{2C_{ij}} \left( \omega^D (r_{ij}) \left( \vec{v}_i \cdot \vec{v}_j \right)^2 - \frac{\gamma^2}{m_i} - \omega^R (r_{ij}) \left( \vec{v}_i \cdot \vec{v}_j \right) \right)$$

$$q_{ij}^C = \kappa_{ij} \omega^H C_i \left( \frac{1}{T_i} - \frac{1}{T_j} \right)$$

$$q_{ij}^R = \alpha_{ij} \omega^HR \left( r_{ij} \right) \phi (\Delta t)^{-1/2}$$

$$\kappa_{ij} = C_i^2 k_0 (T_i + T_j)^2 / 4k_B$$

$$\alpha_{ij} = \sqrt{2k_B \nu}$$

$$s_c = 0.41 + 1.9(T_i T_j - 1)$$

$$\omega^D (r_{ij}) = \begin{cases} 1 & (r_{ij} < r_c) \\ 0 & (r_{ij} \geq r_c) \end{cases}$$

$$\omega^R (r_{ij}) = \omega^D (r_{ij})^{1/2}$$

where $\kappa_{ij}$ and $\alpha_{ij}$ are the strengths of the conductive and random heat fluxes, respectively; $k_0$ is described as the mesoscopic thermal conductivity; $s_c$ is a correlation of the Schmidt number; and $\omega^D$ and $\omega^R$ are weight functions. It is worth mentioning that, in many articles on the energy conservation DPD method, the relationship between $k_0$ and macrothermal conductivity is controversial. In earlier...
...articles,26–29 \( k_p \) was considered to be thermal conductivity, and the relationship between \( k_p \) and \( k_s \) was different. In 2010, Abu-Nada30 developed an equation defining the relationship between \( k_p \) and \( k_s \) (eq 13). In 2014, Li et al.31 published a method to calculate \( k_p \) using the Prandtl number and viscosity. However, the viscosity is not stable in most MDPD simulations, which constitutes a common weakness of the MDPD method.18 Furthermore, in industrial applications, thermal conductivity is more available than the Prandtl number. Therefore, defining the relationship between \( k_p \) and macrothermal conductivity for the MDPDE method was required and will be discussed later.

**Ice Nucleation Model.** During the four stages of liquid droplet freezing, the precooling and cooling stages can be estimated by solving the internal heat equation. The physical properties of water and ice were considered: density, estimated by solving the internal heat equation. The properties of ice and were required and will be discussed later.

The changes in these properties with changing temperatures were considered.34,35 Mesoscopically, the freezing probability of two liquid particles inside a supercooling droplet, nucleation stage, can be expressed by 

\[
\begin{align*}
  T(e) = & T_L/C_v; \quad T > T_e + L/C_v \\
  T_i; \quad T_e + L/C_v \geq T \geq T_e \\
  T_f; \quad T < T_e
\end{align*}
\]

The recalescence particle will not be completely nucleated until the latent heat has been exhausted, and the temperature is below \( T_e \) (at which point it is called a nucleated particle). When two nucleated particles have temperatures below \( T_e \), their dynamic interaction and heat transfer are controlled by the physical properties of their solid phase (ice). In this study, the interaction of ice particles was simulated by a spring damping model. Compared to the interaction of liquids (eqs 1–6), the random parameter for the solid phase was set to zero (\( \xi = 0 \)), and the dissipation parameter, which represents viscosity, was set extremely high at \( \gamma_s = 5\rho_l \). The Young’s modulus of ice particles did not match reality. Besides, the strong influence of the environment and re-icing process have not been considered in this study. For example, during the re-icing process, there might be no recalescence stage. Related influences were summarized in Jung et al.’s36 and Chu et al.’s37 study in detail. These issues will be further discussed in subsequent research.

**Scaling Methodology.** The scaling of length and temperature depends on the practical application. To simulate a droplet of 7.2 \( \mu L \), the length unit was characterized as \( k_B = 1 \times 4 \) m and the temperature unit as \( T_R = 300 \) K. The Boltzmann constant (\( k_B = 1.38 \times 23 \) J K\(^{-1}\)) was usually set to \( k_B = 1 \), and 3.9e15 H2O molecules were considered as a single DPD bead. Based on our previous work,21 the mass, time, and energy units were characterized as follows:

\[
\begin{align*}
  M_R &= L_R^3 \rho_k/\rho \\
  t_R &= (M_R \sigma_0/\sigma_{fl})^{0.5} \\
  E_R &= k_B T_R
\end{align*}
\]

where \( R \) represents the scaling unit; \( \rho \) represents the real value; the surface tension coefficient \( \sigma_0 \) is 0.072 N m\(^{-1}\); and \( \sigma_{fl} \) can be calculated from the following equation:

\[
\sigma_{fl} = -\frac{\pi}{240}(0.42ar^2\rho^2 + 0.003br^4\rho^3)
\]

For a good view of ice shape deformation, the number density of droplets in this study was set to \( \rho = 8.6 \). Correspondingly, we set \( A_L = -200 \), \( B_L = 25 \), and \( B_I = 27.5 \). In this way, \( \rho_L = 0.917/\rho \) and matches the experimental data.15 From eqs 20–23, \( t_R \) is equal to 3.28e–4s. The total computational time steps can be calculated by the target simulation time divided by the time step \( \Delta t \) and DPD time unit \( t_R \). Considering the fact that the entire cooling and freezing process usually lasted hundreds of seconds, \( t_R = 3.28e–4s \) was too small for the droplet freezing simulation. To prevent massive computational cost, \( t_R \) was set to 0.1 s, which resulted in an unreal surface tension coefficient (from eq 21, the surface tension coefficient fitted by \( t_R \) differs from the real value). Gravity and surface tension contribute to the shape of a droplet on a solid surface.

During recalescence, the temperature did not change until the latent heat \( L \) (333 kJ kg\(^{-1}\)) was exhausted.15 In other words, for frozen and recalescence liquid particles,
Therefore, the Bond number was maintained to correct for the effect of the unreal true unit
\[
\frac{\rho g}{\sigma} = \frac{\rho_0 g R^2}{\sigma_0}
\]  
(24)
Based on eq 24, gravity was set to \( g = 0.01 \). Through dimensional analysis, heat capacity can be characterized as
\[
C_v = \frac{C_0}{k_0 \mu}
\]  
(25)
Ignoring viscous heat and random heat, from eqs 11 and 13, we can roughly estimate this with a hypothetical unit volume and unit temperature difference as follows
\[
\rho \frac{C^2_0 k_0 (T_f^2 + T_i^2)}{4k_0 T_i T_f} \Delta T \sim \left[ \frac{E_R}{T_K} \right]
\]  
(26)
Through dimensional analysis of macrothermal conductivity \( \lambda \), we know that with a unit length and unit temperature difference
\[
\lambda \Delta T T_K \sim \left[ \frac{J}{s} \right]
\]  
(27)
From eqs 25–27, we found that
\[
k_0 \sim \frac{\lambda k_0 R \mu}{C^2_0}
\]  
(28)
Considering the influence of weight functions, there should be a coefficient \( x \) to correct \( k_0 \). From the following validation by a classic thermal conduction problem, the coefficient \( x \) is approximately 34.4. The physical properties used for model predictions are summarized in Table 1.

### Table 1. MDPDE Parameters (DPD Units)

| name             | symbol | value          |
|------------------|--------|----------------|
| number density   | \( \rho_v \), \( \rho_l \) | 8.6, 7.9       |
| attractive coeff. | \( A_v \), \( A_l \) | \(-200, -185\) |
| repulsive coeff. | \( B_v \), \( B_l \) | 25, 25         |
| dissipation coeff.| \( r_v \), \( r_l \) | 2.0, 10.0      |
| heat capacity    | \( C_v \), \( C_l \) | 3.5e16, 1.6e16 |
| thermal conductivity | \( k_v \), \( k_l \) | 5.24/C_0, 47.3/C_0 |
| cut-off range | \( r_v \), \( r_l \) | 1              |
| Boltzmann temp.  | \( k_0 T \) | 1              |
| equilibrium temp. | \( T_e \) | 0.91           |
| nucleation temp. | \( T_n \) | 0.857          |
| latent heat      | \( L \) | 0.27C_0       |
| time step        | \( \Delta t \) | 0.01           |
| length unit      | \( l_v \) | 1e-4 m         |
| time unit        | \( t_v \) | 0.1 s          |
| mass unit        | \( M_v \) | 1.2e-8 kg      |
| energy unit      | \( E_v \) | 4.14e-21 J     |
| temperature unit | \( T_v \) | 300 K          |

### RESULTS

Valuation of Thermal Conductivity. To validate our approach, a classic thermal conduction problem was simulated. As shown in Figure 1, in a two-dimensional (2-D) square computational region (\( 45 \times 20 \)), 7800 liquid particles were uniformly distributed with a density of \( \rho_l \) and a temperature of 1.2 (DPD units). The simulation system is a bulk system with reflection boundaries. The dynamic parameters we used are listed in Table 2. This system was designed for the thermo-function test, and the dynamic parameters could be flexible. In the first step of the simulation, the temperature of the particles in the lowest two layers (particles with coordinate between \( y = 0 \) and \( y = 2/\sqrt{1/\rho_l} \) was maintained at 0.8 to act as a cold source. Afterward, the whole region would begin to cool. To focus on the heat transfer, the solidification process was ignored. Theoretically, this problem can be solved analytically by the heat conduction equation
\[
\frac{dT}{dt} = \lambda \frac{\partial^2 T}{\partial y^2}
\]  
(29)
where the thermal conductivity \( \lambda \) and heat capacity \( C_v \) were 0.55 J m\(^{-1}\) K\(^{-1}\) s\(^{-1}\) and 4.2e6 J K\(^{-1}\) m\(^{-3}\), respectively, in the real unit.

From our simulation, both the temperature distribution along the heat transfer direction (as shown in Figure 2) and the evolution of the average temperature of the whole region (as shown in Figure 3) were in good agreement with the analytical solution.

Thermal conduction of liquid was simulated with different number densities (\( \rho = 4.0, 8.6, 10.0 \)), different scaling units (mesoscopic, \( l_v = 0.1 \) mm; microscopic, \( l_v = 10 \) nm), and different dimensions (three-dimensional, 3-D). For liquid models with different number densities, the \( C_v \) and \( k_0 \) were different in the DPD unit based on eqs 25 and 28. The simulation on the microscopic scale was produced with \( l_v = 10 \) nm, \( t_v = 1e-4s \), simulation box: 450 nm \( \times \) 200 nm. The average temperature was compared with the analytical solution. In 3D simulation, the simulation box was set as the \( 10 \times 10 \times 10 \) DPD unit. The temperature evolution was also compared with the analytical solution. As presented in Figure 4, all simulation results showed close agreement with the analytical results. Therefore, we assume that the scaling methodology proposed in this study is valid.

Droplet Freezing on a Cold Surface. The freezing of a 7.2 \( \mu L \) droplet on a hydrophobic surface (contact angle \( \theta_c = 110^\circ \)) was simulated. The initial temperature of the droplet was 0.91 (0°C), and the cold surface was maintained at 0.857 (\(-16^\circ C\)). The wettability of the cold surface was controlled by adjusting the attractive and repulsive coefficients for surface–liquid interaction (for \( \theta_c = 70, 90, 110, 130, \) and 

150\(^\circ \), \( A_v = -60, -48, -36, -22, -10 \) respectively; \( B_v = 25 \)).

Figure 5 shows the temperature evolution and liquid–ice interface movement of a droplet freezing on a cold surface of \(-16^\circ C, 110^\circ \), during the recalescence, solidification, and cooling stages. The MDPDE result exhibits good agreement with Chaudhary’s research. The difference between the experimental data and numerical results could be caused by the insert temperature sensor. As the extension of the ice phase, the difference in temperature inside the droplet reduced, which induced the increase of equipment error. The experimental data for “center freezing height” are not available in Chaudhary’s research. but it can be measured using a high-speed camera. The topmost temperature distribution and shape deformation of the ice-drop are shown in Figure 6. In frame (A), a droplet before recalescence usually had a nearly uniform internal temperature. In frame (B), the droplet reaches \( T_e \) very quickly at the beginning of the recalescence stage. In frames (C) and (D), as the droplet cooled, the ice–
liquid interfaces moved upward. The temperature of the liquid region remained at $T_e$, while a variable temperature distribution is shown in the solid region. In frames (E) and (F), because the solid phase of a droplet had larger thermal conductivity and smaller heat capacity than in the liquid phase, the droplet cooled rapidly. This series of observed changes is identical to our previous experimental study.8

Next, the freezing of a droplet on surfaces with various wettabilities was simulated. The topmost temperature evolution of the entire solidification stage is shown in Figure 7. In the beginning, the droplet was set to have a temperature of $0 \degree C$. The initiation time of recalcensure was determined to be $0 \, s$. After $0 \, s$, the time for a droplet to complete solidification was called the freezing time. The temperature did not fall until the latent heat was exhausted. Once the latent heat was exhausted by the surroundings, the recalcensure particle was nucleated. Therefore, the length of time that the topmost temperature maintained $T_e$ can be assumed to be the freezing time. On hydrophilic surfaces, the interface between a droplet and a cold surface was large, and the droplet height (thermal conduction length) was small. In Gong et al.’s study,16 the reason why the hydrophobic material could delay droplet freezing was described as the fact that the decrease of the contact area (induced by wettability) delayed the solidification rate. Using our model, this phenomenon shall be analyzed differently. First, with the decrease of the contact area, the cooling rate during the precooling stage was delayed, and this can also be seen in Gong et al.’s study.16 Second, the decrease of thermoconduction (induced by the contact area) affected the release of latent heat, which extended the time of the solidification stage. In other words, hydrophobic surfaces can both delay the droplet’s freezing and slow down its nucleation rate.

**DISCUSSION**

Ice Deformation After Freezing. When a droplet froze on a hydrophilic ($\theta_c = 70\degree$) and a hydrophobic ($\theta_c = 110\degree$) surface, ice deformation was recorded. The attractive coefficient and repulsive coefficient of the droplet model was $-50.0$, $-200.0$, $-250.0$. For pure water, under normal atmospheric pressure, the density of ice was $917 \text{ kg m}^{-3}$. However, when the droplet was mixed with other chemical components, the density could be variable. A large range of density change can be numerically computed by changing the attractive and repulsive parameters in our model. The freezing process of droplets with different solid-phase densities (from $1000$ to $593 \text{ kg m}^{-3}$) was simulated (with the droplets’ initial temperature being $0.91 \text{ (0 \degree C)} and surface temperature being $0.857 \text{ (–16 \degree C)}$. Related coefficients and ice densities are shown in Table 3.

Figure 8 shows ice shapes with different ice densities. Along the direction of droplet height, the droplet can be considered

Table 2. Main Dynamic Parameters for the Test System

| parameters      | symbol | value   |
|-----------------|--------|---------|
| number density  | $\rho_l$ | 4.0, 6.6, 10.0 |
| attractive coeff | $A_l$  | $-50.0$, $-200.0$, $-250.0$ |
| repulsive coeff  | $B_l$  | 25.0    |
| dissipation coeff | $\gamma$ | 2.0 |
| random coeff     | $\xi$  | 2.0     |

![Figure 1. Visualization of cooling liquid particles at different times (t, time in DPD unit, t_R = 0.1 s).](https://example.com/figure1)

![Figure 2. Comparison of temperature distribution along the y-direction at different times (t, DPD unit, t_R = 0.1 s) between the analytical (left) and numerical (right) results (“theo” represents theoretical; “simu” represents “simulation”).](https://example.com/figure2)

![Figure 3. Comparison of the average temperature evolution between the analytical (lines) and MDPDE numerical (points) results.](https://example.com/figure3)
to be composed of cylinders with different perimeters. During the solidification process, the cylinders freeze from the bottom to the top. With the same surface tension coefficient, cylinders with larger perimeters have higher surface tensions. Therefore, the top of the droplet usually has a large deformation. As long as the ice density was larger than the droplet density, we observe an obvious pointy tip on the top of the ice-drop. The MDPDE droplet freezing model can predict the phase change-induced deformation at any density ratio ($\rho_\ast = \rho_M/R/\rho_L$). The more serious the density changes, correspondingly more obvious conical ice was seen. The interaction between a cold surface and ice was identical to that between ice (nucleated) particles. Therefore, as the droplet solidified, the droplet-surface interface line extended, as well. In previous theoretical studies, the ice tip formation can be deduced analytically when the density change was between 1000 and 917 kg m$^{-3}$. To simplify the derivation process, the liquid–surface interface line (which was not fixed intentionally in this model) was simplified as unmovable in theoretical studies. Numerically, we can also set the liquid–surface interface line to be unmovable and this will not change the regular ice deformation.

Crystal Nucleation Process. In previous studies about the solidification stage of a droplet, a nucleation temperature $T_n$ was applied to determine the initiation of the recalcitrance stage, and the temperature of all liquid
particles reached equilibrium temperature $T_e$ at the beginning of recalescence. Based on Bigg's research, a droplet at nucleation temperature is at its maximum freezing probability. When the environmental conditions were conducive to a droplet freezing, the freezing probability (in other words, the nucleation probability $Q$) could be very high, and the droplet particles were nucleated almost simultaneously, which agreed with the previous theory. However, when the temperature of a cold source was not near $T_n$, or when the ambient temperature was much higher than $T_n$, the nucleation probability could be very low, which means that the previous theory would no longer be suitable. In this article, we provide a new model to study droplet freezing when the freezing probability is low (due to environmental conditions) and when nucleation probability is not uniformly distributed. In most experiments, before recalescence, the temperature inside the droplet was almost uniform. In this model, $T_n$ was also applied as a condition of supercooling. Every time a liquid droplet interacted with another, there was a probability $Q$ that it would be initiated into the recalescence stage with a temperature of $T_e$ and have latent heat added to its enthalpy. $Q$ is related to the cooling environment of the droplet, and the value of $Q$ influenced the time of precooling stage. Mainly, the

**Table 3. Attractive and Repulsive Parameters for Ice Models with Different Densities**

| attractive coefficient | repulsive coefficient | number density | mass density (kg m$^{-3}$) |
|------------------------|----------------------|----------------|---------------------------|
| $-200$                 | 25                   | 8.6 (base)     | 1000 (base)               |
| $-185$                 | 25                   | 8.2            | 953                       |
| $-170$                 | 25                   | 7.9            | 917                       |
| $-135$                 | 25                   | 6.6            | 767                       |
| $-95$                  | 25                   | 5.1            | 593                       |

**Figure 6.** Temperature distribution inside a droplet at different time steps ($\theta = 110^\circ$).

**Figure 7.** Topmost temperature evolution of a droplet freezing on surfaces with various wettabilties.

**Figure 8.** Ice-drop deformation of droplets with different ice densities (left: on a hydrophobic surface ($\theta = 110^\circ$), right: on a hydrophilic surface ($\theta = 90^\circ$)).

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deicing method was by reducing the contact time of liquid and cold substrate. Therefore, the time of precooling determines whether a droplet can freeze on the deicing material. However, if the precooling time is negligible, Zhang et al.’s VOF model43 and Tembely et al.’s model44 are recommended. By setting the probability \( Q \) to be 1, the simulation result in our model will be similar to that in their models. During the recalescence stage, particle temperature does not decrease until the latent heat is exhausted. Once the temperature of the recalescence particle was below \( T_e \), a nucleus formed. The nucleated particle can also continue to activate the recalescence of other particles.

**Figure 9.** Temperature distribution (left) and nucleation process (center) during droplet freezing (contact angle 150°), and flow chart of particle nucleation (right).
Figure 9 shows a droplet composed of liquid particles, all having a temperature of 0.857 (−16 °C), while the temperature of the cold surface was also set to 0.857 (−16 °C). Because of the low $Q$ (which was set to 1e−4%), nucleation did not begin. In this study, the model we proposed was a local-parameter-based method. The droplet was simplified to be isotropy, and every liquid particle was initialized to the recalescence stage with a probability of $Q$ (see eq 18). Recalescence particles were not nucleated until the latent heat $L$ of it was exhausted by the low-temperature liquid around it. When the particle was nucleated, the physical parameters of the DPD particle was changed from liquid parameters to solid parameters. Then, the nuclei began initializing the recalescence of particles around it (in Figure 9, when $t = 0.49$ s, a recalescence region is observed). At the same time, the temperature inside the droplet was no longer uniform. As the recalescence particles were cooled by surrounding liquid particles, more particles were nucleated, leading to the expansion of the recalescence region. Most of the particles then began recalescence (Figure 9, 0.91 s), and almost all regions of the droplet showed a temperature of $T_c$. A nucleated particle initialized the recalescence of the surrounding particles, so there was always a nucleus at the center of a recalescence region. Particles at the edge of the recalescence region were cooled first and were more easily nucleated. Therefore, in recalescence regions, nucleated particles were loosely distributed. This can be thought to be the initial state of the ice structure. The interactions between recalescence particles and nucleated particles were based on the interactions of liquid. Therefore, the ice structure in the initial state was similar to a liquid. Afterward, once the recalescence region reached the cold surface (Figure 9, 1.87 s), the latent heat was consumed quickly (the cold surface was set to have a constant temperature), and thus the particles were nucleated quickly, and the nucleated particles were tightly distributed (Figure 9, 1.87 s). Regions with tightly distributed nuclei were defined as solid-phase regions. This was the final state of the ice structure, which can be thought as a rigid structure. When the solid phase first appeared, the interface of liquid—solid might be oblique (1.87 s, 2.8 s), due to the randomness of nucleation. Particles closer to the surface had a quicker heat transfer rate, which resulted in a quicker nucleation rate. Therefore, after many time steps, the liquid—solid interphase tended to be a circular arc perpendicular to the liquid—surface interface (6.64 s). As long as the surface had the minimum temperature, the droplet froze from bottom to top (14.63 s). Due to the density difference between liquid and solid states, the last region to freeze froze into a sharp tip at the top of the droplet (18.67 s). The flow chart of the nucleation model is presented below. Our simulation showed an example of a nonequilibrium solidification, in which the large temperature perturbation enforces the system to crystallize. The simulation of equilibrium solid—liquid transitions requires sampling schemes to surmount the liquid—solid free energy barrier, which will be investigated in our future study.

The nucleation model proposed in this study requires a nucleation probability, which can only be determined by a molecular-level simulation. However, it can be predicted statistically by foreign matter content, droplet size, etc. As mentioned in our previous study, although the solidification occurred in tens of seconds, when the nucleation was low, the time of the precooling stage could be hundreds of seconds. Therefore, when the nucleation probability is low (for example, as with supercooled droplets undergoing deformation), the time of the precooling stage was greatly increased. It is worth mentioning that although the first nuclei appeared at a random part of the droplet, the obvious solid phase usually appeared from the solid substrate. Inside the recalescence region, particles at the edge of the region always cooled first, which lead to the loosely distributed nucleus in this region. Therefore, the solid phase during the recalescence stage was invisible. But once the recalescence region extended to the solid substrate with a permanent temperature, the whole region was cooled quickly, and a visible solid phase with a closely distributed nucleus appeared. Recalescence did not begin as soon as the droplet temperature reached its critical value, which might induce the freezing time in numerical simulations that do not match the experimental data. Moreover, when the nucleation probability inside a droplet is not uniform (for example, as with heterogeneous liquid droplets), ice formation could be quite atypical. These situations can be easily simulated by the nucleation model proposed above.

In our simulations, the heat transfer of ambient air was ignored. There are two ways to simulate thermal conduction between liquid and ambient air. (1) Heat is conducted directly to the droplet near the liquid—gas interface. This method requires the deformation of a droplet to be small for the interface of liquid—gas to be easily determined, and the temperature of ambient air can be considered to be a stable value. (2) Gas particles are applied to simulate the liquid—gas heat transfer. With gas particles, the interface can be predicted precisely, especially when a droplet is greatly deformed by inertia and surface tension, and this method can also simulate the temperature distribution of ambient air. However, it is unnecessary to expend effort simulating the movement of air particles that have little contribution to the dynamic behaviors of a droplet (considering that the simulation of surface tension does not need gas particles in the MDPD method). The appropriate ambient thermal conduction method can be chosen for each specific situation.

## CONCLUSIONS

This study presents, to the best of our knowledge, the first demonstration of the capability of the MDPDE method to simulate the heat transfer and ice crystal nucleus deformation of the entire droplet freezing process. This model can accurately predict the freezing time and ice deformation of liquid droplets, which provides a powerful tool to study the liquid—solid phase change. In the simulation of droplet freezing on the cold substrate, substrate wettability has two effects on droplet freezing: the cooling rate during the precooling stage and the length of solidification time. Furthermore, the evolvement of the ice structure can be summarized as follows. Prior to the recalescence stage, a random area of the droplet was initialized (induced by nucleation probability). With the release of latent heat, a recalescence region with a high temperature could be observed. Once the latent heat was exhausted, more nucleation was initialized, which led to the rapid expansion of the recalescence region. Soon afterward, the whole droplet reached the equilibrium temperature. The edges of the recalescence region cooled first, so new nuclei appeared mostly at these edges, which led to loosely distributed nuclei inside the region. Once the recalescence expanded to the interface of the cold source, the whole recalescence region around the cold source was cooled. At this point, tightly distributed nuclei could be seen,
which signifies the beginning of the solidification stage. This explains why solidification usually appears at the interface of a cold source. Depending on the distance from the cold source, a solid phase with tightly distributed nuclei expanded from proximal to distal.

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Notes
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