

# Investigation of the nucleation temperature of different heat exchanger surfaces in an ice store

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## ABSTRACT

During loading ice stores, an ice layer forms on the heat exchanger surface once the surface reaches nucleation temperature. The growing ice layer increases the heat conduction resistance; the loading performance decreases.

In this work, the loading performance shall be optimized by changing the surface structure of the heat exchanger to lower the nucleation temperature. The ice store is loaded with an ice-free heat exchanger while ice grows apart from the heat exchanger.

The nucleation temperatures of heat exchangers of different materials with different surface roughness's and hydrophobic plasma coatings are examined in a model ice store. Furthermore, the nucleation temperatures of the heat exchanger surfaces are calculated using the classical nucleation theory and are compared to the experiments.

It is shown that the smoothest heat exchanger surface with a hydrophobic plasma coating lowers the nucleation temperature best. The loading performance is optimized.

Keywords: Coating (Materials), Cooling Load, Icing, Nucleation, Supercooling, Surface Temperature

## 1. INTRODUCTION

Renewable energies should be used for energy supply to minimize the climate change. The fluctuating supply of renewable energy sources requires energy storage to uncouple the energy demand from the energy supply. One possibility of energy storage is to use ice stores in combination with a cooling device for the air conditioning of buildings. They are used as thermal storages to increase the availability of the cooling supply. At the Institute of Thermodynamics and Thermal Engineering (ITW), an ammonia-water chiller was developed for solar cooling in combination with an ice store. By using ammonia as refrigerant, cold water temperatures of less than 0 °C are reachable and ice growth is possible. The ice store uncouples the cooling supply from the solar radiation and allows a more regular operation of the absorption chiller (Koller et al. 2007; Koller et al. 2012; Zetzsche et al. 2010). Ice stores are characterised by a high storage capacity because of the high enthalpy of fusion of ice of 333 kJ/kg, and small thermal losses. During loading ice stores, an ice layer forms on the heat exchanger surface when the surface temperature comes below the nucleation temperature. The growing ice layer increases the heat conduction resistance; the loading performance of the ice store decreases.

The idea in this work is to control the nucleation mechanism by modifying the heat exchanger's surface. Ideally, the water in the ice store can be supercooled while the ice growth is initiated at nucleation spots apart of the heat exchanger surface. This leads to a better loading performance of the ice store. The storage capacity increases because the ice store can be frozen with smaller heat exchangers.

In this paper, the influence of the surface structure and material on the nucleation temperature is examined. The nucleation temperature of the heat exchanger surface is calculated using the classical nucleation theory. The fundamentals of the model for the nucleation temperature calculation and theoretical results are discussed. Furthermore, the nucleation temperature is examined experimentally by measuring the maximum supercooling of the storage water during a loading procedure of a model ice store. First preliminary results of the experiments will be presented.

## 2. MODELLING OF THE NUCLEATION TEMPERATURE

Nucleation can occur homogeneously or heterogeneously. In the ice store, heterogeneous nucleation exists on the heat exchanger surface, as the heat exchanger surface is the coldest part in the ice store; see Fig. 1.

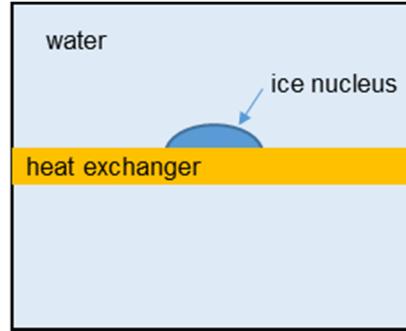


Figure 1: Ice nucleus on the heat exchanger tube in an ice store

The nucleation temperature is calculated in EES (Engineering Equation Solver) using the classical nucleation theory. This theory traces back to the work of Volmer and Weber (1926), Farkas (1927), Becker and Döring (1935) and Volmer (1939). The theory was developed for condensation, e.g. the phase change from vapour to liquid. Turnbull and Fisher (1949) transferred it to the phase change from liquid to solid, as it is for ice nucleation in supercooled water. Fundamental assumptions of the theory are a spherical nucleus; density and surface tension can be described with macroscopic values. Further standard works used for the following remarks are from Fletcher (1958), Dufour and Defay (1963), Defay and Prigogine (1966), Fletcher (1970), Hobbs (1974), Debenedetti (1996), Pruppacher and Klett (1997), Kashchiev (2000) and Vehkamäki (2011).

For the growth of an ice nucleus in supercooled water, molar reorientations at constant pressure and temperature occur. Water-to-water bonds are broken and water-to-ice bonds are created. A water molecule has to break away from its equilibrium position in water and find its equilibrium position in the ice structure. For the diffusion of the water molecule across the water-ice-boundary layer an activation energy must be overcome. The nucleation rate specifies the rate that a built nucleus grows by molecule flow and initiates phase change. The nucleation rate defines how many critical nuclei are built within a second in a defined volume. The heterogeneous nucleation rate  $J^{het}$  in supercooled water is defined by Eq. (1).

$$J^{het} = \frac{N_C \cdot k_B \cdot T_{H_2O}}{h} \cdot \frac{v_{ice}}{v_{H_2O}} \cdot \sqrt{\frac{4 \cdot \sigma_{H_2O,ice}}{k_B \cdot T_{H_2O}}} \cdot e^{-\frac{\Delta F_G^{het}}{k_B \cdot T_{H_2O}}} \cdot e^{-\frac{\Delta F_a}{k_B \cdot T_{H_2O}}} \quad \text{Eq. (1)}$$

During loading an ice store with the water volume  $V_{H_2O,St}$ , the time when the water has  $T_o = 0 \text{ } ^\circ\text{C}$  is  $t_o$ . The time when the nucleation temperature  $T_N$  is reached is  $t_N$ . Then ice growth starts. Assuming that water freezes when one critical nucleus is built, Eq. (2) is valid.

$$\int_{t_o}^{t_N} V_{H_2O,St} \cdot J^{hom} \cdot dt = 1 \quad \text{Eq. (2)}$$

With a constant cooling rate  $C = -dT/dt$ , the nucleation temperature  $T_N$  can be calculated by Eq. (3).

$$-\frac{V_{H_2O,St}}{C} \int_{T_o}^{T_N} J^{hom} \cdot dT_{H_2O} = 1 \quad \text{Eq. (3)}$$

For the specific volume of water  $v_{H_2O}$ , the specific enthalpy of fusion of ice  $\Delta h_f$ , the interfacial tension between water and ice  $\sigma_{H_2O,ice}$ , the free activation energy for the diffusion of a water molecule

through the ice-water-boundary-layer  $\Delta F_a$ , correlations from the literature listed above are used. The free energy of formation of a critical nucleus for heterogeneous nucleation  $\Delta F_G^{het}$  is calculated by Eq. (4):

$$\Delta F_G^{het} = \frac{1}{3} \cdot (\sigma_{H_2O,ice} \cdot A_{H_2O,ice} + \sigma_{ice,HE} \cdot A_{ice,HE} - \sigma_{H_2O,HE} \cdot A_{H_2O,HE}) \quad \text{Eq. (4)}$$

The contact area between water and heat exchanger equals, after the ice nucleus growth, the contact area between ice and heat exchanger, see Eq. (5).

$$A_{H_2O,HE} = A_{ice,HE} \quad \text{Eq. (5)}$$

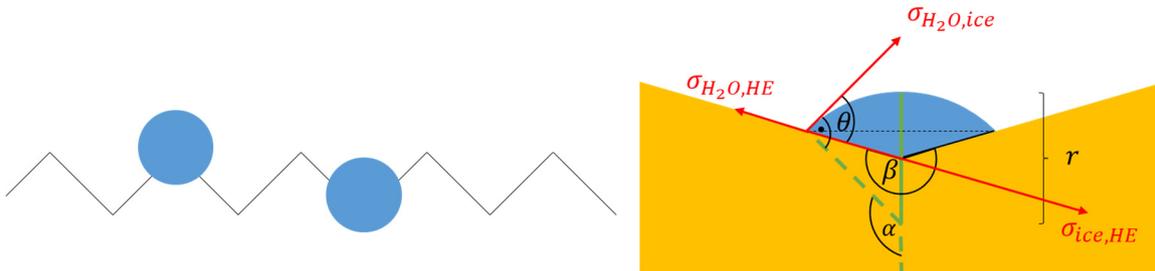
The equation of Young describes the equilibrium of forces on a drop in a thermodynamic equilibrium. According to Young, a correlation exists between the contact angle  $\theta$  and the interfacial tensions; see Eq. (6).

$$\cos \theta = \frac{\sigma_{H_2O,HE} - \sigma_{ice,HE}}{\sigma_{H_2O,ice}} \quad \text{Eq. (6)}$$

Resulting Eq. (7) for the free energy of formation  $\Delta F_G^{het}$ :

$$\Delta F_G^{het} = \frac{1}{3} \cdot \sigma_{H_2O,ice} (A_{H_2O,ice} - A_{Eis,HE} \cdot \cos \theta) \quad \text{Eq. (7)}$$

The contact areas between water and ice and the heat exchanger depend on the structure of the heat exchanger surface. The surface of a rough heat exchanger can be convex or concave; the ice nucleus can grow on a peak or in a notch, see Fig. 2. Besides, in Fig. 2, the geometrical coherences of an ice nucleus growing on a rough heat exchanger surface are visible.



**Figure 2: Critical ice nucleus in water on a rough heat exchanger surface for heterogeneous nucleation**

The surface area of the ice lens  $A_{ice,H_2O}$  (i.e. the contact area between water and ice) and the contact area between ice nucleus and heat exchanger surface  $A_{ice,HE}$  are calculated by Eq. (8) and (9). The radius of the ice nucleus  $r$ , the contact angle  $\theta$ , the curvature radius of the heat exchanger surface  $\beta$  and the position angle of the ice nucleus  $\alpha$  are used.

$$A_{ice,H_2O}^{het} = 2\pi r^2 \cdot (1 - \cos \alpha) \quad \text{Eq. (8)}$$

$$A_{ice,HE}^{het} = \pi \cdot r^2 \cdot \frac{\sin^2 \alpha}{\sin \frac{\beta}{2}} \quad \text{Eq. (9)}$$

It results Eq. (10) for the free energy of formation of a critical nucleus for heterogeneous nucleation  $\Delta F_G^{het}$ .

$$\Delta F_G^{het} = \frac{1}{3} \cdot \sigma_{H_2O,ice} \cdot \pi \cdot r_G^2 \cdot \left( 2 - 3 \sin\left(\frac{\beta}{2} - \theta\right) + \sin^3\left(\frac{\beta}{2} - \theta\right) - \cos^3\left(\frac{\beta}{2} - \theta\right) \cdot \cot\frac{\beta}{2} \right) \quad \text{Eq. (10)}$$

Comparing the free energy of formation of a critical nucleus for heterogeneous nucleation in Eq. (10) to homogeneous nucleation ( $\Delta F_G^{hom} = \frac{4}{3} \cdot \sigma_{H_2O,ice} \cdot \pi \cdot r_G^2$ ), it turns out in Eq. (11) that the free energy of formation for heterogeneous nucleation is the free energy of formation for homogeneous nucleation multiplied by the geometry factor  $f(\beta, \theta)$  (Li et al. 2017).

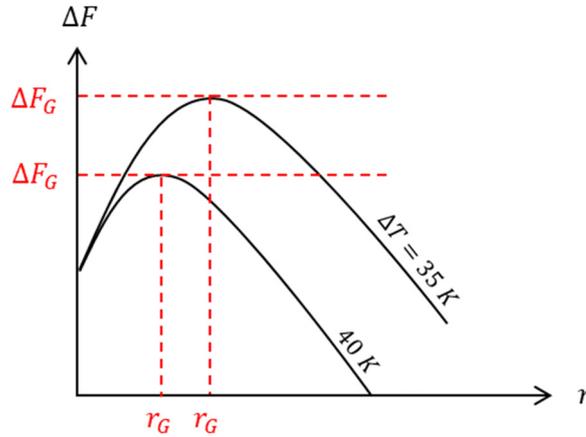
$$\begin{aligned} \Delta F_G^{het} &= f(\beta, \theta) \cdot \Delta F_G^{hom} \\ &= \frac{1}{4} \left( 2 - 3 \sin\left(\frac{\beta}{2} - \theta\right) + \sin^3\left(\frac{\beta}{2} - \theta\right) - \cos^3\left(\frac{\beta}{2} - \theta\right) \cdot \cot\frac{\beta}{2} \right) \cdot \Delta F_G^{hom} \end{aligned} \quad \text{Eq. (11)}$$

The boundary conditions for the formation of a stable nucleus in a notch of the heat exchanger surface are listed in Eq. (12)

$$0 < \beta \leq 180^\circ \quad 90^\circ - \frac{\beta}{2} < \theta < 90^\circ + \frac{\beta}{2} \quad \beta > \alpha > 0^\circ \quad \text{Eq. (12)}$$

The boundary conditions for a stable ice nucleus on a peak of the heat exchanger surface are defined in Eq. (13).

$$180^\circ < \beta < 360^\circ \quad \frac{\beta}{2} - 90^\circ < \theta < 270^\circ - \frac{\beta}{2} \quad 180^\circ > \alpha > \beta - 180^\circ \quad \text{Eq. (13)}$$



**Figure 3: Free energy of formation of a nucleus  $\Delta F$  depending on the radius of the nucleus  $r$  for different supercoolings  $\Delta T$**

The free energy of formation of an ice nucleus  $\Delta F$  consists of the required energy to build the new surface of the growing ice nucleus and the gained volume work by releasing the enthalpy of fusion of ice. The free energy of formation of a nucleus versus the nucleus radius for different supercooling is drawn in Fig. 3. For the formation of a critical nucleus, the free energy of formation has its maximum and the critical radius  $r_G$  is:

$$r_G = \frac{2 \cdot \sigma_{H_2O,ice} \cdot v_{ice}}{\Delta h_f \cdot \frac{T_o - T_{H_2O}}{T_o}} \quad \text{Eq. (14)}$$

The nucleation temperature of the heat exchanger surface during the cooling process of the ice store can be calculated considering all these information's in Eq. (3). The values of the model ice store for experimental investigations are used for the theoretical calculation.

### 3. THEORETICAL RESULTS FOR THE NUCLEATION TEMPERATURE

Fig. 4 shows the geometry factor  $f(\beta, \theta)$  and the nucleation temperature  $T_N$  versus the contact angle  $\theta$  for different angles of curvature of the heat exchanger surface  $\beta$ , calculated with the above presented model in EES. Exemplary geometrical cases for the formation of stable ice nuclei on heat exchanger surfaces with varied curvature angles  $\beta$  and varied contact angles  $\theta$  are presented in Table 1.

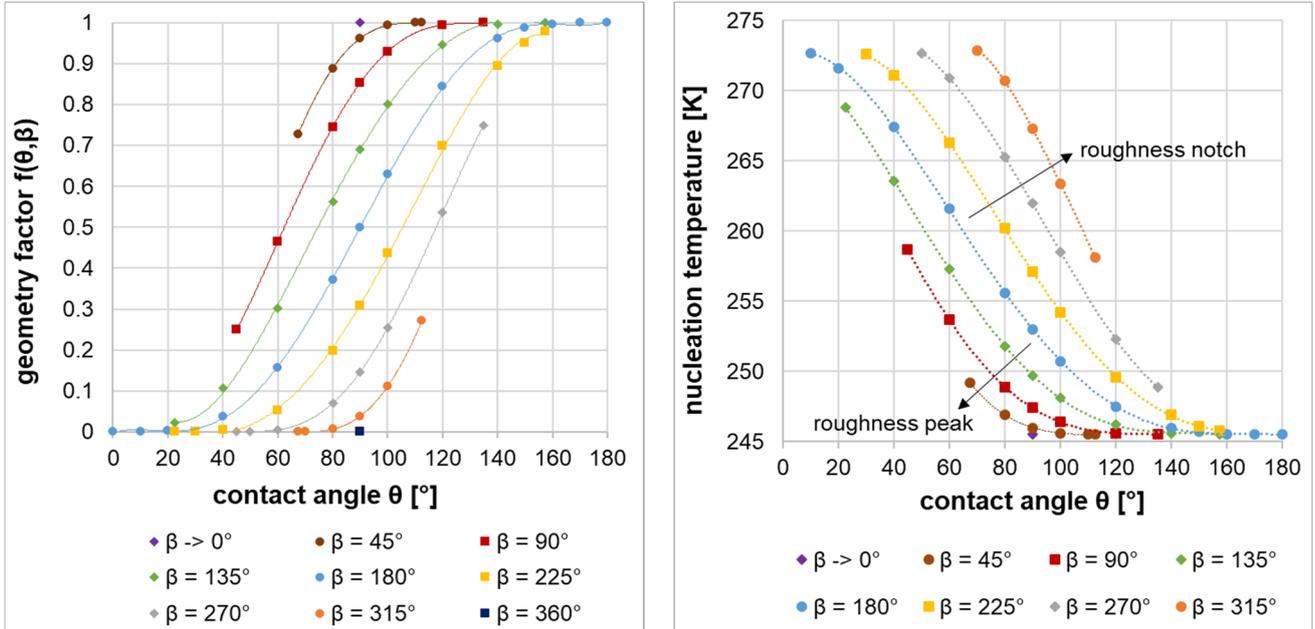


Figure 4: Geometry factor and nucleation temperature over the contact angle  $\theta$  for different angles of curvature of the heat exchanger surface  $\beta$

Table 1: Exemplary cases for the formation of stable ice nuclei on heat exchanger surfaces with varied curvature angles  $\beta$  and varied contact angles  $\theta$

	$\theta = 0^\circ$	$\theta = 45^\circ$	$\theta = 90^\circ$	$\theta = 135^\circ$	$\theta = 180^\circ$
$\beta \rightarrow 0^\circ$	X	X		X	X
$\beta = 90^\circ$	X				X
$\beta = 180^\circ$					
$\beta = 270^\circ$	X				X
$\beta \rightarrow 360^\circ$	X	X		X	X

The nucleation temperature is lowest when homogeneous nucleation can occur. Therefore, the geometry factor must be one. This is the case for decreasing  $\beta$  and growing  $\theta$ . Then, the contact area between ice and heat exchanger is small and nearly a full ice sphere has to be built. The minimum reachable nucleation temperature is 246 K for a heat exchanger surface with the most pointed peak. However, such a heat exchanger surface also forms a narrow notch where nucleation is initiated already at a low supercooling. Therefore, it is best for the lowering of the nucleation temperature to use the smoothest heat exchanger surface ( $\beta = 0^\circ$ ) with the largest possible contact angle ( $\theta \rightarrow 180^\circ$ ).

#### 4. EXPERIMENTAL RESULTS FOR THE NUCLEATION TEMPERATURE

The experimental setup was presented by Oechsle and Spindler (2016). In a model ice store filled with ultrapure water, demineralized water or tap water different heat exchanger tubes are examined. They differ in their materials (copper, aluminium, stainless steel), their surface roughness's  $R_a$  and  $R_z$  (electropolished, sandblasted) and their surface plasma coatings. Ethanol flows through the heat exchangers. At the beginning of a loading procedure of the model ice store the ethanol and the water have a temperature of 7 °C. Then, the temperature of the ethanol is set to -2 °C for 6 hours. Afterwards the temperature is reduced in steps of 0.1 K every 30 minutes until ice growth starts at the heat exchanger surface. The minimum water temperature in the model ice store is measured. This leads to the maximum supercooling of the water  $\Delta T = T_0 - T_N$  and approximately to the nucleation temperature  $T_N$ . For each heat exchanger with each water quality, 10 experiments are done and the mean nucleation temperature is defined. The characteristics of the different heat exchangers are listed in Table 2. First preliminary experimental results for the maximum supercooling reached with the different heat exchangers are listed in Table 3.

**Table 2: Characteristics of the different heat exchanger surfaces**

Heat exchanger surfaces	Copper (Cu)		Aluminium		Stainless steel	
	$R_a$ [ $\mu\text{m}$ ]	$R_z$ [ $\mu\text{m}$ ]	$R_a$ [ $\mu\text{m}$ ]	$R_z$ [ $\mu\text{m}$ ]	$R_a$ [ $\mu\text{m}$ ]	$R_z$ [ $\mu\text{m}$ ]
<b>Electropolished</b>	0.280	1.786	0.238	1.615	1.07	6.56
<b>Fine sandblasted</b>	0.3	0.705	-	-	-	-
<b>Middle sandblasted</b>	0.985	1.945	-	-	-	-
<b>Electropolished and plasma coated (<math>\theta = 86.3^\circ</math>)</b>	0.102	0.636	-	-	-	-

**Table 3: Mean maximum reached supercooling with the different heat exchangers during a loading procedure of the model ice store**

Heat exchanger surface	Ultrapure water	Demineralized water	Tap water
<b>Cu electropolished</b>	$0.9 \pm 1.0$ °C	$0.3 \pm 0.5$ °C	$1.3 \pm 0.2$ °C
<b>Cu fine sandblasted</b>	$0.9 \pm 0.4$ °C	-	-
<b>Cu electropolished and plasma coated</b>	$1.3 \pm 0.4$ °C	$1.0 \pm 0.4$ °C	$2.2 \pm 0.3$ °C

It turns out, that the smooth electropolished copper surface with plasma coating reaches the highest supercooling. That means it lowers the nucleation temperature best. The lightly alkaline tap water ( $pH \sim 8.2$ ) allows a higher supercooling than the lightly acidic ultrapure water ( $pH \sim 6.5$ ). The neutral demineralized water ( $pH \sim 7.4$ ) leads to the lowest supercooling. The ultrapure water has an electrical conductivity of  $0.24 - 0.4 \mu\text{S} \cdot \text{cm}^{-1}$ , demineralized water of  $10.8 - 13.3 \mu\text{S} \cdot \text{cm}^{-1}$  and tap water of  $281 - 331 \mu\text{S} \cdot \text{cm}^{-1}$ .

Detailed water analyses regarding the electrical conductivity, the pH number and the chemical and biological composition will follow. Furthermore, the contact angle of each heat exchanger surface has to be defined in the following research.

## 5. CONCLUSION AND OUTLOOK

The comparison between experimental und theoretical results for the nucleation temperature shows a good qualitative agreement. The smoothest heat exchanger surface with a hydrophobic plasma coating lowers the nucleation temperature best. The loading performance is optimized.

Regarding the quantitative values, a detailed comparison has to be done. From the roughness profiles of the different heat exchanger surfaces, the angle of curvature of the heat exchanger surface  $\beta$  has to be calculated. The different materials or plasma coatings define the contact angle  $\theta$ , that has to be determined. Then, the nucleation temperature of each heat exchanger surface can be calculated and compared to the nucleation temperatures reached experimentally.

Further experiments will be conducted with the parameter variation of the heat exchanger surface listed in Table 2.

## NOMENCLATURE

$A_{ice,HE}$	Contact area between ice nucleus and heat exchanger ( $m^2$ )	$T_N$	Nucleation temperature (K)
$A_{H_2O,ice}$	Contact area between ice nucleus and water ( $m^2$ )	$v_{ice}$	Specific volume of ice ( $m^3 \times kg^{-1}$ )
$A_{H_2O,HE}$	Contact area between water and heat exchanger ( $m^2$ )	$v_{H_2O}$	Specific volume of water ( $m^3 \times kg^{-1}$ )
$C$	Cooling rate ( $5,6 \times 10^{-5} K \times s^{-1}$ )	$V_{H_2O,St}$	Water volume in the ice store ( $m^3$ )
$f(\beta, \theta)$	Geometry factor	$\Delta F$	Free energy of formation of a nucleus (J)
$h$	Plank constant ( $6.626 \times 10^{-34} J \times s$ )	$\Delta F_a$	Free activation energy for the diffusion of a water molecule through the water-ice-boundary layer (J)
$J^{het}$	Heterogeneous nucleation rate ( $m^{-3} \times s^{-1}$ )	$\Delta F_G$	Free energy of formation of a critical nucleus (J)
$k_B$	Boltzmann constant ( $1.381 \times 10^{-23} J \times K^{-1}$ )	$\Delta F_G^{het}$	Free energy of formation for a critical nucleus for heterogeneous nucleation (J)
$N_C$	Number of water molecules in contact with ice surface ( $5.3 \times 10^{18} m^{-2}$ )	$\Delta F_G^{hom}$	Free energy of formation for a critical nucleus for homogeneous nucleation (J)
$r$	Radius of ice nucleus (m)	$\Delta h_f$	Specific enthalpy of fusion of ice ( $J \times kg^{-1}$ )
$r_G$	Critical radius of ice nucleus (m)	$\Delta T$	Supercooling (K) = $T_0 - T_N$
$t$	Time (s)	$\alpha$	Position angle of the ice nucleus ( $^\circ$ )
$t_0$	Time when the water has $T_0 = 0 \text{ }^\circ C$ (s)	$\beta$	Angle of curvature of the heat exchanger surface ( $^\circ$ )
$t_N$	Time when the water has $T_N$ (s)	$\theta$	Contact angle ( $^\circ$ )
$T$	Temperature (K)	$\sigma_{H_2O,ice}$	Interfacial tension between water and ice nucleus ( $J \times m^{-2}$ )
$T_0$	Melting temperature of water (273.15 K)	$\sigma_{ice,HE}$	Interfacial tension between ice nucleus and heat exchanger ( $J \times m^{-2}$ )
$T_{H_2O}$	Water temperature (K)	$\sigma_{H_2O,HE}$	Interfacial tension between water and heat exchanger ( $J \times m^{-2}$ )

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