Ultrasonic-Assisted Freezing of Micro-sized Water Droplets

Shaolei Gai

BSc (MechEng) (SAU); MSc (MechEng) (SAU)

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Statement of Originality

I hereby certify that the work embodied in the thesis is my own work, conducted under normal supervision.

The thesis contains no material which has been accepted, or is being examined, for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made. I give consent to the final version of my thesis being made available worldwide when deposited in the University's Digital Repository, subject to the provisions of the Copyright Act 1968 and any approved embargo.

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I hereby certify that the work embodied in this thesis contains published paper/s/scholarly work of which I am a joint author. I have included as part of the thesis a written declaration endorsed in writing by my supervisor, attesting to my contribution to the joint publication/s/scholarly work.

By signing below I confirm that Shaolei Gai contributed to the papers/ publications entitled:

(1) "LBM modelling of supercooled water freezing with inclusion of the recalescence stage"

	Shaolei Gai contribution	Supervisory team contribution
Conception and design	75%	25%
Analysis and interpretation	70%	30%
Drafting and production	70%	30%

(2) "Ice nucleation of water droplet containing solid particles under weak ultrasonic vibration"

	Shaolei Gai contribution	Supervisory team contribution
Conception and design	75%	25%
Analysis and interpretation	70%	30%
Drafting and production	70%	30%

(3) "A theoretical model for predicting homogeneous ice nucleation rate based on molecular kinetic energy distribution"

	Shaolei Gai contribution	Supervisory team contribution
Conception and design	75%	25%
Analysis and interpretation	75%	25%
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(4) "LBM study of ice nucleation induced by the collapse of cavitation bubbles"

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(5) "Effect of ultrasonic vibration on the nucleation onset of temperature of micro-sized water droplets"

	Shaolei Gai contribution	Supervisory team contribution
Conception and design	75%	25%
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Signature: **Elham Doroodchi**

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Publications

Journal articles

1. **Shaolei Gai,** Zhengbiao Peng, Behdad Moghtaderi, Jianglong Yu, & Elham Doroodchi. (**2020**). LBM modelling of supercooled water freezing with inclusion of the recalescence stage. *International Journal of Heat and Mass Transfer*, *146*, 118839. **(Q1, IF:4.947)**

2. **Shaolei Gai,** Zhengbiao Peng, Behdad Moghtaderi, Jianglong Yu, & Elham Doroodchi. (**2020**). Ice nucleation of water droplet containing solid particles under weak ultrasonic vibration. *Ultrasonics Sonochemistry*, *70*, 105301. **(Q1, IF:6.513)**

3. **Shaolei Gai,** Zhengbiao Peng, Behdad Moghtaderi, Jianglong Yu, & Elham Doroodchi. (**2020**). A theoretical model for predicting homogeneous ice nucleation rate based on molecular kinetic energy distribution. *Journal of the Atmospheric Sciences*. (Under review)

4. **Shaolei Gai,** Zhengbiao Peng, Behdad Moghtaderi, Jianglong Yu, & Elham Doroodchi. (**2020**). LBM study of ice nucleation induced by the collapse of cavitation bubbles. *Ultrasonics Sonochemistry*. (Under review)

5. **Shaolei Gai,** Zhengbiao Peng, Behdad Moghtaderi, Jianglong Yu, & Elham Doroodchi. (**2020**). Experimental Study on the ultrasonic-assisted freezing of micro-sized water droplets. (In preparation)

Conference papers

1. **Shaolei Gai,** Zhengbiao Peng, Behdad Moghtaderi, Jianglong Yu, & Elham Doroodchi. (**2018**). Effect of ultrasonic vibration on the nucleation onset of temperature of micro-sized water droplets. *Chemeca 2018*, 234.

Abstract

This research is concerned with a combined theoretical, experimental and numerical study of the ultrasonic-assisted freezing of micro-sized water droplets. The main objectives of the study are to gain an improved understanding of ice nucleation and the freezing of micro-sized water droplets induced by the high pressures from acoustic cavitation, and the subsequent effects on the freezing temperatures of the droplets. This work is motivated by the need to develop effective approaches to generating engineered ice particles with uniform sizes and spherical shapes for a range of industrial applications, such as in air-conditioning systems, medical cooling, food storage, ice pigging, and the broader field of cold energy storage.

In this study, a theoretical framework was developed to describe the relationship between ice nucleation and pressure. Specifically, fundamental improvements were incorporated into the existing models to capture the transition of the ice-water interface using an approach based on the distribution of the molecular kinetic energy which, in turn, eliminated the need to specify the ice-water interface energy and activation energy typically required in conventional methods. A good agreement was obtained between the predictions of the model and the experimental data from the literature for temperatures down to 190 K, indicating that the model was able to capture all of the essential elements of the ice nucleation phenomenon using a simplified approach. With the measurable parameters as the inputs, including the enthalpy of fusion, the hydrogen-bond energy, the pressure-dependent melting temperatures and the pressure-dependent densities of the solids/liquids, this theoretical framework can be readily extended and applied to analyse the nucleation of other liquids with hydrogen-bonds.

The experimental work is focused on the adaptation of the classic ice nucleation triggering techniques, which are based on acoustic cavitation, to systems with confined volumes of water (i.e., micro-sized droplets). In particular, two mechanical triggering methods were developed. In the first method, the fine solid particles submerged in a droplet were used to provide free sites for the inception of cavitation bubbles. In the second method, cavitation bubbles were formed within a continuous medium carrying the suspended droplets. Both methods used acoustic vibrations to trigger the ice nucleation. In the first method, it was found that the fraction of the frozen droplets increased with an increase in the concentration of the particle numbers, the intensity of the vibrations and the vibration induction time. It was evident that the nucleation sites in this approach were limited to the regions between the solid particles and the vibrating substrate which, in turn, indicated that the contact pressures due to the collisions of the particles with the substrate greatly influenced the onset of the ice nucleation. In the second method, the fraction of the frozen droplets was also found to increase with an increase in the intensity of the vibrations and the vibration induction time. The experimental observations showed that the sites of the onset of the ice nucleation were on the droplet's surface, where strong interactions were encountered between the cavitation bubbles (formed in the continuous phase) and the droplets (in the dispersed phase). It was evident that the cavitation bubbles triggered the onset of the ice nucleation.

Numerical studies based on the lattice Boltzmann method (LBM) were carried out to gain a better understanding of the underlying mesoscale physics of the ice nucleation and freezing processes for the above approaches. Specifically, the study developed a model which coupled the conventional pseudo-potential multi-relaxation-time LBM (MRT-LBM) with a thermal LBM to investigate the dynamics of the cavitation bubbles, including their growth and collapse and the subsequent ice nucleation and freezing processes. The thermal LBM was extended by: (i) the inclusion of the recalescence stage (rapid growth of dendritic ice); and (ii) the inclusion of a criterion for the pressure-dependent onset of the ice nucleation. In this model, the Stefan number was used to determine the initial ice fraction for the entire spectrum of the degrees of supercooling in the recalescence stage. The Simon-Glatzel equation was applied to correlate the ice melting curve with the local pressure field which, in turn, governed the onset of the ice nucleation. Both the data in the literature data and the experimental data collected as part of this study were used to validate the model. It was found that the deviations fell within the limits of experimental error.

The model was then used to gain insights into a number of phenomena, including: (i) the effects of the recalescence stage on the freezing process; (ii) the ice nucleation induced by the cavitation bubbles; (iii) the evolution of the pressures of the cavitation bubbles inside the crevices; and (iv) the evolution of the pressures on the surfaces of the droplets in the vicinity of the collapsing cavitation bubbles. The simulation results showed that the inclusion of the recalescence stage had a significant effect on the accuracy of predicting ice-water interface evolution for supercooling degrees greater than 20 K. Given that the freezing of a small droplet often bears a supercooling degree of more than 30 K, and the local supercooling degree could be significantly increased by the high pressures created by the collapse of the cavitation bubbles, therefore an accurate description of the freezing can be achieved only when the recalescence stage has been taken into account. Simulation results also captured the sudden rise in local temperature following the rapid (isentropic) process of cavitation bubble collapse. The local temperature rose significantly exceeded the ice melting temperature preventing the freezing process to proceed. These results suggest that maintaining a sufficiently large initial supercooling degree or use of additional mechanisms to force the ice crystals to migrate to the low-temperature regions are essential to achieve complete freezing of water droplets. The collapse dynamics of the air bubbles trapped in the crevices on the surfaces of the solid particles was found to be sensitive to the morphological characteristics of the crevices, with the collapse of the bubbles in a hemispherical crevice generating the highest pressures. More importantly, the results provided a potential theoretical explanation on how the presence of solid particles assists with the initialisation of the ice nucleation in a droplet. Lastly, the simulation results showed that the onset of the ice nucleation on the surfaces of the droplets was strongly dependent on the distance between the bubble collapse point and the surface of the droplet. The simulation results were used to develop a correlation for predicting the minimum distance required to initiate ice nucleation in the droplet as a function of the key operating parameters, including the sizes of the cavitation bubbles and the amplitudes of the external pressures.

The effectiveness of the method of triggering the ice nucleation with the cavitation bubbles for continuous production of micro-sized ice particles dispersed in an immiscible liquid was examined experimentally. Specifically, the yield and quality of ice particles, in terms of the fractions of the frozen droplets, the distributions of the particle sizes and the roundness ratios of the ice particles, were examined as a function of the characteristics of the ultrasonic vibrations, namely the power output of the sonicator, the duty cycle of the vibrations and the offset distance of the sonicator probe. It was found that the production yield could be increased with increases in the power output of the sonicator, the duty cycle of the vibrations and the offset distance of the sonicator, but that it was decreased with a reduction in the temperature of the cooling module. However, the increase in the yield led to a loss of quality as the mean diameter of the water droplets used for producing the ice particles was in a range from 535 μm to 567 μm. After the ice nucleation using the cavitation bubbles, the mean diameters of the ice particles produced were measured in a range from 450 μm to 590 μm. The freezing temperature achieved was as high as $269\ K$ with a fraction of frozen droplets of 2% and a roundness ratio for the ice particles of 1. The highest fraction of frozen droplets was about 92% which was obtained at $262\ K$, whereas the roundness ratio of the ice particles decreased drastically to around 45%.

The results of the present study should prove useful in the application of the ultrasonic vibration-assisted nucleation of supercooled liquids in other fields, such as freezing of saline water droplets, solidification of molten metals, and freezing of biomaterials, in which the supercooling phenomenon is often encountered.

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Nomenclature

Symbol	**Description**	**Units**
D_p	Solid particle diameter	μm
E_k	Molecular kinetic energy	J/mol
E_ice	Hydrogen bond energy	J/mol
E_v	Vibration intensity	$\mathrm{W/cm^2}$
f_α	Discrete velocity distribution	-
f_ice	Fraction of frozen droplets	-
f_n	Net flux of water molecules that could potentially attach to the IG surface	-
ΔG	Free energy of critical ice nucleus formation	J/mol
Δg	Free energy of activation for the diffusion of water molecules across the ice-water interface	J/mol
h_i	Discrete temperature distribution	-
J_h	Homogeneous ice nucleation rate	$\mathrm{cm^{-3}\ s^{-1}}$
N_ag	Avogadro constant	-
N_c	Number concentration of IG	-
P_EOS	Reduced pressure from the equation of state	-
p_max	Maximum collapse pressure by a cavitation bubble	GPa
P_p	Sonicator power output	-
q_o	Oil flowrate	mL/h
q_w	Water flowrate	mL/h
R_r	Roundness ratio	-

R_{ig}	Initial IG radius	nm
T_{hom}	Homogeneous ice nucleation onset temperature	K
T_{m}	Melting temperature	K
T_{nuc}	Ice nucleation temperature	K
T_{c}	Cooling temperature	

Abbreviations

COP	Coefficient of performance	-
CNT	Classical nucleation theory	-
EoS	Equations of state	-
HoN	Homogeneous ice nucleation	-
HeN	Heterogeneous ice nucleation	-
HB	Hydrogen bonds	-
IG	Ice germ	-
LBM	Lattice Boltzmann Method	-
MRT	Multi-relaxation-time	-
MD	Molecular dynamic	-
MBD	Maxwell Boltzmann distribution	-
SCC	Specific chiller capacity	-
Ste	Stefan number	-

Greek Letters

$\tilde{\alpha}$	Thermal diffusivity	-
k	Boltzmann constant	J/K
λ	Standoff distance	-

$\Delta\mu$	Chemical-potential difference between ice and liquid water	J
$\sigma_{\mathrm{i/w}}$	Ice-water interface tension	N/m
τ	Relaxation time	-
φ	Water molecule fraction that can form HBs	-
$\emptyset$	Source term	-

Subscripts

α	Discrete velocity direction	-
c	Concentration for N_c	-
cri	Critical value	-
hom	Homogeneous	-
i	Discrete velocity direction	-
inm	Ice nucleation module	-
max	Maximum value	-
nuc	Nucleation	-

Superscripts

eq	Equilibrium	-