Experimental and numerical studies on freezing of droplets under effects of nanoparticles and magnetic fields

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**EXPERIMENTAL AND NUMERICAL STUDIES
ON FREEZING OF DROPLETS UNDER
EFFECTS OF NANOPARTICLES AND
MAGNETIC FIELDS**

ZHANG HUI

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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ZHANG HUI

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

A thesis submitted to Nanyang Technological University
in partial fulfilment of the requirements for the degree of
Doctor of Philosophy

Dec, 2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

July-15-2020

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Zhang Hui

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July-28-2020

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Date

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Prof. Yang Chun, Charles

Authorship Attribution Statement

*(B) This thesis contains material from two paper(s) published in the following peer-reviewed journal(s) in which I am listed as an author.

Chapter 5 is published as Zhang, H., Zhao, Y. G., Fang, W. Z., Zhang, C. Y., Zhu, F. Q., Jin, L. W., and Yang, C. Active control of the freezing process of a ferrofluid droplet with magnetic fields. *Applied Thermal Engineering* (2020), 115444. <https://doi.org/10.1016/j.applthermaleng.2020.115444>

The contributions of the co-authors are as follows:

- I designed and built up the experimental setup and performed all the experiments in the Energy Systems Laboratory.
- I analysed the experimental data and prepared the manuscript.
- Prof. Yang supervised this paper project and edited the manuscript.
- The manuscript was revised by all co-authors.

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The contributions of the co-authors are as follows:

- I designed and built up the experimental setup and performed all the experimental works in the Energy Systems Laboratory.
- I conducted numerical simulations with the help of Dr Fang.
- Prof. Yang supervised this paper project.
- Dr Fang and I prepared the manuscript draft and the manuscript was revised by Prof. Yang Chun and Dr Zhang Chaoyang.

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Date

.....
Zhang Hui

Abstract

The freezing of substances on supercooled surfaces is ubiquitous in both nature and industry. Studying the freezing process of a single droplet is significant from both fundamental and practical viewpoints. Most existing studies focus on the freezing process of a single pure water droplet, and tremendous progress has been made in understanding the mechanisms involved in this process. However, the freezing behaviours of nanofluid droplets have received less attention. Furthermore, the presence of foreign particles significantly changes the properties of these systems, and these particles present new challenges for the analysis of the freezing related phenomena due to the complex particle-particle and particle-fluid interactions. This study aims to advance the understanding of the freezing dynamics of nanofluid droplets and to explore methods for controlling the freezing process of nanofluid droplets under magnetic conditions. In this thesis, the study of the freezing process of a nanofluid droplet is divided into two parts. In the first part of this study, the freezing behaviour of a nanofluid droplet is investigated both experimentally and numerically. Experimental observations have shown that the morphology of a frozen nanofluid droplet is different from that of a frozen water droplet. A flat plateau has been found to form on the top of a nanofluid droplet upon the completion of freezing, unlike the pointy tip that always appears on a frozen water droplet. This new phenomenon is attributed to the outward Marangoni flow induced by the gradient of particles along the liquid-air interface of the droplet, which can drive the liquid from the central region to the periphery of the freezing front. Experimental studies of the droplet volume, initial volumetric concentration, substrate temperature, and effects of particle size on the shape change feature of a freezing nanofluid droplet have been carried out. In addition, a scaling model has been proposed to reveal the underlying physics of this new phenomenon. Meanwhile, a regime map describing the morphologies of frozen nanofluid droplets has been developed. Furthermore, a two-

dimensional numerical simulation based on the lattice Boltzmann (LB) method has been carried out. In the simulation, a multiphase solidification model is used to simulate the freezing of a droplet, and the immersed boundary method is applied to describe the small particles inside the droplet. The plateau feature can be well predicted with the LB method that has been developed in this research. The simulation results show that particles are rejected by the freezing front during the freezing process and accumulated near the freezing front. The outward movement of liquid in the central region can be observed in the simulated results for the velocity distribution.

In the second parts of this study, both experimental and numerical methods are employed to investigate the effect of magnetic field on nanofluid droplets freezing. First, an active method involving the use of an applied magnetic field to control the deformation and freezing process of sessile ferrofluids droplet is developed. By changing the direction and magnitude of the magnetic field, the shape of the ferrofluid droplet can be elongated or squeezed. Consequently, the droplet freezing time can be extended and shortened under the magnetic lift and squeeze conditions, respectively. Additionally, the shape variation of a ferrofluid droplet under a magnetic field is analysed by employing the modified Young-Laplace equation. Analytical models are proposed to explain the deformation feature of the liquid ferrofluid droplet. Meanwhile, a scaling analysis is conducted to examine a relationship between the freezing time and the frozen droplet height. Secondly, numerical and scaling analyses of the freezing process for ferrofluid droplets under magnetic field effects are performed. A new LB model is proposed and the model takes magnetic force and stress into consideration. It is found that the effect of the magnetic field gradient is much larger than that of the magnetisation. Scaling models have been developed to describe the acceleration of the freezing front in a ferrofluid droplet near the completion of freezing. The simulated morphologies of ferrofluid droplets agree well with the experimental snapshots.

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Publications Arising from This Thesis

1. Zhang, H., Zhao, Y. G., Fang, W. Z., Zhang, C. Y., Zhu, F. Q., Jin, L. W., and Yang, C. (2020). Active control of the freezing process of a ferrofluid droplet with magnetic fields. *Applied Thermal Engineering*, 115444.
2. Fang, W. Z., Zhang, H., Zhang, C. Y., and Yang, C. (2020). Freezing process of ferrofluid droplets: Numerical and scaling analyses. *Physical Review Fluids*, 5(5), 053601.

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1. Zhang, H. and Yang C. (2019). Dynamic Freezing of Single Nanofluid Droplet on a Subcooled Substrate. 6th ASME International Conference of Micro/Nanoscale Heat and Mass Transfer, July 8-10, Daliang, China
2. Zhang, H., Zhao, Y. G. and C. Yang (2018). Active Control of Freezing a Sessile Ferrofluid Droplet on a Subcooled Solid Surface. 16th International Heat Transfer Conference (IHTC-16), August 10-15, 2018, Beijing, China
3. Zhang, C. Y., Zhang, H., Fang, W. Z., Zhao, Y. G., and Yang, C. (2020). Axisymmetric lattice Boltzmann model for simulating the freezing process of a sessile water droplet with volume change. *Physical Review E*, 101(2), 023314.
4. Zhao, Y. G., Zhang H. and C. Yang (2018). “Wetting Transition of Sessile and Condensate Droplets on Copper-based Superhydrophobic Surfaces.” *International Journal of Heat and Mass Transfer* 127: 280-288.
5. Zhao, Y. G., Zhu, F. Q., Zhang, H., New, T. H., Jin, L. W., and Yang, C. (2019). Triple condensate halo from a single water droplet impacting upon a cold surface. *Applied Physics Letters*, 114(18), 183703.

Nomenclature

b	The radius of curvature at the droplet's apex (m)
C_0	Volumetric concentration
d	Mean diameter of particles (m)
g	Gravity acceleration (m/s ²)
F_m	Magnetic force per unit volume (N/m)
G	Free energy (J)
h	Height (m)
H	Magnetic field strength (A/m)
k	Boltzmann constant (J/K)
k_{ice}	Thermal conductivity of ice (W/m K)
L	Latent heat of solidification (J/kg)
M_p	Saturation magnetisation for magnetite (A/m)
q	Heat flux (W/m ²)
P_{atm}	Atmospheric pressure (Pa)
V	Velocity (m/s)
r	Radius (m)
s	Arc length (m)
t	Time (s)
T	Temperature (K)

Greek Symbols

φ	Volumetric fraction
μ_0	Permeability of vacuum (N/A ²)
ϕ	The correction factor of heterogeneous nucleation
θ	Contact angle
γ	Interfacial tension (N/m)
ρ	Density (kg/m ³)
ν	Kinematic viscosity (m ² /s)
μ	Dynamic viscosity (Pa · s)

Subscripts

<i>b</i>	Baseline
<i>f</i>	Freezing
<i>ini</i>	Initial
<i>l</i>	Liquid
<i>p</i>	Particle
<i>s</i>	Solid
<i>subs</i>	Substrate

Chapter 1: Introduction

1.1. Background and motivation

Water covers more than 70% of the Earth's surface. There are three different forms of water in nature—liquid, water vapour, and ice. The phase change processes among the three states of water are melting, sublimation, deposition, condensation, evaporation, and freezing. The freezing and melting of water are associated with the release or the absorption of large quantities of energy. These properties make water the most used material in the refrigeration cycle, energy storage devices, and many other applications.

Water-based phase change materials (PCMs) can be used to store energy in a latent heat storage system. However, the supercooling behaviour of water and its relatively low thermal conductivity are two major drawbacks in water-based PCMs. Nanofluids are colloidal suspensions containing nano-sized particles in the base fluid [1, 2]. When nanoparticles are present, the thermal properties of water, especially the thermal conductivity of the colloidal system, are improved [3, 4]. In the past two decades, nanofluids have been employed to develop new PCMs with high thermal conductivity [5, 6]. Many studies have investigated the thermal performances of nanofluid PCMs, and their results indicate that the dispersed nanoparticles in PCMs can decrease the degree of supercooling of these materials [7, 8]. Most previous studies have focused on the heat transfer characteristics of nanofluids or nanofluid PCMs. However, little attention has been paid to the characteristics of nanoparticles during the phase change process.

The solidification of colloidal suspensions is a ubiquitous phenomenon in nature, such as in the freezing of soils or the formation of ice on the sea, and many industrial applications, such as in frozen food engineering, cellular cryopreservation, the fabrication of metal matrix composites, and freeze-casting [9]. The freezing process of a colloidal suspension is very

different from that of pure water due to the complex interactions between the dispersed particles and the liquid-solid interfaces. The engulfment/rejection of particles and the alignment of particles due to the freezing front can always occur during the solidification process in colloidal suspensions [10-12].

In some situations, all particles are engulfed in the solid phase in such a manner as to achieve a uniform distribution of these particles, such as in the processing of metal matrix composites [13]. In other situations, the particles are treated as undesirable impurities that should be rejected, such as in the fabrication of silicon wafers [14]. With the development of materials processing technology, segregating particles via a freezing front can be used to control the growth of crystals and the formation of different microstructures and architectures via the ice-templating method [15-17]. Thus, understanding the interactions between particles and the freezing front is of fundamental and practical interest in the development of the aforementioned fields.

Generally, the size, concentration, and wettability of the particles [18-20], the additives [21], the cooling rate, temperature gradient [22-24] and external fields [25, 26] can influence the solidification behaviour of colloidal suspensions in terms of the distribution of particles, the growth direction of crystals, and the microstructures of the final materials. Many efforts have been made to understand the solidification dynamics in a large-scale colloidal system; however, less attention has been paid to the freezing process of a colloidal droplet containing nanoparticles. In terms of fundamental research, studying the freezing of a nanofluid droplet can provide a holistic understanding of how to control the solidification process for colloidal suspensions.

On the other hand, the freezing of water and colloidal suspensions can sometimes become dangerous phenomena that can have negative effects on nature and industrial processes. The

upheaval of frozen soil can result in damage to oil pipelines [27], and ice accumulation on surfaces due to the continuous freezing of water droplets can result in serious damage in many applications. For example, undesirable aircraft icing is considered as one of the major factors in accidents in some situations [28]. Moreover, ice formation on power transmission lines and wind turbine blades in cold regions challenges the safety and integrity of the equipment [29].

To decrease the negative impact caused by the freezing phenomenon, many anti-icing and de-icing studies have been conducted over the past two decades. Using the Joule effect to heat the ice layer is one typical de-icing method for transmission lines [30]. A traditional anti-icing method involves the utilisation of chemicals, such as NaCl mixed with an organic solvent [31]. The freezing temperature of water decreases with the addition of specific compounds, which results in the prevention of ice formation. Recently, incorporating micro- and nano-fabrication methods into the development of anti-icing surfaces has become very popular. A superhydrophobic surface with fabricated nanostructures or microstructures can prevent the accumulation of water droplets, and such a surface has been reported to have good anti-icing abilities [32, 33]. With its micro-scale or nano-scale structures, its surface texture allows it to trap more air and minimise the contact area between a droplet and its surface, thus retarding ice nucleation. However, in most situations, only passive control of the freezing behaviour of water droplets can be achieved on these surfaces due to their fixed structures. Few studies have been reported on the active control of the freezing temperature using very strong external fields [34, 35].

To further understand the physics of freezing, many efforts have also been made to examine the freezing of a single water droplet [36, 37]. Studying the freezing behaviour of a sessile or impact droplet is very important to the development of more efficient freezing control methods. To date, many studies have focused on the freezing process of sessile droplets and droplet

impact on cold substrates. Furthermore, theoretical models have been developed to explain the formation of the pointy tip on a frozen water droplet [38-41]. It is found that the density ratio between the ice and liquid is important for tip formation. Recent studies have shown that the presence of saline or other contaminants in a water droplet changes the tip angle of the frozen droplet [42-44]. However, very little attention has been paid to the freezing dynamics of water droplets with nanoparticles.

To close the research gaps identified in previous investigations, the freezing behaviour of a nanofluid droplet is investigated in this study by carrying out fundamental and systematical experiments and numerical simulations to explore the underlying mechanism of this phenomenon. Water is chosen as the host fluid since it is used widely in many applications; hence, studying its freezing process is of great practical interests.

1.2. Research objective and scope

The main objective of this study is to reveal and characterise the underlying mechanisms of the nanofluid droplet freezing phenomenon. Fundamental and systematic investigations are carried out experimentally and numerically to explore the freezing process of nanofluid droplets under both the absence and presence of magnetic field conditions. To achieve this objective, the scope of this thesis is as follows:

- Investigating the freezing of a nanofluid droplet deposited on a supercooled substrate and proposing scaling models to analyse the mechanisms underlying the shape change feature of a frozen nanofluid droplet.
- Developing numerical models to simulate the particle-particle and particle-freezing front interactions during the freezing process of a nanofluid droplet.

- Exploring the effect of an external magnetic field on freezing of a nanofluid droplet and presenting scaling analyses of the deformation feature and freezing behaviour of a nanofluid droplet.
- Developing numerical models to simulate the deformation and freezing of a nanofluid droplet under magnetic fields.

1.3. Outline of the thesis

To achieve the research objective of this thesis, its two related parts are carried out sequentially. The first two research chapters focus on experimental and numerical investigations of the freezing of a deposited nanofluid droplet. Then the following two chapters investigate the effects of a magnetic field on the freezing process of nanofluids experimentally and numerically. The complete thesis contains seven chapters:

Chapter 1 introduces the background and motivation for this study. Recent research on PCMs and the freezing of colloidal suspensions and water droplets are reviewed briefly. The main objective and scope of this study are stated clearly.

Chapter 2 presents a literature review on the fundamentals of freezing phenomena, including the relevant background on, and the freezing of water and colloidal suspensions. Previous research work on nucleation, surface wettability, icing, and freezing are reviewed.

Chapter 3 presents experimental studies on the freezing of a nanofluid droplet deposited on a supercooled substrate. The effects of droplet volume, particle volumetric concentration, particle size, and substrate temperature on the freezing propagation and the shape change feature of a freezing droplet are investigated systematically. Scaling analyses are also presented to explain the observed phenomena.

Chapter 4 reports the results of numerical studies on the freezing of nanofluid droplets with different particle volumetric concentrations on a surface based on the developed LB model. More detailed investigations of the dynamic freezing process are carried out to study the effect of surface wettability. The simulated results are found in reasonable agreement with the experimental data.

Chapter 5 presents systematic experimental studies of the freezing of nanofluid droplets under magnetic field effects. The deformation features and the freezing behaviours of ferrofluid droplets are controlled actively by varying the direction and magnitude of the magnetic field. Scaling models are also developed to explain the observed phenomena.

Chapter 6 investigates the effect of a magnetic field on the freezing of ferrofluid droplets numerically. Scaling analyses are also performed to explain the different characteristics of the propagation of the freezing front during the freezing process.

Chapter 7 provides a summary of the major research findings in this study and outlines possible future work.

Chapter 2: Literature review

In this chapter, the fundamentals of the freezing phenomenon, including nucleation, contact angle, and wetting are introduced. Then experimental and numerical studies that have been conducted on freezing water droplets will be discussed. Finally, a broad review of the research work on the freezing of colloidal suspensions will be presented.

2.1. Fundamentals of freezing

2.1.1. Ice nucleation

During the freezing process, nuclei come out of the solution through nucleation. These nuclei are centres of crystallisation within the system. If there are not enough nuclei in the system, the development of ice crystals will not start. Nucleation can sometimes happen spontaneously. Otherwise, artificial stimuli, such as agitation, ultrasonic irradiation, and a pressure change, can also influence the occurrence of nucleation.

The formation of nuclei in a system without crystals is defined as primary nucleation [45]. There are two types of primary nucleation: homogeneous nucleation and heterogeneous nucleation. Homogeneous nucleation only occurs in a system that contains no impurities. On the contrary, heterogeneous nucleation takes place in the presence of contaminants in the system [45]. In most industrial applications, heterogeneous nucleation is a very commonly encountered phenomenon. When crystals already exist in a suspension, the generation of new nuclei is due to the pre-existing nuclei in the system, and such a nucleation process is defined as secondary nucleation.

Due to the energy necessary for the creation of a new interface, a free energy barrier exists during the nucleation process [46]. Overcoming this energy barrier is necessary for the

generation of the first nuclei. The free energy barrier in homogeneous nucleation is given by [47]:

$$\Delta G = \Delta G_S + \Delta G_V \quad (2-1)$$

Here ΔG_S represents the absorption of energy for the creation of the new interface, and ΔG_V represents the release of energy due to the phase change [48].

If the shape of the nuclei is assumed to be a sphere, ΔG_S can be calculated as [48]:

$$\Delta G_S = 4\pi r^2 \gamma_{sl}, \quad (2-2)$$

where r is the radius of the sphere, and γ_{sl} is the interfacial energy(J/m²).

The release of energy ΔG_V can be expressed as [47, 48]:

$$\Delta G_V = -\frac{4}{3}\pi r^3 \frac{\Delta H_f \Delta T}{T^*} \quad (2-3)$$

where ΔH_f is the latent heat of vaporisation (J/m³), T^* is the equilibrium temperature during the freezing process (K), and $\Delta T = T^* - T$ is the degree of subcooling (K).

The effect of the radius of the nucleus on free energy is shown in Figure 2-1.

Figure 2-1 Relationship between the free energy and the radius of the nucleus

For simplicity, the results will be given for $\Delta H_f = 3.9 \times 10^8 \text{ J/m}^3$, $\Delta T = 30 \text{ K}$, $T^* = 270 \text{ K}$, and $\gamma_{sl} = 3.6 \times 10^{-2} \text{ J/m}^3$ only. The absolute values of ΔG_V and ΔG_S increase with the increase in nucleus radius. The sum of ΔG_V and ΔG_S increases at first, then decreases with further increases in the radius. Since the two terms have opposite signs and both of them are functions of r , the free energy barrier ΔG must have a maximum value (See the curve of ΔG in Figure 2-1). The radius resulting in the maximum ΔG is defined as the critical radius, r_c . It corresponds to the smallest radius for crystal growth in the nucleation process. Substituting the above equations into Eq. (2-1) yields:

$$\Delta G_V = \Delta G = 4\pi r^2 \gamma_{sl} - \frac{4}{3}\pi r^3 \frac{\Delta H_f \Delta T}{T^*} \quad (2-4)$$

Differentiating Eq. (2-4) with respect to r and setting $\frac{d\Delta G}{dr} = 0$, the expression for the critical radius, r_c , is obtained:

$$r_c = \frac{2r_{sl}T^*}{\Delta H_f \Delta T} \quad (2-5)$$

When the nucleus reaches the critical radius, new crystals form. In a fixed system, γ_{sl} , ΔH_f , and T^* are usually constant. From Eqs. (2-4) and (2-5), it can be observed that the critical radius and free energy go down with the increase in the degree of supercooling. The variation in the critical radius with the supercooling temperature can be obtained by setting $\Delta H_f = 3.9 \times 10^8$ J/m³, $\Delta T = 30$ K, $T^* = 270$ K, and $\gamma_{sl} = 3.6 \times 10^{-2}$ J/m² in Eq. (2-5). Using the same parameters and setting $r_c = 1.65$ nm, the relationship between the free energy and the degree of supercooling can also be obtained. Figure 2-2 shows the relationships between the degree of supercooling and the critical radius and the degree of supercooling and the free energy barrier.

Figure 2-2 Variations in the critical radius and the free energy barrier with the degree of supercooling

In the low supercooling condition, an increase in the degree of supercooling results in a steep decrease in the critical radius. However, the decrease in the radius slows at higher supercooling temperatures. From the definition of the degree of supercooling, the higher the degree of supercooling, the lower the temperature of the system. Therefore, the results in Figure 2-2

indicate that the critical radius becomes smaller in the more moderate temperature condition. Hence, the formation of the crystal phase is more straightforward.

Homogeneous nucleation is not very common in nature and industry because a perfectly clean system is very difficult to obtain. Even in laboratories with excellent filters, the preparation of a solution without impurities is almost impossible. The contaminants or foreign particles in a system can influence the free energy barrier in the nucleation process. In some situations, the existence of contaminants acts as an accelerator for nucleation, which leads to a decrease in the critical free energy barrier. Therefore, in a heterogeneous system, nucleation can occur at a lower degree of supercooling compared to homogeneous nucleation. The critical free energy required for the growth of crystals under heterogeneous conditions can be calculated by using the following equation [46]:

$$\Delta G_{het,crit} = \phi \Delta G_{hom,crit}, \quad (2-6)$$

where ϕ is a correction factor with a value less than 1. The expression for the factor ϕ in heterogeneous nucleation is [46]:

$$\phi = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4}, \quad (2-7)$$

where θ is the contact angle.

Substituting $\Delta H_f = 3.9 \times 10^8 \text{ J/m}^3$, $\Delta T = 30 \text{ K}$, $T^* = 270 \text{ K}$, and $\gamma_{sl} = 3.6 \times 10^{-2} \text{ J/m}^2$ into Eq. (2-4), setting the contact angle $\theta = 30^\circ, 60^\circ, 90^\circ, 120^\circ$, and using Eqs. (2-6) - (2.7) yields the value of the free energy in heterogeneous nucleation under different nucleus size conditions. Figure 2-3 shows a comparison of free energy barriers for heterogeneous and homogeneous nucleation. Since the correction factor is smaller than 1.0, the free energy barrier in heterogeneous nucleation is smaller than that in homogeneous nucleation. This trend can be seen clearly in Figure 2-3. Unlike the changes in the free energy barrier, the critical nucleus size is the same for two nucleation processes.

Figure 2-3 Free energy barriers for heterogeneous nucleation and homogeneous nucleation as functions of the nucleus radius for different contact angles

2.1.2. Freezing front propagation

The advancing freezing front appears at the end of the nucleation process. The propagation of the freezing front is a very important feature in freezing dynamics. In the 19th century, Stefan proposed a theoretical model to describe the propagation of a flat water-ice interface in a liquid system. Many studies have analysed the freezing process of a pure water droplet by treating it as a one-dimensional Stefan problem [49, 50]. The methods used in their analyses for the propagation of the freezing front are briefly introduced in this section.

If a quasi-steady approximation is employed, the energy conservation equation on the solid ice side can be written as:

$$\frac{\partial^2 T}{\partial z^2} = 0, \quad (2-8)$$

which reflects a linear temperature distribution in the solid ice region.

If the temperature of the liquid phase is assumed to remain at the solidification temperature T_m , the latent heat released by the liquid water can be primarily conducted to the solid ice part, yielding:

$$k_s \frac{\partial T}{\partial z} = \rho_s L \frac{\partial h}{\partial t}, \quad (2-9)$$

where k_s and ρ_s are the thermal conductivity and density of ice, respectively, L is the latent heat, and $\frac{\partial h}{\partial t}$ represents the freezing front velocity.

Since the temperature at the droplet bottom is almost equal to the substrate temperature T_{sub} , combining Eq. (2-8) and Eq. (2-9) and integrating both sides of Eq. (2-9) with respect to t yields:

$$h = t^{-0.5} \sqrt{\frac{2(T_m - T_{sub})k_s}{L\rho_s}} \quad (2-10)$$

Based on Eq. (2-10), the height of the freezing front h can be calculated a function of time t . The predicted results have been shown to be in good agreement with the experimental data [49, 50]. These studies have proved the accuracy of the Stefan's model for calculating the movement of the flat interface. Recently, Fang et al. have developed a new scaling model to analyse the propagation of a concave freezing front in a ferrofluid droplet based on Stefan's method [51]. The model proposed by Fang et al. can more accurately predict the evolution of the freezing front near the completion of freezing.

2.1.3. Contact angle and surface wettability

The profile of a small droplet on a horizontal surface can be described by using the angle of the liquid-solid-vapour interface. This angle is known as the contact angle and is the result of the interaction between the liquid-solid and the liquid-vapour interfaces. From a geometric

perspective, the contact angle is the tangential angle between the free surface of the droplet and the solid substrate.

Schematics of static contact angles formed by sessile droplets resting on homogeneous surfaces are shown in Figure 2-4. The small contact angle in Figure 2-4 (a) indicates that the spreading of the liquid droplet on the surface is favourable, while the large contact angle in Figure 2-4 (b) means that the spreading process is partially inhibited. Hence, the spreading state of a droplet on a surface changes when the contact angle changes [52, 53]. A droplet would spread completely on the surface for $\theta = 0^\circ$. It would partially spread out on the surface for $0^\circ < \theta < 180^\circ$. If $\theta = 180^\circ$, no spread would not occur.

Figure 2-4 Illustration of static contact angles and surface tensions acting on sessile water droplets

The contact angle of a sessile droplet indicates surface wettability. Table 2.1 summarises examples of solid surfaces with different wettability classifications. Four kinds of solid surfaces with different wettability classifications are shown, namely, superhydrophobic surfaces, hydrophilic surfaces, hydrophobic surfaces, and superhydrophobic surfaces. Large contact angles indicate that the wetting of the surface is retarded. The contact angles on smooth and homogeneous surfaces usually vary from 30° to 150° [46]. With the development of surface texturing technology, the contact angles on hydrophobic/hydrophilic materials can be further increased or decreased to achieve superhydrophobic/superhydrophilic states. In recent years, many efforts have been devoted to the fabrication of micro-/nano-structures on

superhydrophobic surfaces [54, 55]. Over the past decades, many studies have reported that superhydrophobic surfaces can exhibit excellent anti-icing performances due to their self-removal of droplets [33, 56].

Table 2.1 Illustration of solid surfaces with different wettability

Contact angle	Wettability	Illustration
$\theta \leq 30^\circ$	Superhydrophilic
$30^\circ < \theta \leq 90^\circ$	Hydrophilic
$90^\circ < \theta \leq 150^\circ$	Hydrophobic
$150^\circ < \theta \leq 180^\circ$	Superhydrophobic

The wetting state of droplets on a surface with micro-/nano- structures is different from that on a smooth surface. When air is concentrated on the structure beneath the liquid droplet, the Cassie-Baxter state is favourable. To the contrary, the droplet is in the Wenzel state when liquid is trapped on the structure. The schematics of these two wetting states are depicted in Figure 2-5.

Figure 2-5 Schematics of the Wenzel and Cassie – Baxter states

As shown in Figure 2-5, the droplet contacts the textured surface directly in the Wenzel state, while it will not thoroughly wet the surface in the Cassie-Baxter state due to the formation of a liquid-air-solid interface. The earliest recognition of a wetting state on a rough surface was provided by Wenzel [57]. He reported that if the wetting process of droplets on a surface is favourable, then the wettability of this surface will be enhanced when the surface becomes rough. He also noticed that roughness on a surface would strengthen its wetting resistance if the wettability on the original surface was reduced. Wenzel attributed the change in wettability to the surface area difference between a smooth surface and a rough surface. The expression for the contact angle in the Wenzel state is:

$$\cos \theta_{wen} = \cos \theta \cdot r \quad (2-11)$$

This expression is also called the Wenzel equation. Here, θ_{wen} is the contact angle on a rough surface, θ is the contact angle on a smooth surface, and r is the surface roughness factor [57]

which represents the ratio between the actual area for the rough surface and the projected area for the smooth surface.

Wenzel described the contact angle on a rough homogeneous surface, but he did not consider the trapping of air on a solid surface. When Cassie and Baxter studied the wetting process of droplets on porous surfaces, they took the influence of air pockets into account. A thoroughly wetted state will not occur when air remains trapped on a porous surface [58]. They derived the famous Cassie- Baxter equation to calculate the contact angle:

$$\cos \theta_{C-B} = \cos \theta \cdot f^S + (1 - f^S) , \quad (2-12)$$

where f^S is the area fraction of the solid on the interface, and θ is the contact angle on a smooth surface.

If the droplet is in the Wenzel state, it shows high contact angle hysteresis and pinning of the contact line can be observed [59, 60]. Studying the transition mechanism between the Wenzel state and the Cassie-Baxter state is of great importance in achieving the continuous removal of droplets on a superhydrophobic surface [61].

2.2. Freezing of water droplets

Studying the freezing process of a single water droplet paves the way for understanding the fundamental physics of the freezing phenomenon. Many numerical and experimental studies on the analysis of droplet morphology, the prediction of the temperature distribution, and the effects of surface wettability and external fields on the freezing behaviour of droplets have been conducted over a long period of time [62-66].

The freezing process of a sessile water droplet on a supercooled surface takes place in four distinct stages: pre-cooling, recalescence, isothermal freezing, and ice cooling [66-68]. In the first stage of freezing, the droplet remains in the liquid phase. The temperature of the droplet

decreases from its initial temperature to a pre-recalescence temperature (T_r) below the equilibrium temperature (T_e). The pre-cooling state is terminated when the nucleation of ice occurs. During the recalescence stage, the rapid growth of crystal nuclei releases latent heat, which leads to a droplet temperature increase to the equilibrium temperature in a very short time. In addition, a fraction of the liquid becomes ice, and the droplet loses its transparency at the end of this stage [69-71]. In the isothermal freezing state, a freezing front initially arises from the bottom of the droplet and moves continuously toward the top of the droplet. The temperature of the droplet remains at the equilibrium temperature (T_e) until the freezing front reaches the apex of the droplet. During the solid cooling stage, the temperature of the frozen droplet is further reduced to the temperature of the cold substrate. The temperature changes taking place in the aforementioned four stages are shown in Figure 2-6.

Figure 2-6 Evolution of the temperature in the freezing process of a droplet

2.2.1. Theoretical and numerical studies of the formation of a pointy tip

Focusing on the freezing of a water droplet on a supercooled substrate, many theoretical and numerical studies have been carried out to predict the shape change feature of a frozen water droplet. One of the most important features in water droplet freezing is the formation of the tip

[63, 71-74]. This universal tip has been proven to be the result of volume expansion [39, 40, 65]. Figure 2-7 displays the morphologies of liquid and frozen droplets on a cold solid surface.

Figure 2-7 Schematics of the shapes of the water and frozen droplets, respectively

Anderson et al. [72] observed the formation of pointy tips and inflexion points on frozen water droplets in their experiments. They then proposed a theoretical model to predict the shape of a frozen droplet based on four different boundary conditions for the solidified front. Figure 2-8 shows the schematic of a solidified droplet from their theoretical model. Here, θ is the angle between the solidified front and the tangent to the solid-vapour interface, and θ_g is the growth angle. The initial contact angle of the liquid droplet is defined to be θ_0 in their model.

Figure 2-8 Schematic of a water droplet describing the characteristics of the freezing front

The four boundary conditions in their model are: (1) constant contact angle ($\theta = \theta_g$), (2) fixed contact line (θ is dynamic, $\theta_g = 0$), (3) fixed growth angle (θ is dynamic, θ_g is a constant other than zero), and (4) dynamic growth angle (θ and θ_g are dynamic). Using these conditions, they successfully predicted the inflexion point in a frozen water droplet with the dynamic growth angle. Their theoretical results also show that the position of the inflexion point is dependent on the substrate temperature, which is in good agreement with the experimental data.

A simplified mathematical model was proposed by Snoeijer and Brunet to calculate the shape of frozen droplet [38]. They established the relationship between the radius of the freezing front, the volume, and the contact angle of the unfrozen droplet. The geometric model of the droplet used in their analysis is shown in Figure 2-9.

Figure 2-9 The geometric model of a water droplet during the freezing process. The freezing front is assumed to be flat, and the shape of the liquid part is considered to be part of a sphere

In their theoretical model, the unfrozen part of the water droplet was considered to be part of a sphere, and the freezing front was treated as a flat interface. The shape of the frozen droplet could then be expressed as a function of the density ratio between ice and water (v):

$$\frac{d\theta}{dz} = -\frac{1}{R} [v(1 + \cos \theta)^2 - 2 \cos \theta - \cos^2 \theta] \quad (2-13)$$

Based on Eq. (2-13), the formation of the tip on a freezing water droplet can be explained under both large contact angle ($\theta = 133^\circ$) and small contact angle ($\theta = 30^\circ$) conditions. Their

numerical results showed that the tip feature can appear on a freezing droplet whenever $v \leq 0.75$. Although this critical value (0.75) differs from the real density ratio between ice and water (0.917), their study provided an explanation for the formation of the pointy tip.

In most of the studies up to this point, a flat freezing front was used in the derivation process. Hence, none of their derivations was able to reflect the shape of a frozen droplet perfectly because the freezing front is concave, but not flat.

Marín et al. [40] developed a new theoretical model to predict the tip singularity that used a concave freezing front. Their calculated results showed that the formation of the tip occurs when $v < 1$, not the 0.75 obtained by Snoeijer and Brunet. Based on Marín et al.'s study, Schetnikov et al. developed a numerical model to calculate the vertex angle in a frozen droplet [41]. In this model, the freezing front is assumed to have a concave shape, and the centre of this concave shape is located at the apex of the frozen droplet. Using the model, they obtained the relationship between the vertex angle (α) and the ice/water density ratio. The calculated tip angle was 130° when $v = 0.917$, and this result was in good agreement with the average value of the tip angles measured during their experiments.

A comprehensive model was proposed by Tembely and Dolatabadi [65]. They simulated the freezing of a water droplet while taking droplet-substrate and droplet-air interactions into account but made no assumptions concerning the freezing growth angle. They also adopted disjoining pressure, the full mean curvature expression, and the Gibbs-Thomson relation in their analysis. The volume expansion, concave freezing front, and the tip singularity can be well predicted using their model. Zhang et al. [74] employed the concave freezing front assumption and developed a new model by accounting for gravity and the supercooling effect. In addition, they used a correlation to calculate the angle between the freezing front and the

liquid-air interface. They were then able to predict the formation of the pointy tip and the angle was calculated as 144° in their studies.

Recently, Zhang et al. [75] applied the LB method to simulate the freezing process of a water droplet while taking the volume expansion effect into consideration. The formation of the tip can be observed in their simulations. In addition, their numerical results showed that the angle between the freezing and liquid-air interfaces cannot be maintained at 90° , which is a departure from Marin et al.'s study.

The tip singularity on a frozen water droplet under asymmetric conditions was proved by Ismail and Waghmare [76]. The droplet was placed on a tilted substrate to achieve an asymmetric shape. They then proposed a theoretical model to predict the location of the tip, and it matched well with the experimental data. Vu et al. [77] studied the freezing process of a water droplet on an inclined surface numerically. They discovered that the tip angle is dependent on the tilt angle of the surface and the initial morphology of the droplet.

2.2.2. Experimental studies of effects of surface wettability and roughness on the freezing of water droplets

The micro-/nano-structures of surfaces play vital roles in the freezing of a water droplet, as ice nucleation and the freezing time of water droplets have been reported to be affected by the surface hydrophobicity/hydrophilicity. In this section, the effects of surface wettability and roughness on water droplet freezing will be reviewed briefly.

The ice nucleation rate is one of the most important factors for controlling freezing. It is affected significantly by the energy barrier, which, in turn, is dependent on the degree of supercooling, the droplet contact angle, and the surface morphologies. A lower nucleation rate usually represents a freezing delay.

Few studies have examined lower nucleation rates or longer freezing delay times on hydrophilic surfaces. Jung et al. [69] investigated the freezing delay for droplets on hydrophilic/superhydrophobic surfaces. The longest delays occurred on hydrophilic surfaces with nanoscale roughness. Similarly, the nucleation rate on a hydrophilic silicon surface was observed to be lower than those on hydrophobic surfaces [78]. Authors from the same group further compared the ice nucleation rate on the hydrophobic/hydrophilic surface and revealed the dominant of interfacial water for ice nucleation [79]. Their results indicate that a hydrophilic surface exhibits a lower ice nucleation rate. Hao et al. [80] found that both the surface wettability and roughness impact the freezing delay for water droplets. The freezing delays on all smooth surfaces with nanoscale roughness are longer than those on superhydrophobic surfaces with larger roughness. To provide a reasonable explanation for the above results, Hao et al. calculated the free energy barriers for these surfaces qualitatively. The results of their calculations indicated that the free energy barrier is greater for surfaces with less roughness. A longer freezing delay on a slightly hydrophilic surface was also observed in Rahimi et al.'s experiments [81]. Besides, they pointed out that the surface chemistry plays a very important role in ice formation.

In contrast to the conclusions reached in the studies above, most studies have shown that longer freezing delays for water droplets occur on hydrophobic/superhydrophobic surfaces [62, 82-85]. Huang et al. [62] investigated the freezing process for a single droplet on surfaces with different contact angles. They applied surface coatings and used immersion methods to fabricate hydrophobic surfaces. The contact angles of the droplet on these surfaces range from 97.2° to 154.9° . A fixed droplet volume ($6\ \mu\text{l}$) was used in their experiments. Delayed freezing was observed on all hydrophobic surfaces, and the frost growth rate was found to be faster for frozen droplets on hydrophobic surfaces. The effect of surface wettability on the nucleation kinetics of sessile water droplets at constant volume ($25\ \mu\text{l}$) was investigated by Boinovich et

al. [82]. Freezing delays occurred on both hydrophilic and superhydrophobic surfaces. The longest freezing delay of several hours was reached on superhydrophobic aluminium surfaces at -8 °C. A lower nucleation rate was observed on a superhydrophobic surface in Shen et al.'s experiments [83]. To fabricate the superhydrophobic surface, hierarchical structures were added to the base substrate using sandblasting and hydrothermal technology. The surface was then further modified with heptadecafluorodecyl trimethoxysilane (FAS-17).

Rahimi et al. [43] studied the effect of topology on the freezing delay. Their experimental results showed that the freezing delay is longer on a surface with relatively greater roughness. When the surface roughness is much greater than that needed for nucleation, surface wettability dominates the free energy barrier value. The free energy barrier increases with an increasing contact angle. Similarly, Wang and Wang's experimental results [70] showed that the freezing of sessile water droplets on a hydrophobic silicon surface with micro-pillars was delayed compared to that on polished silicon. Yamada et al. [86] found that the freezing delay for a sessile water droplet increases with the hydrophobicity of the surface. Recently, the ice-nucleation rates on five different coated superhydrophobic surfaces were investigated by Wu et al. [84]. Their experimental results indicate that the surface with the lowest surface roughness and uniformly distributed particles can exhibit the lowest nucleation rate.

Another important feature in the freezing process of water droplets is the droplet freezing time. With a decrease in the contact area between the water droplet and substrate, extended freezing time is possible on superhydrophobic surfaces [56, 85].

Studies have shown that an increase in the freezing time for a water droplet can occur when relatively smooth surfaces are coated with monolayers or nanoparticle composites. The freezing times for small droplets on a hydrophobic silicon wafer were found to be longer than those of big droplets on a hydrophilic silicon wafer [87]. The difference in surface wettability was obtained by coating the wafers with two types of self-assembled monolayers. Zhang et al.

[36] studied the phase changes of water droplets on substrates with different contact angles numerically and experimentally. The aluminium surface used in their experiments was coated with carbon nanotube/polydimethylsiloxane. Both the numerical and experimental results indicated that the freezing time of a water droplet increases with an increase in the contact angle. Xu et al. [88] synthesised a superhydrophobic film on a glass surface and studied the freezing process of a water droplet on a bare glass surface and this superhydrophobic surface under different temperature conditions. It can be observed from their experimental results that the freezing time of a water droplet increases remarkably on the superhydrophobic glass surface. The freezing times for a water droplet on superhydrophobic surfaces with different micro-/nano-structures have been reported to be extended. Tourkine et al. [89] found that the freezing time for a water droplet on a superhydrophobic surface with microstructures was three to five times longer than that for a droplet on the same flat surface. When they tilted these two kinds of surfaces at a small angle, the droplets left the superhydrophobic surface with a microstructure without freezing, while the pinning and freezing of droplets occurred on the flat surface. Lv and Zhang [90] fabricated a superhydrophobic aluminium alloy surface using chemical etching and surface modification. Their results indicate that the freezing time for a water droplet on a superhydrophobic surface is two times longer than that on a hydrophilic surface. Nguyen et al. [56] investigated the effects of a nanopillar's height and diameter on the anti-icing performance of superhydrophobic glass substrates. The longest freezing time occurred on the surfaces with the smallest pillar diameter under their experimental conditions. Their experimental results also indicated that the variation in pillar height is not very significant in terms of the freezing time. Barthwal and Lim [91] fabricated a dual-scale superhydrophobic aluminium surface using chemical etching and the anodization method. The surface was then modified with polydimethylsiloxane. The icing time for a water droplet on their fabricated surface was extended to four times that for a bare aluminium surface. Pan et al. [92] fabricated

hierarchical structures on a CF/PEEK composite and modified the surface with trimethoxysilane. The freezing time of a water droplet on this fabricated superhydrophobic surface was almost ten times longer than that on the untreated surface. Recently, a bioinspired superhydrophobic surface aligned with vertical TiO₂ nanopillars exhibited excellent anti-icing properties in that the freezing time for water droplets was three times longer than that on a *Berberis thunbergii* leaf surface [93].

2.2.3. Experimental studies of effects of external fields on the freezing of water droplets

Studies on freezing under electrical field conditions can be dated back to Dufour's discovery of the electrofreezing phenomenon in the 19th century [94]. His experimental results showed that the freezing temperature of water is increased when an electrical field is applied.

However, the experimental results on the effect of an electrical field on ice nucleation are conflicting. A few studies have shown that the ice nucleation temperature is not influenced by an electrical field [95, 96]. However, most studies have concluded that an applied electrical field can promote nucleation or increase the freezing temperature [97-100].

Two typical methods are used to generate electrical fields in electrofreezing studies. In the first method, the electrodes are immersed in the sample (direct contact method) with the presence of the current, whereas, in the second method, there is no electric current in the sample (indirect contact method).

Hozumi et al. [101] investigated the freezing of supercooled water using different electrode materials. The electrodes were arranged in the water sample. It was discovered that the inclusion of an electric field could lead to ice nucleation when a small degree of supercooling was present. The highest freezing temperature was obtained when aluminium was used as the electrode. Nakajima et al. studied the freezing of supercooled droplets under an electric field

[102]. In their experiment, a silicon wafer was coated with Au and connected directly to a DC power supply. They found that the movement of the contact line induced by electrification could promote ice nucleation. Yang et al. [103] explored the nucleation mechanism for water droplets under electric fields. In this series of experiments, the electrode was in contact with the droplet, and the substrate was placed on a conducting plate. They applied high voltages ranging from 600 V to 1000 V via a DC power supply. The experimental results indicated that nucleation occurred at a higher temperature as the result of moving the contact line with electrowetting.

When using the direct contact method, it is difficult to separate the influences of the electric field and the current flow on freezing. Thus, many researchers have employed the indirect contact method by, for example, using parallel plate electrodes [97, 98], keeping the electrodes away from the sample, or placing a dielectric layer below the sample [34, 100]. Carpenter and Bahadur studied the electrofreezing of water droplets under a high electric field strength (80 V/ μm) [34]. In particular, they examined the influence of an electric field on the freezing temperature under the current flow absence condition. They discovered that there were no further enhancements of the freezing temperature when the electric field intensity increased beyond 20 V/ μm . Zhang et al. [99] investigated the nucleation of water droplets under an electric field consisting of a cylindrical shell electrode and a cylinder electrode. Their experimental results showed that the promotion of ice nucleation occurs under magnetic field conditions and that this phenomenon is independent of the electric field direction. Fallah-Joshaqani et al. [100] investigated the freezing parameters of different types of solutions under electric field conditions. The decrease in the nucleation time and increase in the nucleation temperature of pure water occurs when the static electric field intensity reaches 6.4×10^5 V/m. Recently, Teng et al. [104] systematically reviewed the development of electrowetting for

droplet manipulation and covered such topics as electrofreezing, droplet permeation, droplet oscillation, and capillary bridges.

When an external magnetic field is applied, the variations in the physicochemical properties of water, such as the pH value, the surface tension, and the hydrogen bond, can be investigated [105-107]. Cai et al. measured some of the properties of water under magnetic field conditions [105]. Their experimental results showed that the surface tension of water decreased and more hydrogen bonds formed after the magnetic treatment. To the contrary, an increase in the surface tension was observed in Iino and Fujimura's experiments with magnetic field strengths of up to 10 T. They also reported an increase in the surface tension of heavy water [106]. A recent study measured the surface tensions of different pendant droplets. The results showed that the surface tension of a pendant droplet is unaffected by a magnetic field [107].

Magnetic-field-induced changes in the physicochemical properties of water can lead to corresponding changes in its freezing behaviour in some situations. A slight increase in the freezing temperature was observed by Inaba et al. when the magnetic field strength was set to 6T [35]. Niino et al. [108] reported an increase in the degree of supercooling for a saline solution under a 1.2 mT magnetic field as the frequency increased to 200 kHz. To the contrary, some researchers found that a magnetic field cannot affect the freezing temperature of water. Naito et al. [109] reported that the supercooling of water is unaffected by low-frequency (30 Hz) electromagnetic fields at 0.5mT. Using a static magnetic field, Zhao et al. [110] studied the freezing behaviour of different aqueous solutions under weak magnetic field strength. The nucleation temperature of water in the presence of the magnetic field was found to be the same as that in the absence of the magnetic field. Otero et al. [111] obtained similar results under static magnetic field conditions. They also studied the effects of oscillating magnetic fields (OMFs) on the supercooling and freezing kinetics of pure water. Their experimental results

showed that the nucleation time of water did not change under a 0.8mT OMF at frequencies between 20 Hz and 2000 Hz [112].

In the studies above, the focus was on the effect of the magnetic field on water itself. The influence of the magnetic field when not in contact with water has seldom been studied. Ivall et al. developed an excellent icephobic surface using a ferrofluid layer and called it a magnetic slippery surface. The new surface significantly reduced ice adhesion and freezing formation temperature under weak magnetic field conditions [113]. Masoudi et al. [114] further developed a non-Newtonian magnetic slippery surface based on Irajizad et al.'s study [113]. This surface exhibits excellent antiscaling and anti-icing properties under shear flow conditions. To solve the weak binding issue encountered by the magnetic fluid on a general surface, Wang et al. [115] developed a new magnetic fluid surface on a porous anodic aluminium oxide template. The freezing delay time on this new surface was found to be two times that on a superhydrophobic surface. In addition, the new surface has far better anti-icing durability than most magnetic slippery surfaces.

A recent study conducted by Qin et al. showed that external magnetic fields have significant impacts on both the ice nucleation time and the thickness of the frost layer on the surface [116]. In particular, an increased ice nucleation time and a reduced layer thickness were recorded.

2.3. Freezing of colloidal suspensions

In nature and industrial applications, the freezing of a colloidal system is a frequently encountered process. It can be seen in ice formation in seawater, the cryopreservation of cells, the freezing of food, energy storage, metallurgy, and ice-templating [9, 117, 118]. The interactions between particles/bubbles/cells and the freezing front make the freezing process of a colloidal system rather different from that for pure water. In some situations, the particles/bubbles/cells need to be engulfed by the freezing interface to achieve a uniform

distribution of these objects in the solid phase. In other cases, these objects need to be rejected by the freezing front and redistributed by the crystals. In all cases, understanding the mechanisms of this freezing process is important for controlling the particle distribution, crystal structures, and the interface morphologies. The complex interactions between particles and solidification interfaces present challenges for understanding the underlying mechanism.

On the other hand, the presence of particles can also change the thermal conductivity of a colloidal system [119-125]. The presence of graphite nanotubes has been reported to reduce the solidification time of colloids [125]. Increasing the volume fraction of multi-wall carbon nanotubes in colloidal suspensions results in a further decrease in the solidification time due to the increased thermal conductivity [121]. Similar conclusions have been reached by other researchers [122-124].

2.3.1. Experimental studies of the freezing of colloidal suspensions

The rejection or engulfment of particles during the freezing process of colloids is dominated significantly by the moving velocity of the freezing front. Particles will be engulfed by the freezing front when the propagation velocity of the freezing front exceeds the critical velocity. Studying particle engulfment/rejection is important for understanding the freezing mechanism of colloidal suspensions. The first part in this section discusses experimental studies of the critical velocity. Subsequently, the pushing/engulfment of particles can affect the stabilities and morphologies of the freezing fronts and crystal structures. Understanding the formation and building of the ice growth structures is very important for the fabrication of microporous and dense materials. Thus, in the second part of this section, experimental studies of the morphologies of ice crystals in the freezing process of colloidal suspensions and their application in the fabrication of advanced materials are introduced.

In any system containing foreign particles, there exists a critical velocity during the solidification process, as reported in many experiments [126-132]. Corte [126] studied the particle migration principle in the freezing process experimentally. In the transparent cylindrical cabinet used in the experiment, the freezing began at the bottom part of the cylinder, which was in contact with a cold aluminium plate. The radii of the sand particles used in the test ranged from 0.1-7 mm. Particle size and the freezing rate are critical factors in particle migration. The migration of small particles occurred under almost all the freezing rates used in the experiment. However, particles with larger radii migrated in a narrow range of the freezing rate only. The probability of particle migration decreased with increases in the freezing rate. Corte [132] also studied the sorting behaviour of particles during freezing and thawing cycles and came to a similar conclusion.

Uhlmann et al. [127] first proposed the concept of critical velocity when studying the interactions between particles and a solid-liquid interface. They used water and other organic materials as solvents in their investigations of the freezing of colloidal systems. Their experimental results indicated that particles would be pushed by the interface or trapped in the solid phase at different freezing rates and that there was a critical value for the propagation velocity of the freezing front that could mark the transition between pushing and trapping. They concluded that the critical velocity decreases with increasing particle size when larger particles are present ($> 100 \mu\text{m}$). Furthermore, particle size does not influence the value of the critical velocity when the particle is very small ($< 15 \mu\text{m}$).

Water is a widely used solvent in the freezing of colloidal suspensions. Much attention has been paid to experimental studies of the critical velocity in aqueous solutions. Cisse and Bolling [133] performed systematic studies on the freezing of water suspension. The particles used in their experiments were Cu, Al, W, SiO_2 , and C. The radii of these particles ranged from $2.5 \mu\text{m}$ to $62.5 \mu\text{m}$. They discovered that the critical velocity decreases with increasing particle

radius and decreasing temperature gradient. The authors also reported that the particle type and the presence of air in the water impact the critical velocity. An experimental study of the surface thermodynamic effect on the engulfment of particles was conducted by Omenyi and Neumann [134]. Their experimental results showed that hydrophobic particles are engulfed by the freezing front while the hydrophilic particles are rejected under the same freezing rate conditions. Körber et al. [135] investigated the pushing/engulfment transition in spherical latex particles in aqueous solutions. They found that the critical velocity for large-sized particles was smaller than that for small-sized particles. Their experimental results also indicated that the engulfment of particles can affect the morphology of the freezing front. In a study of a colloidal system involving starch and water, the particle pushing/trapping transition occurred when the velocity of the freezing front increased [136]. The engulfment of particles by the freezing front has been observed in the process of ice-templating under large freezing rate or temperature gradient conditions [16, 17, 128-130, 137].

Many experimental studies focusing on the freezing of a metal matrix with particles have also reported the engulfment of particles when the velocity of the freezing front is larger than the critical velocity. Stefanescu et al. [138] found that SiC particles can be entrapped in the Al-Mg matrix at a high solidification rate. Juretzko et al. [139] investigated the interactions between particles and the freezing front in two metal/particle systems. Their experimental results showed that there is a relation between the critical velocity and the particle type. Youssef [140] measured the critical velocity of TiB_2 particles in aluminium and observed lower critical velocities as the particle concentrations became greater. The transition from rejection to engulfment of $48\text{ }\mu\text{m}$ Al_2O_3 particles in an aluminium-based composite was reported to occur by Hecht and Rex [141] when the freezing rate was greater than $0.33\text{ }\mu\text{m/s}$.

The effect of convection on particle engulfment/pushing has also been investigated by many researchers. Sen et al. [142] found that the effect of natural convection led to an increase in the

critical velocity. Stefanescu et al. [143] measured the critical velocity under microgravity conditions and obtained a conclusion similar to that of Sen et al. [142]. The freezing process of silicon with SiC particles was investigated by Friedrich et al. [144] and Friedrich and Müller [145], and they found a lower critical velocity under microgravity conditions. This phenomenon is caused by the reduced natural convection, which leads to a decrease in the lift force on the particles under microgravity conditions.

The engulfment and rejection of particles were found to change the morphology and the stability of the freezing front in the freezing processes for aqueous and metal composite systems. Peppin et al. [24, 146, 147] investigated the morphologies of the freezing fronts in various aqueous suspensions experimentally and included an instability analysis of the freezing front. Their experimental results showed that the morphology of the freezing front is dependent on the freezing conditions, the particle type, and the particle concentration. In the case of colloidal suspensions with montmorillonite, a planar freezing front can be observed at a very slow freezing rate ($T_b = -3\text{ }^{\circ}\text{C}$; here, T_b is the temperature of the base), and it is possible to observe that all particles are rejected by the freezing front. With the increase in the freezing rate ($T_b = -20\text{ }^{\circ}\text{C}$), the morphology of the ice front becomes unstable, and the particles follow different distribution patterns determined by the ice. When the particle concentration is the same as that for the low cooling rate, a dendritic ice structure can be observed at $T_b = -20\text{ }^{\circ}\text{C}$. If the particle concentration is increased to 50% wt, a more complex polygonal structure is formed. When using different concentrations of kaolinite clay as the solute in an aqueous solution, they observed variations in the morphology of the freezing front [146]. The morphologies of the freezing fronts in Peppin et al.'s experiments are shown in Figure 2-10.

Deville et al. [148] used the so-called tomography reconstruction technology to observe the unstable and metastable domains in the freezing process for aqueous colloids. Ammonium polymethacrylate anionic dispersant and alumina powder were dispersed in the water-based

suspension. The three-dimensional X-ray tomography results for the ice crystals are shown in Figures 2-11(a) – 2-11(b).

Figure 2-10 The morphologies of freezing fronts in the freezing of aqueous suspensions with montmorillonite clay (a) – (c) and kaolinite clay (d)-(f) [146, 147].

The existence of transverse crystals, which are normal to the freezing direction, indicates the appearance of unstable structures in the observed domain in Figure 2-11(a). Global instabilities (denoted by black arrows) and localised instabilities (denoted by white arrows) are used to describe these unstable structures. The degree of particle engulfment is reduced due to the presence of global instabilities. As can be seen from their experimental data, localised instabilities only occur between the crystals. Meanwhile, they observed metastable ice crystals when increasing the particle size in the suspensions or the freezing rate. Figure 2-11(b) shows the homogeneous ice crystals and the absence of a transverse structure. They explained that the presence of these instabilities was the result of the partial diffusion of the particles. Based on their study, Lasalle et al. [20] investigated the underlying mechanism for the formation of defects and flocculation in the freezing process of colloids with 300 nm alumina powders. They pointed out that defects/flocculation can result in the appearance of unstable freezing fronts.

(a) Ice crystals in a 0.2 μm -particle colloid under unstable conditions

(b) Ice crystals in a 1.3 μm -particle colloid under metastable conditions

Figure 2-11 Three-dimensional ice crystals in colloidal suspensions obtained by X-ray tomography [148]

Waschkies et al. [137] investigated the transition in the interface morphology in the freezing process of alumina suspensions. The particle diameters in the experiments ranged from 0.25 to 15 μm . At a low freezing rate, the interface had a planar shape. At a high freezing rate, a lamellar freezing front was observed. Anderson and Worster [149] investigated the effect of the freezing rate on the steady-state ice segregation patterns in the freezing process of aqueous dispersions with 320 nm alumina powders. Wang et al. [150] studied the interface instability in the freezing of water-based colloids with 50 nm alumina powders via *in situ* observation of the onset of the initial instability. They proposed three interface instability modes based on their experimental results. You et al. [151] observed the growth of ice lenses as the result of an unstable freezing front. They thought the instability was caused by the particle-induced supercooled region in front of the advancing interface. They also investigated the interface instabilities and the steady morphologies in the freezing of colloidal suspensions with 20 nm alumina particles [11]. At a low freezing rate (1.6 $\mu\text{m/s}$), the freezing front of the suspensions became unstable. The engulfment/pushing of particles in the freezing process for porous alloys has also been reported to affect the morphology of the freezing front [152, 153].

The material processing technique based on the freezing of colloids is usually called ice-templating or freeze-casting. Experimental studies on ice-templating have attracted considerable attention over the past two decades due to the versatility and controllability of this method [12, 154, 155, 156]. A typical ice-templating process, including freezing, sublimation, post-treatment and post-fabrication is shown in Figure 2-12 [12]. Particles/polymers/fibres are rejected by the freezing fronts and redistributed between crystals. After sublimation, a porous material is obtained and then treated further with sintering or other methods.

Figure 2-12 A schematic of the ice-templating process [12]

Changing the freezing conditions, solutes, or external field conditions in the ice-templating process can result in the formation of various micro-/macro- structures in porous materials. Figure 2-13 provides a schematic view of the assembled structures in the ice-templating process. This technique has been used widely for the fabrication of ceramics, metals, composites, polymers, carbon materials, porous materials, and aerogels [9, 156, 157].

Figure 2-13 The assembled micro-/macro-structures in the ice-templating process [156]

Both dense and porous ceramics have been investigated in studies on ice-templating. Ice-templated materials, such as alumina [18], mullite [158], zirconia [159], titania [160], and silicon nitride [161], exhibit excellent mechanical and thermal properties. When using the traditional freeze-casting methods, the microstructures in the porous ceramics are aligned in a single direction. Recently, Su et al. [162] developed a new freeze-casting method to fabricate radial-concentric structures in ceramics with enhanced axial compressive moduli and splitting tensile strengths. A new polymer–ceramic composite consisting of ceramic scaffolds ($\text{Al}_2\text{W}_3\text{O}_{12}$) and poly(methylmethacrylate) has been developed by Ellis et al. [163]. This ice-templated composite has very low thermal expansion ($2 \times 10^{-6} \text{ K}^{-1}$).

In addition to the fabrication of templated ceramics, the ice-templating technique has also been used to process polymers materials for biomedical applications [164]. A unidirectional porosity in polymers can be obtained by using ice-templated materials [165]. Moreover, experimental investigations focusing on the fabrication of metals with unique properties and carbon materials with high porosities have been widely conducted [166, 167]. Mimicking the structures found in natural materials to achieve many useful physical properties has attracted much interest in many engineering fields. There have also been interests in applying ice-templating technology

to the fabrication of bioinspired materials with layered structures in recent years. Nacre-like composite structures can be produced by using nanoparticles, macromolecules (polymer chains or nanofibers), and nanosheets as the solutes in the ice-templating process, as shown in Figure 2-14 [154, 168-171].

Figure 2-14 Schematics of the ice-templating technique for the fabrication of bioinspired nanocomposites with the nanoparticles, macromolecules, and nanosheets [154, 168-171].

Very few studies have reported on the disappearance of the tip singularity or the change of the tip angle in the frozen water droplet with impurities, such as salt (NaCl), the polymer polyethylene glycol, and the surfactant tetradecyltrimethylammonium bromide [42, 44]. Furthermore, systematic experimental studies are lacking, and the physical mechanism underlying these phenomena are still unclear.

2.3.2. Theoretical studies of the particle engulfment transition in the freezing of colloidal suspensions

There is a long history of studying the particle engulfment transition in the freezing of colloids in terms of the critical velocity. A variety of theoretical models for the prediction of the critical velocity have been developed over the past years. Table 2.2 summarises these models and the physical parameters used to calculate the critical velocity, including the viscosity of the liquid

(η), particle radius (R), fluid atomic diameter (a_0), thermal conductivity of the liquid (k_l) and solid (k_p), and interfacial energy (γ). The critical velocity satisfies the $\left(\frac{1}{R}\right)^4$ relation in most of the derived models.

The first model for calculating the critical velocity was proposed by Uhlmann et al. [127]. They assumed that the repulsive force dominates the particle-interface interaction when the particle-solid surface free energy is greater than the sum of the particle-liquid and liquid-interface surface free energies. It was also assumed that the particles are engulfed in the freezing front when the viscous drag exceeds the repulsive force. They obtained expressions for the critical velocities for different particle sizes and solvent materials. The predicted values of the critical velocity were in good agreement with their experimental results. Uhlmann et al.'s model was modified by Bolling and Cissé [172], who took into account the roughness of the particles and gravity. They defined a bump radius R_b and derived different expressions to calculate the critical velocity according to the relative size of the particles compared to R_b .

Chernov et al. [173, 174] first considered the effect of the disjoining pressure induced by the van der Waals interaction and evaluated the shape changes in the freezing front due to heat flow perturbations. Separate analytical expressions were obtained for large particles and small particles. Stefanescu et al. [138] proposed a theoretical model for calculating the critical velocity of ceramic particles in metal matrix composites. The different thermal conductivities of the liquid (k_l) and solid (k_p) were considered in this model. The calculated results were shown to be slightly higher than the results obtained in the experiments. Taking the temperature gradients and the influence of the particles into account, Pötschke and Rogge [175] developed a theoretical model to describe the critical velocity. This model can predict the pushing of latex particles by the freezing front in water well.

Shangguan et al. [176] extended Stefanescu et al.'s model [138] with a more accurate description of the particle-induced shape changes in the freezing front. Based on their model, they created a regime map to describe the engulfment and pushing behaviours of particles in various metallic systems under different freezing rate conditions. Stefanescu [143] investigated the interaction between zirconia particles and the freezing front in pure aluminium under microgravity conditions, then further modified Shang et al.'s model based on the experimental results. In Kim and Rohatgi's study [177], the disjoining pressure acting on the particle was considered to be a repulsive force that needed to be balanced by the attractive drag force in order to achieve the critical condition. The critical velocity was modelled as a function of the curvature of the interface and the particle radius. Azouni and Casses [178] developed an analytical model for the calculation of the critical velocity. The surface properties of the particles were considered in their model. Kaptay [179] investigated the interaction of ceramic particles and the freezing front and proposed an analytical model to calculate the critical velocity. A new quantity $\Delta\gamma_{cls} = 2\gamma_{cs} - \gamma_{cl} - \gamma_{sl}$ was developed to evaluate the sign of the interfacial force exerted on a particle. The repulsive force induced by the freezing front and the viscous force is considered in this model, and it can predict the experimentally observed critical velocity in an alumina system with 250 μm ZrO_2 particles well.

A great deal of progress has been made by Rempel and Worster [180]. They proposed that the velocities of particles be treated as functions of the pre-melted film thickness. In addition, the interfacial interactions are described more fundamentally in their analysis. The thermal conductivities of the particles, solid, and liquid are assumed to be the same. In the force balance analysis for a single particle, they included the thermomolecular force by integrating the thermomolecular pressure and the lubrication force associated with liquid pressure. The particle velocity reaches the maximum value at a special film thickness, and this value also corresponds to the critical velocity value. Later, they modified their model to take the Gibbs-

Thomson effect on the temperature at the freezing front and the effects of other power-law interactions (except for the van der Waals interaction) on intermolecular forces into account [181].

A theoretical analysis of particle-interface interactions has recently been performed by Park et al. [182] with the consideration of the temperature gradient and latent heat. The engulfment of spherical particles and bubbles were studied in their study. They calculated the particle velocity and predicted the deformation of the freezing front induced by the particles by considering the van der Waals interactions, different liquid and particle thermal conductivities, solid-liquid interfacial energy, liquid film, and latent heat. In this model, the critical velocity equals the maximum value of the particle velocity. Kao et al. [183] developed scaling models to predict particle pushing and engulfment in different systems, such as saline, aluminium-copper alloy, and water systems. Their results have shown that the particle velocity is reduced as a result of the constitutional undercooling induced by the presence of the solutes.

The aforementioned analytical and scaling models have been applied widely in the prediction of particle behaviours, and good agreements with some of the recent experimental studies can be observed [153, 184]. Many numerical simulations have also been conducted to investigate the interactions between particles and the freezing front [185-189]. However, these works cannot provide direct predictions of the critical velocity.

Table 2.2 Theoretical models for the critical velocity

Model	Critical velocity for particle engulfment	Dependence on the particle radius
Uhlmann et al. [127]	$V_c = \left(\frac{n+1}{2}\right) \left(\frac{La_0 \Omega D_1}{k_b T R^2}\right)$	$\left(\frac{1}{R}\right)^2$
Bolling and Cissé [172]	$V_c = \left(\frac{4\psi(\alpha)k_b a_0 T \gamma_{sl}}{9\pi\eta^2 R^3}\right)^{1/2}, R < R_b$ $V_c = \frac{6\alpha k_b T \gamma_{sl}}{\pi\eta R_b g \Delta \rho R^3}, R \gg R_b$	$\left(\frac{1}{R}\right)^{3/2}, R < R_b$ $\left(\frac{1}{R}\right)^3, R \gg R_b$
Chernov et al. [173, 174]	$V_c = \frac{0.14 B^{2/3} \gamma_{sl}^{1/3}}{\eta R^{4/3}}, R < 500 \mu\text{m}$ $V_c = \frac{0.15 B}{\eta R l}, R \geq 500 \mu\text{m}$	$\left(\frac{1}{R}\right)^{4/3}, R < 500 \mu\text{m}$ $\frac{1}{R}, R \geq 500 \mu\text{m}$
Stefanescu et al. [138]	$V_c = \frac{h_0 \Delta \gamma_0}{6\eta(n-1)R} \left(2 - \frac{k_p}{k_l}\right), n = 2 - 7$	$\frac{1}{R}$
Pötschke and Rogge [175]	$V_c = \frac{1.3 \Delta \gamma_0}{\eta} \left[\frac{1}{16 \left(\frac{R}{a_0}\right)^2 \left(\frac{k_p}{k_l}\right) \left(15 \frac{k_p}{k_l} + x\right) + x^2} \right]^{1/2}$	/
Shangguan et al. [176]	$V_c = \frac{a_0 k_l \Delta \gamma_0}{3\eta k_p (n-1)R} \left(\frac{n-1}{n}\right)^n$	$\frac{1}{R}$
Stefanescu et al. [143]	$V_c = \left(\frac{a_0^2 k_l \Delta \gamma_0}{3\eta k_p R}\right)^{1/2}$	$\left(\frac{1}{R}\right)^{1/2}$
Kim and Rohatgi [177]	$V_c = \frac{a_0 \Delta \gamma_0}{18\eta} \left(\frac{\kappa R + 1}{R}\right)$	/
Azouni and Casses [178]	$V_c = -\frac{A}{36\eta\pi h \beta R} - \frac{2}{9} R h \times \frac{(\rho_p - \rho_l)g}{\beta\eta}, \text{ planar front}$ $V_c = -\frac{A \pm \alpha}{36\eta\pi h \beta R} - \frac{2}{9} R h \times \frac{(\rho_p - \rho_l)g(1 \pm \alpha)^2}{\beta\eta}, \text{ curved front}$	/
Kaptay [179]	$V_c = \frac{0.157}{\eta} (2\gamma_{cs} - \gamma_{cl} - \gamma_{sl})^{2/3} \gamma_{sl}^{1/3} \left(\frac{a_0}{R}\right)^{4/3}$	$\left(\frac{1}{R}\right)^{4/3}$
Rempel and Worster [180]	$V_c \sim \left(\frac{A_{sw}^2 \gamma_{sl}}{6^5 \pi^2 \mu^3 R^4}\right)^{1/3}$	$\left(\frac{1}{R}\right)^{4/3}$
Park et al. [182]	$V_c = \frac{1}{6\mu R} \left[\frac{L_v A^3 G}{(6\pi)^3 T_m} \right]^{1/4} u_{max}(\gamma, k_p/k_m)$	$\frac{1}{R}$
Kao et al. [183]	$V_c \sim G_T^{0.01} \gamma^{0.3} A^{0.69} \frac{\rho_l}{\eta \rho_s R^{1.35}}$	$\left(\frac{1}{R}\right)^{1.35}$

2.3.3. Application of external fields in the freezing of colloidal suspensions

External fields (magnetic, electric and acoustic) have been applied extensively in the ice-templating process to control the particle distribution and the microstructures of the templated materials over the past two decades [25, 26, 155-157, 190-192]. Figure 2-15 gives a schematic view of the different microstructures and particle distributions in ice-templated materials under external fields.

Most of the studies have focused on the effects of the magnetic field on the freezing of colloids. The formation of bridges between lamellar walls, the alignment of particles, and variations in pore size have all been observed under different magnetic conditions [15, 26, 190, 191]. When a single permanent magnet was oriented axially with respect to the freezing direction, a unique banding pattern based on Fe_3O_4 -rich regions (brown) and Fe_3O_4 -poor regions (white) can be obtained along the vertical axis on the templated scaffolds, as shown in Figure 2-15 (a.1) and (a.5) [191]. The magnetic field strength is close to 0 near the top and bottom of the ring magnet; therefore, the Fe_3O_4 particles in these locations are attracted to other regions (the upper and lower regions), leading to the formation of the brown-white banding. A cross-section of one of the Fe_3O_4 -rich regions exhibits a core-shell feature, while a more uniform microstructure can be seen in the Fe_3O_4 -poor regions. When the magnetic field is applied in the radial direction, a continuous banding pattern along the freezing direction is obtained [191]. Figure 2-15 (a.2) shows the configuration of the magnetic field. Similar to the morphology of the cross-section under axial magnetic field conditions, a core-shell structure is formed on the final scaffolds (see Figure 2-15 (a.6)). The accumulation of Fe_3O_4 particles is caused by the large magnetic field strength in the outer perimeter of the cylinder. Porter et al. studied the freezing of different types of ceramics with Fe_3O_4 particles under rotating magnetic field conditions [26, 190]. The schematic of their magnetic field is shown in Figure 2-15 (a.3). They found an unusual helical structure in the templated scaffolds (See Figure 2-15 (a.7)). The angle and thickness of the

helix can be further manipulated by changing the rotation speed of the permanent magnets and the freezing rate. The templated composites exhibit excellent torsional properties compared to the composites without the helical structure. When the magnetic field direction is perpendicular to the freezing direction, as shown Figure 2-15 (a.4), a combination of lamellar walls and mineral bridges structures can be observed in the scaffolds under the transverse magnetic field condition [15, 156, 157, 191, 193]. With the presence of the wall and bridge alignments in the microstructures, the compressive properties of the composites are enhanced.

Electrical effects on the freezing of colloidal suspensions have also been investigated. A tilted growth direction of ice crystals was found by Tang et al. under relatively weak electrical field conditions [25]. The direction of the electrical gradient was perpendicular to the freezing direction. On the other hand, an increase in the size of the lamellar walls was observed in Tang et al.'s experiments under stronger transverse electrical field conditions [194]. They also observed the enhancement of compressive properties along the electrical field direction. When the electrical field is parallel to the freezing direction, a combination of porous and dense structures can be obtained in the final ceramic pieces [195]. The application of an acoustic field can result in the formation of a concentric ring pattern. These rings represent the high/low particle density regions caused by the standing pressure waves [192]. The hardness of the templated material is higher than that of the scaffolds without the acoustic fields.

In this chapter, the fundamental freezing phenomena, including the nucleation theory, propagation of freezing front, and surface wettability, were introduced. Then a systematic literature review on the freezing of a water droplet was conducted. The related physical mechanism of the tip singularity was described. Moreover, previous researches on the effects of surface wettability, roughness, and external fields on the freezing of water droplets were reviewed. Finally, the experimental and theoretical studies on the freezing of colloidal suspensions focusing on the critical velocity and the application of external fields in the ice-templating process were introduced systematically.

Based on the literature review of the freezing of water droplets and colloidal suspensions, some insights can be gleaned, as follows:

- I. Most of the existing studies have paid attention to the freezing of colloidal suspensions in relatively large systems, such as rectangular or cylindrical channels. Very few experimental studies have investigated the freezing of small-scale colloidal systems systematically, particularly those involving nanofluid droplets. The physical mechanisms in the freezing process of a nanofluid droplet remain elusive.
- II. Theoretical and numerical studies have been conducted to explain the formation of the pointy tip on a freezing pure water droplet; however, a numerical investigation on the freezing of a nanofluid droplet is still lacking.
- III. Most of the existing passive freezing control methods have focused on the fabrication of superhydrophobic surfaces with complex structures and different degrees of roughness. The application of an external field as an alternative freezing control method has attracted much interest. However, few experimental studies have investigated the active control of the freezing process using weak external fields and no definitive method has been found. Furthermore, analyses of the freezing process under any successful method would need to be completed, that is, a scaling analysis and numerical simulation would need to be conducted.

These research gaps provide the motivation for the studies conducted in this thesis. To fill up these gaps, systematic studies on the freezing of nanofluid droplets are carried out both experimentally and numerically. The studies can be divided into two parts: the freezing of a deposited nanofluid droplet in the absence of external field, and the application of an external field on the freezing of a sessile nanofluid droplet. These studies and their results are discussed in the next four chapters

Chapter 3: Experimental study of the freezing process of nanofluid droplets with no external field

This section examines the freezing process of a nanofluid droplet experimentally. The results indicate that a flat plateau is formed on the top of a frozen nanofluid droplet and that this unique shape change feature depends on the particle type, volumetric concentration, and size as well as the substrate temperature.

3.1. Introduction

Freezing is a very ubiquitous phenomenon in the natural environment, causing ice accumulations in wind turbines [196], on aircraft [28, 197], and in seawater [198]. The liquid-solid phase change process is also found in many industrial processes, for example, the freeze casting of the scaffold in tissue engineering [199], the solidification of silicon in the fabrication of semiconductors [200], and the spray-drying technology used in food processing [201]. Therefore, understanding the underlying mechanism in the solidification process is very crucial for the control of ice-induced difficulties as well as the advancement of new technology in the industrial fields mentioned above.

The analysis of a single droplet can provide a more fundamental understanding of the solidification process than examining a large-scale macrosystem. Accordingly, numerous works focusing on the solidification behaviour of single droplets of water [36, 64, 74], metals [202], and liquid marbles [203], among others, have been conducted over the past decade.

The freezing process of a water droplet can be observed after the droplet is placed on a cold substrate. At the completion of freezing, a single pointy tip will form on the frozen droplet, which is a universal phenomenon [40, 76]. Various models have been developed to explain this experimental observation, and many efforts have also been put into the analysis of heat transfer

in a water droplet during the freezing process [62, 80, 82, 87]. It has been concluded that the contact angles of a water droplet play a very important role in the freezing process. The shape change features exhibited by silicon, iron, and wax droplets during solidification on cold substrates have also been investigated [204-206]. In these cases, the tip does not appear at the apex of the droplet at the end of solidification. Recently, the disappearance of this freezing singularity in water has been observed when increasing the sodium chloride concentration in saline droplets [42].

The solidification process in colloidal systems has received a great deal of attention in studies of fabrication routes for porous ceramics, complex composites, and reinforced alloys [16, 20, 207]. The presence of foreign particles in the solidification process can influence the formation of aligned structures in the solid phase and change its mechanical properties. In addition to their influence on the solid structure, they can also affect the heat transfer characteristics of the system. The dispersion of nanoparticles in liquids will influence their thermal properties as well as their solidification behaviours. The nanofluids' phase change materials have much better thermal conductivities than conventional phase change materials [119, 120]. The cooling rate and thermal energy storage of the phase change material can also be enhanced by adding nanoparticles to the host material [208].

The solidification of nanofluids is more complicated than that of pure water due to the interactions between particles and particles or particles and the interface. Particle size and shape, as well as the solidification rate, are shown to influence the interface shape and crystal structures [136, 152, 209]. The interactions between particles and the solidification front have been studied. Particles can be trapped or rejected by the interface during the solidification process. Previous theoretical and experimental research indicates that large particles are more easily trapped by the interface than small particles under the same conditions [144, 186, 209].

However, the effect of particle size on the solidification of a nanofluid droplet is still not very clear. Only a few studies have investigated the phase change process of a droplet containing different types of particles. Different morphologies are formed in a sessile nanofluid droplet with a multiwall carbon nanotube during the freezing process [210]. The rejection of carbon nanotubes was observed under higher substrate temperature conditions ($T_{sub} = -5\text{ }^{\circ}\text{C}$) in the experiment. However, the mechanism for the formation of the crystallisation morphology in a nanofluid is still not completely understood.

In this chapter, an experimental study on the freezing behaviour of deposited nanofluid droplets was conducted. The focus of the present study is to understand the mechanism for this freezing behaviour. Hence, the effect of droplet volume, particle volumetric concentration, particle size, and substrate temperature on droplet freezing time and droplet morphology during the freezing process were investigated.

3.2. Experimental setup and procedure

A cooling unit with a temperature control system, an enclosed chamber with a gas supply system, a droplet generation system, and an imaging system were fabricated to study the freezing process of nanofluid droplets, as shown Figure 3-1.

The cooling unit comprises a heat sink and a Peltier cooler model (9500/127/100B, Ferrotec, USA) to cool the substrates. A hollow aluminium block with Teflon layers (15 mm thickness) on the outside was connected to a recirculating cooler (Polyscience, USA) to form the heat sink. Teflon was used as the insulation material to decrease the heat loss from the heat sink to the ambient environment. A Peltier cooler model connected to a DC power source (GPC-3060D, GWINSTEK) was used to further decrease the temperature of the substrate. It was tightly bonded to the top of the aluminium block using thermal paste (OT-201, Omega engineering).

Two thermocouples (Type-T, 0.2 mm, RS PRO, accuracy ± 1.0 °C) were installed between the Peltier cooler and the substrate to measure the substrate temperature. The Peltier cooler model and heat sink were used to adjust the substrate temperature via adjustments to the temperature of the recirculating cooler and the current/voltage in the Peltier. In this study, the substrate temperature was varied from -12.5 °C to 31.3 °C (accuracy ± 1.0 °C).

An enclosed chamber (15 cm $\times$ 15 cm $\times$ 10 cm) was used to avoid the condensation of water vapour on the substrate environment during the experiment. The surrounding walls of the chamber were made from acrylic sheets (1 cm thickness) to provide proper illumination conditions for image acquisition. The chamber was connected to N₂ gas supply equipment, and the pressure inside the chamber was balanced with the outside pressure via a check valve on an acrylic sheet. Before starting the experiment, the water vapour inside the chamber was removed by filling the chamber with nitrogen gas for 5 minutes.

The droplet generation system contained a micropipette and height gauge. Used in place of a syringe pump for droplet generation, a micropipette can eliminate the volume variation due to particle size. The droplet was generated at the tip of the micropipette, which was fixed on the extended part of the height gauge. The deposition height of the droplet was adjusted via the height gauge, and the droplet was generated at a location close to the substrate. The Weber number was approximately 3 in the experiments ($We = \rho u^2 R / \gamma$, where ρ is the density, u is the velocity and R is the radius of the droplet and γ is the surface tension).

An imaging system consisting a high-speed camera (3260 frames per second at full resolution of 1280 $\times$ 800, M310, Phantom, USA) with a Nikon zoom lens and an LED light source (CLS150, Leica) for providing good illumination was used to capture the freezing process of the deposited nanofluid droplets at a rate of 25 frames per second.

The nanofluid samples in the experiments were prepared by dispersing different types and sizes nanoparticles (US Research Nanomaterials), such as TiO_2 and Fe_3O_4 , into deionised water. Before adding particles into the system, a beaker containing the distilled water was placed in a vacuum chamber to remove the gas. The particle radii varied from 5 nm to 800 nm, and the volumetric concentration of the nanofluid samples varied from 0.03% to 2%. All the nanofluid samples were stirred for 20 minutes on a magnetic stirrer (Thermo Fisher Scientific) and kept in an ultrasonic cleaner for 1 hour (Sonicator 3000, 20 kHz and 80 kW, MISONIX) before the freezing experiments.

A thin copper plate with a thickness of 1 mm was employed as the substrate due to its excellent thermal conductivity. The freezing process for each droplet was repeated five times under each experimental condition, and error bars were obtained based on these measurements.

Figure 3-1 Schematic of the experimental test system

3.3. Flat plateau formed on the top of frozen nanofluid droplets

3.3.1. Singularity in frozen water droplets

Experiments have been conducted to investigate the freezing process for deposited water droplets of different volumes on a supercooled substrate ($-21.5\text{ }^{\circ}\text{C}$). The geometries of these water droplets at two dimensionless times are shown in Figure 3-2. Here, $t^* = t / t_{total}$. t_{total} represents the freezing time for each droplet, with t indicating time. As can be seen from Figure 3-2, a pointy tip is formed at the apex when a droplet completes its freezing process, indicating that the shape change feature of water droplets is independent of volume.

Figure 3-2 Selected images of the morphologies of water droplets with different volumes during the freezing process

The tip angle was calculated using a theoretical model while assuming the self-similar geometry of the freezing front at the final stage of freezing [40, 41]. The schematic of the two-

dimensional droplet geometry during the final stage of freezing is shown in Figure 3-3. Based on the assumptions, (1) the unfrozen liquid ($V_a + V_b$) becomes a portion of a sphere that is centred on the final pointy tip, and (2) the freezing front assumes a concave shape and is perpendicular to the ice-air interface.

Figure 3-3 Schematic of a droplet during the final stage of freezing

The unfrozen water contains two parts, (1) the volume below the crater, V_a , and (2) the volume above the crater, V_b . Their volumes can be expressed as

$$V_a = \frac{1}{3}\pi R^3 \frac{(2 + \cos\alpha)(1 - \cos\alpha)^2}{\sin^3\alpha} \quad (3-1)$$

$$V_b = \frac{1}{3}\pi R^3 \frac{(2 + \cos\beta)(1 - \cos\beta)^2}{\sin^3\beta} \quad (3-2)$$

When the freezing is completed, the ice is filled with the conical area and the volume of the frozen ice is $V_{ice} = V_a + V_c$, where V_c is given by

$$V_c = \frac{1}{3}\pi R^3 \frac{1}{\tan\alpha} \quad (3-3)$$

The relationship between the unfrozen liquid and frozen ice satisfies

$$\frac{\rho_{ice}}{\rho_{water}} = \frac{V_a + V_b}{V_a + V_c} \quad (3-4)$$

Since $\alpha + \beta = 90^\circ$ and the volume expansion $\rho_{ice} / \rho_{water} = 0.917$, the value of $\alpha = 65^\circ$ can be obtained numerically. Accordingly, the calculated tip angle is 135° . The comparisons between the measured tip angles for different droplet volumes and the theoretical calculations are shown

in Figure 3-4. The divergence between the measurements and the theoretical calculations is caused by the change in the volume expansion ratio in the experiment (i.e., $\rho_{\text{ice}} / \rho_{\text{water}} \neq 0.917$).

Figure 3-4 Comparison of the calculated tip angles with the experimental measurements for different droplet volumes

After investigating the effect of volume on the singularity of the tip formation, the substrate temperature's effect on the freezing behaviour of water droplets was studied. A fixed-volume (6 μl) water droplet was deposited on the substrate at different temperatures. The morphologies of the droplet at the initial stage and at the end of the freezing process are shown in Figure 3-5. The variation in the arrested contact angles of the droplet with the decreasing substrate temperature is in agreement with a previous study by De Ruiter et al. [211]. The changes in the arrested contact angle and substrate temperature do not affect the formation of the pointy tip.

Figure 3-5 Selected images of water droplets (6.0 μL ± 0.12 μL) during the freezing process under different substrate temperature conditions

As shown in Figure 3-6, the tip angle remains nearly constant as the substrate temperature changes, which indicates that the angle is independent of the freezing rate. The calculated tip angle can predict the experimental measurements well.

Figure 3-6 Comparison of the calculated tip angles with the experimental measurements under different substrate temperature conditions

3.3.2. Shape change features of frozen nanofluid droplets

Tip formation in a freezing water droplet is independent of the droplet volume, substrate temperature, and the arrested contact angle. However, when a nanofluid droplet is deposited on a supercooled surface, its freezing behaviour is different from that of a pure water droplet. Interestingly, the pointy tip disappears in freezing nanofluid droplets and a flat plateau is observed when droplets complete the freezing process. Figure 3-7 shows the morphology of nanofluid droplets with different particle types and the same particle volumetric concentrations (0.3%) during the freezing process. At the early stage of freezing ($t^* = 0.2$), the unfrozen part and frozen part in a nanofluid droplet are similar to those in a water droplet. Large differences in the droplet shapes can be observed at the end of the freezing process ($t^* = 1$). The pointy tip at the apex of a water droplet is replaced by a flat plateau in all the nanofluid droplets in the

experiments. The experimental results also indicate that the radius of the plateau and the shape of the droplet depends on the properties of the particles.

Figure 3-7 Morphologies of nanofluid droplets ($6.0 \mu\text{L} \pm 0.12 \mu\text{L}$) with different types of particles at the initial stages ($t^* = 0.2$) and final stages ($t^* = 1$) of freezing.

To explore the mechanism of the appearance of the plateau in freezing nanofluid droplets further, the freezing process for a nanofluid droplet was investigated in a Hele-Shaw cell device. The Hele-Shaw cell is a device that consisted of 2 acrylic sheets separated by a spacer. The 2-D freezing experiments can be conducted in the Hele-Shaw cell device. The movement of the freezing front and the formation of the plateau can be observed clearly in the two-dimensional area. The schematic of the Hele-Shaw cell with a droplet is shown in Figure 3-8. The bottom of the Hele-Shaw cell was bonded to the Peltier cooler model using thermal paste. The device consisted of a copper base and two pieces of acrylic glass (10 mm in width). A nanofluid droplet was deposited on the top of a copper strip (1 mm in width) at the middle of the base using a blunt-tip syringe. The freezing process was observed through the sidewall of the Hele-Shaw cell device.

Figure 3-8 Schematic of the Hele-Shaw cell with the deposited droplet

Figure 3-9 shows the evolution of the freezing front in a water droplet and a TiO_2 nanofluid droplet ($12.0 \mu\text{L} \pm 0.12 \mu\text{L}$, $r_p = 15 \text{ nm}$) with 0.1% volumetric concentrations in the Hele-Shaw cell. The liquid phases and solid ice phases can be identified via their different transparencies. In the case of a water droplet freezing, air is separated out from the liquid, and many bubbles are formed in the ice phase. In the case of a nanofluid droplet freezing, particles are pushed out by the freezing front. The unfrozen liquid has been transported to the outside of the droplet at a certain stage (as can be seen from $t^* = 0.5$ for the 0.1% TiO_2 droplet). Finally, the plateau is formed when nanofluid droplets complete freezing.

Figure 3-9 Evolution of the freezing fronts in a Hele-Shaw cell

The particle rejections lead to the accumulation of particles around the vicinity of the freezing front. Previous studies have shown that the surface tension of nanofluids is a function of particle concentrations [212, 213]. Therefore, in the case of the freezing of nanofluid droplets,

the higher particle concentrations near the freezing front can create a surface tension gradient along the free surface of the liquid droplet. Accordingly, a Marangoni flow is formed, and part of the liquid in the central region is transported to the outside region. Hence, the rejection of particles is a very important reason for the generation of a surface tension gradient as well as the Marangoni flow. The extent of the particle rejection by the freezing front is influenced by the initial particle volumetric concentration, the freezing rate, and the particle size [16, 130, 147]. Therefore, systematic experiments have been conducted to investigate the effect of these factors on the freezing behaviour of nanofluid droplets.

3.4. Effects of particle volumetric concentration

The previous discussions have shown that the Marangoni flow induced by the particle accumulation on the freezing front is an important reason for the formation of a plateau on nanofluid droplets. The initial particle volumetric concentration can affect the number of particles near the freezing front and the particle distribution in the liquid droplet; therefore, the effect of the particle volumetric concentration on freezing behaviour is studied in this section. Nanofluid droplets (TiO_2 , $r_p = 5 \text{ nm}$) at three volumes were generated via the micropipette (3.5 μL , 6.0 μL , $8.0 \pm 0.12 \mu\text{L}$). The substrate temperature was fixed at -21.5°C , and the particle volumetric concentration varied from 0.03% to 2.0%.

Figure 3-10 shows the final shapes of 5 nm TiO_2 nanofluid droplets during the freezing process. As can be seen from the figure, a plateau can appear in both smaller droplets with lower particle concentrations and larger droplets with higher particle concentrations. The increase in the radius of the plateau can be observed in Figure 3-10 because more particles are rejected by the freezing front when droplet volumes and particles volumetric concentrations increase, causing more liquid to be transported away from the centre to the outer edges via the Marangoni flow.

Figure 3-10 Selected images of the morphology of nanofluid droplets (TiO_2 , $r_p = 5$ nm) with different volumes and particle volumetric concentrations at the end of freezing

The dynamic freezing behaviours of different volumes of water droplets and nanofluid droplets were compared. The morphologies of droplets with different volumetric concentrations at four different stages, that is, the initial freezing stage ($t = 0.28$ s), the stage before half of the freezing occurs, the stage after half of the freezing occurs, and the end of the freezing stage, are shown in Figures 3-11, 3-12, and 3-13. The variation in the total freezing time of nanofluid droplets is greater than that for water droplets with the same volume; this trend can still be observed when the droplet volume changes from $3.5 \mu\text{l}$ to $8 \mu\text{l}$ (Accuracy $\pm 0.12 \mu\text{L}$). The acceleration of the freezing process in nanofluid droplets can be attributed to two factors. Firstly, the dispersion of nanoparticles in the colloidal droplet system enhances the heat transfer properties that shorten the total freezing time. Secondly, the particle rejection-induced Marangoni flow transports liquid from the centre of the droplet to the outside region, which can decrease the height of the liquid part of the droplet during the freezing process. With a decrease in droplet height, the freezing time can be shortened. As can be seen from Figures 3-11, 3-12, and 3-13, the height of the 0.1% nanofluid droplets after half freezing is almost the same as that before

half freezing. A decrease in droplet height is even observed for the 1.5% nanofluid droplets during the freezing process. Note that the height of the water droplet increases monotonously during the freezing process. With the increase in particle volumetric concentration, more particles can be rejected by the freezing front, which can lead to a larger surface tension gradient in the droplet's free surface. As a result of the Marangoni effect, more liquid is transported from the centre to the outward section of the droplet near the freezing front region. Therefore, the height of the droplet at the end of freezing decreases with increasing particle volumetric concentrations.

Figure 3-11 Dynamic freezing process for a 3.5 μl water droplet and nanofluid droplets (TiO₂, $r_p = 5$ nm) with different particle volumetric concentrations (0.1% and 2.0%)

Figure 3-12 Dynamic freezing process for a 6.0 μl water droplet and nanofluid droplets (TiO_2 , $r_p=5$ nm) with different particle volumetric concentrations (0.1% and 2.0%)

Figure 3-13 Dynamic freezing process for an 8.0 μl water droplet and nanofluid droplets (TiO_2 , $r_p=5$ nm) with different particle volumetric concentrations (0.1% and 2.0%)

The effects of droplet volumes and particle volumetric concentrations on droplet freezing time are shown in Figure 3-14. The experimental observation shows that the height of the frozen water droplet is smaller than that of the pure water droplet. The freezing time can scale according to $t_f \sim h^2 K(L, k_{ice}, T)$, where h is the height of the frozen droplet, L is the latent heat of fusion, k_{ice} is the thermal conductivity of ice, and T is the temperature difference. Meanwhile, the presence of nanoparticles changes the thermal conductivity of the system. Therefore, a combined effect of the increase in the thermal conductivity and the decrease in frozen droplet height leads to the acceleration of the freezing process in nanofluid droplets.

Figure 3-14 Differences in the total freezing times for nanofluid droplets with different particle volumetric concentrations and droplet volumes

Figures 3-15, 3-16, and 3-17, respectively, show the digitalised geometric profiles of 3.5 µl, 6.0 µl, and 8.0 µl water droplets as well as nanofluid droplets (TiO_2 , $r_p = 5$ nm) with 0.1% and 1.5% volumetric concentrations during the freezing process. For the water droplets with different volumes, the droplet surface in the centre region always moves upward during the freezing process. Finally, a tip is formed in water droplets as freezing is completed. The dimensionless heights of water droplets (h/r_b) at the final stages are greater than those at the initial stages. Here, r_b represents the radius of the baseline of the droplet. However, for 0.1% nanofluid droplets, the movement of the droplet surface in the centre region almost stops completely after $t = 1.28$ s. With the increase in particle volumetric concentration, a downward movement in the droplet profile can be seen in the 1.5% nanofluid droplets during the freezing process. As can be seen from Figures 3-15, 3-16, and 3-17, a flat plateau forms in nanofluid droplets, and the dimensionless heights of the nanofluid droplets when freezing is completed are close to (0.1% particle concentration) or less than (1.5% particle concentration) the heights at the initial stage. Because the increase in particle volumetric concentration leads to a larger

surface tension gradient in the droplet surface that can generate a Marangoni flow, more liquid in the centre region moves downward and outward, which can change the direction of movement for the droplet profile in the centre region.

(a) Digitalised geometric profiles of a 3.5 μl water droplet

(b) Digitalised geometric profiles of a 3.5 μl 0.1% nanofluid droplet

(c) Digitalised geometric profiles of a 3.5 μl 1.5% nanofluid droplet

Figure 3-15 The digitalised geometric profiles for 3.5 μl water and nanofluid droplets (TiO_2 , $r_p = 5 \text{ nm}$)

(a) Digitalised geometric profiles of a 6.0 μl water droplet

(b) Digitalised geometric profiles of a 6.0 µl 0.1% nanofluid droplet

(c) Digitalised geometric profiles of a 6.0 µl 1.5% nanofluid droplet

Figure 3-16 The digitalised geometric profiles for 6.0 µl water and nanofluid droplets (TiO_2 , $r_p = 5$ nm)

(a) Digitalised geometric profiles of an 8.0 µl water droplet

(b) Digitalised geometric profiles of an 8.0 µl 0.1% nanofluid droplet

(c) Digitalised geometric profiles of an 8.0 µl 1.5% nanofluid droplet

Figure 3-17 The digitalised geometric profiles for 8.0 µl water and nanofluid droplets (TiO_2 , $r_p = 5$ nm)

The previous experimental results show that the variations in droplet volume and particle volumetric concentration result in two typical shapes for nanofluid droplets at the end of freezing; the schematics for the shapes of nanofluid droplets with low ($C_0 < 1.0\%$) and high particle concentrations ($C_0 \geq 1.0\%$) of particles are shown in Figure 3-18 (a) and 3-18 (b), respectively.

Figure 3-18 Schematics for the shapes of frozen nanofluid droplets with different initial particle volumetric concentrations (C_0): (a) the geometric profile of a frozen nanofluid droplet when the $C_0 < 1.0\%$ and (b) The geometric profile of a frozen nanofluid droplet when the $C_0 \geq 1.0\%$

A geometric model is proposed for calculating the volume of the liquid that is transported from the central region to the outer region. The top region of the nanofluid droplet at the end of the freezing process is assumed to be a circular, truncated cone (a trapezoid in 2-D view). If the liquid in the central part cannot be transported to the outside, the top region of the nanofluid droplet is assumed to be conical in shape (a triangle in 2-D view), that is, similar to the top

region of a pure water droplet. Based on these assumptions, the volume of the top cone in the centre of a droplet can be expressed as

$$V_{centre} = \frac{1}{3}\pi r_c^2 h \quad (3-5)$$

The volumes of the large truncated cone (the radius of the upper base is r_t) and small truncated cone (the radius of the upper base is r_c) can be respectively expressed as

$$V_{truncated\ cone-l} = \frac{1}{3}\pi(r_b^2 + r_t^2 + r_b r_t)H \quad (3-6)$$

$$V_{truncated\ cone-s} = \frac{1}{3}\pi(r_b^2 + r_c^2 + r_b r_c)H \quad (3-7)$$

Using the conservation of mass, the volume transported from the centre is equivalent to the increased volume on the outside. Therefore, the volume of the top triangle region (with dots) is equal to the volume of the sideward annulus (with vertical lines).

$$V_{centre} = V_{truncated\ cone-l} - V_{truncated\ cone-s} \quad (3-8)$$

Because the two triangles are similar, it yields

$$\frac{r_c}{r_b} = \frac{h}{h + H} \quad (3-9)$$

The ratio r_t/r_b is assumed to be λ . Substituting Eq. (3-5) – Eq. (3-7) and Eq. (3-9) into Eq. (3-8), the following relationship between r_t/r_b and r_c/r_b can be obtained

$$\frac{r_c}{r_b} = \frac{\lambda + \lambda^2}{1 + \lambda + \lambda^2} \quad (3-10)$$

Therefore, the ratio between the transported liquid in the centre and the volume of the large triangle region can be calculated as

$$\frac{\Delta V}{V} = \frac{V_{centre}}{V_{centre} + V_{truncated\ cone-s}} = \frac{\frac{1}{3}\pi r_c^2 h}{\frac{1}{3}\pi r_b^2 (h + H)} = \frac{r_c^3}{r_b^3} = \left(\frac{\lambda + \lambda^2}{1 + \lambda + \lambda^2} \right)^3 \quad (3-11)$$

A scaling model was developed to analyse the relationship between the initial particle volumetric concentration and the transported liquid from the central region. The following assumptions were used in the analysis: (1) Particles rejected by the freezing front can form a relatively highly concentrated layer near the freezing front in the liquid phase. (2) The particle volumetric concentration at the apex of the droplet equals the initial particle volumetric concentration C_0 during the freezing process. (3) The particle volumetric concentration varies linearly along the liquid-air free surface. (4) The liquid is transported from the central region due to the velocity component in the horizontal direction of the Marangoni flow only. (5) The thermal conductivity of solid ice is independent of the particle volumetric concentration.

The particle volumetric concentration along the liquid-air free surface can be expressed as

$$C(Z) = C_F(Z_0) - \frac{C_F(Z_0) - C_0}{s(r_0, Z_0)} s(r, z), \quad (3-12)$$

where $s(r, z)$ is the arc length of the unfrozen liquid in the nanofluid droplet, and $C_F(Z_0)$ is the particle volumetric concentration on the liquid side near the freezing front.

The surface tension is a function of the particle volumetric concentration [212-215]; therefore, the scales of the surface tension gradient along the liquid-air interface of the unfrozen part can be expressed as

$$\nabla_s \gamma \sim F(r, z, s) C_0 \quad (3-13)$$

The Marangoni stress is balanced by the viscous stress, which can be expressed as

$$\nabla_s \gamma = \mu \left(\frac{\partial u}{\partial z} \right), \quad (3-14)$$

where u is the velocity component in the horizontal direction.

Substituting Eq. (3-13) into Eq. (3-14), the scales of the horizontal velocity u can be obtained as

$$u \sim \frac{F(r, z, s)}{\mu} C_0 \quad (3-15)$$

The transported liquid in the central region is the result of the horizontal flow and can be calculated as

$$\Delta V = \int_0^{t_f} 2\pi r h_l \bar{u} dt, \quad (3-16)$$

where t_f is the total freezing time of the liquid; r and h_l are the radius and height of the unfrozen liquid part, respectively; and $\bar{u}$ is the average velocity in the liquid region, which can be calculated as

$$\bar{u} = \frac{1}{h_l} \int_0^{h_l} u dz \quad (3-17)$$

The scales of t_f can be expressed as

$$t_f \sim \frac{G(R, \theta)}{k_{ice}} H(L, T), \quad (3-18)$$

where k_{ice} is the thermal conductivity of the ice in a nanofluid droplet, L is the latent heat of fusion, and T is the substrate temperature.

Substituting Eq. (3-15), Eq. (3-17), and Eq. (3-18) into Eq. (3-16) yields

$$\Delta V \sim \frac{1}{k_{ice}} \frac{1}{\mu} G(R, \theta) H(T, L) F(r, z, s) C_0 \quad (3-19)$$

Therefore, the ratio between the transported liquid from the central region and the volume of the truncated cone ($\Delta V/V$) can be expressed as

$$\frac{\Delta V}{V} = F C_0 \quad (3-20)$$

Based on the results of the geometric and scaling models, the shape change feature of a nanofluid droplet can be expressed as a function of the initial particle volumetric concentration

$$\left(\frac{\lambda + \lambda^2}{1 + \lambda + \lambda^2} \right)^3 = FC_0, \quad (3-21)$$

where the coefficient F can be obtained using a linear fitting method.

The calculated results of the models are compared to the experimental observations in Figure 3-19. The scaling model can predict the shape change features of nanofluid droplets with low particle volumetric concentrations ($C_0 < 1.0\%$) well. However, the theoretical calculations and experimental data differ at higher particle volumetric concentrations ($C_0 \geq 1.0\%$) because of the accumulation of particles in the liquid phase near the freezing front increases to a constant packing density at high particle volumetric concentrations [10, 148, 216, 217]. Further increases in the initial concentration cannot change the concentration near the freezing front. As a result, the particle concentration and surface tension gradient along the liquid-air interface are kept constant, causing the volume of the liquid transported from the central region to the outside to remain unchanged.

Figure 3-19 The shape change feature of a nanofluid droplet with variations in the initial particle volumetric concentration

3.5. Effects of particle size and substrate temperature

The effect of the particle volumetric concentration on the freezing process of nanofluid droplets is discussed in the previous section. A flat plateau is formed on the top of a nanofluid droplet as the freezing process is completed, and this unique shape change feature is caused by a Marangoni flow that transports liquid from the central region to the outward region. The rejection of particles by the freezing front is very influential in the generation of this Marangoni flow. Many studies have shown that the velocity of the freezing front and the radii of the nanoparticles can affect the rejection/engulfment of particles [143, 188, 189, 218]. In this study, the velocity of the freezing front in a TiO₂ nanofluid droplet can be altered by adjusting the substrate temperature and the radii of the particles in nanofluid droplets, which vary from 5 nm to 800 nm. The effect of particle size and substrate temperature on the freezing process for nanofluid droplets is investigated experimentally in this section.

The morphologies of TiO₂ nanofluid droplets with different particle sizes (r_p) on cold substrates at the end of the freezing process are shown in Figure 3-20. When the substrate temperature is -12.5 °C, a plateau appears on the top of nanofluid droplets, indicating that the freezing front can always reject particles in nanofluid droplets and that the formation of the plateau is independent of the particle size under this temperature condition. Two non-dimensional parameters are used to analyse the shape change of a droplet during the freezing process quantitatively. The shape factor of the freezing front is defined as the ratio of the radius of the freezing front (r_f) and the radius of the droplet baseline (r_b). Dimensionless time is defined as $t^* (t/t_f)$, where t_f is the total freezing time of the droplet. Figure 3-20 (b) shows the variation in the shape factor with respect to dimensionless time. As can be seen from the figure, the shape factor is smaller than 1 during the freezing process, which indicates that the radius of the freezing front is always smaller than that of the droplet baseline. There is little difference in the shape factors of nanofluid droplets at the end of the freezing process, which means that the

volumes of liquid transported from the central regions due to Marangoni flows are almost similar. Therefore, the effect of particle sizes on the shape change feature of a nanofluid droplet is not very significant under this substrate temperature condition. As a result of the similar shape change features, little variation in the freezing times of nanofluid droplets is observed in Figure 3-20 (c) as the particle size changes.

Figure 3-20 The effect of particle size on the shape change features of nanofluid droplets ($6.0 \mu\text{L} \pm 0.12 \mu\text{L}$) during the freezing process when the substrate temperature is -12.5°C . (a) Select morphologies of the nanofluid droplets at the end of freezing. (b) Evolution of the shape factor during the freezing process. (c) Differences in the freezing times of nanofluid droplets with different particle sizes.

As can be seen from Figure 3-21 (a), the shape change feature of the TiO_2 nanofluid droplet changes with increasing particle size under -17.5°C substrate temperature conditions. The plateau is still observed for nanofluid droplets with 5 nm and 15 nm TiO_2 particles. The appearance of pointy tips on the apexes of nanofluid droplets with 100 nm and 800 nm TiO_2 particles suggests that the morphologies of the two frozen nanofluids droplet differ from those of the small-sized particles. The formation of a triangular shape is observed in the upper part of frozen nanofluid droplets with larger-sized particles. The tip angles of the triangles in nanofluid droplets with 100 nm and 800 nm TiO_2 particles are 144.5° and 142.7° , respectively. The formation of plateaus and triangles on nanofluid droplets at the end of the freezing period represents different degrees of Marangoni effects and particle rejection by the freezing front. Fewer particles are rejected when the plateau feature is less obvious. The relationship between dimensionless time and the shape factor under the -17.5°C substrate temperature condition is shown in Figure 3-21 (b). Rapid decreases in the shape factors are observed for nanofluid droplets with 100 nm and 800 nm TiO_2 particles at the final stage of freezing due to the formation of triangles. The different shape change features of nanofluid droplets under this substrate temperature condition also result in a divergence in freezing behaviours. The nanofluid droplets with 100 nm and 800 nm TiO_2 particles take a longer amount of time to completes freezing because the triangle in the apex increases the heights of the frozen droplets.

Figure 3-21 The effect of particle size on the shape change feature for nanofluid droplets ($6.0 \mu\text{L} \pm 0.12 \mu\text{L}$) during the freezing process when the substrate temperature is -17.5°C . (a) Select morphologies of the nanofluid droplets at the end of freezing. (b) Evolution of the shape factor during the freezing process. (c) Differences in the freezing times of nanofluid droplets with different particle sizes.

If the temperature of the substrate continues to decrease, the difference between the morphologies of frozen nanofluid droplets with small-sized particles and those with large-sized particles becomes more obvious. Figure 3-22 (a) depicts the morphologies of nanofluid droplets with four sizes of TiO_2 particles at the completion of freezing under -31.3°C substrate temperature conditions. Plateaus still form on the apexes of nanofluid droplets with 5 nm and 15 nm TiO_2 particles. However, as the particle size decreases, the shape change features on the upper parts of the frozen droplets are similar to those observed for a pure water droplet, as shown in Figure 3-13. The tip angles of frozen nanofluid droplets with 100 nm and 800 nm

TiO₂ particles are 129.1° and 131.5°, respectively, which are both close to the value of the tip angle of a frozen water droplet (130°). However, these tip angles are smaller than the tip angles of nanofluid droplets with 100 nm and 800 nm TiO₂ particles under the -17.5 °C substrate temperature conditions. The shapes of the frozen nanofluid droplets with large-sized particles are similar to that of the frozen pure water droplet, which indicates that the effect of Marangoni flow is almost negligible at this temperature. Therefore, very few particles are rejected by the freezing front during the freezing process. Figure 3-22 (b) compares the shape factors of droplets with four sizes of nanoparticles quantitatively. Similar to the results found for the -12.5 °C and -17.5 °C conditions, with the upward propagation of the freezing front, the values of the shape factors for all nanofluid droplets decrease. However, the slopes of the shape factors of nanofluid droplets with large-sized particles are much steeper than those of nanofluid droplets with 5 nm and 15 nm particles after half of the freezing process. The effect of particle size on the shape change feature can be observed after $t^* = 0.5$, where $t^* = t/t_f$. The different freezing times of nanofluid droplets with four particle sizes can be seen from Figure 3-22 (c); these differences are attributed to the variations in the morphologies of the frozen droplets.

Figure 3-22 The effect of particle size on the shape change features of nanofluid droplets ($6.0 \mu\text{L} \pm 0.12 \mu\text{L}$) during the freezing process when the substrate temperature is -31.3°C . (a) Select morphologies of the nanofluid droplets at the end of freezing. (b) Evolution of the shape factor during the freezing process. (c) Differences in the freezing times for nanofluid droplets with different particle sizes

The effect of temperature on the morphologies of nanofluid droplets ($6.0 \mu\text{L} \pm 0.12 \mu\text{L}$) with four particle sizes was investigated at five substrate temperature conditions. The selected morphologies of the nanofluid droplets ($6.0 \mu\text{L} \pm 0.12 \mu\text{L}$) with 5 nm TiO_2 particles at the two temperature conditions $T = -12.5^\circ\text{C}$ and $T = -31.3^\circ\text{C}$ are shown in Figures 3-23 (a) and 3-23 (b). The progression of nanofluid droplet freezing was tracked via image sequencing during the four stages of the freezing process. The geometry of the droplets shortly after the beginning of freezing is presented in the image at $t^* = 0.1$. The droplet morphologies before and after half of the freezing have taken place are illustrated in the images at $t^* = 0.3$ and 0.7 , respectively. The shapes of the droplets near the completion of freezing are shown for $t^* = 0.9$. As can be seen from Figures 3-23 (a) and 3-23 (b), the droplet contact angle is a function of substrate temperature. The arrest of the droplet contact line is faster on substrates at lower temperatures, which results in an increase in the contact angle [211]. The height of the droplet decreases from $t^* = 0.3$ to $t^* = 0.9$, which suggests the effect of the Marangoni flow due to the particle rejection is stronger than the effect of volumetric expansion. The disappearance of the liquid phase is observed at both temperature conditions when $t^* = 0.9$, indicating that the formation of the

plateau on the top of nanofluid droplets with 5 nm TiO₂ particles is independent of the substrate temperature.

Figure 3-23 Evolution of the morphologies in the freezing process of a TiO₂ nanofluid droplet (5 nm TiO₂ particles) with the 0.3% volumetric concentration at a cold substrate setting of (a) -12.5 °C and (b) -31.3 °C

The morphologies of nanofluid droplets ($6.0 \mu\text{L} \pm 0.12 \mu\text{L}$) with 15 nm TiO₂ particles during the freezing process are shown in Figure 3-24. The height of the droplet decreases from $t^* = 0.7$ to $t^* = 0.9$ for both substrate temperature conditions. The disappearance of the liquid phase near the completion of freezing can be observed for both cases. It could be concluded that the upward propagation of the freezing front during the final stage of freezing can occur.

Figure 3-24 Evolution of the morphologies in the freezing process of a nanofluid droplet (15 nm TiO₂ particles) with the 0.3% volumetric concentration in a cold substrate setting of: (a) -12.5 °C, and (b) -31.3 °C

The effects of the substrate temperature on the interface heights of nanofluid droplets with 5 nm and 15 nm TiO₂ particles are shown in Figures 3-25 (a) and 3-25 (b). The height of the

interface (ih) at each time moment was normalised by the droplet height at the completion of freezing ($h_{t^*=1}$). The slopes of the dimensionless interface heights decrease during the freezing process under the five substrate temperature conditions.

The droplet height change feature due to freezing is evaluated using the vertical expansion ratio, defined to be the height of the frozen droplet (h_f) relative to the height of the droplet very shortly after the onset of the freezing (h_{ini}). The effects of the substrate temperature on the droplet height changes are shown in Figures 3-25 (c) and 3-25 (d). The differences in the vertical expansion ratios for nanofluid droplets with decreasing substrate temperatures are smaller than 0.05, which indicates that the effect of the substrate temperature is not significant on the height change feature for nanofluid droplets with small-sized particles. All the vertical expansion ratios of the nanofluid droplets are smaller than that of pure water droplets due to the formation of the plateau during the completion of freezing.

Figure 3-25 Time evolutions of the dimensionless interface heights of (a) Nanofluid droplets (5 nm TiO_2 particles) and (b) Nanofluid droplets (15 nm TiO_2 particles) with 0.3% volumetric concentrations. The vertical expansion ratios of (c) Nanofluid droplets (5 nm TiO_2 particles) and (d) Nanofluid droplets (15 nm TiO_2 particles) with 0.3% volumetric concentrations

The image sequences for freezing nanofluid droplets ($6.0 \mu\text{L} \pm 0.12 \mu\text{L}$) with 100 nm and 800 nm TiO_2 particles are shown in Figure 3-26 and Figure 3-27. The morphologies of these nanofluid droplets change significantly with the decrease of the substrate temperature. In the initial ($t^* = 0.1$) and early stage ($t^* = 0.3$) freezing stages, only an increase in the contact angles of the nanofluid droplets can be observed when the substrate temperature decreases. With the upward movement of the freezing front, three different geometric profiles in the upper region of the nanofluid droplets become distinguishable after half of the freezing. With the disappearance of the liquid phase near the completion of freezing, plateaus were observed at the -12.5°C substrate temperature setting. The Marangoni flow can transport liquid from the central region to the outside region due to the particle segregation. With a decrease in substrate temperature from -17.5°C to -31.3°C , the velocity of the freezing interface increases in both the nanofluid droplets with 100 nm and 800 nm TiO_2 particles. When the velocity of an interface reaches a critical value, particles can be trapped by the interface. This velocity value is defined as the critical velocity [16, 127, 131, 142, 176]. The effect of the Marangoni flow due to the particle concentration difference along the liquid-air interface decreases when fewer particles are rejected by the interface, leading to the disappearance of the plateau near the completion of freezing. Therefore, the morphologies of nanofluid droplets were observed to vary from triangle-shaped regions at -17.5°C to dome-shaped regions at -31.3°C , becoming more and more like pure water droplets.

Figure 3-26 Evolution of the morphologies in the freezing process for a nanofluid droplet (100 nm TiO_2 particles) with the 0.3% volumetric concentration at a cold substrate setting of: (a) $-12.5\text{ }^\circ\text{C}$, (b) $-17.5\text{ }^\circ\text{C}$, (c) $-21.5\text{ }^\circ\text{C}$, and (d) $-31.3\text{ }^\circ\text{C}$

The movements of the freezing interfaces during the freezing process for nanofluid droplets ($6.0\text{ }\mu\text{L} \pm 0.12\text{ }\mu\text{L}$) with 100 nm and 800 nm TiO_2 particles under five substrate temperature conditions are compared. The variations in the dimensionless interface heights for these droplets with respect to the dimensionless freezing time is shown in Figures 3-28 (a) and 3-28 (b). More steeply increasing slopes for the dimensionless interface heights can be observed near the completion of freezing when the temperature of the substrate is lower than $-17.5\text{ }^\circ\text{C}$ due to the changes in the droplet geometric profiles in the upper regions shown in Figures 3-26 and 3-27.

Figure 3-27 Evolution of the morphologies in the freezing process for a nanofluid droplet (800 nm TiO_2 particles) with the 0.3% volumetric concentration at a cold substrate setting of: (a) $-12.5\text{ }^\circ\text{C}$, (b) $-17.5\text{ }^\circ\text{C}$, (c) $-21.5\text{ }^\circ\text{C}$, and (d) $-31.3\text{ }^\circ\text{C}$

The height change features of nanofluid droplets with 100 nm and 800 nm TiO_2 particles at different temperature settings are compared in Figure 3-28. The smallest height change factors (h_f / h_{ini}) for the nanofluid droplets were observed at $-12.5\text{ }^\circ\text{C}$ due to the formation of plateaus, which are absent at other temperature settings. The number of particles near the freezing front in the liquid phase has a significant impact on the effect of Marangoni flow. With a decrease in substrate temperature, fewer particles are rejected by the freezing front. Therefore, less liquid can be moved from the central region, and the height change factor increases. At the lowest substrate temperature setting, the height change factors for these nanofluid droplets are close to that of pure water droplets, which indicates that very little particle segregation has occurred under this condition.

Figure 3-28 Evolution of the dimensionless interface heights of (a) Nanofluid droplets (100 nm TiO_2 particles) and (b) Nanofluid droplets (800 nm TiO_2 particles) with 0.3% volumetric concentrations. The vertical expansion ratios of (c) Nanofluid droplets (100 nm TiO_2 particles) and (d) Nanofluid droplets (800 nm TiO_2 particles) with 0.3% volumetric concentrations.

The transport of the liquid from the central region to the outside region can decrease the droplet height. The difference between the height of a droplet at the current time moment ($h_{t^*=i}$) and the previous time moment ($h_{t^*=i-0.1}$) is transformed into a dimensionless expression using the height of the frozen droplet ($h_{t^*=1}$). The non-dimensional parameters $dp^* = (h_{t^*=i} - h_{t^*=i-0.1})/h_{t^*=1}$ for nanofluid droplets with four particle sizes under five substrate temperature conditions during the freezing process are shown in Figure 3-29. If $dp^* < 0$, the height of a nanofluid droplet decreases from $t^* = i-1$ to $t^* = i$, indicating that the liquid in the central region is transported to the outside region due to a Marangoni flow. As can be seen from Figure 3-29 (a) and 3-29 (b), the effect of temperature on the heights of 5 nm and 15 nm nanofluid droplets during the freezing process is not significant. The value of dp^* at $t^* = 0.9$ is below 0, which can represent the formation of a plateau at the completion of freezing. The freezing process is not completed after the liquid phase (shown in Figure 3.23 – Figure 3.24) disappears at $t^* = 0.9$ because there are liquid residuals near the concave freezing front (shown in Figure 3.3). Therefore, the value of dp^* is larger than 0 due to the upward propagation of the freezing front during the final stage of freezing.

As can be seen from Figure 3-29 (c) and 3-29 (d), the variations in the heights of the 100 nm and 800 nm nanofluid droplets during the freezing process depend strongly on the substrate

temperature. At $-21.5\text{ }^{\circ}\text{C}$, $-26.5\text{ }^{\circ}\text{C}$, and $-31.3\text{ }^{\circ}\text{C}$, the values of dp^* of the 100 nm and 800 nm nanofluid droplets are greater than 0 during the freezing process, indicating that the effect of Marangoni flow can be neglected because very few particles are rejected by the freezing interface due to the increasing freezing velocity. However, the dp^* becomes less than 0 at $t^*=0.5$ under the $-12.5\text{ }^{\circ}\text{C}$ and $-17.5\text{ }^{\circ}\text{C}$ temperature conditions, which indicates that the liquid is transported from the central region to the outside region from $t^*=0.4$ onward. However, the values of dp^* exceed 0 at $-17.5\text{ }^{\circ}\text{C}$ when $t^*=0.8$. Meanwhile, the liquid phase is still observed in the upper parts of the droplets in Figure 3.26 – Figure 3.27, suggesting that the liquid in the central part cannot be moved to the outside region after $t^*=0.7$. Although particles are rejected during the freezing process, a pointy tip can still be observed in the nanofluid droplets at the completion of freezing under this temperature condition. With the disappearance of the liquid phase at $t^*=0.9$ at a substrate temperature of $-12.5\text{ }^{\circ}\text{C}$, plateaus can still be formed on the frozen nanofluid droplets, even if the values dp^* are greater than 0 from $t^*=0.9$ onward.

Figure 3-29 Droplet height variations in the freezing processes of nanofluid droplets (5 nm, 15 nm, 100 nm, and 800 nm TiO_2 particles) with 0.3% volumetric concentrations

Particles can be engulfed in the solid ice phase when the speed of the freezing front exceeds a limit value, which is defined as the critical velocity [130, 185, 187, 189, 218]. With fewer particles being rejected by the freezing interface, the effect of the Marangoni flow decreases, and the morphologies of nanofluid droplets change. A regime map describing the relationship between the velocity of the freezing front and the morphologies of nanofluid droplets is shown in Figure 3-30. The change in the velocity is the result of the substrate temperature. Many studies have shown that the critical velocity is inversely related to particle size [153, 179, 181, 182]. Based on this fact, a simplified scaling model is provided to analyse the critical velocity as a function of the particle size:

$$V_{cr} \sim Er^{-M} \quad (3-22)$$

where r is the radius of the nanoparticles, E and M are two factors that are independent of this radius.

After taking the logarithm of both sides, Eq. (3-22) becomes:

$$\log_{10} V_{cr} \sim E - M \log_{10} r \quad (3-23)$$

The values of E and M can be obtained via curve fitting based on the experimental data.

Meanwhile, the critical velocity can also be calculated by using the model proposed by Rempel

and Worster [181]. The two lines in Figure 3-30 represent the critical velocity as a function of particle size. As can be seen from the regime map, the shapes of the nanofluid droplets exhibit the plateau feature in the regions below the fitting lines. Because the velocity of the freezing front is less than the critical velocity under these conditions, particles can be rejected to the liquid phase near the freezing front, which leads to the generation of a Marangoni flow. When the velocity of the freezing front becomes larger than the critical velocity, the number of particles rejected by the freezing front is reduced, and the effect of Marangoni flow is no longer obvious. Therefore, the pointy tip feature becomes more and more obvious in the region far beyond the curve fitting. In Rempel and Worster's study, it is assumed that the thermal conductivities of water and solid particles are identical, perhaps resulting in the differences between the directly fitted results and Rempel and Worster's model.

Figure 3-30 The regime map reflecting the relationship between the morphologies of nanofluid droplets with different sizes of particles and freezing rates.

3.6. Summary

The freezing process of a nanofluid droplet deposited on a cold substrate has been studied experimentally in this chapter. The results show that the freezing behaviour of a nanofluid droplet is different from that of a pure water droplet. In the latter case, a pointy tip always appears on the apex of the frozen droplet which is independent of the droplet's volume and the substrate temperature. A theoretical model based on the self-similar geometry of a pure water droplet near the completion of freezing is adopted to explain the constant value of the tip angle. In the case of nanofluid droplets, a plateau is formed on the top of a frozen nanofluid droplet at the completion of the freezing process, while tip singularity is not observed. This new phenomenon not only occurs in one special type of nanofluid droplets but also in nanofluid droplets with different types of particles.

A scaling model has been developed to explain the formation of the plateau, and the relationship between the degree of shape change in the nanofluid droplet and the initial particle volumetric concentration has been analysed. With large numbers of particles accumulating near the freezing front in the liquid phase due to particle rejection, a surface tension gradient along the liquid-air interface of a droplet is generated, which can lead to a Marangoni flow that brings the liquid from the central part to the outside region of the droplet. As a result of this effect, a plateau is observed in the final shape of a frozen nanofluid droplet. The calculated shape change factor of a nanofluid droplet using the proposed scaling model is in good agreement with the experimental observations when the initial volumetric concentration is less than 1%. With further increases in particle concentration, the calculated results differ from the experimental data due to the constant packing density of particles near the freezing front.

The experimental observations indicate that the substrate temperature can have an important impact on the formation of the plateau found on some frozen nanofluid droplets. The shape

change feature of nanofluid droplets with large-sized particles is found to be strongly dependent on the substrate temperature. With a decrease in the substrate temperature, the velocity of the freezing front increases, and plateaus gradually cease to form on top of the droplets. A regime map is developed using the moving velocity of the freezing front and the size of the nanoparticles to describe the profiles of frozen nanofluid droplets based on the experimental results of this study. In the regime below the fitting line, the plateau feature can be observed regardless of the size of the particles in the nanofluid droplets. The current study may provide new insights into the dynamic control of droplet shape in the phase change process.

Chapter 4: Numerical study of the freezing process of nanofluid droplets with no external field

In this chapter, a new lattice Boltzmann (LB) model was developed to investigate the freezing process of a nanofluid droplet numerically. The mathematical models in the LB model will be introduced first. Secondly, the numerical results from the new LB model are compared to the experimental observations to validate this new model. Lastly, the effects of particle volumetric concentration and the contact angle on the shape change feature of freezing nanofluid droplets are studied numerically.

4.1. Introduction

Even though the experimental work in Chapter 3 provided many straightforward results on the freezing behaviour of nanofluid droplets, detailed information, such as particle distribution and fluid flow inside a nanofluid droplet during the freezing process, is difficult to acquire due to the small scale of the particles. For this reason, a numerical simulation is adopted as an alternative tool with which to study the freezing process of nanofluid droplets. Among the current numerical methods used to explain multiphase flows, the lattice Boltzmann method (LBM) is considered to be one of the most powerful approaches for the simulation of phase change problems, such as condensation [219], melting [220], boiling [221, 222], and freezing [223], due to its high computational efficiency and good ability to handle arbitrary geometries. Recently, an axisymmetric LB model was developed to simulate the freezing process of a pure water droplet which took into consideration the volume expansion effect caused by the density difference between liquid and ice [75].

Ladd firstly proposed an LB model to simulate particulate suspensions [224, 225]. In these studies, the solid particles were defined by a boundary surface, and the lattice nodes on either side of boundary surfaces were treated as fluids. Over the past two decades, many efforts have

been put into using Ladd's model in other areas, such as the heat transfer characteristics in nanofluids [226, 227], the impact dynamics for droplets hitting a layer of solid particles [228], the evaporation of a colloidal droplet [229], and the fluid dynamics in a droplet [230]. However, most of these works were conducted under single-phase conditions, and the sizes of the particles used in the simulations were much greater than those of nanoparticles. As a result of these two issues, it is difficult to apply the previous LB models to simulations involving the freezing of nanofluid droplets.

Peskin [231] firstly proposed the immersed boundary method (IBM) to deal with the complex interfaces inside fluids. In IBM, the boundaries are treated as Lagrangian nodes, and the flow field is represented by fixed Eulerian coordinates. Feng et al. combined the IBM and LB methods and developed a new LB model to simulate the interaction between a fluid and particles in colloidal suspensions [232]. Due to its flexibility in dealing with non-slip interfaces, many IBM-LB models have been developed to track the deformation and movement of particles in particulate flows [232, 233]. However, to the best of the author's knowledge, very few IBM-LB models have been used in solving phase change problems.

In this study, a new LB model was developed by combining the axisymmetric LB model for the freezing of water droplet with IBM. Hence, a 2-D LBM simulation was carried out to investigate the freezing process of a nanofluid droplet on a cold substrate numerically. The radius and height of the freezing front obtained from the simulation are in good agreement with the experimental data, which validates the accuracy of the developed model. Next, the effect of particle volumetric concentration and the surface wettability on the freezing shape change feature was examined and reasonable results were obtained.

4.2. Theory and mathematical model

4.2.1. Thermal lattice Boltzmann model for a pure water droplet

The Shan-Chen (SC) multiphase LB model [234] was adopted to track the liquid-air interface in a 2-D Cartesian coordinate system. The density distribution function can be written as the following equation in the classical two-dimensional, nine-speed (D2Q9) lattice form with a Bhatnagar–Gross–Krook (BGK) collision operator

$$f_{\alpha}(\mathbf{x} + \mathbf{e}_{\alpha}\delta_t, t + \delta_t) - f_{\alpha}(\mathbf{x}, t) = (1 - B) \left[-\frac{1}{\tau} (f_{\alpha}(\mathbf{x}, t) - f_{\alpha}^{eq}(\mathbf{x}, t)) + \Delta f_{\alpha}(\mathbf{x}, t) \right] + B\Omega_{\alpha}^s + \delta V_{\alpha} \quad (4-1)$$

with

$$\Omega_{\alpha}^s = f_{\bar{\alpha}}(\mathbf{x}, t) - f_{\alpha}(\mathbf{x}, t) + f_{\alpha}^{eq}(\rho, \mathbf{u}_s) - f_{\bar{\alpha}}^{eq}(\rho, \mathbf{u}), \quad (4-2)$$

where $f_{\alpha}(\mathbf{x}, t)$ is the particle distribution function at position $\mathbf{x}$ and time t , and the subscript α ($\alpha=0, 1, \dots, 8$) represents 9 lattice velocities in 9 directions. Here, τ is the relaxation time for the density distribution function and can be written as $\tau = 3\nu + 0.5$, where ν is the kinematic viscosity. Next, $\bar{\alpha}$ represents the opposite direction from α in Eq. (4-2). Finally, B is a weighting factor related to the volume fraction of the ice phase (f_s) on each lattice node and can be expressed as

$$B = \frac{\tau - 0.5}{0.5 - f_s + \tau}, \quad (4-3)$$

where f_{α}^{eq} is the corresponding density equilibrium distribution function in the α direction and is given as

$$f_{\alpha}^{eq} = \omega_{\alpha} \rho \left[1 + \frac{\mathbf{e}_{\alpha} \cdot \mathbf{u}}{c_s^2} + \frac{(\mathbf{e}_{\alpha} \cdot \mathbf{u})^2}{2c_s^4} - \frac{\mathbf{u}^2}{2c_s^2} \right], \quad (4-4)$$

with $\mathbf{e}_\alpha$ representing the discrete velocities, ω_α being the weighting coefficient, and c_s being the lattice sound speed.

The $\Delta f_\alpha(\mathbf{x}, t)$ in Eq. (4-1) represents the body force term and can be expressed by [221, 235]

$$\Delta f_\alpha(\mathbf{x}, t) = f_\alpha^{eq} \left(\rho(\mathbf{x}, t), \mathbf{u} + \frac{\mathbf{F} \delta_t}{\rho} \right) - f_\alpha^{eq}(\rho(\mathbf{x}, t), \mathbf{u}), \quad (4-5)$$

where $\mathbf{F}$ represents the total body force on the particles, including the fluid-fluid interaction force $\mathbf{F}_f$, fluid-solid interaction force $\mathbf{F}_s$, and fluid-particle interaction force $\mathbf{F}_p$. The expression of the total force can be given as $\mathbf{F} = \mathbf{F}_f + \mathbf{F}_s + \mathbf{F}_p$. The effect of gravity is not considered in this simulation due to the small Bond number for the droplets ($Bo \approx 0.3$).

The δV_α in Eq. (4-1) is an additional source term representing the volume change due to the density difference between liquid and solid. It can be given by [75]

$$\delta V_\alpha = f_\alpha^{eq} ((1 - \gamma) \rho \frac{\partial f_s}{\partial t}, \tilde{\mathbf{u}}), \quad (4-6)$$

where $\tilde{\mathbf{u}}$ represents the real fluid velocity and can be expressed as

$$\tilde{\mathbf{u}} = \sum_\alpha \frac{\mathbf{e}_\alpha f_\alpha}{\rho} + \frac{\mathbf{F} \delta_t}{2\rho} \quad (4-7)$$

The total density ρ and macro velocity $\mathbf{u}$ of each lattice node in Eqs. (4-1), (4-2), (4-3), and (4-5) can be calculated from

$$\rho = \sum_\alpha f_\alpha \quad (4-8)$$

$$\mathbf{u} = \frac{\sum_\alpha \mathbf{e}_\alpha f_\alpha}{\rho} \quad (4-9)$$

The added source term δV_α can lead to the solid ice density becoming larger than the liquid density ρ_l in some situations. In these cases, the density equilibrium distribution function f_α^{eq} must be corrected to achieve the conservation of mass. The corrected f_α^{eq} is given by Zhang et al.'s model [75]

$$f_{\alpha}^{eq} = \begin{cases} \omega_{\alpha} \rho_l \left[1 + \frac{\mathbf{e}_{\alpha} \cdot \mathbf{u}}{c_s^2} + \frac{(\mathbf{e}_{\alpha} \cdot \mathbf{u})^2}{2c_s^4} - \frac{\mathbf{u}^2}{2c_s^2} \right] & \alpha = 0 \\ \omega_{\alpha} \frac{\rho - \omega_0 \rho_l}{1 - \omega_0} \left[1 + \frac{\mathbf{e}_{\alpha} \cdot \mathbf{u}}{c_s^2} + \frac{(\mathbf{e}_{\alpha} \cdot \mathbf{u})^2}{2c_s^4} - \frac{\mathbf{u}^2}{2c_s^2} \right] & \alpha \neq 0 \end{cases} \quad (4-10)$$

The total density of solid ice also needs to be revised in the current study due to the volume expansion. The real density is calculated with

$$\tilde{\rho} = \rho(1 - f_s + \gamma f_s) \quad (4-11)$$

4.2.2. The enthalpy-based lattice Boltzmann model

The evolution equation of the temperature equilibrium distribution function is expressed as

$$g_{\alpha}(\mathbf{x} + \mathbf{e}_{\alpha} \delta_t, t + \delta_t) - g_{\alpha}(\mathbf{x}, t) = -\frac{1}{\tau_T} \left(g_{\alpha}(\mathbf{x}, t) - g_{\alpha}^{eq}(\mathbf{x}, t) \right) + \delta_t \omega_{\alpha} \phi, \quad (4-12)$$

where τ_T is the relaxation time of the temperature, which is defined as

$$\tau_T = \frac{3k}{\tilde{\rho} c_p} + 0.5, \quad (4-13)$$

where k and c_p are the thermal conductivity and specific heat at constant pressure, respectively.

In Eq. (4-12), g_{α}^{eq} is the temperature equilibrium distribution function, which is given as

$$g_{\alpha}^{eq} = \omega_{\alpha} T \left[1 + \frac{\mathbf{e}_{\alpha} \cdot \tilde{\mathbf{u}}}{c_s^2} + \frac{(\mathbf{e}_{\alpha} \cdot \tilde{\mathbf{u}})^2}{2c_s^4} - \frac{\tilde{\mathbf{u}}^2}{2c_s^2} \right], \quad (4-14)$$

where T is the macro temperature that can be defined as

$$T = \sum_{\alpha} g_{\alpha} \quad (4-15)$$

Next, ϕ represents the thermal source term in Eq. 4-12, which is given by Zhang et al. [75]

$$\phi = \left[\frac{1}{\tilde{\rho}c_p} \nabla \cdot (k \nabla T) - \nabla \cdot \left(\frac{k}{\tilde{\rho}c_p} \nabla T \right) \right] + \frac{\Delta H_{ls}}{c_p} \frac{\partial f_s}{\partial t}, \quad (4-16)$$

where ΔH_{ls} is the latent heat of the liquid-solid phase change, which can be calculated as

$$\Delta H_{ls} = H_l - H_s, \quad (4-17)$$

where H_l is the enthalpy of liquid at the onset of freezing, and H_s is the enthalpy of the solid at the completion of freezing.

The total enthalpy value in the computational domain is related to the fraction of solid and the temperature and is given by [236]

$$H = f_s c_{p,s} T + (1 - f_s) c_{p,f} T + f_s \Delta H_{ls}, \quad (4-18)$$

where the volume fraction of the solid f_s can be written as

$$f_s = \begin{cases} 0 & H \geq H_l \\ \frac{H - H_s}{H_l - H_s} & H_s < H < H_l \\ 1 & H \leq H_s \end{cases} \quad (4-19)$$

4.2.3. The immersed boundary method

Figure 4-1 shows a schematic of the IBM. The particle surfaces are described by Lagrangian nodes, and the fluid domain is represented by fixed Eulerian coordinates [237]. As shown in Figure 4-1, the Lagrangian node is much smaller than the lattice length in Eulerian coordinates; therefore, the Lagrangian nodes in the simulation can be considered to be the particles in a nanofluid droplet. Spherically shaped particles with diameter d_p are considered in this simulation. The number of particles used in the simulation is set to be N_B .

Figure 4-1 Schematic illustration of an immersed boundary method-Lattice Boltzmann model

The relationship between the velocity at a Lagrangian node and the Eulerian lattice node can be expressed by [238]

$$\mathbf{u}_B^*(\mathbf{X}_B, t + \delta_t) = \sum_{i,j} \tilde{\mathbf{u}}(\mathbf{x}_{ij}, t + \delta_t) D_{ij}(\mathbf{x}_{ij} - \mathbf{X}_B) \delta_x \delta_y, \quad (4-20)$$

where $\mathbf{u}_B^*$ is the temporal velocity of the Lagrangian nodes, $\tilde{\mathbf{u}}$ is the real velocity at $\mathbf{x}_{ij}$, $\mathbf{X}_B = (X_B, Y_B)$ is the Lagrangian node, and $\mathbf{x}_{ij} = (x_i, x_j)$ is the Eulerian lattice (with indices i and j).

In Eq. (4-20), D_{ij} is the distribution function given by Peskin [239]

$$D_{ij}(\mathbf{x}_{ij} - \mathbf{X}_B) = \frac{1}{h^2} \delta_h \left(\frac{x_i - X_B}{h} \right) \cdot \delta_h \left(\frac{x_j - Y_B}{h} \right) \quad (4-21)$$

with

$$\delta_h(r) = \begin{cases} \frac{1}{4h} \left(1 + \cos \left(\frac{\pi r}{2} \right) \right), & |r| \leq 2 \\ 0, & |r| > 2 \end{cases}, \quad (4-22)$$

where $h=1$ represents the lattice spacing.

The no-slip boundary conditions must be satisfied when the IBM is adopted to simulate the interactions between the particles and fluid. Therefore, some body forces near the Lagrangian nodes are added and distributed via the Dirac delta distribution function [232].

The body force density at the Lagrangian nodes is given by Kang and Hassan [240]

$$\mathbf{F}_B(\mathbf{X}_B, t + \delta_t) = 2\rho_p \frac{\mathbf{U}_B(\mathbf{X}_B, t + \delta_t) - \mathbf{u}_B^*(\mathbf{X}_B, t + \delta_t)}{\delta_t}, \quad (4-23)$$

where $\mathbf{U}_B$ and $\mathbf{u}_B^*$ are the real velocity and the temporal velocity, respectively, at the Lagrangian node $\mathbf{X}_B$ at time $t + \delta_t$.

The body force at the Eulerian node $\mathbf{x}_{ij}$ is given as

$$\mathbf{F}_b(\mathbf{x}_{ij}, t + \delta_t) = \sum_B \mathbf{F}_B(\mathbf{X}_B, t + \delta_t) D_{ij}(\mathbf{x}_{ij} - \mathbf{X}_B) \Delta s_l, \quad (4-24)$$

where Δs_l represents the arc length of the boundary element, which is calculated as

$$\Delta s_l = \frac{\pi d_p}{N_B} \quad (4-25)$$

This is an additional hydrodynamic force on the lattice nodes, that is, a part of the fluid-particle interaction force $\mathbf{F}_p$.

The movement of a particle can be calculated based on the Newton's law of motion. The centre of the particle is denoted $\mathbf{X}_p$. The total force and torque on the particle can be expressed as

$$\mathbf{F}_p(\mathbf{X}_p) = \sum_B \mathbf{F}_B(\mathbf{X}_B) \Delta s_l = M_p \frac{d\mathbf{U}_p}{dt}, \quad (4-26)$$

where $\mathbf{U}_p$ is the translational velocity, and M_p represents the mass of the particle.

The torque on the particle can be calculated as

$$\mathbf{T}_p = \sum_B (\mathbf{X}_B - \mathbf{X}_p) \times \mathbf{F}_B(\mathbf{X}_B) \Delta s_l = I_p \frac{d\mathbf{\Omega}_p}{dt}, \quad (4-27)$$

where $\mathbf{\Omega}_p$ is the angular velocity, and I_p is the moment of the particle.

Then the positions of the particles at every step can be tracked with $d\mathbf{X}_p/dt = \mathbf{U}_p$.

The velocity $\mathbf{U}_B$ at a Lagrangian point can be calculated from $\mathbf{U}_p$ and $\mathbf{\Omega}_p$

$$\mathbf{U}_B(\mathbf{X}_B) = \mathbf{U}_p + \mathbf{\Omega}_p \times (\mathbf{X}_B - \mathbf{X}_p) \quad (4-28)$$

The interactions between the fluid and particles were discussed previously. However, the existence of particle-particle, particle-ice, and particle-gas interactions in a droplet during the freezing process can present challenges regarding the analysis of the interaction forces on a particle. In this study, all particles are assumed to be driven into the liquid phase due to the rejection of the ice and gas phase. An additional repulsive force is added to a single particle based on the Lennard-Jones potential model used to analyse the interactions caused by the wall, gas/ice phase, and other particles [241].

$$\mathbf{F}_m^{p-p}(\mathbf{X}_p) = \begin{cases} \varepsilon \sum_{n, n \neq m} \left[\left(\frac{2r_p}{X_R^{m,n}} \right)^{2\hat{n}} - 2 \left(\frac{2r_p}{X_R^{m,n}} \right)^{\hat{n}} \right] \frac{\mathbf{X}_p^m - \mathbf{X}_p^n}{(2r_p)^2}, & X_R^{m,n} \leq 2r_p + \zeta \\ 0, & X_R^{m,n} > 2r_p + \zeta \end{cases} \quad (4-29)$$

$$\mathbf{F}_m^{p-w|g|s}(\mathbf{X}_p) = \begin{cases} \varepsilon \sum_n \left[\left(\frac{r_p}{X_R^{m,w|g|s}} \right)^{2\hat{n}} - 2 \left(\frac{r_p}{X_R^{m,w|g|s}} \right)^{\hat{n}} \right] \frac{\mathbf{X}_p^m - \mathbf{X}_{w|g|s}}{r_p^2}, & X_R^{m,w|g|s} \leq 2r_p + \zeta \\ 0, & X_R^{m,w|g|s} > 2r_p + \zeta \end{cases}, \quad (4-30)$$

where $\varepsilon = r_p^2$, $\hat{n}$ is related to the particle collision elasticity and is set to $\hat{n} = 1$, and ζ is the threshold, that is, $\zeta = 2d_p$. The subscript/superscript m represents the particle the force is being applied on, n represents any other particle, and $w|g|s$ represent the wall, gas interface, or ice interface.

In Eq. (4-29) and Eq. (4-30), $X_R^{m,n} = 2|\mathbf{X}_p^m - \mathbf{X}_p^n|$ and $X_R^{m,w|g|s} = 2|\mathbf{X}_p^m - \mathbf{X}_{w|g|s}|$. Here, $\mathbf{X}_p^m$ and $\mathbf{X}_p^n$ represent the positions of two particles, and $\mathbf{X}_{w|g|s}$ is the position of the wall ($\mathbf{X}_w$), the liquid-gas interface ($\mathbf{X}_g$), or the liquid-ice interface ($\mathbf{X}_s$).

A hypothetical concentration distribution function $\xi_p(\mathbf{x}_{ij})$ is used on the Eulerian nodes and is based on the Dirac delta function in the calculation of the forces on a single particle.

Referring to Zhang et al.'s study [221], the capillary force exerted on a particle is written as

$$\mathbf{F}_c^p(\mathbf{X}_p) = \sum_{ij} \left[-\gamma D_{ij}(\mathbf{x}_{ij} - \mathbf{X}_p) \sum_{\mathbf{x}'} G_p(\mathbf{x}, \mathbf{x}') \psi(\mathbf{x}') \right], \quad (4-31)$$

where γ is the weighting factor related to the particle size and considered to be $\gamma = 1$; G_p represents the interaction strength between the fluid and particles, which is given as -0.6 in this study; $\mathbf{x}'$ represents the nodes surrounding $\mathbf{x}$; and $\psi(\mathbf{x})$ is the effective mass, which can be calculated with $\psi(\mathbf{x}) = \sqrt{(p - \rho/3)/3}$.

With consideration for all the discussed forces, the total force exerting on a particle in Eq. (4-26) can be written as

$$\mathbf{F}_p(\mathbf{X}_p) = \sum_B \mathbf{F}_B(\mathbf{X}_B) \Delta s_l + \mathbf{F}_m^{p-p}(\mathbf{X}_p) + \mathbf{F}_m^{p-w}(\mathbf{X}_p) + \mathbf{F}_m^{p-g}(\mathbf{X}_p) + \mathbf{F}_m^{p-s}(\mathbf{X}_p) + \mathbf{F}_c^p(\mathbf{X}_p) \quad (4-32)$$

To calculate the capillary force on each fluid lattice induced by the surrounding particles, the sum of the total force on all particles around a fluid lattice can be calculated as

$$\mathbf{F}_{c,p}(\mathbf{x}) = \sum_p \left[\sum_B \frac{1}{N_B} \mathbf{F}_p(\mathbf{X}_p) D_{ij}(\mathbf{x}_{ij} - \mathbf{X}_B) \Delta s_l \right] \quad (4-33)$$

In the calculation, the total force on one particle is separated equally on its neighbouring boundary points.

In summary, the effect of the particles on the fluid flow represented by the Eulerian nodes can be expressed by considering the body force $\mathbf{F}_b(\mathbf{x}_{ij}, t + \delta_t)$ in Eq. (4-24) and the capillary force $\mathbf{F}_{c,p}(\mathbf{x})$ in Eq. (4-33). The effect of the body force on the macro velocity field can be neglected due to the small size of the particles used in this simulation. Therefore, this force is not included in the calculation of total velocity.

4.3. Description of the simulation

4.3.1. Computational domains and boundary conditions

Figure 4.2 shows the schematic of the computational domain with 100×120 lattice nodes. A droplet with small particles is located on the top of a cold substrate.

The symmetric boundary condition is employed on the left side of the domain. A flat wall with a height of 10 lattice units is set on the bottom side of the domain, and a constant temperature is applied at the wall. The conjugate heat transfer between the droplet and the top of the wall is treated as in Li et al.'s model [242]. The wall and thermal isolation boundary conditions are applied on the right and upside of the domain.

Figure 4-2 Schematics of the computational domain for a nanofluid droplet freezing on a cold substrate

4.3.2. Initial conditions

A liquid droplet with a radius of 100 lattice units (corresponding to the contact angle $\theta = 90^\circ$) and a gas phase are initially incorporated into the domain. As pointed out by Gong and Cheng [223], the Peng-Robinson equation of state (PR-EOS) should be adopted to initialise the multiphase LB model, that is

$$p = \frac{\rho R_g T_0}{1 - b\rho} - \frac{a\rho^2 \varepsilon(T_0)}{1 + 2b\rho - b^2\rho^2} \quad (4-34)$$

with

$$\varepsilon(T_0) = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - (\sqrt{\frac{T_0}{T_c}})]^2, \quad (4-35)$$

where R_g is the gas constant, T_0 is the initial temperature, T_c is the critical temperature, ω is the acentric factor, a is the attraction parameter, and b is the repulsion parameter. In this simulation, a , b , ω , and R_g are set to be 2/49, 2/21, 0.344, and 1, respectively. The effect of temperature on the liquid density during the freezing process of a droplet is not considered; therefore, the density ratio between the liquid and gas phases depends only on T_0 , which is given as $T_0 = 0.85 T_c$.

The initialisation of the density field is very important for the stability of the simulation. The initial densities of the liquid droplet and gas are chosen to be $\rho_l = 6.64$ and $\rho_g = 0.32$, respectively. The liquid-gas interface density can be initialised using a flowing expression based on Xu et al.'s model [243]

$$\rho = \frac{1}{2}(\rho_l + \rho_g) - \frac{1}{2}(\rho_l - \rho_g) \times \tanh\left(\frac{2\sqrt{(r - r_0)^2 + (z - z_0)^2} - R_0}{W}\right), \quad (4-36)$$

where W is the thickness of the interface and is chosen to be 5 lattice units, and the centre of the droplet is at (r_0, z_0) .

The diffuse-interface method is used to simulate the different wetting conditions on the top of the substrate. The effective mass fraction of the wall lattice ($\psi_{i,0}$) can be calculated from the effective mass values at the neighbouring lattices ($\psi_{i,2}$, $\psi_{i+1,1}$) above it based on Ding and Splet's model [244]

$$\psi_{i,0} = \psi_{i,2} + \tan\left(\frac{\pi}{2} - \theta\right) |\psi_{i+1,1} - \psi_{i-1,1}|, \quad (4-37)$$

where the first index ($i-1$, i , and $i+1$) and the second index (0, 1, and 2) represent the coordinates tangential and normal to the wall, respectively. Zero denotes the lattice on the wall, while 1 and 2 denote the lattices on the first and second layers above the top of the wall. When a contact angle θ is given, the wetting condition on the surface can be discretised via Eq. (4-37).

The particle distribution in the liquid droplet is initialised using the generation loop shown in Figure 4-3. Based on this generation method, particles are uniformly distributed in the liquid droplet before the onset of freezing. The diameter of a particle is 0.1 lattice unit. The Lagrangian nodes number N_b is given as 6.

Figure 4-3 Flow chart of the particle initialisation procedure in the simulation

4.4. Results and discussions

In this section, the simulation results for the freezing process of a nanofluid droplet are discussed in three parts. Firstly, the developed LBM was validated with the experimental data and good agreement was found. After validating the model, the effect of the initial concentration of particles on the freezing process of a nanofluid droplet was investigated numerically. Lastly, the new LBM was used to examine the freezing behaviour of a nanofluid droplet with different contact angles on the substrate.

4.4.1. Model validation

The developed LB method was first applied to simulate the freezing process of a nanofluid droplet, and the results were compared to the experimental data. In the experiment, nanofluids

with 100 nm TiO₂ nanoparticles were used. The volumetric concentration of the particles was 0.3%, the volume of the droplet was 6 μ l, the substrate temperature was maintained at -14.5 °C, and the initial droplet temperature T_0 was 25 °C. The contact angle of the droplet was measured as 60°; this value was also used as the initial contact angle of the droplet in the simulation. The total particle number was set to be 200 in the simulation to guarantee that the particle volumetric concentration ($\Phi = 0.3\%$) was the same as that for the nanofluid droplet in the experiment. The temperature on the bottom of the substrate was gradually decreased to T_w in 1000 calculation steps when the temperature of the droplet at the baseline reached T_f the freezing process on the droplet began.

Figure 4-4 shows the evolution of the droplet shape during the freezing process. The simulated droplet profiles were compared to the experimental observations at four dimensionless time moments (t^*), where $t^* = t/t_f$. t is the transient time at the given moment, and t_f is the total freezing time of the nanofluid droplet from the onset of freezing to the completion of freezing. As can be seen from the Figure 4-4, a plateau is observed on the top of the simulated droplet at $t^* = 1$, which indicates that the new LB method can successfully predict the most important shape change feature of a frozen nanofluid droplet. A decrease in the droplet height at the central part of the droplet from $t^* = 4/9$ to $t^* = 6/9$ can be directly observed in both experimental snapshots and the simulated droplet profiles, although there is some difference between the numerical and experimental results in terms of droplet height values. The divergence of the two droplet profiles can be explained as follows: the particle distribution field, the particle shape, and the number of particles in the simulation are not exactly the same as in the real nanofluid droplet due to the limitations of the current numerical model. These properties are very significant for the interactions between the particles and fluid during the phase change process [209]. As a result, the simulated droplet shapes are not exactly the same as the real droplet shapes.

Figure 4-4 Comparisons of nanofluid droplet shape profiles given by the simulation (images right) and the experiment (images left) at various time moments

The variation in the interface height and interface radius during the freezing process is investigated quantitatively to analyse the freezing dynamics of the freezing front in a nanofluid droplet. The height and radius of the interface at each time moment are normalised by the height of the frozen droplet and the radius of the droplet at baseline, respectively. The two simulated normalised parameters are compared to the experimental results in Figure 4-5. The numerical results show good agreement with the experimental data in terms of the evolution of the normalised interface height. The slope of the normalised interface height decreases with time, representing a reduced freezing front velocity during the freezing process. A monotonous decrease in the normalised interface height can be found in both the experimental and numerical results. The values of the normalised interface height diverge near the final stage of freezing (after $t^* = 6/9$). A rapid decrease in the simulated results can be seen due to the formation of a relatively higher part in the freezing front, which is not observed in the droplet profile at the completion of freezing.

Figure 4-5 Comparisons of the normalised interface heights and normalised interface radii given by the LB method and experimental measurements during the freezing process

4.4.2. The particle distribution and velocity profiles

Based on the results shown in Figures 4-4 and 4-5, the accuracy of the newly developed model is proven. On the other hand, applying the new LBM to simulate the freezing process of a nanofluid droplet can provide more detailed information on the particle distribution and velocity field, which is challenging to observe in experiments due to the very small-scale particle sizes.

Figure 4-6 shows the distribution of the particles in the liquid phase at different time moments during the freezing process. The height and radius in the coordinate are normalised with respect to the radius of the droplet baseline. The blue colour represents the ice phase in a nanofluid droplet, while the white colour inside the droplet denotes the liquid phase. A freezing front with a concave shape can be observed from the simulation, which has also been seen in the freezing of a pure water droplet in a Hele-Shaw cell [40]. At the initial stage of freezing ($t^* = 1/9$), particles are rejected by the freezing front, and the particle distribution is relatively uniform compared to the distributions in other time moments. When the freezing front moves, this uniform distribution is affected. As can be seen from Figure 4-6 (b), the number of particles at the advancing freezing front is greater than in the other regions in the liquid phase. The velocity of the freezing front at its periphery is greater than that in the centre, that is, more particles can accumulate in this region. The liquid in the central part of the droplet is moved to the outside region, partly due to the capillary force caused by the particle accumulation near the freezing front. At $t^* = 7/9$, some particles are trapped in the ice phase, and the top of the droplet becomes relatively flat, with the liquid phase in a cap. At the completion of freezing, a plateau is formed with two slope regions that is similar to the plateau of the nanofluid droplet in experiments.

Figure 4-6 The particle distribution field in a nanofluid droplet during the freezing process at various time moments

The fluid flow in a nanofluid droplet during the freezing process is different from that in a pure water droplet. Using the newly developed LB model, a visualisation of the flow inside the droplet can be achieved. The velocity profile in a nanofluid droplet at $t^* = 0.4$ is shown in Figure 4-7. Here, the green contour represents the magnitude of the velocity, and the red arrow represents the velocity vector. Downward and outward fluid flows are observed in the liquid phase, which can drive the liquid from the central region to the outside region. In this simulation, the interactions between the particles and fluid are described with the capillary force. With the accumulation of particles near the freezing front (shown in Figure 4-6), the capillary force can drive the liquid to the region with a relatively high particle concentration. The maximum velocity of the liquid appears on the periphery of the freezing front, where the number of accumulated particles is also very high.

Figure 4-7 The velocity field in a nanofluid droplet at $t^* = 0.4$ during the freezing process

With the downward and horizontal movement of the liquid caused by the particle-fluid interactions, the height of the nanofluid droplet is decreased. However, the droplet expansion

due to the density difference can increase the droplet height. A droplet expansion ration is employed to analyse the droplet height dynamics during the freezing process. This dimensionless parameter is defined as the ratio between the height of the droplet at the current dimensionless time ($t^* = i$) and that at the previous time ($t^* = i-0.056$). The variation in the droplet expansion ratio ($h_i / h_{i-0.056}$) with t^* as shown in Figure 4-8. When $h_i / h_{i-0.056} > 1$, the height of droplet increases from $t^* = i-0.056$ to $t^* = i$, and the effect of the droplet expansion is more obvious. When $h_i / h_{i-0.056} < 1$, the droplet height decreases during this time period, and the effect of the capillary force becomes significant. A droplet expansion region can be observed at the initial stage of freezing ($t^* < 0.389$), with the droplet expansion dominating the droplet height change feature during this period. As more and more particles accumulate near the freezing front, the effect of the capillary force on droplet height can overcome the effect of the droplet expansion. Accordingly, a region without droplet expansion appears.

Figure 4-8 The droplet expansion ratio versus dimensionless time

4.4.3. Effects of the particle volumetric concentration

The effect of the particle volumetric concentration on the freezing of a nanofluid droplet is investigated using the newly developed model. Figure 4-9 shows select LBM results for a nanofluid droplet with a fixed contact angle ($\theta = 70^\circ$) and different particle volumetric concentrations (Φ) at the completion of freezing. The red areas represent the particle concentrations. A plateau region can be observed on the top of all nanofluid droplets, and the radius of the plateau is dependent on the particle concentration. At $\Phi = 0.09\%$, the particles have mostly accumulated on the top of the plateau, leading to the formation of a relatively flat plateau. At high particle volumetric concentrations ($\Phi > 0.45\%$), particle accumulations can also be found in the side regions far below the top plateau, which indicates that particles are trapped in the ice phase during the freezing process with increases in particle concentrations. This particle distribution field also changes the plateau region on a frozen nanofluid droplet, giving it a concave shape under these conditions.

Figure 4-9 Morphologies of, and particle distributions in, a nanofluid droplet with a fixed contact angle at the completion of freezing: (a) $\Phi = 0.09\%$, (b) $\Phi = 0.18\%$, (c) $\Phi = 0.45\%$, (d) $\Phi = 0.63\%$, and (e) $\Phi = 0.72\%$.

A quantitative analysis of the effect of the particle volumetric concentration on the shape change feature of a freezing nanofluid droplet is performed. Two dimensionless factors, the height change factor of the droplet, and the radius change factor of the plateau, are used in the following discussions. Figure 4-10 (a) shows the variations in height change factors for the droplets as the result of increases in the particle volumetric concentration for two contact angles. The height change factor of a droplet is defined as the ratio between the height of a frozen nanofluid droplet ($h_{particle}$) and the height of a frozen water droplet (h_{water}) with the same contact angle. This factor represents the degree of deviation of a nanofluid droplet's height from a water droplet's height at the completion of freezing. If $h_{particle}/h_{water} = 1$, then the presence of particles has not resulted in any change in the nanofluid droplet height. At $\Phi =$

0.09%, the values of $h_{particle}/h_{water}$ for both nanofluid droplets are slightly smaller than 1. The decrease in the frozen droplet height is not obvious under a relatively low Φ . A monotonic decrease in the $h_{particle}/h_{water}$ with increasing Φ can be found in both cases due to the enhanced particle-fluid interactions under high Φ conditions. The effect of the particle volumetric concentration on the plateau radius is shown in Figure 4-10 (b). The plateau radius (r_{top}) is non-dimensionalized, with the maximum radius (r_{max}) found in the frozen nanofluid droplet. The value of this dimensionless parameter represents the size of the plateau. The values of r_{top}/r_{max} are around 0.15 at $\Phi = 0.09\%$ for both droplets, while the maximum r_{top}/r_{max} is 0.65 at $\Phi = 0.72\%$. The increase in Φ leads to a monotonic increase in the plateau radius. This conclusion is verified through the shape of the nanofluid droplets in Figure 4-9. The slopes of $h_{particle}/h_{particle}$ and r_{top}/r_{max} become smaller after $\Phi > 0.45\%$ for both contact angles. This phenomenon can be explained by the particle distribution in the top region of a frozen droplet. There is not much difference in the particle concentration value and the distribution profile after Φ reaches 0.45% in Figure 4-9. As a result, the effect of Φ on the above two dimensionless parameters becomes weaker in the high Φ region.

(a) The height change factor for the droplet versus the particle volumetric concentration

(b) The radius change factor for the plateau versus the particle volumetric concentration

Figure 4-10 The variations in the shape change factor with the initial particle volumetric concentration for nanofluid droplets with contact angles $\theta = 70^\circ$ and 110°

4.4.4. Effects of the droplet contact angle

To examine the effect of the droplet contact angle on the freezing shape change feature of a nanofluid droplet, the surface wettability is altered based on Ding and Splet's model, which was described in Section 4.3.2. Figure 4-11 shows the simulated droplet profiles and the particle distribution field at the completion of freezing under different contact angle (θ) conditions. A plateau region appears on the top of the frozen droplet, where particle accumulations are also observed in all cases. The coordinate in Figure 4-11 is normalised with respect to the droplet baseline when the contact angle $\theta = 40^\circ$. With an increase in θ , both the droplet baseline and the plateau radius decrease. A relatively higher particle concentration can be observed in the periphery of the top plateau in the simulated results for all droplets, which is similar to the coffee ring phenomenon observed in droplet evaporation experiments [245].

Figure 4-11 Morphologies of, and particle distributions in nanofluid droplets with different contact angles and fixed volumetric particle concentrations ($\Phi = 0.36\%$) at the completion of freezing

To study the freezing dynamics of nanofluid droplets with different contact angles further, the variation in the simulated dimensionless plateau radius (r_{top}/r_{max}) and the height change factor of the droplet ($h_{particle}/h_{water}$) with θ will be examined. As can be seen from Figure 4-12, the value of r_{top}/r_{max} ranges from 0.46 to 0.58 under the given contact angle conditions.

Meanwhile, a relatively small variation in the $h_{particle}/h_{water}$ value can also be found when the droplet's contact angle is changed. From these simulation results, it can be concluded that the effect of the contact angle on the shape change feature is not as significant as the effect of the particle volumetric concentration under the current simulation conditions. The morphologies of the droplets in Figures 4-11 (d) and 4-11 (e) indicates that the height of the frozen droplet remains nearly constant when $\theta > 90^\circ$, explaining the decrease in $h_{particle}/h_{water}$ after $\theta > 90^\circ$ in Figure 4-12.

Figure 4-12 The variations in the dimensionless plateau radius (r_{top}/r_{max}) and the droplet height change factor ($h_{particle}/h_{water}$) with droplet contact angles

4.5. Summary

In this chapter, a new lattice Boltzmann model was proposed to simulate the freezing process of a nanofluid droplet. The freezing was simulated by using the thermal LB model for water droplets while considering volume expansion and the enthalpy-based LB model. The particles

inside the droplets were described via the IBM. The interactions between the particles and fluid were described with the capillary force.

The formation of the plateau can be well predicted in the simulation. The simulated normalised interface height is in good agreement with the experimental data. The distribution of particles in a droplet is very complicated and cannot be described precisely by the current simulation. Therefore, the deviations between the simulation and experiment concerning the normalised radius become large at the later stage of freezing.

The numerical simulation results show that particles are pushed by the freezing front during the freezing process, which leads to the formation of a particle layer near the freezing front on the liquid side. The velocity distribution in the nanofluid droplet has proved that the liquid in the central region can be driven to the outside region due to the accumulation of particles in the periphery of the freezing front.

In higher particle volumetric concentration regions, the decrease in the height shape change factor ($h_{particle}/h_{water}$) and the increase in the radius change factor (r_{top}/r_{max}) slow down due to the similar distributions of the particles on the top of the frozen droplet. When the particle concentration varies from 0.09% to 0.72%, the predicted values of $h_{particle}/h_{water}$ and r_{top}/r_{max} range from 0.975 to 0.725 and 0.15 to 0.65, respectively, which indicates the impact of the particle concentration is very significant in relation to the shape change feature of frozen nanofluid droplets.

The simulated results for droplets on a hydrophilic surface indicate that the values of $h_{particle}/h_{water}$ and r_{top}/r_{max} remain almost unchanged. Compared to the variations in these two parameters in the simulation results for different particle concentrations, the $h_{particle}/h_{water}$ changes from 0.88 to 0.78, and the r_{top}/r_{max} changes from 0.46 to 0.59, which indicates that the

effect of the contact angle is not very important in terms of the shape changes in frozen nanofluid droplets.

The results of this numerical study provide more details on the freezing process of a nanofluid droplet which could not be observed in the previous experimental study in Chapter 4. The study complements the physical understanding of the mechanisms involved in the freezing process of nanofluid droplets.

Chapter 5: Experimental study of the freezing process of nanofluid droplets under magnetic fields

The results in Chapters 3 and 4 have highlighted the unique shape change feature of a nanofluid droplet on a supercooled surface. To explore the underlying mechanisms of the freezing of a nanofluid droplet further, the effect of an external magnetic field on the freezing process of a nanofluid droplet is investigated experimentally in this chapter.

5.1. Introduction

Droplet solidification is a ubiquitous phenomenon related to numerous industrial processes, such as microencapsulation [246], pharmaceutical [247], food processing [248], spray coating [249], soldering [250] and additive manufacturing [251]. Understanding the underlying physics of droplet solidification and controlling its process are of both fundamental and practical importance. Substantial studies have been reported regarding the solidification of metallic [252, 253], non-metallic (e.g., wax [254], silicon [206]) and water droplets [255, 256] on cold solid substrates.

Freezing of water droplets is a typical solidification phenomenon that not only occurs in nature but also has relevance to many technological systems; aircraft, heat pumps, wind turbines, and HVAC equipment just a few to name [255, 255]. Most existing studies of the droplet freezing on cold solid surfaces focus on the effects of surface wettability and roughness [70, 80, 87, 257, 258]. Passive strategies, such as surface coating and surface topography tailoring were used to control the droplet freezing process [80, 257, 258]. The freezing time and ice nucleation of water droplets are reported to be dependent on the surface wettability [80, 258]. On the other hand, active freezing control methods using externally applied fields such as ultrasonic, electric and magnetic fields were developed [34, 35, 103, 259, 260]. Gao et al. studied the ultrasonic

field effect on the water droplet freezing process [259], and their experiments showed that the droplet temperature can be lowered by 2 °C under the ultrasonic intensity of 100 W/m². Effects of electric [34, 103] and magnetic [35, 260] fields on water droplet freezing were also investigated and these studies showed that the presence of an electric or magnetic field can promote ice nucleation and increase the freezing temperature under high electric (the electric field strength > 10 V/μm) or magnetic fields (the magnetic field strength > 6 T). Usually, high external field strengths were used in these studies.

Ferrofluids are stable colloidal suspensions with magnetic nanoparticles dispersed in liquid carrier [261, 262]. They are used in microfluidic applications for the purpose of droplet manipulations due to their strong and rapid response to the magnetic field and their magnetically controllable properties [263]. Studies have been reported to investigate the magnetic field effects on the shape change and motion of sessile ferrofluid droplets [263, 264] and the dynamic behaviours of impacting ferrofluid droplets [265, 266]. However, to the best of the author's knowledge, the freezing of a ferrofluid droplet under the magnetic field and the freezing control of droplet has not been reported in the literature.

In this work, the use of weak magnetic fields to actively control the freezing process of a ferrofluid droplet on a cold substrate surface is reported. Specifically, through applying magnetic lift or squeeze conditions, the elongation and squeezing of the shape of the ferrofluid droplet can be achieved respectively, and thus the droplet freezing time can be extended or shortened accordingly. Additionally, the variation of the ferrofluid droplet profile with the magnetic field by using the modified Young-Laplace equation with consideration of an additional magnetic force is analysed and the effect of the magnetic field on the height of liquid ferrofluid droplet is presented. A scaling analysis was performed to describe the observed relationship between the freezing time and the frozen droplet height.

5.2. Experimental setup and procedure

Figure 5-1 (a) shows a schematic of the experimental test rig used for studying the freezing process of a sessile ferrofluid droplet on a cold substrate surface under an applied magnetic field. A cooling unit consisting of a thermoelectric cooler (9500/127/100B, Ferrotec, USA) and a recirculating cooler (Polyscience, USA) is used to cool a copper strip. The temperature of the copper strip is measured by using a thermocouple (Type-T, 0.2 mm, RS PRO, accuracy ± 1.0 °C) connected to a temperature display. Typical experimental steps are illustrated in Figure 5-1 (b) and they are described in brief as follows. 1) the temperature of the copper strip is cooled down to - 6 °C; 2) a micropipette (Thermo Fisher Scientific, USA) is used to deposit a ferrofluid droplet with a preset volume of 4.5 ± 0.12 μL on the centre region of a copper substrate; 3) the droplet is put together with the substrate onto the cold copper strip; 4) the magnet is moved to close to the strip to exert a magnetic force on the droplet and a high-speed camera (3260 frames per second at full resolution of 1280x800, M310, Phantom, USA) is used to capture images at a frame rate of 25 fps. Figure 5-1 (c) shows the forces exerted on the ferrofluid droplet under both magnetic lift and squeeze conditions. The interactions of the gravity force, magnetic force, and interfacial tension result in the deformation of the droplet. For the author's freezing study here, a water-based ferrofluid (EMG 507, Ferrotec, USA) is used. The ferrofluid is diamagnetic and has a negative magnetic susceptibility [265, 266]. Hence, the direction of the magnetic force is opposite to the gravitational force under the magnetic lift case (-), and it is in the same direction as the gravitational force under the magnetic squeeze case (+).

(a) Experimental test rig

(b) Experimental steps

(c) Forces exerting on a ferrofluid droplet

Figure 5-1 (a) Schematic of the experimental test rig used for studying the freezing process of a sessile ferrofluid droplet on a cold substrate surface under an applied magnetic field. (b) Experimental procedures under the magnetic lift and squeeze conditions. (c) Illustration of the forces exerting on a ferrofluid droplet under different magnetic conditions

An electromagnetic (Magnetic Sensor Systems, USA) and a permanent magnet (Titan Magnetics, Singapore) are used respectively to create magnetic lift and squeeze conditions to control the sessile ferrofluid droplet. For the magnetic lift case, the distance between the electromagnet and the substrate is fixed as 6 mm. Different magnetic field strengths are obtained by altering

the electric current in the electromagnet. For the magnetic squeeze case, the strength of the magnetic field is adjusted by changing the distance between the permanent magnet and the substrate from 2.3 mm to 11.5 mm. The magnetic field strength is measured by using a Gauss meter (GM07 Gauss Meter, Hirst Magnetics, United Kingdom). The measurement details and data of the measured magnetic field strength are provided in Figure 5-2 and Table 5-1.

Figure 5-2 Measured strength of magnetic fields for both magnetic lift and squeeze conditions

Table 5-1 The magnetic field strength as a function of z , obtained by 5th order polynomial fitting

Magnetic lift	L1	$12.4 + 4.66 \times 10^3 z - 2.86 \times 10^6 z^2 + 6.13 \times 10^8 z^3 - 6.14 \times 10^{10} z^4 + 2.37 \times 10^{12} z^5$
	L2	$24.0 + 1.40 \times 10^2 z - 1.12 \times 10^6 z^2 + 2.49 \times 10^8 z^3 - 2.55 \times 10^{10} z^4 + 1.03 \times 10^{12} z^5$
	L3	$34.6 + 7.58 \times 10^2 z - 1.5 \times 10^6 z^2 + 2.55 \times 10^8 z^3 - 2.04 \times 10^{10} z^4 + 6.83 \times 10^{11} z^5$
	L4	$34.1 + 1.58 \times 10^4 z - 8.79 \times 10^6 z^2 + 1.82 \times 10^9 z^3 - 1.80 \times 10^{11} z^4 + 6.96 \times 10^{12} z^5$
	L5	$53.4 + 7.8 \times 10^3 z - 5.99 \times 10^6 z^2 + 1.27 \times 10^9 z^3 - 1.28 \times 10^{11} z^4 + 5 \times 10^{12} z^5$
	L6	$66.3 + 5.24 \times 10^3 z - 4.74 \times 10^6 z^2 + 8.97 \times 10^8 z^3 - 8.12 \times 10^{10} z^4 + 3 \times 10^{12} z^5$
	L7	$72.7 + 1.18 \times 10^4 z - 8.37 \times 10^6 z^2 + 1.71 \times 10^9 z^3 - 1.68 \times 10^{11} z^4 + 6.57 \times 10^{12} z^5$
	L8	$86.2 + 8.46 \times 10^3 z - 6.78 \times 10^6 z^2 + 1.24 \times 10^9 z^3 - 1.05 \times 10^{11} z^4 + 3.54 \times 10^{12} z^5$

	L9	$83.2 + 2.19 \times 10^4 z - 1.33 \times 10^7 z^2 + 2.63 \times 10^9 z^3 - 2.48 \times 10^{11} z^4 + 9.16 \times 10^{12} z^5$
Magnetic squeeze	Si	$253.9 - 6.88 \times 10^4 z + 9.21 \times 10^6 z^2 - 6.92 \times 10^8 z^3 + 2.77 \times 10^{10} z^4 - 4.57 \times 10^{11} z^5$

According to the manufacturer (Ferrotec, USA), the density ρ , volume fraction ϕ , and mean diameter of particle d of the EMG 507 ferrofluid used in the experiments are 1.12 g/cm^3 , 1.8% , and 10 nm , respectively. The surface tension ($\sigma = 34.8 \pm 0.5 \text{ mN/m}$) of the ferrofluid was measured using a “First Ten Angstroms (FTA) 200” system. Since copper has a relatively high thermal conductivity, commercially available copper (99.9% purity, 1 mm thickness) plates are used and are cut into small pieces with their dimensions of $2 \text{ cm} \times 2 \text{ cm}$ as the substrates. The substrates are cleaned in an ultrasonic bath with acetone and ethanol, respectively, and followed by a rinse with deionised water. The substrates are coated with a trichloro (1H, 1H, 2H, 2H-perfluorooctyl) silane monolayer (Sigma Aldrich), and the contact angle of the surface is $90.5 \pm 0.5^\circ$. Prior to the experiment, each substrate is dried on a hotplate and then a ferrofluid droplet is deposited on the substrate surface. All experiments are conducted in a small, air-conditioned room with its temperature and relative humidity maintained at $23 \pm 1.5^\circ \text{C}$ and $45 \pm 5\%$, respectively.

5.3. Freezing behaviour of nanofluid droplets under magnetic fields

5.3.1. Profiles of a ferrofluid droplet under magnetic field effects

In the experiments, the diameter of the magnets is more than 10 times larger than that of ferrofluid droplets. Based on the previous studies that used the similar geometric sizes of magnets and ferrofluid droplets [263, 267], the magnetic field strength can be considered to be uniform in the horizontal plane, and it only varies along the z direction. The presence of the magnetic field

generates an attractive force on the ferrofluid droplet, and the magnetic force per unit volume is given by [267-269]

$$F_m = \mu_0 \phi M_p L(\psi) \frac{dH}{dz} \quad (5-1)$$

where μ_0 is the magnetic permeability in vacuum, ϕ is the volumetric fraction, M_p is the saturation magnetisation of magnetite, H is the strength of the magnetic field. For calculations, the gradient of magnetic field strength is determined by using a 5th order polynomial curve to fit the measured magnetic field strength as a function of the distance from the magnet in the z direction. The detailed information of the magnetic field strength is shown in Figure 5-2 and Table 5-1.

In Eq. (5-1) $L(\psi)$ is the Langevin function, and the complete form of $L(\psi)$ is expressed as

$$L(\psi) = \coth \psi - \frac{1}{\psi} \quad (5-2)$$

where $\psi = \frac{\pi}{6k} \mu_0 M_p H d^3 \frac{1}{T}$, k is the Boltzmann constant, T is the temperature of the ferrofluid, and d is the mean diameter of Fe_3O_4 particles.

Because the response time of magnetisation is much shorter than the freezing time in this work, the ferrofluid droplet profile under the magnetic field can be determined by using the modified Young-Laplace equation with the inclusion of an additional magnetic force, but without consideration of the freezing phase change effect. Figure 5-3 shows the coordinate system used for the analysis of the ferrofluid droplet. At the droplet's apex ($z = 0$), the Young-Laplace equation is written as [270]

$$P_{l,0} - P_{atm} = \sigma \frac{2}{b} \quad (5-3)$$

where $P_{l,0}$ is the pressure inside the droplet at $z = 0$, P_{atm} is atmospheric pressure, b is the radius of curvature at the droplet's apex, and s is the surface tension.

Figure 5-3 Schematic of a sessile ferrofluid droplet on a copper substrate with the coordinate system

The pressure difference at an arbitrary height z across the droplet surface is described by the Young-Laplace equation as [270]

$$P_{l,z} - P_{atm} = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (5-4)$$

where $P_{l,z}$ is the pressure inside the droplet at z , R_1 and R_2 respectively are the first and second principal radii of the droplet at z , with their expression given by

$$\frac{1}{R_1} = \frac{d\alpha}{ds} \quad (5-5)$$

$$\frac{1}{R_2} = \frac{\sin \alpha(s)}{x(s)} \quad (6)$$

where α is the tangential angle at z , s is the arc length at z .

The pressure inside the droplet with consideration of magnetic and gravity forces is given by

$$P_{l,z} = P_{l,0} + \rho_l g z \pm \int_0^z F_M(z') dz' \quad (5-7)$$

Substituting Eqs. (5-5) – Eq. (5-7) into Eq. (5-4) yields

$$P_{l,0} + \rho_l g z \pm \int_0^z F_M(z') dz' - P_{atm} = \sigma \left(\frac{d\alpha}{ds} + \frac{\sin \alpha(s)}{x(s)} \right) \quad (5-8)$$

Combining Eq. (5-3) and Eq. (5-8) yields the modified Young-Laplace equation at z

$$\rho_l g z + \int_0^z F_M(z') dz' + \sigma \frac{2}{b} = \sigma \left(\frac{d\alpha}{ds} + \frac{\sin \alpha(s)}{x(s)} \right) \quad (5-9)$$

Noting that

$$\frac{dx}{ds} = \cos \alpha \quad (5-10)$$

$$\frac{dz}{ds} = \sin \alpha \quad (5-11)$$

The 4th order Runge-Kutta method is used to solve Eq. (5-9) – Eq. (5-11) such that the droplet profiles under different magnetic field conditions can be obtained. The boundary and constrained conditions used for solving differential equations are the contact angle (θ) of the ferrofluid and the droplet volume (4.5 μ l). The contact angles of ferrofluids under magnetic field is shown in Figure 5-4. In the calculations, an initial value of b is given at first, and then

used to calculate $P_{l,0}$. Afterwards, the value of α gradually increases until it reaches the given contact angle such that the droplet profile can be obtained. Through several iterations, the values of b and $P_{l,0}$ as well as the height and base diameter of the droplet can be finally determined once the calculated droplet volume matches its given value ($4.5 \mu\text{l}$).

Figure 5-4 Variations of the measured contact angle with the strength of the magnetic field

Figures 5-5 (a) and 5-5 (b) respectively shows the calculated droplet profiles under the magnetic lift and squeeze conditions. Because of the attractive magnetic force exerting on the ferrofluid droplet, the magnetic lift /squeeze condition is created when placing the magnet above/below the droplet. With the increase of the magnetic field strength, for the selected magnetic lift cases (The magnitude of field strength: $B_0 = 0 < L_2 < L_5 < L_7 < L_9$), the droplet becomes more elongated (Figure 5-5 (a)) due to the upward magnetic force; while for the selected magnetic squeeze cases (The magnitude of field strength: $B_0 = 0 < S_1 < S_2 < S_5 < S_7$), the droplet shows a more flattened feature (Figure 5-5 (b)) due to the downward magnetic force. The normalised height of droplet is defined as the ratio of the droplet height under the magnetic field (h_{Li} or h_{Si}) to that in the absence of a magnetic field (h_{B0}). Figures 5-5 (c) and 5-5 (d) respectively shows the comparisons of the normalised height of droplet between the experiments and the calculations versus the magnetic field strength for the magnetic lift and

squeeze conditions, and reasonable agreements can be seen. It is found that when increasing the magnitude of magnetic field strength, the normalised height of droplet monotonically increases for the magnetic lift case (h_{Li}/h_{B0} , Figure 5-5 (c)) and decreases for the magnetic squeeze case (h_{Si}/h_{B0} , Figure 5-5 (d))

Figure 5-5 Calculated shapes of a ferrofluid droplet under various (a) magnetic lift conditions (Li) and (b) magnetic squeeze conditions (Si). Comparisons of the experimental and calculated results for the normalised height versus magnetic field strength under (c) magnetic lift conditions and (d) magnetic squeeze conditions.

Of note, the differences between the calculations and the experiments becomes larger under high magnetic field; this happens for both the magnetic lift and squeeze conditions. Such discrepancies could be attributed to two issues. First, the actual magnetic field strength inside the droplet would be different from that used in the calculations. It is known that the magnetisation of the ferrofluid droplet can alter the original local magnetic field strength [261]. However, because of the difficulty in measuring the magnetic field strengths inside and near the ferrofluid droplet, the measurements were conducted in the absence of the ferrofluid droplet.

The difference between the actual magnetic field and the measured magnetic field (used in the calculations) becomes more significant at the high magnetic field. Second, the possible variation of the surface tension of ferrofluid droplet with the strength of the magnetic field is neglected [271, 272]. In this work, the surface tension of ferrofluid is measured without inclusion of the magnetic field, because it is difficult to measure the surface tension under the magnetic lift and squeeze conditions. In the calculations, the fixed value of 34.8 mN/m is used based on the measured surface tension which certainly would change when increasing the magnetic field. Therefore, these two issues lead to higher calculated dimensionless heights of droplets under magnetic lift conditions and lower calculated dimensionless heights of droplets under magnetic squeeze conditions under the high magnetic field.

To analyse the relationship between the normalised height (h_{Li}/h_{B0}) and the magnetic field strength (H), a scaling analysis was performed under both magnetic lift and squeeze conditions based on the following assumptions: (1) The effect of gravity on the deformation of a droplet is not considered due to the small volume of the ferrofluid droplet. (2) The variation of $L(\Psi)$ inside the droplet is neglected. (3) The profile of ferrofluid droplet is assumed to be a prolate spheroid shape under magnetic lift conditions. (4) The profile of ferrofluid droplet is assumed to be an oblate spheroid shape under magnetic squeeze conditions. The schematics of the morphologies of a ferrofluid droplet under magnetic lift and squeeze conditions are shown in Figure 5-6.

Figure 5-6 The schematics of the droplet morphologies under (a) magnetic lift and (b) squeeze conditions

Based on the above assumptions, Eq. (5-9) can be rewritten as

$$\sigma\kappa_B - \sigma\kappa_A = \mu_0\phi M_p L(\Psi)(H_m(B) - H_m(A)), \quad (5-12)$$

where $\kappa_A = \frac{1}{a} + \frac{a}{b^2}$ is the curvature at A, and $\kappa_B = 2\frac{b}{a^2}$ is the curvature at B.

Equation (5-12) can be rewritten as

$$\left(2\frac{b}{a^2} - \frac{1}{a} - \frac{a}{b^2}\right) = \frac{\mu_0\phi M_p L(\Psi)[H_m(A) - H_m(B)]}{\sigma} \quad (5-13)$$

Since the volume of a ferrofluid droplet is conserved, it can be rewritten as

$$\frac{2}{3}R_0^3\pi = \frac{2}{3}a^2b\pi, \quad (5-14)$$

where R_0 is the radius of a ferrofluid droplet in the absence of a magnetic field. Substituting

Eq. (5-14) into Eq. (5-13) results in

$$2\left(\frac{b}{R_0}\right)^2 - \sqrt{\frac{b}{R_0}} - \left(\frac{b}{R_0}\right)^{-2.5} = \frac{R_0\mu_0\phi M_p L(\Psi)[H_m(A) - H_m(B)]}{\sigma} \quad (5-15)$$

Under the current experimental condition, the contact angle of the ferrofluid droplet in the absence of a magnetic field is $90.5 \pm 0.5^\circ$, with $R_0 \approx h_{B0}$. In the case of magnetic lift conditions, $b = h_{Li}$. Thus, $b/R_0 \approx h_{Li}/h_0$

Therefore, the relation between b/R_0 and the magnetic field strength at the bottom of the droplet can be expressed as

$$H_m(A) \approx H_m(B) - \frac{\sigma}{R_0 \mu_0 \phi M_p L(\Psi)} \left[2 \left(\frac{h_{Li}}{h_{B0}} \right)^2 - \sqrt{\frac{h_{Li}}{h_{B0}}} - \left(\frac{h_{Li}}{h_{B0}} \right)^{-2.5} \right] \quad (5-16)$$

In the case of high magnetic field strength under magnetic lift conditions, the shape of the ferrofluid droplet cannot be considered to be a prolate spheroid. The curvature at the apex of the droplet can still be calculated with $\kappa_B = 2 \frac{b}{a^2}$. However, the curvature at the baseline of the droplet cannot be calculated directly. The value of this curvature κ_A is given as $\kappa_A = \frac{1}{R_0} (2 - \omega Bo_m)$ [51].

Substituting the values of κ_A and κ_B into Eq. (5-12), the relation between b/R_0 and $H_m(A)$ under high magnetic strength conditions can be expressed as

$$H_m(A) \approx H_m(B) - \frac{\sigma}{R_0 \mu_0 \phi M_p L(\Psi)} \left[\left(\frac{h_{Li}}{h_{B0}} \right)^2 - 1 \right] \frac{2}{1 - \omega} \quad (5-17)$$

Equations (5-16) and (5-17) provide the analytical models needed to describe the normalised height of a liquid ferrofluid droplet under magnetic lift conditions. These models ($\omega = 0.5$) are in good agreement with the experimental data presented in Figure 5-5 (c).

When the magnet is placed below the ferrofluid droplet, a flattened droplet can be observed in Figure 5-5 (b). Analogous to the derivation of Eq. (5-16), the relationship between Bo_m and b/R_0 under magnetic squeeze cases can be expressed as

$$\frac{\mu_0 \phi M_p L(\Psi) [H_m(A) - H_m(B)]}{\sigma} = \sqrt{\frac{b}{R_0}} + \left(\frac{b}{R_0}\right)^{-2.5} - 2 \left(\frac{b}{R_0}\right)^2 \quad (5-18)$$

In the case of magnetic squeeze, $R_0 \approx h_{B0}$, and $b = h_{Si}$. Eq. (5-19) can be rewritten as

$$H_m(A) \approx H_m(B) + \frac{\sigma}{R_0 \mu_0 \phi M_p L(\Psi)} \left[\sqrt{\frac{h_{Si}}{h_{B0}}} + \left(\frac{h_{Si}}{h_{B0}}\right)^{-2.5} - 2 \left(\frac{h_{Si}}{h_{B0}}\right)^2 \right] \quad (5-19)$$

With an increase in magnetic strength under magnetic squeeze conditions, the shape of ferrofluid droplet becomes a pancake, while the assumption of an oblate spheroid shape becomes inapplicable. Therefore, Eq. (5-19) cannot be used in these cases.

Based on Hodges et al.'s model, the force balance in the droplet can be written as [273]

$$P_d - Bo_m z = \kappa_r + \kappa_\theta, \quad (5-20)$$

where P_d is the dimensionless internal pressure, $\kappa_r = \frac{-z_{rr}}{(1+z_r^2)^{3/2}}$ and $\kappa_\theta = \frac{1}{r} \frac{-z_r}{(1+z_r^2)^{1/2}}$. Bo_m is the magnetic Bond number. The variation in Bo_m inside the droplet is not considered in the following analysis. Thus, the value of Bo_m can be given by $Bo_m = R_0 \mu_0 \phi M_p L(\Psi) [H_m(A) - H_m(B)] / \sigma$. The value of κ_θ can be neglected on the side of the pancake droplet. Integrating both sides of Eq. (5-20) with respect to z yields

$$P_d z - \frac{1}{2} Bo_m z^2 = (1 + z_x^2)^{-0.5} - (1 + z_x^2)^{-0.5} \Big|_{z=0}, \quad (5-21)$$

where $z = 0$ represents the location of the droplet baseline.

Under the current experimental conditions, the value of $(1 + z_x^2)^{-0.5} \Big|_{z=0} \rightarrow 0$ due to the contact angle of the droplet under magnetic squeeze conditions being almost equal to 90° .

Equation (5-21) can be rewritten as

$$P_d z - \frac{1}{2} Bo_m z^2 = (1 + z_x^2)^{-0.5} \quad (5-22)$$

At the apex of the droplet, $z_x = 0$; thus, Eq. (5-22) can be given as

$$P_d \frac{h_{Si}}{R_0} - \frac{1}{2} Bo_m \left(\frac{h_{Si}}{R_0} \right)^2 = 0 \quad (5-22)$$

When the high magnetic field strength is high, the flattened shape at the apex also results in $\kappa_r \rightarrow 0$. Equation (5-20) can be rewritten as

$$P_d - Bo_m \frac{h_{Si}}{R_0} = 0 \quad (5-24)$$

Combining Eq. (5-23) and Eq. (5-24) yields

$$\frac{h_{Si}}{h_{B0}} \approx \frac{h_{Si}}{R_0} = \sqrt{2} Bo_m^{-0.5} \quad (5-25)$$

Therefore, the relationship between $\frac{h_{Si}}{h_{B0}}$ and $H_m(A)$ under the magnetic squeeze condition in the high magnetic strength region can be given as

$$H_m(A) \approx H_m(B) + \frac{2\sigma}{R_0 \mu_0 \phi M_p L(\Psi)} \left(\frac{h_{Si}}{h_{B0}} \right)^{-2} \quad (5-26)$$

Equations (5-19) and (5-26) can well predict the variation in the normalised height with the magnetic field strength under magnetic squeeze conditions in Figure 5-5 (d).

5.3.2. Freezing of a ferrofluid droplet under magnetic field effects

Figures 5-7 (a) – 5-7 (d) are the snapshot images showing the shapes of freezing ferrofluid droplets for different magnetic field strengths under the magnetic lift ($L2 < L4 < L6 < L8$) and squeeze ($S1 < S2 < S5 < S7$) conditions. Specifically, the dynamic shapes of droplets at two

time moments (1/6 and 5/6), normalised with respect to the entire freezing time under applied magnetic fields, are presented. Noticeably, a comparison of the snapshot images between two different times under the same magnetic field shows the occurrence of the volume expansion due to the smaller ice density. With the progress of time, the volume expansion results in larger droplet heights under all applied magnetic field conditions. Meanwhile, compared to the magnetic squeeze cases, a stronger enhancement in the droplet height during the freezing process can be observed in the magnetic lift cases. Because the magnet is placed above the droplet in the magnetic lift cases, and the attractive force becomes larger when the apex of the droplet is closer to the magnet during the freezing process due to the expansion in the vertical direction. Additionally, it is noted that different from the frozen pure water sessile droplets that exhibit pointy with a sharp tip [38, 40, 41, 65, 75, 76, 274, 275], in the experiments, however, the tip angle was not noticeably observed. Based on the understanding, the unobserved tip angle is attributed to the following reasons: Firstly, it is due to the presence of Fe_3O_4 particles. The open literature studies amply showed that the presence of impurities in water, such as carbon nanotubes, NaCl, and tetradecyltrimethylammonium bromide, can alter the final shape of frozen droplets as well as the value of tip angles, even leading to the disappearing freezing singularity [42, 44, 113]. Secondly, the volume expansion caused by the density difference between ice and water is believed to be a major factor for the tip angle formation [38, 40, 41, 65, 75, 76, 274, 275]. For the pure water droplet case, the angle of the pointy tip is about 130° when the density ratio of ice to water is 0.917 [44]. In this study, the density ratio of ice to the liquid of ferrofluid increases to 0.948. The theoretical value of the tip angle under this condition would be estimated as 145° , if adopting the analytical model derived in the pure water case [41, 76]. The increase of the tip angle also makes the tip singularity not be noticeably observed. Thirdly, when an external magnetic field is imposed, the interaction between the magnetic field and the Fe_3O_4 particles can cause the redistribution of particles; this in turn will alter the local

surface tension and thus affect the tip angle. As the formation of a tip angle for the frozen droplets is a complicated phenomenon, further research is needed to understand why the tip angle was not noticeably formed under these experimental conditions.

Figure 5-7 Snapshot images showing the shapes of freezing ferrofluid droplets for different magnetic field conditions. (a) - (b) at two dimensionless time moments ($t^* = 1/6$ and $5/6$) in the freezing process under magnetic lift conditions. (c) - (d) at two dimensionless time moments ($t^* = 1/6$ and $5/6$) in the freezing process under magnetic squeeze conditions. The dimensionless time t^* is defined as the ratio of a specific time to the entire freezing time of a ferrofluid droplet under the same magnetic field.

After digitising the snapshot images, the quantitative results in terms of the expansion ratio in the vertical direction is obtained, which can be defined as the frozen droplet height (h_{f-Li} or h_{f-Si}) divided by the initial liquid droplet height (h_{Li} or h_{Si}) under the same applied magnetic field. Then the plots of such vertical expansion ratio versus the magnitude of magnetic field strength under the magnetic lift and squeeze conditions are depicted in Figures 5-8 (a) and 5-8 (b), respectively. In addition, the dependence of the dimensionless freezing height, defined as the ratio of the frozen

droplet height under an applied magnetic field (h_{f-Li} or h_{f-Si}) to that in the absence of a magnetic field (h_{f-B0}), on the magnitude of magnetic field strength is also presented in Figure 5-8 (a) and 5-8 (b).

Figure 5-8 The dimensionless freezing height and the vertical expansion ratio versus the magnetic field strength under (a) magnetic lift conditions and (b) magnetic squeeze conditions. The dimensionless freezing height is the ratio of the frozen droplet height under an applied magnetic field (h_{f-Li} or h_{f-Si}) to that in the absence of a magnetic field (h_{f-B0}), and the vertical expansion ratio is defined as the frozen droplet height divided by the initial liquid droplet height under the same applied magnetic fields.

For the magnetic lift cases, the expansion ratio is resulted mainly from two effects: 1) the density difference between ice and water, and 2) the interaction between the magnetic field and the ferrofluid; both effects are favourable with the vertical expansion of freezing droplet. Specifically, the second effect is associated with the enhanced magnetic force due to the redistribution of Fe_3O_4 particles and the elongated ferrofluid droplet. Under the magnetic lift conditions, the magnetic force pulls Fe_3O_4 particles to be accumulated in the upper region of the droplet [276]. Such particle accumulation increases the concentration of particles, which according to Eq. (5-1), in turn leads to a stronger magnetic force and hence the more elongated droplet. Therefore, with increasing the magnetic field, much higher expansion ratio and larger dimensionless freezing height during the freezing process can be observed, especially in the relatively higher magnetic field region. For the magnetic squeeze case, the expansion ratio is resulted mainly from the density difference between ice and water and this can be justified by

a nearly constant value of about 1.1 for the expansion ratio shown in Figure 5-8 (b) (note: the theoretical value for the density ratio of water to ice is 1.09). As the magnet is placed underneath the substrate, the magnetic force is in the downward direction, causing the droplet squeeze which is against the vertical expansion. Consequently, the expansion ratio essentially exhibits no noticeable dependence on the magnetic field strength.

The variation of the dimensionless freezing time with the magnetic field strength is depicted in Figures 5-9 (a) and 5-9 (b) for the magnetic lift and squeeze conditions respectively. The dimensionless freezing time is defined as the entire freezing time under a magnetic field (t_{Li} or t_{Si}) divided by that in the absence of a magnetic field (t_{B0}). Clearly, the freezing time is extended for the magnetic lift situation and shortened for the magnetic squeeze situation. Notably, the inclusion of Figures 5-9 (a) and 5-9 (b) also contain the square ratio of the frozen droplet height that is shown as the right-hand side of the vertical coordinate.

Figure 5-9 Variations of the ferrofluid droplet freezing time and the square ratio of the frozen droplet height with applied magnetic fields under (a) magnetic lift conditions and (b) magnetic squeeze conditions. The dimensionless freezing time is defined as the entire freezing time under a magnetic field (t_{Li} or t_{Si}) divided by that in the absence of a magnetic field (t_{B0}).

Interestingly, the freezing time and the square ratio of the frozen droplet height exhibit nearly the same trend of the magnetic field dependence in both Figures 5-9 (a) and 5-9 (b). To interpret this trend, a scaling model is used and the following assumptions are made [36, 72, 73]: (1) Negligible convection heat transfer in the liquid region. (2) One-dimensional heat conduction in

the solid. (3) The quasi-steady approximation for the heat conduction. (4) The constant temperatures at the freezing interface as T_f and at the bottom substrate surface as T_{subs} . Then, the energy-balance equation at the solid-liquid interface can be written as [277]

$$q_{ice|z} - q_{w|z} = -\rho_{ice} L v_{inter|z}, \quad (5-27)$$

where L is the latent heat of fusion per unit mass, $q_{ice|z}$ is the interfacial heat flux in the solid ice side, $q_{w|z}$ is the interfacial heat flux on the liquid fluid side, and $v_{inter|z}$ is the velocity of the interface in the z direction. Using assumption 1, $q_{w|z} = 0$ can be derived. $q_{ice|z}$ can be obtained using the Fourier's law for the one-dimensional case as $q_{ice|z} = -k_{ice} \frac{dT}{dz}$ with k_{ice} being the thermal conductivity of ice. Making use of assumptions 3 and 4,

$$q_{ice|z} = -k_{ice} \frac{T_f - T_{subs}}{h}$$

The interfacial velocity can be expressed as

$$v_{inter|z} = \frac{dh}{dt}, \quad (5-28)$$

where h is the height of the freezing front at time t . Then, Eq. (5-28) becomes

$$k_{ice} \frac{T_f - T_{subs}}{h} = \rho_{ice} L \frac{dh}{dt} \quad (5-29)$$

Substituting constant freezing and substrate temperatures into Eq. (5-29), and then integrating both sides of the equation, it yields:

$$h = \sqrt{2t \frac{k_{ice} (T_f - T_{subs})}{\rho_{ice} L}} \quad (5-30)$$

When the freezing process completes, the height of the freezing front is the height of the frozen droplet ($t_{f-Li(B0, Si)}$) and the time is the total freezing time ($t_{f-Li(B0, Si)}$). Eq. (5-30) can be rewritten as

$$t_{f-Li(B0, Si)} = h_{f-Li(B0, Si)}^2 \frac{\rho_{ice} L}{2(T_f - T_{subs})k_{ice}} \quad (5-31)$$

Given the same ρ_{ice} , L , T_f , T_{subs} , and k_{ice} under the experimental conditions, the following relationships for the magnetic lift and squeeze conditions can be obtained, respectively as.

$$\frac{t_{Li}}{t_{B0}} = \frac{h_{f-Li}^2}{h_{f-B0}^2} \text{ and } \frac{t_{Si}}{t_{B0}} = \frac{h_{f-Si}^2}{h_{f-B0}^2} \quad (5-32)$$

As can be seen in Figure 5-9 (b), the experimental measuring square ratio of the height of the frozen droplet is in good agreement with the ratio of the total freezing time in both magnetic lift and squeeze conditions. The reason for the experimental observation shown in Figures 5-9 (a) and 5-9 (b) can be explained using Eq. (5-32).

Clearly, Eq. (5-32) can correlate two sets of the experimental data depicted in Figure 5-9 (a) and Figure 5-9 (b): one is the dimensionless freezing time denoted by empty symbols on the left-hand side of the vertical coordinate, and the other is the square ratio of frozen droplet height denoted by solid symbols on the right-hand side of the vertical coordinate. The trends of these two sets of data can be well described by Eq. (5-32).

5.4. Summary

The freezing processes of ferrofluid droplets on cold substrates has been studied in this chapter. The results show that the shape of a ferrofluid droplet can be elongated or squeezed and its freezing time extended or shortened under magnetic lift and squeeze conditions, respectively.

The initial ferrofluid droplet profiles can be described via a modified Young-Laplace equation with consideration for the magnetic force but without consideration for the freezing phase change effect. The calculated shapes of liquid ferrofluid droplets are in good agreement with the experimental observations under both magnetic lift and squeeze conditions. Analytical models were proposed to describe the relationship between the height of a liquid ferrofluid droplet and the magnetic field strength.

Under the magnetic lift conditions with applied magnetic field strengths varying from about 10 to 55 kA/m, the frozen droplet height was found to increase from approximately 1.08 times to 1.6 times the frozen droplet height in the absence of a magnetic field, leading to increases in the freezing time of up to 2.4 times longer. Under the magnetic squeeze conditions with applied magnetic field strengths varying from about 20 to 135 kA/m, the frozen droplet height was found to decrease from around 95% to 55% of the frozen droplet height in the absence of a magnetic field, leading to the freezing time becoming at most 0.3 times shorter. Moreover, it was also found that the expansion ratio, defined as the ratio of the frozen droplet height to the initial liquid droplet height under the same applied magnetic field, increases with increasing magnetic field strength under the magnetic lift conditions but is independent of the magnetic field strength under the magnetic squeeze conditions. Finally, a scaling analysis was presented to explain the experimentally obtained dependencies of both the dimensionless freezing time and the square of the frozen droplet height upon the magnetic field strength.

This study advances the understanding of the freezing process of a nanofluid droplet under magnetic field conditions. The outcome of this study can pave the way for the development of active methods for controlling the shape of, and time to, freezing droplets through externally applied external fields. It may also shed light on the development of new technologies for the fabrication of micro-sized elements using nanofluids with external magnetic fields.

Chapter 6: Numerical study of the freezing process of nanofluid droplets under magnetic fields

A series of experiments have been conducted to study the freezing process of a ferrofluid droplet under different magnetic field conditions. However, detailed information, such as the temperature distribution inside the ferrofluid droplet, was not provided by the experimental studies described in Chapter 5. In this chapter, a numerical investigation of the freezing process of a ferrofluid droplet is performed based on LBM, and some analytical models are derived to explain the propagation of the freezing front in a ferrofluid droplet.

6.1. Introduction

The experimental results in Chapter 5 have shown that the morphology of a ferrofluid droplet and its freezing process can be actively manipulated by changing the magnitude and direction of an external magnetic field. The volumetric expansion of, and the magnetic force exerted on, a ferrofluid droplet are two important factors that affect its shape change feature. In the case of a pure water droplet, the density ratio between solid ice and liquid water results in a specific value of the volume expansion (0.917). The height of the droplet is observed to increase during the freezing process, and a pointy tip is formed at the completion of freezing. Many studies have shown the universality of this tip [38, 40]. However, very few studies have considered the effect of the droplet height on the freezing time. A new theoretical model was developed by Zhang et al. to analyse the effect of volumetric expansion on the final shape of a frozen water droplet [278]. They calculated the droplet freezing time based on a fixed droplet morphology while neglecting the evolution of a dynamic droplet morphology. Recently, a front-tracking method was proposed by Vu et al. to predict the freezing behaviour of a water droplet [274]. These authors did consider the dynamic morphology evolution due to volumetric expansion. However, two prescribed parameters (contact angle and tri-junction growth angle) are required

to close their model. In this chapter, an improved LB model is adopted to simulate the freezing process of a ferrofluid droplet directly that takes volumetric expansion into account.

The experimental results in Chapter 5 indicate that the deformation of a ferrofluid droplet under a magnetic field is the result of the magnetic force, the surface tension, and gravity. It is very important to understand how the ferrofluid droplet responds to the external magnetic field in the analysis of its freezing behaviours. However, using an experimental method limits the amount of information that can be provided. On the other hand, numerical methods can produce more details concerning the evolution of droplet morphology during the freezing process under magnetic field conditions. In this chapter, a numerical analysis is performed to investigate the variation in droplet morphology in response to a magnetic field.

A simple scaling model with $t \sim h^2$ is adopted to analyse the variation in droplet freezing time under magnetic field conditions. Here, h represents the height of the freezing front and t represents the freezing time. This scaling method is also widely applied to analyse the propagation of the freezing front [49, 73, 74]. The derivation of this model is based on the flat freezing front assumption. However, the shape of the freezing front is concave in a real droplet [36, 40, 87]. A recent study also proved that the acceleration of the freezing front near the final stage of freezing cannot be predicted correctly using this scaling method. Therefore, a more comprehensive analysis is needed regarding the propagation of the freezing front near the completion of freezing.

In this numerical study, a new multiphase flow LB model is developed with consideration for the magnetic and volume expansion effects to simulate the freezing process of a ferrofluid droplet under magnetic lift and squeeze conditions. In addition, analytical and scaling analyses are performed to explain the freezing behaviour of ferrofluid droplets.

6.2. Theory and mathematical model

In this section, the multiphase flow and the heat transfer models used in the current study to describe the deformation and freezing processes of a ferrofluid droplet will be introduced.

6.2.1. Multiphase flow lattice Boltzmann model

A D2Q9 multiphase flow LB model is adopted to simulate the fluid flow. The evolution equation of the density distribution function can be written as [279]

$$f_i(\mathbf{x} + \mathbf{c}_i \Delta t, t + \Delta t) - f_i(\mathbf{x}, t) = -\frac{1}{\tau_f} [f_i(\mathbf{x}, t) - f_i^{eq}(\mathbf{x}, t)] + \Delta t F_i + \Delta t \omega_i S_\rho, \quad (6-1)$$

where x denotes the position, t is time, f_i is the density distribution function along the i direction, and f^{eq} is the equilibrium distribution function given by

$$f_i^{eq} = \omega_i \rho \left[1 + \frac{3}{c^2} (\mathbf{c}_i \cdot \mathbf{u}) + \frac{9}{2c^4} (\mathbf{c}_i \cdot \mathbf{u})^2 - \frac{3}{2c^2} u^2 \right], \quad (6-2)$$

where ω_i is the weight coefficient for a different direction, $\omega_0 = 4/9$, $\omega_1 = \omega_2 = \omega_3 = \omega_4 = 1/9$, $\omega_5 = \omega_6 \dots = \omega_8 = 1/36$, and c_i is the discrete velocity in the i direction

$$\mathbf{c}_i = \begin{cases} (0,0)c & i = 0 \\ (\pm 1, 0)c, (0, \pm 1)c, & i = 1, \dots, 4, \\ (\pm 1, \pm 1)c & i = 5, \dots, 8 \end{cases} \quad (6-3)$$

where $c = \Delta x / \Delta t$, Δx and Δt are the space step and time step, respectively.

The kinematic viscosity can be given by

$$\nu = \frac{1}{3} (\tau_f - 0.5) \frac{\Delta x^2}{\Delta t}, \quad (6-4)$$

where τ_f is the relaxation time.

The macroscopic density and velocity can be defined as follows

$$\rho = \sum_i f_i \quad (6-5)$$

$$\rho \mathbf{u} = \sum_i f_i \mathbf{e}_i + \frac{\Delta t}{2} \mathbf{F}, \quad (6-6)$$

where $\mathbf{F} = (F_x, F_y)$ denotes the total force exerted on the fluid particle, which includes the fluid-fluid molecular interaction force ($\mathbf{F}_f$), fluid-solid interaction force ($\mathbf{F}_s$), and other body force ($\mathbf{F}_b$) encompassing, among others, the magnetic force $\mathbf{F}_m$ and gravity $\mathbf{F}_g$.

The expression for $\mathbf{F}_f$ can be given by Fang et al.'s model [280]

$$\mathbf{F}_f = -G\psi(\mathbf{x}) \sum_i w(|\mathbf{e}_i|^2) \psi(\mathbf{x} + \mathbf{e}_i) \mathbf{e}_i, \quad (6-7)$$

where G is the interaction strength, $w(|\mathbf{e}_i|^2)$ represents the weight function, and ψ is the pseudopotential function, which can be defined as

$$\psi(\mathbf{x}) = \sqrt{2(p_{\text{EOS}} - \rho c_s^2) / Gc^2}, \quad (6-8)$$

where P_{EOS} is the non-ideal equation of state. In this study, the Peng-Robinson equation of state is adopted, that is

$$p_{\text{EOS}} = \frac{\rho RT}{1 - b\rho} - \frac{a\phi(T)}{1 + 2b\rho - b^2\rho^2} \quad (6-9)$$

$$\phi(T) = \left[1 + \left(0.37464 + 1.54226\omega - 0.26992\omega^2 \right) \left(1 - \sqrt{T/T_c} \right) \right]^2,$$

where $a = 0.45724R^2T_c^2 / p_c$, and $b = 0.0778RT_c / p_c$. Here, the saturation temperature is set to $T_s = 0.85 T_c$, the gas constant is set to $R = 1$, and the acentric factor $\omega = 0.344$.

The fluid-solid interaction force can be obtained via Fang et al.'s model [280]

$$\mathbf{F}_s = -G_w \psi(\mathbf{x}) \sum_i w(|\mathbf{e}_i|^2) \psi(\mathbf{x}) s(\mathbf{x} + \mathbf{e}_i) \mathbf{e}_i, \quad (6-10)$$

where s is the indicator function which is equal to 0 for fluids and 1 for solids, and G_w can be used to change the surface wettability.

In Eq. (6-1), the force term F_i can be given by Guo et al.'s model [281]

$$F_i = \omega_i \left(1 - \frac{1}{2\tau_f} \right) \left(\frac{\mathbf{c}_i - \mathbf{u}'}{c_s^2} + \frac{\mathbf{c}_i \cdot \mathbf{u}'}{c_s^4} \mathbf{c}_i \right) \cdot \mathbf{F}, \quad (6-11)$$

where $\mathbf{u}' = \mathbf{u} + \varepsilon \mathbf{F} / (\nu \psi)$ is the modified velocity, and ε is set to be 0.105 in this simulation.

The magnetic force is given by [268, 282]

$$\mathbf{F}_m = \mu_0 M \nabla H_m \quad (6-12)$$

$$M = \varphi M_p L(\xi) \quad (6-13)$$

$$L(\xi) = \coth \xi - \frac{1}{\xi} \quad (6-14)$$

$$\xi = \frac{\pi}{6k_0} \mu_0 M_p H_m d^3 \frac{1}{T}, \quad (6-15)$$

where μ_0 is the magnetic permeability in a vacuum, ∇H_m is the gradient of the magnetic field strength, φ is the concentration of the Fe_3O_4 particles, M_p is the saturation magnetisation of

magnetite, k_0 is the Boltzmann constant, T is the temperature of the ferrofluid, and d is the mean diameter of the Fe_3O_4 particles.

The gravitational force can be obtained with

$$\mathbf{F}_g = \rho \mathbf{g} \quad (6-16)$$

A source term is added in Eq. (6-1) to take the volume expansion into consideration

$$S_\rho = \frac{\partial \varphi_s}{\partial t} \rho (1 - v), \quad (6-17)$$

where φ_s represents the volume fraction of the solid ice phase, and v is the density ratio between ice and liquid, which is given as $v = \rho_s / \rho_l$. Physically, the source term should be added to the nodes where the solid-liquid phase change occurs (freezing front). However, the incremental mass at these local nodes cannot propagate immediately towards other liquid nodes since they will be frozen soon. To the conservation of mass for the entire domain, the source term is evenly divided into those nodes occupied by the water phase.

6.2.2. Phase change lattice Boltzmann model

Analogous to the multiphase flow model, the evolution equation for the temperature distribution function can be expressed as

$$g_i(\mathbf{x} + \mathbf{c}_i \Delta t, t + \Delta t) - g_i(\mathbf{x}, t) = -\frac{1}{\tau_T} \left[g_i(\mathbf{x}, t) - g_i^{eq}(\mathbf{x}, t) \right] + \Delta t \omega_i S_T, \quad (6-18)$$

where g_i is the temperature distribution function, τ_T is the relaxation time for the temperature, and g_i^{eq} is the corresponding equilibrium temperature distribution function, calculated by

$$g_i^{eq} = T \left(\omega_i + \frac{1}{2} \mathbf{c}_i \cdot \mathbf{u} \right), \quad (6-19)$$

where ω_i is the weight coefficient, which is given as

$$\omega_i = \begin{cases} \omega_0 & i = 0 \\ (1 - \omega_0) / 4 & i = 1, 2, 3, 4 \end{cases} \quad (6-20)$$

and the macroscopic temperature is defined as

$$T = \sum_i g_i \quad (6-21)$$

The thermal diffusivity can be written as

$$a = \frac{1}{2} (1 - \omega_0) \left(\tau_T - \frac{1}{2} \right) \frac{\Delta x^2}{\Delta t} \quad (6-22)$$

S_T denotes the source term in Eq. (6-18), which is given by [283, 284]

$$S_T = \frac{L_f}{c_p} \frac{\varphi_s - \varphi_{s,0}}{\Delta t}, \quad (6-23)$$

where L_f is the latent heat of the liquid-solid phase change, c_p is the specific heat at constant pressure, φ_s is the volume fraction for the solid phase at the current time step, and $\varphi_{s,0}$ is the fraction at the previous time step.

The enthalpy can be calculated with the temperature and solid volume fraction as

$$En = c_{p,s} T \varphi_s + c_{p,w} T (1 - \varphi_s) + L_f (1 - \varphi_s), \quad (6-24)$$

where $c_{p,s}$ is the specific heat of the solid, and $c_{p,w}$ is the specific heat of water. The solid volume fraction is defined as

$$\varphi_s = \begin{cases} 0 & En < En_s \\ \frac{En - En_s}{En_l - En_s} & En_s \leq En \leq En_l \\ 1 & En > En_l \end{cases}, \quad (6-25)$$

where En_s and En_l are the enthalpies of the solid and liquid, respectively.

In this study, the interface treatment for the conjugated heat transfer is given by Li et al.'s model [285]

$$\begin{aligned} g_{\vec{i}}(\mathbf{x}_l, t + \Delta t) &= \frac{1-\beta}{1+\beta} g_{\vec{i}}^*(\mathbf{x}_l, t) + \frac{2\beta}{1+\beta} g_{\vec{i}}^*(\mathbf{x}_s, t) \\ g_{\vec{i}}(\mathbf{x}_s, t + \Delta t) &= -\frac{1-\beta}{1+\beta} g_{\vec{i}}^*(\mathbf{x}_s, t) + \frac{2}{1+\beta} g_{\vec{i}}^*(\mathbf{x}_l, t) \end{aligned} \quad (6-26)$$

On the left-hand side of Eq. (6-26), $\vec{i}$ and i represent two opposite directions. On the right-hand side, in the definition of $\beta = (\rho c_p)_s / (\rho c_p)_l$, the subscripts s and l represent the solid and fluid domains, respectively, and the symbol $*$ represents the state before streaming.

6.2.3. Simulation description

Thermal conductivity and diffusivity are very important for the simulation of the freezing process of a ferrofluid droplet. In this study, Wang and Pan's model is adopted to calculate the effective properties of the ferrofluid [286]

$$\frac{\phi_e}{\phi_l} = 1 + \frac{3(\alpha - 1)\varphi}{(\alpha + 2) - (\alpha - 1)\varphi}, \quad (6-27)$$

where ϕ_e indicates the effective property, ϕ_l is the property of the water or solid ice phase, ϕ is the volume fraction of the Fe_3O_4 particles, and α is defined as $\alpha = \phi_f / \phi_l$, where ϕ_f is the property of the Fe_3O_4 particles. The latent heat of the ferrofluid can be calculated as

$$L_f = L_w(1 - \phi), \quad (6-28)$$

where L_w represents the latent heat of pure water.

As described in Chapter 5, the deformation features and freezing behaviour of a ferrofluid droplet under magnetic lift and squeeze conditions have been studied experimentally. In this chapter, the simulation of the ferrofluid droplet is performed under these magnetic field conditions.

The schematic of the 2-D computational domains for the simulation of ferrofluid droplet under magnetic lift and squeeze conditions are shown in Figures 6-1 (a) – 6-1 (b). For the magnetic lift condition, the size of the computational domain was set as 201×201 lattice units, while a 301×301 domain was used for magnetic squeeze cases. The physical length of each unit cell was $25 \mu\text{m}$. The grid-independent results for droplet shape and freezing time were reached under the above grid sizes.

Figure 6-1 Schematic of the computational domains and forces exerted on a ferrofluid droplet under (a) the magnetic lift condition and (b) the magnetic squeeze condition

6.3. Results and discussions

6.3.1. Model validation

The verification and validation of the multiphase flow LB model and the phase change LB model are discussed in this section. A suspension droplet problem and a one-dimensional solidification in a semi-infinite region are used to as the two benchmark cases in the study.

For the validation of the multiphase flow model, the simulation results for a suspension droplet surrounded by a vapour phase were analysed. In the simulation, periodic boundary conditions were used. The relationship between the pressure difference (ΔP) and the droplet radius (R) can be obtained from the simulation. On the other hand, the Laplace equation gives an analytical expression, namely, $\Delta P = \sigma/R$, for their relationship, where σ is the surface tension. As can be seen from Figure 6-2 (a), the pressure difference between the liquid phase and vapour phase increases linearly with $1/R$, which is in good agreement with the results found with the Laplace equation. The simulated surface tension of the droplet can also be calculated as 0.168 N/m at the given saturation temperature condition. This value was proven to be correct via Cai

et al.'s model [287]. Based on this simulated surface tension value, a lattice unit can be converted to the real physical unit via the same Bond numbers.

For the validation of the phase change LB model, a two-phase Stefan problem was simulated. The initial temperature of the computational domain was set to be T_i and was higher than the freezing temperature T_m . Next, a lower temperature T_0 ($T_i > T_0$) was provided for the left boundary. Subsequently, the freezing front appeared on the left side and propagated to the right side of the boundary.

The spatial location of the freezing front is given by [288]

$$x_m(t) = 2\lambda\sqrt{a_s t}, \quad (6-29)$$

where t is the time, and λ is a parameter that can be determined by the following transcendental equation

$$\frac{e^{-\lambda^2}}{\operatorname{erf}(\lambda)} + \frac{k_l}{k_s} \left(\frac{a_s}{a_l}\right)^{1/2} \frac{T_m - T_i}{T_m - T_0} \frac{e^{-\lambda^2(a_s/a_l)}}{\operatorname{erfc}(\lambda\sqrt{a_s/a_l})} = \frac{\lambda L_f \sqrt{\pi}}{C_s(T_m - T_0)}, \quad (6-30)$$

where a is the thermal diffusivity, and k is the thermal conductivity. The subscripts s and l represent the solid and liquid phases, respectively.

The temperature for the solid phase $T_s(x, t)$ can be calculated as [288]

$$\frac{T_s(x, t) - T_0}{T_m - T_0} = \frac{\operatorname{erf}(x/(2\sqrt{a_s t}))}{\operatorname{erf}(\lambda)} \quad (6-31)$$

and the temperature for the liquid phase $T_l(x, t)$ is obtained by

$$\frac{T_l(x, t) - T_i}{T_m - T_i} = \frac{\operatorname{erfc}(x/(2\sqrt{a_l t}))}{\operatorname{erfc}(\lambda\sqrt{a_s/a_l})} \quad (6-32)$$

If the initial temperature equals the freezing temperature, the previous two-phase freezing problems can be treated as a single-phase Stefan problem, and Eq. (6-30) is reduced to

$$\frac{e^{-\lambda^2}}{\operatorname{erf}(\lambda)} = \frac{\lambda L_f \sqrt{\pi}}{C_s(T_m - T_0)} = \frac{\lambda \sqrt{\pi}}{St} \quad (6-33)$$

Here, $a_s = 0.005 \text{ m}^2/\text{s}$, $a_l = 0.001 \text{ m}^2/\text{s}$, the Stefan number $St = C_s(T_m - T_0)/L_f = 1$, and $Fo = a_s t / L_x^2 = 0.625$. The analytical results of the temperature distribution can be given by Eq. (6-31) – Eq. (6-33).

The variation in temperature in the domain can also be obtained by the numerical phase change LB model. In this simulation, Li et al.'s model [285] is used for the conjugate heat transfer (Eq. 6-26). If the solid volume fraction $\varphi_s = 0$, the node is in the liquid region. On the contrary, the node is in the solid part when $\varphi_s > 0$.

The analytical results for the temperature distribution and the simulated results were compared. As can be seen from Figure 6-2 (b), the numerical results can well predict the variation in temperature along the x direction under both single-phase conditions ($T_i = T_m = 0 \text{ K}$) and the two-phase condition ($T_i > T_m = 0 \text{ K}$). Thus, a faster propagation of the freezing front can be obtained under the single-phase condition compared to the two-phase condition.

Figure 6-2. Verification and validation of the multiphase LB model and the phase change LB model. (a) The simulation results for a suspension droplet surrounded by vapour. (b) The simulation results for the freezing process in a 1-D semi-infinite region (T_m is the freezing temperature, and T_i is the initial temperature in the liquid phase)

6.3.2. Droplet freezing in the absence of a magnetic field

The discussion in Section 6.3.1 indicates the accuracy of the LB model in this study. In this section, the validated LB model is applied to simulate the deformation and freezing process of a ferrofluid droplet in the absence of a magnetic field.

The effect of the volume expansion ratio on the height change feature of the droplet is analysed first. A dimensionless parameter is used to evaluate the height change of the droplet during the freezing process and is defined as the ratio of the height of the initial droplet (H_f) and that of the frozen droplet (H_d). As can be seen from Figure 6-3, H_f/H_d increases with the volume

expansion ratio. The volume expansion ratio of the ferrofluid droplet is measured as 1.052 in the absence of a magnetic field. The simulated results for H_f/H_d are in good agreement with the experimental data at the given volume expansion ratio.

Figure 6-3. The simulated results of the dimensionless height of the frozen droplet (H_f/H_d) at different volume expansion ratios (ρ_l/ρ_s) in the absence of a magnetic field.

Both the temperature distribution inside the droplet and the heat flux across the freezing front can impact a droplet's freezing behaviour. A recalescence stage exists in the freezing process of a droplet [67, 87]. During it, the droplet exhibits lower transparency, and the temperature of the droplet increases rapidly to the equilibrium temperature $T_m = 0$ at the end of this stage. After the recalescence process, the isothermal freezing stage begins. Both the equilibrium temperature [87] and the surrounding temperature [36] have been used as the initial temperature inside ($T_{i,d}$) the droplet in previous numerical studies. In the current simulation, the effect of the initial droplet temperature on the propagation of the freezing front was investigated. Both the numerical and analytical analysis were performed. The substrate temperature and environmental temperature used in the simulation were $-6\text{ }^{\circ}\text{C}$ and $22\text{ }^{\circ}\text{C}$, respectively. The comparison of the simulated results with the experimental data is shown in Figure 6-4. The dimensionless form of the height of the freezing front (h) is given by h/R_0 , where R_0 is the radius of a ferrofluid droplet in the absence of a magnetic field, as shown in the inset. The time

t is represented by the Fourier number, which is defined as $Fo = a_s t / R_0^2$. The increase in the freezing rate can be seen from the numerical results when the initial temperature varies from 22 °C to 0 °C due to the sensible heat transfer at $T_{i,d} = 22$ °C. The divergence between the numerical and experimental results is very small at $T_{i,d} = 0$ °C as compared to that at $T_{i,d} = 22$ °C. Therefore, the initial temperature of the droplet was chosen to be $T_{i,d} = 0$ °C in the remaining simulations and analytical studies.

The analytical analysis of the propagation of the freezing front is introduced in the next section. Based on Eq. (6-29), the position of the freezing front at the beginning stage of the freezing process can be given as

$$h/R_0 = 2\lambda\sqrt{Fo}, \quad (6-34)$$

where Fo is Fourier number, and λ can be calculated with Eq. (6-32) and Eq. (6-33). For the single-phase Stefan problem, if $St = Cs(Tm - Tw)/Lf \ll 1$, then the value of λ can be given by

$$\lambda \approx \sqrt{St/2} \quad (6-35)$$

Figure 6-4. The evolution of the dimensionless height (h/R_0) during freezing in the absence of a magnetic field. The black solid line was obtained via Eq. (6-34), and the green dashed line was given by Eq. (6-47).

As can be seen from Figure 6-4, the analytical result of Eq. (6-34) can well predict the experimental data at the beginning stage of freezing. However, this analytical model cannot predict the increase in the propagation rate near the final stage of freezing. A more comprehensive model should be developed to explain the acceleration of the freezing front.

The energy conservation equation at the freezing front can be given by

$$q_s - q_l = \rho_s L_f \frac{dh}{dt}, \quad (6-36)$$

where q_s is the heat flux at the freezing front computed from the solid side, and q_l is heat flux in the liquid phase. Figure 6-5 (a) shows the simulated results for the temperature distribution along the centreline of the computational domain. The value of Fo in Figure 6-5 (a) represents the simulated results for the dimensionless time moment, where L_y is the length of the domain in the vertical direction. The variation in the simulated heat flux with the dimensionless height of the freezing front (h/R_0) is depicted in Figure 6-5 (b). When the temperature value at the given position is smaller than 0°C, this position is treated as the solid ice region. With increasing Fo , more solid ice region can be observed in Figure 6-5 (a). The temperature increases to 0 °C at first and stays at this value for some time before continuing to increase until it reaches the environmental temperature. The simulation result also indicates that the temperature of the liquid phase in the droplet is kept close to 0 °C because the temperature difference between the liquid phase and the freezing front is very small. The heat flux at the freezing front on the liquid side (q_l) can be treated as 0. This conclusion can also be proved with the simulation results shown in Figure 6-5 (b).

A linear temperature gradient can be found in the solid ice region at the initial stage of freezing corresponding to the smaller Fo in Figure 6-5 (a). Based on this temperature distribution, the

heat flux q_s can be calculated via Fourier's law of heat conduction: $q_s = k_s(T_m - T_w)/h$. The energy conservation equation can be changed to

$$h/R_0 = \sqrt{2StFo} \quad (6-37)$$

The temperature of the solid ice region becomes nonlinear at large Fo ($Fo = 12.31$), which corresponds to the time moment near the completion of freezing. Concave isothermal lines can also be found in the temperature contour for this moment. The simulated results in Figure 6-5 (b) also indicate that the value of q_s increases near the completion of freezing. It could be concluded that Eq. (6-34) is no longer suitable for predicting the acceleration of the freezing front at these stages. Recently, Fang et al. proposed a model based on the self-similar geometry of the droplet near the completion of freezing to describe the propagation of the freezing front [51]. Figure 6-6 shows the schematic of the droplet profile in spherical coordinates.

The propagation velocity of the freezing front is determined by

$$\rho_s L_f \frac{dr}{dt} = k_i \frac{\partial T}{\partial r}, \quad (6-38)$$

where L_f is the latent heat.

The temperature distribution in this region can be expressed as [275]

$$\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} = 0 \quad (6-39)$$

Therefore, the general solution for temperature T can be $T = \alpha/r + \beta$, where α and β are time-dependent variables.

Based on the boundary condition at $r = r(t)$, $T = T_m$, and at $r = r_0$, $T = T_0$, the value of α can be calculated as $\alpha = (T_m - T_0)r(t)r_0/(r_0 - r(t))$.

The temperature gradient at $r = r(t)$ can be calculated as

$$\frac{\partial T}{\partial r} \big|_{r=r(t)} = -\frac{\alpha}{r(t)^2} = -\frac{(T_m - T_0)r_0}{(r_0 - r(t))r(t)} \quad (6-40)$$

The energy equation in spherical coordinate gives

$$r^2 \frac{\partial T}{\partial r} \big|_{r=r(t)} = r_0^2 \frac{\partial T}{\partial r} \big|_{r=r_0} \quad (6-41)$$

The temperature gradient at $r = r_0$ satisfies

$$\frac{\partial T}{\partial r} \big|_{r=r_0} = \frac{T_0 - T_w}{z_0} \quad (6-42)$$

Substituting Eq. (6-41) – Eq. (6-42) into Eq. (6-40), the temperature difference can be calculated as

$$\frac{(T_m - T_0)}{(T_0 - T_w)} = -\frac{(r_0 - r(t))r_0}{r(t)z_0} \quad (6-43)$$

Eq. (6-43) can be rewritten as

$$\frac{(T_m - T_0)}{(T_0 - T_w) + (T_m - T_0)} = \frac{(T_m - T_0)}{(T_m - T_w)} = -\frac{(r_0 - r(t))r_0}{r(t)z_0 + (r_0 - r(t))r_0} \quad (6-44)$$

Substituting Eq. (6-44) into Eq. (6-40), the temperature gradient can be expressed as

$$\frac{\partial T}{\partial r} = -\frac{(T_m - T_w)r_0^2}{r(t)[z_0r(t) + r_0^2 - r_0r(t)]} \quad (6-45)$$

Set $x = r(t)/r_0$ and $t' = t/t_1$, where $t_1 = r_0^2 \rho_s L_f / (2k_i(T_m - T_w))$ represents the time scale for the propagation of the freezing front in spherical coordinates. Then substituting Eq. (6-45) into Eq. (6-38) gives

$$\frac{dx}{dt'} = -\frac{1}{2x[\eta x + 1 - x]}, \quad (6-46)$$

where $\eta = z_0/r_0$, with z_0 and r_0 being the initial location and the radius of the freezing front in the spherical coordinate, respectively. Integrating both sides of Eq. (6-46) gives

$$t'(x) = t'(1) + (2/3\eta + 1/3) - [2/3(\eta - 1)x^3 + x^2], \quad (6-47)$$

where $t'(1)$ is the moment when Eq. (6-47) is applicable.

Since $r(t) = z_0 + r_0 - h$, $Fo = a_s t / R_0^2$, $Fo = a_s t / R_0^2$, and $St = C_s(T_m - T_0)/L_f$, the expressions for x and $t'(x)$ can be rewritten as

$$x = \left(\frac{z_0 + r_0}{R_0} - \frac{h}{R_0} \right) \frac{R_0}{r_0} \quad (6-48)$$

$$t'(x) = \frac{2Fo \cdot St}{r_0^2 / R_0^2} \quad (6-49)$$

If $t'(1)=15.73$ ($t=14.47$ s) is set as the initial moment when the freezing front becomes concave, the corresponding η can be calculated as $\eta = 3.907$. The results in Figure 6-4 indicate that Eq. (6-47) can predict the acceleration of the propagation of the freezing front near the completion of freezing well.

Figure 6-5. The numerical results for (a) the temperature distribution along the vertical centreline of the computational domain and (b) the heat flux at the substrate and at the freezing front in the liquid phase and solid phase

Figure 6-6 Schematic of the droplet profile near the completion of freezing in spherical coordinates. Here, z_0 is the vertical location of the freezing front at the initial moment.

6.3.3. Magnetic squeeze cases

In this section, the simulation results for the deformation and freezing behaviour of a ferrofluid droplet under magnetic squeeze conditions are discussed.

When the magnet is placed below the ferrofluid droplet, the deformation of the droplet is determined by two factors: (1) the gradient of the magnetic field, and (2) the magnetisation of the droplet [289]. In the previous experimental study in Chapter 5, only the effect of the magnetic field gradient is considered. In this numerical work, the influence of magnetisation on the profile of the ferrofluid droplet is also analysed by adding an additional magnetic stress term (μ_0/M_n^2) at the air-droplet interface based on Rowghanian et al.'s model [290], where M_n is the normal component of magnetisation [264, 290].

Two dimensionless Bond numbers Bo_m and Bo_s are used to represent the magnetic force induced by the magnetic field gradient and the magnetic stress due to the magnetisation, respectively.

The definition of Bo_m is given by [269]

$$Bo_m = \mu_0 M |\nabla H_m| R_0^2 / \sigma \approx \mu_0 M |H_m(z_i) - H_m(z_i + R_0)| R_0 / \sigma, \quad (6-50)$$

where ∇H_m is the gradient of the magnetic field. The value of Bo_s can be calculated as [40]

$$Bo_s = \mu_0 M^2 R_0 / (2\sigma) \quad (6-51)$$

The maximum value of $Bo_m = 13.14$, which is much larger than that of $Bo_s = 1.23$ under the current magnetic squeeze conditions. Therefore, the deformation of a ferrofluid droplet is dominated by the magnetic force induced by the gradient of the magnetic field. The deformation feature of a liquid ferrofluid droplet before the onset of freezing is evaluated by the dimensionless height of the droplet (H_d / H_{d0}), where H_d represents the height of the

ferrofluid droplet under magnetic conditions. The comparison of the simulated results and the experimental data is shown in Figure 6-7. Bo_e is the effective magnetic Bond number given by $Bo_e = Bo_m - Bo_s$. With consideration for the magnetisation effect, the shape of a ferrofluid droplet is elongated [289], which results in the increase in H_d/H_{d0} in the simulation. It can be concluded that the predicted shape change feature is in good agreement with the experimental data when both the magnetic field gradient and the magnetic stress are included in the simulation.

Figure 6-7. Simulated and experimental results for the deformation of a ferrofluid droplet before the onset of freezing under magnetic squeeze conditions.

A comparison between the simulated droplet profiles and the snapshots of ferrofluid droplets taken during the experiments is shown in Figure 6-8. The squeezing of the ferrofluid droplets can be observed in both the simulations and experiments. With the increase in the magnetic field strength, the radius of the ferrofluid droplet increases, while the height decreases. The current numerical model can predict the morphology of the droplet well under the given magnetic squeeze conditions.

Figure 6-8. The snapshots of a frozen ferrofluid droplet (images left) and the simulated droplet profiles (images right) under different magnetic squeeze conditions

The freezing dynamic of a ferrofluid droplet is evaluated via the temperature distribution in the vertical centreline of the domain and the evolution of the freezing front during the freezing process. When $Bo_e = 6.37$, the variation in temperature as a function of the dimensionless distance (y/L_y) at different time moments is shown in Figure 6-9 (a). The temperature increases linearly inside the solid ice phase along the y direction in all the given time moments. As can be seen from the temperature contours (inset), the isothermal line is not as concave as it is in the absence of a magnetic field. Based on the previous discussion in Section 6.3.2, the propagation of the freezing front during the freezing process can be predicted well by Eq. (6-34), as supported by the results in Figure 6-9 (b).

Figure 6-9. The freezing dynamics of a ferrofluid droplet under magnetic squeeze conditions. (a) Temperature distributions along the centreline of the domain for different dimensionless time moments (Fo) when $Bo_e = 6.67$. (b) The dimensionless height of the freezing front (h/R_0) at different Fo

The freezing behaviour of a ferrofluid droplet under magnetic squeeze conditions is analysed using the dimensionless height (H_f/H_{f0}) of the frozen droplet and the dimensionless freezing time (t_f/t_{f0}). H_f and H_{f0} are the heights of the frozen droplet under magnetic field conditions and in the absence of a magnetic field, respectively. Here, t_f and t_{f0} are the corresponding total freezing times for the above two cases. As can be seen from Figure 6-10, the simulated results for H_f/H_{f0} and t_f/t_{f0} are in good agreement with the experimental data. In addition, the variation in t_f/t_{f0} can also be described well via the scaling $t_f/t_0 = (H_f/H_{f0})^2$ due to the linear variation of the temperature in solid ice (shown in Figure 6-9).

Figure 6-10. The freezing behaviour of a ferrofluid droplet under magnetic squeeze conditions. (a) The variation in the dimensionless height (H_f/H_{f0}) of frozen droplets due to different effective magnetic Bond numbers Bo_e (b) The dimensionless freezing time (t_f/t_0) as a function of Bo_e

6.3.4. Magnetic lift cases

When the magnet is placed above the droplet, the magnetic force exerted on the ferrofluid droplet becomes an upward force, which can lead to the elongation of the droplet and extended total freezing time. The migration of the particles in the liquid ferrofluid under magnetic lift conditions has been investigated by other researchers [276]. When the magnetic field is strong, a splitting of the droplet can be observed due to particle migration [276]. Since the distribution of the particles in the liquid phase is very important in these cases, the Maxwell-Boltzmann distribution law is used in the simulation to consider the redistribution of the Fe_3O_4 particles [269], namely

$$\varphi = \varphi_0 e^{\mu_0 M H_m \pi d^3 / (6 k_0 T)}, \quad (6-52)$$

where φ_0 represents the particle concentration at the magnetic strength $H_m = 0$.

The effective Bond number Bo_e varies from 0 to 3.65 under magnetic lift conditions. The selected morphologies of ferrofluid droplets before the onset of freezing and at the completion of freezing are shown in Figure 6-11 (a) – Figure 6-11 (b). The predicted droplet shape is found to be in a good agreement with the snapshots of ferrofluid droplets before the onset of freezing. However, the divergence between the numerical and experimental results becomes obvious under high Bo_e conditions at the completion of freezing. This phenomenon is caused by the complex redistribution of particles during the freezing process. This feature cannot be precisely described by the current Maxwell-Boltzmann distribution law.

Figure 6-11. Comparisons of the morphologies of ferrofluid droplets (a) before the onset of freezing and (b) at the completion of freezing between the experimental data (images left) and the simulated results (images right) under magnetic lift conditions

The variation in the dimensionless height (H_d/H_{d0}) of the liquid ferrofluid droplet due to the effective magnetic Bond number ($Bo_e = Bo_m + Bo_s$) is shown in Figure 6-12. It can be concluded that the deformation feature of the liquid droplet can be predicted well by the current numerical model.

Figure 6-12 The dimensionless height of a droplet (H_d/H_{d0}) versus the Bo_e before the onset of freezing under magnetic lift conditions

As can be seen from Figure 6-13 (a), the temperature distribution along the centreline of the droplet in the solid ice phase increases non-linearly with y/L_d after $Fo = 12.74$ (when $Bo_e = 3.65$). The nonlinear distribution of the temperature at $Fo = 12.74$ can also be seen from the inset. This effect leads to the obvious divergence between the simulated and calculated results found with Eq. (6-34) near the completion of freezing.

Figure 6-13. The freezing dynamics of a ferrofluid droplet under magnetic lift conditions. (a) Temperature distribution along the centreline of the domain at different dimensionless time moments (Fo) when $Bo_e = 3.65$. (b) The dimensionless height of the freezing front (h/R_0) at different Fo

Analogous to the analysis done under the magnetic squeeze condition, comparisons of the freezing behaviour of a ferrofluid droplet between the simulated results and experimental data under the magnetic lift condition are shown in Figure 6-14. The more complicated particle distributions under high Bo_e lead to the divergence between the simulated and experimental results with respect to the dimensionless height of the frozen droplet (Figure 6-14 (a)). Since the height of the frozen droplet is related to the total freezing time, the simulated dimensionless freezing time becomes different from the experimental data with increasing Bo_e . As can be seen from Figure 6-14 (a), with increasing Bo_e , the difference between the analytical model and the

simulation results becomes more obvious. Such results cause the divergence between the scaling $t_f/t_0 = (H_f/H_0)^2$ and the experimental and numerical results.

Figure 6-14 The freezing behaviour of a frozen ferrofluid droplet under magnetic lift conditions. (a) The variation in the dimensionless height (H_f/H_{f0}) of the frozen droplet with the effective magnetic Bond number Bo_e (b) The dimensionless freezing time (t_f/t_0) as a function of Bo_e .

6.4. Summary

In this chapter, the deformation and freezing processes for ferrofluid droplets under magnetic squeeze and lift conditions were investigated numerically based on the lattice Boltzmann method. Scaling models were also proposed to explain the propagation of the freezing front in the ferrofluid droplet.

In the absence of a magnetic field, the scaling analyses show that the propagation of the freezing front follows a $h \sim t^{0.5}$ relation in the initial stage of freezing. However, large divergences between the experimental data and the scaling model can be observed near the final stage of the freezing. A new scaling model has been proposed to describe the acceleration of the freezing front at this stage, and it matches well with the experimental results. The simulation results indicate that the initial temperature inside the droplet ($T_{i,d}$) affects the evolution of the freezing front during the freezing process. The numerical results are in good agreement with the experimental data when $T_{i,d} = 0^\circ\text{C}$.

Under the magnetic squeeze condition, the shape of the ferrofluid droplet is found to be flattened, and the simulated droplet profiles agree well with the experimental observations. The simulated results show that the dimensionless height of the ferrofluid droplet (H_{d0}/H_d) decreases almost linearly with the magnetic Bond number (Bo_m) when the value of Bo_m is low. When Bo_m becomes larger, the propagation of the freezing front can be described by $h \sim t^{0.5}$ for the entire freezing process due to the linear temperature distribution in the solid ice phase and the flattened droplet shape. The effect of the magnetic field on the dimensionless height of the frozen droplet and the dimensionless freezing time can be described well by the numerical models.

Under the magnetic lift condition, the simulated morphologies of the droplet agree approximately with the snapshots of the droplet obtained through the experiments. The migration of particles during the freezing process brings challenges to the simulation. Even when the Maxwell-Boltzmann distribution law is applied, the simulated results differ from the experimental data in the high Bo_m region. A more complicated model is needed to describe the distribution of the particles in this process in the future.

Chapter 7: Conclusions and recommendations for future work

7.1. Conclusions

The current study investigated the freezing process of a nanofluid droplet on a supercooled surface systematically. The investigation in the thesis was divided into two parts: the freezing of a deposited nanofluid droplet in the absence of an external field, and the application of an magnetic field on the freezing of a sessile ferrofluid droplet. Both experimental studies and numerical simulations were carried out for each part. The major conclusions from this study can be drawn as follows:

First, a unique shape feature of frozen nanofluid droplets, which is quite different from that for frozen pure water droplets, was found through a series of experiments. Experiments involving water droplets have shown that the formation of a pointy tip on a pure water droplet is independent of the droplet volume and substrate temperature. However, a flat plateau was found on nanofluid droplets at the completion of freezing. In a series of experiments, the particle concentration, droplet volume, substrate temperature, and particle size were found to have significant impacts on this unique shape change feature of frozen nanofluid droplets. The underlying mechanism of this phenomenon was analysed while taking into consideration an outward Marangoni flow induced by the particle gradient along the droplet surface. A simple scaling model was proposed to explain the relationship between the shape change factor and the initial particle concentration. The predicted results are in good agreement with the experimental data. In addition, three geometrical features in the frozen nanofluid droplets, namely, the plateau, triangle (the combination of the plateau and tip), and pointy tip were found under different temperature and particle size conditions. The underlying mechanism for this phenomenon is related to the engulfment of particles at different freezing rates. A regime map

describing the morphologies of a frozen nanofluid droplet was built based on a scaling analysis of the relationship between the particle size and critical velocity.

Second, a new LB model using the phase-change LB model with volume expansion effect and the entropy-based LB model was developed for the simulation of the freezing process of a nanofluid droplet. The particles were described via the immersed boundary method, and the liquid was assumed to be attracted by the particles due to the capillary force. The simulated results can predict the formation of a plateau and the evolution of the height of the freezing front observed in the experiments well. The numerical results have shown that a particle layer was formed near the advancing freezing front and that the liquid in the central part was driven to the periphery of the droplet due to the accumulation of particles in that region. Obvious variations in the height change factor ($h_{particle}/h_{water}$) and the ratio change factor (r_{top}/r_{max}) can be observed when the particle concentration changes from 0.09% to 0.72%. To the contrary, the contact angle does not have much impact on the shape change factors of nanofluid droplets.

Third, the application of a magnetic field on the freezing of a nanofluid droplet was investigated experimentally. At first, an active method for the control of the freezing process of a ferrofluid droplet using weak magnetic fields was developed. The profile of a liquid ferrofluid droplet under magnetic field conditions can be described via the modified Young-Laplace equation with consideration for the magnetic force due to the very short time span of the magnetisation. The calculated droplet height features were in good agreement with the experimental measurements. A scaling analysis was also used to explain the variation in the droplet height under magnetic lift and squeeze conditions. Specifically, under the magnetic lift conditions, the frozen droplet height was found to be 1.6 times higher than the frozen droplet height in the absence of a magnetic field, leading to an increase in the freezing time of up to 2.4 times longer. Under the magnetic squeeze conditions, the freezing time became at most 0.3 times shorter. Moreover, it was also found that the expansion ratio increases with increasing magnetic field

strength under the magnetic lift conditions, but it is independent of the magnetic field strength under the magnetic squeeze conditions. A scaling model was proposed to explain the experimentally obtained dependence of both the dimensionless freezing time and the square of the frozen droplet height upon the magnetic field strength.

Finally, numerical studies based on the LB method for the freezing process of a ferrofluid droplet were carried out. A scaling analysis was used to describe the evolution of the freezing front in the ferrofluid droplet. Two scaling models were proposed to predict the propagation of the freezing front at the initial stage and later stage of freezing. Under the magnetic squeeze conditions, the simulated results can predict the flattened feature of the ferrofluid droplet observed in the experiments well. Both H_d/H_{d0} and H_f/H_{f0} can be described well by the numerical model. The propagation of the freezing front can be described by $h \sim t^{0.5}$. Under the magnetic lift conditions, the simulated droplet profiles agreed approximately with the snapshots of the droplet obtained experimentally. The simulated values of H_d/H_{d0} and H_f/H_{f0} differed from the experimental data in the high Bo_m region. These derivations are caused by the migration of particles during the freezing process. Even when the Maxwell-Boltzmann distribution law was applied, the complex migration still brought challenges in terms of simulating the deformation and freezing processes of ferrofluid droplets under these conditions.

The results of the fundamental studies focusing on the freezing process of nanofluid droplets were systematically introduced and discussed in this thesis. The current study provides some new insights in controlling the shape and freezing time of droplets with the use of external magnetic field. However, studying the effect of the magnetic field on the freezing process of water is still in the laboratory experimental research stage. There are still many challenges that need to be overcome in the future, such as the limitation of the working fluid materials and the contamination of particles, before it can be applied in the anti-icing or de-icing fields. The unique shape change feature of the frozen nanofluid droplets found in this study may also shed

light on the development of new technologies for the fabrication of micro-sized elements, such as microcells and microreactors with different shapes, using nanofluids with external magnetic fields.

7.2. Recommendations for future work

7.2.1. Further investigations of the underlying physics of nanofluid droplets freezing

In this thesis, the effects of particle size, droplet volume, substrate temperature, and an external field on the freezing of nanofluid droplets were examined in both 2D (the Hele-Shaw cell) and 3D (the sessile and deposited droplets) experiments. The shape change features of frozen droplets have been shown to be dependent of these parameters. Although the current study shows that the liquid in the central part of a droplet is driven to the outside part due to the Marangoni flow induced by the particle concentration gradient. More experimental studies should be conducted in the future to further reveal the physics of this phenomenon. For example, effects of the concentration of surfactants, the shape of the particles, and the arrest contact angle on the freezing behaviours of nanofluid droplets could be investigated.

7.2.2. Measurement of temperature distributions and induced flow fields inside nanofluid droplets

The present experimental studies lack detailed information on temperature distributions and flow fields inside a freezing sessile nanofluid droplet. These unknown parameters bring difficulties in deep understanding the physics of the dynamic freezing process. However, it should also be noted that the small scale of nanofluid droplets and the curved surfaces present challenges for the measurement of the droplet temperature distribution during the freezing

process. In addition, precisely tracking the movement of each nano-sized particle and identifying the concentration of particles is also very challenging. The improved experimental setups in combination with more advanced measuring technologies, such as an infrared camera, confocal scanning and micro-particle image velocimetry could be used in the future to advance the understanding of this phenomenon.

7.2.3. Improvement of the lattice Boltzmann models

The current LB models are unable to predict the phenomena observed in all experiments because the particle distributions and migrations in the simulations are not the same as those occurring in the experiments. Further modifications involving models or functions to describe the distribution of the particles in nanofluid droplets and the movement of particles in the freezing process are needed. In addition, 3D simulations should be conducted in the future to reduce the dimensionality differences between simulations and experiments.

7.2.4. Exploring applications of the novel freezing control technology and fabrication method based on the freezing of nanofluids

The results in this thesis have shown that the freezing conditions, particle size, and magnetic field play significant roles in the freezing time and profiles of frozen nanofluid droplets. The freezing process of droplet could be accelerated or extended by adding nanoparticles or applying magnetic field. Future studies will aim to precisely control the freezing time of droplets to develop the novel freezing manipulation technology. On the other hand, these phenomena shed light on the fabrication of micro-sized units with controllable shapes. The shape of the droplet bottom can be affected by the structures of the substrates. In combine with surface structure tailoring technology, experimental investigations focusing on controlling the shape change feature of micro-sized droplets could be performed for the development of a novel fabrication method. Currently, the water-based nanofluids are used in this study, and

systematic studies focusing on the droplet freezing process of non-Newtonian fluids with suspended particles will be studied in the future. This is significant for finding the potential application in the 3D printing field.

APPENDIX A The source code for the simulation of the freezing process of nanofluid droplets under magnetic fields

```

MODULE START_L
  implicit none
  integer,PARAMETER::NX=201,NY=201
  INTEGER,PARAMETER::LAST=2000000
  integer,dimension(0:NX+1,0:NY+1)::s
  double precision:: DX=1.0d0, DY=1.0d0, DT=1.0d0,phydx,phydy,phydt
  integer iter,I,J,K,L,N
  integer,dimension(0:8,0:8)::M
  double precision,dimension(0:8,0:8)::invM
  integer hleft,hright,chleft,chright,height,cheight
  CHARACTER*20::NAME,fname
  integer,dimension(0:4)::TCX=(/0,1,0,-1,0/)
  integer,dimension(0:4)::TCY=(/0,0,1,0,-1/)
  integer,dimension(0:8)::CX=(/0,1,0,-1,0,1,-1,-1,1/)
  integer,dimension(0:8)::CY=(/0,0,1,0,-1,1,1,-1,-1/)
!----- Multiphase flow-----
  double precision,dimension(0:NX+1,0:NY+1):: RHO,U,V,UP,VP,UPM,VPM
  double precision,dimension(0:NX+1,0:NY+1):: rhocp
  double precision,dimension(0:8,0:NX+1,0:NY+1)::F,FF,FFORCE
  double precision:: BFORCEY1,BFORCEX1,WFORCEX1,WFORCEY1,SFORCEX1,SFORCEY1,FORCEX,FORCEY
  double precision:: waf=-0.00d0,gravx=0d0,gravy=0d0
  double precision,dimension(0:8)::FM1,FFM1,FMEQ1
  double precision:: omega,A,B,RR,G11=-1.d0,c0=1.d0,rhoc,ts
  double precision SUMM,ADDF,ADDF2,SIKMA,FQ1
  double precision denl,deng,width,Ri,DISTANCE,height0
  double precision tc,t,droplet_height,height_ratio
  double precision rhomax,rhomin,usmax,pin,pout
  double precision temp1,temp2,temp3,temp4,z1,z2,feq1,feq2
  double precision tempF,tempf2,tempf3,Volume_ice2,Volume_ice2_p
  double precision
  Volume_drop,Volume_water,Volume_ice,Volume_ice_p,ice_ratio,Volume_inter,Volume_gap,Volume_water_p,Volume_dr
  op_p
  double precision Volume_expansion,CP_fs
!----- Temperature -----
  double precision,dimension(0:NX+1,0:NY+1)::Temperature
  double precision,dimension(0:NX+1,0:NY+1)::tsor
  double precision,dimension(0:4,0:NX+1,0:NY+1)::h,hh
  double precision::heq,diffu
  double precision Tbottom(0:NX+1),Tup
  double
  precision,DIMENSION(0:8)::WI=(/4.d0/9.d0,1.d0/9.d0,1.d0/9.d0,1.d0/9.d0,1.d0/9.d0,1.d0/36.d0,1.d0/36.d0,1.d0/36.d0,1.d0
  /36.d0/)
  double precision,DIMENSION(0:4)::WIT=(/1.d0/3.d0,1.d0/6.d0,1.d0/6.d0,1.d0/6.d0,1.d0/6.d0/)
!----- solid-liquid phase change -----
  double precision,dimension(0:NX+1,0:NY+1)::EN,FRF,FR,FC
  double precision::TAOF,TaoG_1,TaoG_s,TaoG_c
  double precision::TH,TM,R,G1,UM,ENS,ENL,J0
  double precision::PR,RA,STE,FO,porosity
  double precision::CP,LF,BETA
  double precision::Vwater,melting_rate,freezing_height
!----- property -----
  double precision st(0:8) ! for variable thermophysical properties
  double precision visco,viscosity_v,viscosity_l,diff_v,diff_l,diff_ice,Cv_v,Cv_l,Cv ! smoothing at the interface
  double precision tao_l,tao_v,tao_visco,taof_t,taos_t,taofs_t
  double precision diff_ice_p,diff_w_p,diff_v_p,diff_su_p,rhoice,cp_ice,rhocp_w,rhocp_i,rhocp_v,rhocp_su
  double precision lambda_i,lambda_w,lambda_v,lambda_su
  double precision::Tcrit,Tscale,Scale
!----- post-processing: local heat flux and total heat flux-----

```

```

double precision DeDiam
double precision LocalQ(1:NX),TotalQ
=====
double precision::Kb,miu0,Mp,Hm,dia,Ma
double precision::epsilon,Langevin
double precision::volume_f,pi,rbase
double precision::B0,B1,B2,B3,B4,B5,dis,Angle,dropbase
double precision:: ratio(NY),graE,ration0,Dis0,H1,H0,epsilon0,volume_c(NY)
double precision::Fm,DH,Bond_m,Bond_ma,mag_f,surface_tension,Fm_L,surface_tension_L,gravity
LOGICAL, DIMENSION(0:nx+1,0:ny+1)::bonds,walls=.false.,bonds2
integer::m_case
LOGICAL::Initial
END MODULE

=====

PROGRAM MAIN

  USE START_L
  implicit none

  CALL INIT_UV
  CALL INIT_T
  Initial=.true.

  OPEN(20,file='dropheight_ini.dat')

  if(Initial) then
    do ITER=0,25000
      CALL Binex2
      CALL Volume_height
      CALL Main_UV

      if(mod(ITER,200).eq.0) then

        write(*,*) iter, RHO(NX/2,NY/2),height_ratio
        write(20,*) ITER,height_ratio,height_ratio*Ri
      endif

      IF ( mod (iter,1000) .eq. 0) THEN
        WRITE(NAME,*)ITER,".DAT"
        FNAME='rhouv'//TRIM(ADJUSTL(NAME))
        OPEN(4,file=FNAME)
        WRITE(4,*)'VARIABLES="I" "J" "RHO" "T" "U" "V" "FR"'
        WRITE(4,*)'ZONE I=',NX,'J=',NY,'T=POINTS'
        DO J=1,NY
          DO I=1,NX
            WRITE(4,*) I,J,RHO(I,J),Temperature(I,J)-
273.15d0,UP(I,J)*phydx/phydt,VP(I,J)*phydx/phydt,FR(I,J)
          ENDDO
        ENDDO
        CLOSE(4)
      ENDIF
    enddo
  endif

  I=(nx+1)/2
  DO J=height+1,NY
    IF (RHO(I,J)<(deng/2d0+denl/2d0)) THEN
      temp1 = J
      EXIT
    END IF
  END DO
  height0=temp1-height-0.5d0
  write(*,*) 'height0=',height0

  CALL INIT_T

```

```

Initial=.false.
ITER=0
OPEN(14,file='height_ratio.dat')
OPEN(15,file='tem_t.dat')
DO WHILE (ITER.LT.300000)

    CALL Volume_height
    CALL Binex2
    CALL Main_UV

!     if(Volume_water>=Volume_gap) then
!         CALL Main_UV
!     elseif(Volume_water>10d0.and.Volume_water<Volume_gap) then
!         DO I=1,nx
!         DO J=1,ny
!             IF(RHO(I,J)<=(deng/2d0+denl/2d0).and.Volume_water>0.1d0.and.Volume_inter>0.1d0) then
!                 IF (BONDS(I,J).and.RHO(I,J-1)>=(deng/2d0+denl/2d0).and.FR(I,J-1)<0.5d0.and.Volume_ice2_p>0.1d0)
RHO(I,J)=RHO(I,J)+(Volume_ice2 -Volume_ice2_p)/Volume_inter *(1d0-Volume_expansion)*denl
!             ENDIF
!             ENDDO
!             ENDDO
!         else
!             DO J=height+2,ny
!                 IF(RHO((nx+1)/2,J)<=(deng/2d0+denl/2d0).and.Volume_water>0.1d0.and.Volume_inter>0.1d0) then
!                     IF (BONDS((nx+1)/2,J).and.RHO((nx+1)/2,J-1)>=(deng/2d0+denl/2d0).and.FR((nx+1)/2,J-1)<0.5d0)
RHO((nx+1)/2,J)=RHO((nx+1)/2,J)+(Volume_ice2 -Volume_ice2_p)/Volume_inter *(1d0-Volume_expansion)*denl
!                     ENDIF
!                     ENDDO
!                 endif
!             enddo

    CALL Main_T

    Fo = diff_ice_p*phydt*iter/(Ri*phydx)/(Ri*phydx)

    IF (mod(ITER,250).eq.0) WRITE (*,*) ITER,RHO(NX/2,NY/2),Temperature(NX/2,NY/2),Fo
    IF (mod(ITER,10).eq.0) WRITE (15,'(I8,3F20.10)') ITER,Temperature(NX/2+1,height+1)-
273.15d0,Temperature(NX/2+1,height+11)-273.15d0,Temperature(NX/2+1,height+freezing_height+0.5d0)-273.15d0
    IF (mod(ITER,10).eq.0) WRITE (14,'(I8,6F19.8)') ITER,Fo,height_ratio,freezing_height,(Volume_drop-
Volume_water)/Volume_drop,Volume_drop,Volume_water
    IF ( mod (iter,1000) .eq. 0) THEN
        WRITE(NAME,*)ITER,".DAT"
        FNAME='rhouv'//TRIM(ADJUSTL(NAME))
        OPEN(4,file=FNAME)
        WRITE(4,*)'VARIABLES="I" "J" "RHO" "T" "U" "V" "FR"'
        WRITE(4,*)'ZONE I=,NX,J=,NY,T=POINTS'
        DO J=1,NY
        DO I=1,NX
            WRITE(4,*) I,J,RHO(I,J),Temperature(I,J)-
273.15d0,UP(I,J)*phydx/phydt,VP(I,J)*phydx/phydt,FR(I,J)
        ENDDO
        ENDDO
        CLOSE(4)

        ENDIF
        ITER=ITER+1
        ENDDO
        CLOSE(10)
        CLOSE(14)
END PROGRAM

=====

SUBROUTINE INIT_UV
    USE START_L
    implicit none
!----- PR- EOS model parameters -----

```



```

omega=0.344d0
omega=0.37464d0+1.54226d0*omega-0.26992d0*omega*omega
A=2.0d0/49.d0 !/1.8d0
B=2.d0/21.0d0
RR=1.d0
Tc=0.0729d0 !4.051222448563013D-2
Tcrit=647.3d0
Tscale=Tcrit/Tc

rhoc=2.541858d0
T=0.85d0*Tc

ts=T
denl = 6.62933834325514d0
deng = 0.341309526652276d0

!----- property for fluids -----
! viscosity_l=0.125389d0/2d0
! viscosity_v=0.5859d0/2d0
! tao_l=3d0*viscosity_l+0.5d0
! tao_v=3d0*viscosity_v+0.5d0

rbase = 48
tao_visco = 1d0

! st(0)=1.0d0; st(1)=1.0d0/1.2d0; st(2)=1.0d0/1.2d0
! st(3)=1.0d0; st(4)=1.0d0/1.1d0; st(5)=1.0d0
! st(6)=1.0d0/1.1d0
! M(0,:)=(/ 1, 1, 1, 1, 1, 1, 1, 1, 1/)
! M(1,:)=(/-4,-1,-1,-1,-1, 2, 2, 2, 2/)
! M(2,:)=(/ 4,-2,-2,-2,-2, 1, 1, 1, 1/)
! M(3,:)=(/ 0, 1, 0,-1, 0, 1,-1,-1, 1/)
! M(4,:)=(/ 0,-2, 0, 2, 0, 1,-1,-1, 1/)
! M(5,:)=(/ 0, 0, 1, 0,-1, 1, 1,-1,-1/)
! M(6,:)=(/ 0, 0,-2, 0, 2, 1, 1,-1,-1/)
! M(7,:)=(/ 0, 1,-1, 1,-1, 0, 0, 0, 0/)
! M(8,:)=(/ 0, 0, 0, 0, 0, 1,-1, 1,-1/)
! invM(0,:)=(/4,-4, 4, 0, 0, 0, 0, 0, 0/)*1.0d0/36.d0
! invM(1,:)=(/4,-1,-2, 6,-6, 0, 0, 9, 0/)*1.0d0/36.d0
! invM(2,:)=(/4,-1,-2, 0, 0, 6,-6,-9, 0/)*1.0d0/36.d0
! invM(3,:)=(/4,-1,-2,-6, 6, 0, 0, 9, 0/)*1.0d0/36.d0
! invM(4,:)=(/4,-1,-2, 0, 0,-6, 6,-9, 0/)*1.0d0/36.d0
! invM(5,:)=(/4, 2, 1, 6, 3, 6, 3, 0, 9/)*1.0d0/36.d0
! invM(6,:)=(/4, 2, 1,-6,-3, 6, 3, 0,-9/)*1.0d0/36.d0
! invM(7,:)=(/4, 2, 1,-6,-3,-6,-3, 0, 9/)*1.0d0/36.d0
! invM(8,:)=(/4, 2, 1, 6, 3,-6,-3, 0,-9/)*1.0d0/36.d0

U=0.d0
V=0.d0
UP=0.d0
VP=0.d0
FFORCE=0d0

CALL MICROSTRUCTURE

Ri=51.6d0
width=3.d0

DO I=0,NX+1
DO J=0,NY+1

DISTANCE= SQRT(FLOAT((I-(nx+1)/2)**2+(J-(height+1))**2)) !DROPLET LOCATION
temp1=2.d0*(distance-Ri)/width
temp1=(2.d0*exp(temp1)-1.d0)/(2.d0*exp(temp1)+1.d0)

if(s(I,J).eq.0) then
RHO(I,J)=(denl+deng)/2.d0-(denl-deng)/2.d0*temp1

```

```

else
  RHO(I,J)=1.e-8
endif

IF(S(I,J)==1) THEN
  FRF(I,J)=0.d0
  FR(I,J)=0.d0
ELSE
  FRF(I,J)=0.d0
  FR(I,J)=0.d0 ! solid phase volume
END IF

ENDDO
ENDDO

walls((nx+1)/2-rbase:(nx+1)/2+rbase,height+1)=.true.

OPEN(4,file='initialdensity.dat')
WRITE(4,*)'VARIABLES="X" "Y" "RHO"'
WRITE(4,*)'ZONE I=',NX,'J=',NY,'T=POINTS'
DO J=1,NY
DO I=1,NX
  if(s(I,J).eq.1) RHO(I,J)=0.d0
  WRITE(4,*) I,J,RHO(I,J)
ENDDO
ENDDO
CLOSE(4)

!-----
DO I=1,NX
DO J=1,NY
DO K=0,8
  Z1=CX(K)*UP(I,J)+CY(K)*VP(I,J)
  Z2=UP(I,J)**2.d0+VP(I,J)**2.d0
  F(K,I,J)=RHO(I,J)*WI(K)*(1.d0+3.d0*Z1+4.5d0*Z1**2.d0-1.5d0*Z2)
  FF(K,I,J)=F(K,I,J)
ENDDO
ENDDO
ENDDO

DO I=1,NX
DO J=1,NY
IF(s(I,J).eq.1) THEN
  DO K=1,8
    if(s(I+int(CX(K)),J+int(CY(K))).eq.0) FF(k,I,J)=FF(K,I+int(CX(K)),J+int(CY(K)))
  ENDDO
ENDIF
ENDDO
ENDDO

Volume_gap = 80d0
Volume_expansion=0.95d0
Volume_drop= 0d0

DO J= height+1,droplet_height-0.5d0+height
DO I= (nx+1)/2,NX
  IF (RHO(I,J)<(deng/2d0+denl/2d0)) THEN
    temp1 = I
    EXIT
  ENDDO
ENDIF
ENDDO
Volume_drop = Volume_drop + (temp1-(nx+1)/2-0.5)*(temp1-(nx+1)/2-0.5) *3.1415
ENDDO

Volume_ice = 0d0
Volume_ice2 = 0d0
Volume_ice_p = 0d0

```

```

Volume_water = Volume_drop - Volume_ice
ice_ratio = 0d0

END SUBROUTINE

!=====

SUBROUTINE Main_UV
  USE START_L
  implicit none
  double precision FIV
  double precision x
  double precision rhoav
  integer nrhoav
  FIV(X)=SQRT(2.d0*(X**RR*T/(1.d0-b*X)-a*x*x*(1.d0+(omega*(1.d0-sqrt(T/Tc))))**2.d0/(1.d0+2.d0*b*x-
b*b*x*x)-X/3.d0)/g11/c0)
! FIV(X)=SQRT(2.d0*(x**RR*T*(1.d0+b*x/4.d0+(b*x/4.d0)**2.d0-(b*x/4.d0)**3.d0)/(1.d0-b*x/4.d0)**3.d0-a*x**2.d0-
X/3.d0)/g11/c0)

!*****collision*****

      DO I=1,NX
        DO J=1,NY
!          FMEQ1(0)= RHO(I,J)
!          FMEQ1(1)= RHO(I,J)*(-2.0D0+3.0D0*(UP(I,J)**2+VP(I,J)**2))
!          FMEQ1(2)= RHO(I,J)*( 1.0D0-3.0D0*(UP(I,J)**2+VP(I,J)**2))
!          FMEQ1(3)= RHO(I,J)*UP(I,J)
!          FMEQ1(4)=-RHO(I,J)*UP(I,J)
!          FMEQ1(5)= RHO(I,J)*VP(I,J)
!          FMEQ1(6)=-RHO(I,J)*VP(I,J)
!          FMEQ1(7)= RHO(I,J)*(UP(I,J)**2-VP(I,J)**2)
!          FMEQ1(8)= RHO(I,J)*UP(I,J)*VP(I,J)

          IF (S(I,J)==0) THEN
!            visco = viscosity_l*abs(RHO(I,J)-deng)/(denl-deng)+viscosity_v*abs(denl-RHO(I,J))/(denl-deng)
!            if(RHO(I,J)>denl) visco = viscosity_l
!            if(RHO(I,J)<deng) visco = viscosity_v
!            tao_visco = visco*3.0d0 + 0.5d0
!            st(7)=1.d0/ tao_visco
!            st(8)=st(7)

            DO K=0,8
              Z1=CX(K)*UP(I,J)+CY(K)*VP(I,J)
              Z2=UP(I,J)*UP(I,J)+VP(I,J)*VP(I,J)
              FQ1=RHO(I,J)*Wi(K)*(1.d0+3.d0*Z1+4.5d0*Z1**2-1.5d0*Z2)
              FF(K,I,J)=(1.d0-1.d0/tao_visco)*F(K,I,J)+1.d0/tao_visco *FQ1 + FFORCE(K,I,J)
              IF(.not.Initial.and.RHO(I,J).ge.(deng/2d0+denl/2d0).and.Volume_water>0.1d0) then
                IF(FR(I,J)<0.5d0.and.Volume_water>Volume_gap) FF(K,I,J)=(1.d0-
1.d0/tao_visco)*F(K,I,J)+1.d0/tao_visco *FQ1 + FFORCE(K,I,J)+ Wi(K)*(Volume_ice-
Volume_ice_p)/Volume_water*(1d0-Volume_expansion)*RHO(I,J)
                IF(Volume_water<=Volume_gap) THEN
                  IF (BONDS(I,J).and.FR(I,J)<0.5d0.and.Volume_inter>=1d0) FF(K,I,J)=(1.d0-
1.d0/tao_visco)*F(K,I,J)+1.d0/tao_visco *FQ1 + FFORCE(K,I,J)+ Wi(K)*(Volume_water_p -
Volume_water)/Volume_inter *(1d0-Volume_expansion)*RHO(I,J)
                ENDIF
              ENDIF
            ENDDO

!          DO K=0,8
!            SUMM = 0d0
!            DO L=0,8
!              SUMM=SUMM+M(K,L)*F(L,I,J)
!            END DO
!            FM1(K)=SUMM
!            FFM1(K)=FM1(K)-st(K)*(FM1(K)-FMEQ1(K))+FFORCE(K,I,J)
!          ENDDO

```

```

!                                DO K=0,8
!                                SUMM = 0d0
!                                DO L=0,8
!                                SUMM = invM(K,L)*FFM1(L)+SUMM
!                                ENDDO
!                                FF(K,I,J)=SUMM
!                                ENDDO
!                                ENDDO
!                                ENDDO

FF(:,NX+1,:)=FF(:,1,:)
FF(:,0,:)=FF(:,NX,:)

DO I=1,NX
  DO J=1,NY
    IF(S(I,J)==1) THEN
      FF(1,I,J)=F(3,I,J)
      FF(3,I,J)=F(1,I,J)

      FF(2,I,J)=F(4,I,J)
      FF(4,I,J)=F(2,I,J)

      FF(5,I,J)=F(7,I,J)
      FF(7,I,J)=F(5,I,J)

      FF(6,I,J)=F(8,I,J)
      FF(8,I,J)=F(6,I,J)
    END IF
  END DO
END DO

DO I=1,NX
DO J=1,NY
  IF(FR(I,J)>=0.5d0.or.walls(i,j)) THEN
    FF(1,I,J)=F(3,I,J)
    FF(3,I,J)=F(1,I,J)

    FF(2,I,J)=F(4,I,J)
    FF(4,I,J)=F(2,I,J)

    FF(5,I,J)=F(7,I,J)
    FF(7,I,J)=F(5,I,J)

    FF(6,I,J)=F(8,I,J)
    FF(8,I,J)=F(6,I,J)
  END IF
END DO
END DO

DO I=1,NX
  DO J=1,NY
    DO K=0,8
      F(K,I,J)=FF(k,i-CX(k),j-CY(k))
    ENDDO
  ENDDO
ENDDO

DO I=0,NX+1
  F(4,i,NY)= FF(2,i,NY)
  F(7,i,NY)= FF(5,i,NY)
  F(8,i,NY)= FF(6,i,NY)
ENDDO

```

!-----MACROSCOPIC VARIABLES-----

```

DO I=1,NX
DO J=1,NY
IF (s(I,J).eq.0) THEN !
  IF (FR(I,J)<0.5d0.and..not.walls(i,j)) THEN
    RHO(I,J)=sum(F(:,I,J))
    U(I,J)=sum(F(:,I,J)*CX(:))
    V(I,J)=sum(F(:,I,J)*CY(:))
    U(I,J)=U(I,J)/(RHO(I,J)+1.e-30)
    V(I,J)=V(I,J)/(RHO(I,J)+1.e-30)
    IF (RHO(I,J) .le. 0) RHO(I,J)=1e-3
  ELSEIF (FR(I,J)>=0.5d0.or.walls(i,j)) THEN
    ! RHO(I,J)= 0d0
    U(I,J)= 0d0
    V(I,J)= 0d0
    UP(I,J)=0d0
    VP(I,J)=0d0
  ENDIF
ENDIF
ENDDO
ENDDO

RHO(0,:)=RHO(NX,:)
RHO(NX+1,:)=RHO(1,:)

!-----
Temperature(NX+1,:)=Temperature(1,:)
Temperature(0,:)=Temperature(NX,:)

DO I=1,NX
DO J=1,NY
  IF (s(I,J).eq.0) THEN ! .and.FR(I,J)<0.5d0 ! temperature variation, cohesive variation, phase
change
  t=ts
  tempF=4.d0*FIV(RHO(i+1,j))
  ! t=Temperature(i-1,j)
  tempF=tempF-4.d0*FIV(RHO(i-1,j))

  tempF=tempF*(1.d0-s(i-1,j))*(1.d0-s(i+1,j))
  ! if(FR(I-1,J)>=0.5d0.or.FR(I+1,J)>=0.5d0) tempF=0d0

  ! t=Temperature(i+1,j+1)
  tempf2=FIV(RHO(i+1,j+1))
  ! t=Temperature(i-1,j+1)
  tempf2=tempf2-FIV(RHO(i-1,j+1))

  tempf2=tempf2*(1.d0-s(i-1,j+1))*(1.d0-s(i+1,j+1))
  ! if(FR(i-1,j+1)>=0.5d0.or.FR(i+1,j+1)>=0.5d0) tempF2=0d0

  ! t=Temperature(i+1,j-1)
  tempf3=FIV(RHO(i+1,j-1))
  ! t=Temperature(i-1,j-1)
  tempf3=tempf3-FIV(RHO(i-1,j-1))
  tempf3=tempf3*(1.d0-s(i+1,j-1))*(1.d0-s(i-1,j-1))
  ! if(FR(i+1,j-1)>=0.5d0.or.FR(i-1,j-1)>=0.5d0) tempF3=0d0

  IF ( tempF .eq. 0 ) THEN
    tempf2=0.d0
    tempf3=0.d0
  ELSE
    IF (tempf2 .eq. 0 .and. tempf3 .ne. 0) tempf2=tempf3
    IF (tempf3 .eq. 0 .and. tempf2 .ne. 0) tempf3=tempf2
  ENDIF

  ! t=Temperature(I,J)
  SFORCEX1 = -g11*FIV(RHO(I,J))*(tempF+tempf2+tempf3)/12.d0

  ! t=Temperature(I,J+1)

```

```

tempF=4.d0*FIV(RHO(I,J+1))
! t=Temperature(I,J-1)
tempF=tempF-4.d0*FIV(RHO(I,J-1))
tempF=tempF*(1.d0-s(I,J+1))*(1.d0-s(I,J-1))
! if(FR(I,J+1)>=0.5d0.or.FR(I,J-1)>=0.5d0) tempF=0d0

! t=Temperature(i+1,j+1)
tempf2=FIV(RHO(i+1,j+1))
! t=Temperature(i+1,j-1)
tempf2=tempf2-FIV(RHO(i+1,j-1))
tempf2=tempf2*(1.d0-s(i+1,j+1))*(1.d0-s(i+1,j-1))
! if(FR(i+1,j+1)>=0.5d0.or.FR(i+1,j-1)>=0.5d0) tempf2=0d0

! t=Temperature(i-1,j+1)
tempf3=FIV(RHO(i-1,j+1))
! t=Temperature(i-1,j-1)
tempf3=tempf3-FIV(RHO(i-1,j-1))
tempf3=tempf3*(1.d0-s(i-1,j+1))*(1.d0-s(i-1,j-1))
! if(FR(i-1,j+1)>=0.5d0.or.FR(i-1,j-1)>=0.5d0) tempf3=0d0

IF ( tempF .eq. 0 ) THEN
    tempf2=0.d0
    tempf3=0.d0
ELSE
    IF ( tempf2 .eq. 0 .and. tempf3 .ne. 0 ) tempf2=tempf3
    IF ( tempf3 .eq. 0 .and. tempf2 .ne. 0 ) tempf3=tempf2
ENDIF

! t=Temperature(I,J)
SFORCEY1 = -g11*FIV(RHO(I,J))*(tempF+tempf2+tempf3)/12.d0

!-----adhesive force-----
! PHYSICAL REVIEW E 90, 053301 (2014)    Qing Li
if(J==height+1) then
    WFORCEX1=waf*FIV(RHO(I,J))*FIV(RHO(I,J))*(4.d0*S(I+1,J)-4.d0*S(I-1,J)+S(I+1,J+1)+S(I+1,J-1)-S(I-1,J-1)-
S(I-1,J+1))/12d0
    WFORCEY1=-waf*FIV(RHO(I,J))*FIV(RHO(I,J))*(4.d0*S(I,J+1)-4.d0*S(I,J-1)+S(I+1,J+1)+S(I-1,J+1)-S(I+1,J-
1)-S(I-1,J-1))/12d0
endif
!=====magnetic force=====

FORCEX = SFORCEX1 + WFORCEX1 !+BFORCEX1
FORCEY = SFORCEY1 + WFORCEY1 !+ RHO(i,j)*gravity !+BFORCEY1

IF(RHO(I,J)>(deng+denl)/2d0) then    !.not.Initial.and.

Dis = 0.006d0 - (J-height)*phydy

Hm = (B0 + B1*Dis + B2*Dis*Dis + B3*Dis**3 + B4*Dis**4 + B5 * Dis**5)*1D3
DH = (B1 + 2d0*B2*Dis + 3d0*B3*Dis*Dis + 4d0*B4*Dis*Dis*Dis + 5d0*B5*Dis*Dis*Dis*Dis)*1D3

epsilon = PI/6d0/Kb * miu0 * Mp * Hm * dia**3 / 273.15d0
Langevin= (exp(epsilon) + exp(-epsilon))/ (exp(epsilon) - exp(-epsilon)) - 1d0/epsilon

Ma = volume_c(J) * Mp * Langevin
Fm = -miu0 * Ma * DH

surface_tension = 0.0348d0
surface_tension_L = 0.16816d0

Bond_m = Fm * (Ri*phydx) * (Ri*phydx) / surface_tension

Fm_L = Bond_m * surface_tension_L / Ri/Ri

FORCEY = SFORCEY1 + WFORCEY1 - gravity + Fm_L

ENDIF

```

```

IF(BONDS2(I,J)) THEN
IF (I.ne.(nx+1)/2) then
  Angle=atan(dropbase*dropbase/(droplet_height)/(droplet_height)*(J-(height+1))/abs(I-(nx+1)/2))
  FORCEY = FORCEY + Mag_f*sin(angle)**3
  If(I>(nx+1)/2) FORCEX = FORCEX + Mag_f*sin(angle)**2*cos(angle)
  If(I<(nx+1)/2) FORCEX = FORCEX - Mag_f*sin(angle)**2*cos(angle)
ELSEif(I==(nx+1)/2) then
  FORCEY = FORCEY + Mag_f
ENDIF
ENDIF

UP(I,J) = U(I,J) + FORCEX*0.5D0/(RHO(I,J)+1e-30)
VP(I,J) = V(I,J) + FORCEY*0.5D0/(RHO(I,J)+1e-30)

!----- improved forcing scheme-----
! visco = viscosity_1*abs(RHO(I,J)-deng)/(denl-deng)+viscosity_v*abs(denl-RHO(I,J))/(denl-deng)
! if(RHO(I,J)>denl) visco = viscosity_1
! if(RHO(I,J)<denl) visco = viscosity_v
! tao_visco = visco*3.0d0+0.5d0
! st(7)=1.0d0/ tao_visco
! st(8)=st(7)

t= ts !Temperature(I,J)

SIKMA=0.105D0
UPM(I,J) = UP(I,J)+ SIKMA*FORCEX/(tao_visco -0.5d0)/(FIV(RHO(I,J))*FIV(RHO(I,J)))
VPM(I,J) = VP(I,J)+ SIKMA*FORCEY/(tao_visco -0.5d0)/(FIV(RHO(I,J))*FIV(RHO(I,J)))

DO K=0,8
temp1=CX(K)*UPM(I,J)+CY(K)*VPM(I,J)
temp3=CX(K)*FORCEX+CY(K)*FORCEY
temp4=UPM(I,J)*FORCEX+VPM(I,J)*FORCEY
FFORCE(K,I,J)=Wi(K)*(1.0D0-1.0D0/tao_visco/2.0D0)*(3.0d0*temp3+9.0d0*temp1*temp3-3.0d0*temp4)
ENDDO

! ADDF= 12D0*SIKMA*(SFORCEX1*SFORCEX1+SFORCEY1*SFORCEY1)/(1.0D0/st(1)-0.5D0) &
! /(FIV(RHO(I,J))*FIV(RHO(I,J)))
! ADDF2=-12D0*SIKMA*(SFORCEX1*SFORCEX1+SFORCEY1*SFORCEY1)/(1.0D0/st(2)-0.5D0)
&
! /(FIV(RHO(I,J))*FIV(RHO(I,J)))
! FFORCE(0,I,J) = 0D0
! FFORCE(1,I,J) = (1D0-st(1)/2.0D0)*(6D0*UP(I,J)*FORCEX + VP(I,J)*FORCEY + ADDF)
! FFORCE(2,I,J) = (1D0-st(2)/2.0D0)*(-6D0*UP(I,J)*FORCEX+ VP(I,J)*FORCEY + ADDF2)
! FFORCE(3,I,J) = (1D0-st(3)/2.0D0)*FORCEX
! FFORCE(4,I,J) =-(1D0-st(4)/2.0D0)*FORCEX
! FFORCE(5,I,J) = (1D0-st(5)/2.0D0)*FORCEY
! FFORCE(6,I,J) =-(1D0-st(6)/2.0D0)*FORCEY
! FFORCE(7,I,J) = 2D0*(1D0-st(7)/2.0D0)*(UP(I,J)*FORCEX-VP(I,J)*FORCEY)
! FFORCE(8,I,J) = (1D0-st(8)/2.0D0)*(UP(I,J)*FORCEY+VP(I,J)*FORCEX)

ENDIF
ENDDO
ENDDO

END SUBROUTINE

!=====

SUBROUTINE Volume_height

USE START_L
implicit none
double precision:: indis,nstep

I=(nx+1)/2
DO J=height+1,NY

```

```

        IF (RHO(I,J)<(deng/2d0+denl/2d0)) THEN
            temp1 = J
            EXIT
        END IF
    END DO
    droplet_height=J-1+(RHO(I,J-1)-(deng+denl)/2d0)/((RHO(I,J-1)-RHO(I,J))-height
    height_ratio = droplet_height/Ri

    J = 12
    DO I=(nx+1)/2,NY
        IF (RHO(I,J)<(deng/2d0+denl/2d0)) THEN
            temp1 = I
            EXIT
        END IF
    END DO
    dropbase= (temp1-(nx+1)/2-0.5d0)

    I=(nx+1)/2
    DO J=height+1,NY
        IF (FR(I,J)<0.5d0) THEN
            temp1 = J
            EXIT
        END IF
    END DO
    freezing_height= temp1-height-0.5d0

    Volume_ice_p = Volume_ice
    Volume_water_p = Volume_water
    Volume_drop_p = Volume_drop
    Volume_drop = 0d0

    volume_c=volume_f

!   if(.not.Initial) then
!       ratiot = 0d0
!       DO J = height+1,height+droplet_height
!           Dis = 0.006d0 -(J-height)*phydy
!           Hm = (B0 + B1*Dis + B2*Dis*Dis + B3*Dis**3 + B4*Dis**4 + B5 * Dis**5) * 1D3
!           ratio(J) = exp(epsilon0*(Hm-H0)- graE*(J-height)*phydy ) !
!           ratiot = ratiot + ratio(J)
!       ENDDO
!       n0 = volume_f*(droplet_height)/ratiot
!       volume_c=n0*ratio
!
!       open(10,file='conc.dat')
!       DO J=height+1,height+droplet_height
!           write(10,*) J,volume_c(J),volume_c(J)/volume_f
!       ENDDO
!       close(10)
!   endif

    ratiot = 0d0
    DO J= height+1,droplet_height-0.5d0+height
        DO I= (nx+1)/2,NX
            IF (RHO(I,J)<(deng/2d0+denl/2d0)) THEN
                temp1 = I
                EXIT
            ENDIF
        ENDDO
        Volume_drop = Volume_drop + (temp1-(nx+1)/2-0.5)*(temp1-(nx+1)/2-0.5) *3.1415

        Dis = 0.006d0 -(J-height)*phydy
        Hm = (B0 + B1*Dis + B2*Dis*Dis + B3*Dis**3 + B4*Dis**4 + B5 * Dis**5) * 1D3
        ratio(J) = exp(epsilon0*(Hm-H0)- graE*(J-height)*phydy ) !
        ratiot = ratiot + ratio(J)*(temp1-(nx+1)/2-0.5)*(temp1-(nx+1)/2-0.5) *3.1415
    ENDDO

```



```

if(.not.Initial) then

n0 = volume_f*Volume_drop/ratior
volume_c=n0*ratio

if(mod(iter,1000)==0) then
  open(10,file='conc.dat')
  DO J=height+1,height+droplet_height
    write(10,*) J,volume_c(J),volume_c(J)/volume_f
  ENDDO
  close(10)
endif

DO J=height+1,height+droplet_height
  if(volume_c(J)<volume_f) volume_c(J)=volume_f
  if(volume_c(J)>volume_f) then
    if(freezing_height<=7) then
      indis = 14+(freezing_height-7)/7.0*4
      nstep = 6
    elseif(freezing_height>7.and.freezing_height<=14) then
      indis = 18+(freezing_height-7)/7.0*4
      nstep = 6
    elseif(freezing_height>14.and.freezing_height<=21) then
      indis = 22+(freezing_height-14)/7.0*4
      nstep = 6
    elseif(freezing_height>21.and.freezing_height<=28) then
      indis = 26+(freezing_height-21)/7.0*5
      nstep = 6
    elseif(freezing_height>28.and.freezing_height<=35) then
      indis = 30+(freezing_height-28)/7.0*5
      nstep = 6
    elseif(freezing_height>35.and.freezing_height<=42) then
      indis = 35+(freezing_height-35)/7.0*5
      nstep = 6
    elseif(freezing_height>42) then
      indis = 40
      nstep = 6
    endif

    if(J-freezing_height-height-0.5d0-nstep>=0d0) volume_c(J)=volume_f+(volume_c(J)-volume_f)*exp(-(J-
freezing_height-height-0.5d0-nstep)/indis)

  endif
ENDDO

if(mod(iter,1000)==0) then
  open(10,file='conc_m.dat')
  DO J=height+1,height+droplet_height
    write(10,*) J,volume_c(J),volume_c(J)/volume_f
  ENDDO
  close(10)
endif

endif

Volume_water=0d0
DO J= freezing_height+0.5d0+height,droplet_height-0.5d0+height
DO I= (nx+1)/2,NX
  IF (RHO(I,J)<(deng/2d0+denl/2d0).or.FR(I,J)>=0.5d0) THEN
    temp1 = I
    EXIT
  ENDIF
ENDDO
Volume_water = Volume_water + (temp1-(nx+1)/2-0.5)*(temp1-(nx+1)/2-0.5) *3.1415
ENDDO

```

```

Volume_ice= Volume_drop-Volume_water

Volume_inter=0d0
IF(Volume_water<=Volume_gap) THEN
CALL BINEX
DO J= freezing_height+0.5d0+height,droplet_height+0.5d0+height
DO I= (nx+1)/2-Ri,(nx+1)/2+Ri
  IF (BONDS(I,J).and.RHO(I,J-1)>=(deng/2d0+denl/2d0).and.FR(I,J-1)<0.5d0) then !
    Volume_inter = Volume_inter + 1 !3.1415926*(2*(temp1-(nx+1)/2-0.5d0)-1)
  ENDIF
ENDDO
ENDDO

Volume_ice2_p = Volume_ice2

Volume_ice2=0

DO I=(NX+1)/2-Ri-10,(NX+1)/2+Ri+10
DO J= height+1,height+2*RI
  IF (RHO(I,J).ge.(deng/2d0+denl/2d0)) THEN
    Volume_ice2 = Volume_ice2 + FR(I,J)
  END IF
END DO
END DO
ENDIF

IF(iter>2000.and.Volume_drop<Volume_drop_p) Volume_drop = Volume_drop_p
IF(iter>2000.and.Volume_water>Volume_water_p) Volume_water = Volume_water_p
IF(iter>2000.and.Volume_ice<Volume_ice_p) Volume_ice = Volume_ice_p
IF(Volume_inter>Volume_water) Volume_inter=Volume_water
IF (Volume_water>1d0.and.Volume_inter == 0d0) Volume_inter = 1d0

ice_ratio = Volume_ice/Volume_drop

END SUBROUTINE
!=====
SUBROUTINE INIT_T
  USE START_L
  implicit none
  double precision sita
! ----- fluid property,NIST -----

  diff_ice_p = 1.19077967986185D-6 ! m2/s
  diff_w_p = 1.38552689812715D-7 ! m2/s effective
!   rhoice = 992.75d0 ! kg/m3

  diff_l = 0.14804d0/3d0
  diff_v = 0.38149d0/30d0
  diff_ice = diff_l * diff_ice_p/diff_w_p

  scale = diff_w_p / diff_l
  phydx = 2.5D-5 ! m
  phydy = phydx
  phydt = phydx * phydx / scale

  taofs_t = diff_ice*3d0 + 0.5d0 ! ice

  taos_t = 1.95d0 ! subtract

  lambda_i = 2.26368956301413d0
  lambda_w = 0.583426904848706d0

  rhocp_w = lambda_w/diff_w_p !4156.0018d0 * 1120d0
  rhocp_i = lambda_i/diff_ice_p !rhoice * cp_ice

  rhocp_v = rhocp_w/20d0

```

```

rhocp_su = rhocp_i * 10d0

diff_v_p = diff_w_p * diff_v / diff_l
diff_su_p = (taos_t-0.5d0)/3d0/diff_ice * diff_ice_p

lambda_v = rhocp_v * diff_v_p
lambda_su = rhocp_su * diff_su_p

TM = 273.15d0 !rit/Tscale      ! freezing temperature
LF = 334000d0*(1d0-0.018d0)    ! latent heat,J/Kg
CP = 4219d0      ! water specific heat, J/Kg/K
cp_ice = 2050d0    ! J/kg/K
! CP = cp_ice
ENS = cp_ice * TM      ! solid phase, enthalpy
ENL = CP * TM + LF      ! liquid phase, enthalpy

write(*,*) "taofs_t=",taofs_t,"LF=",LF,'ENS=',ENS,'ENL=',ENL
write(*,*) "lambda_i=",lambda_i,"lambda_w=",lambda_w,"lambda_v=",lambda_v,"lambda_su=",lambda_su
write(*,*) 'phydx=',phydx,'phydt=',phydt,'radius=',Ri*phydy

Tbottom(:)= 273.15d0 - 6d0

Tup = 273.15d0 + 22d0

do i=1,nx
do j=1,ny
  Temperature(i,j) = Tup
  if(s(i,j).eq.1) then
    Temperature(i,j) = 273.15d0 - 6d0
  else
    if(RHO(i,j)>(deng+denl)/2) Temperature(i,j) = 273.15d0
  endif
enddo
enddo

print*, 'Tup=',Tup
Temperature(:,NY)=Tup
Temperature(:,NY+1)=Tup
h=0.d0
hh=0.d0
do j=0,NY+1
do i=0,NX+1
do k=0,4
  ! Z1=CX(K)*UP(I,J)+CY(K)*VP(I,J)
  ! Z2=UP(I,J)**2d0+VP(I,J)**2d0
  heq=Temperature(I,J)*WIT(K) !*(1.d0+3.d0*Z1+4.5d0*Z1**2.d0-1.5d0*Z2)
  h(k,I,J)=heq
  hh(k,I,J)=heq
enddo
enddo
enddo

Pi=3.141592657
miu0=4d0*PI*1D-7 ! N/A2 , H/m
Mp=4.46*1D5      ! A/m
dia=1D-8          ! m

Kb = 1.381D-23
volume_f=0.018d0

m_case = 4

select case (m_case)
case (1) ! 2.6 A
  B0 = 83.2d0
  B1 = 21904.98d0

```

```

B2 = -1.32667D7
B3 = 2.632D9
B4 = -2.47885D11
B5 = 9.16493D12
case (2) ! 2.4 A
  B0 = 86.24d0
  B1 = 8463.4d0
  B2 = -6.7835d6
  B3 = 1.24D9
  B4 = -1.0545D11
  B5 = 3.5397D12
case (3) ! 2.1 A
  B0 = 72.73d0
  B1 = 11808.42d0
  B2 = -8.372D6
  B3 = 1.714D9
  B4 = -1.6838D11
  B5 = 6.5669D12
case (4) ! 1.8 A
  B0 = 66.27d0
  B1 = 5234.25d0
  B2 = -4.7397D6
  B3 = 8.968D8
  B4 = -8.12D10
  B5 = 3.001D12
case (5)! 1.5 A
  B0 = 53.42d0
  B1 = 7803.98d0
  B2 = -5.991D6
  B3 = 1.2746D9
  B4 = -1.28D11
  B5 = 4.9975D12
case (6)! 1.2 A
  B0 = 34.13d0
  B1 = 15760.15d0
  B2 = -8.785D6
  B3 = 1.818D9
  B4 = -1.8D11
  B5 = 6.964D12
case (7)! 0.9 A
  B0 = 34.58d0
  B1 = 757.83d0
  B2 = -1.497D6
  B3 = 2.554D8
  B4 = -2.037D10
  B5 = 6.825D11
case (8)! 0.6 A
  B0 = 23.958d0
  B1 = 139.74d0
  B2 = -1.125D6
  B3 = 2.486D8
  B4 = -2.554D10
  B5 = 1.031D12
case (9)! 0.4 A
  B0 = 12.379d0
  B1 = 4658.4d0
  B2 = -2.86D6
  B3 = 6.132D8
  B4 = -6.14D10
  B5 = 2.365D12
end select

Dis = 0.006d0

Hm = (B0 + B1*Dis + B2*Dis*Dis + B3*Dis**3 + B4*Dis**4 + B5 * Dis**5)*1D3
DH = (B1 + 2d0*B2*Dis + 3d0*B3*Dis*Dis + 4d0*B4*Dis*Dis*Dis + 5d0*B5*Dis*Dis*Dis*Dis)*1D3

```

```

epsilon = PI/6d0/Kb * miu0 * Mp * Hm * dia**3 / 273.15d0
Langevin= (exp(epsilon) + exp(-epsilon))/(exp(epsilon) - exp(-epsilon)) - 1d0/epsilon

Ma = volume_f * Mp * Langevin
Fm = -miu0 * Ma * DH

surface_tension = 0.0348d0
surface_tension_L = 0.16816d0

Bond_m = Fm * (Ri*phydx) * (Ri*phydx) / surface_tension
Bond_ma = 0.5d0*miu0*Ma*Ma*(Ri*phydx) / surface_tension

mag_f = Bond_ma* surface_tension_L /Ri
Fm_L = Bond_m * surface_tension_L /Ri/Ri

gravity = Fm_L/Fm *(1120d0*9.8d0)

epsilon0 = PI/6d0/Kb * miu0 * Mp * dia**3 / 273.15d0

Dis0 = 0.006d0
H0 = (B0 + B1*Dis0 + B2*Dis0*Dis0 + B3*Dis0**3 + B4*Dis0**4 + B5 * Dis0**5) * 1D3

graE = 5180 * PI/6d0/Kb * dia**3/ 273.15d0 *9.8d0

Print*,Fm=',Fm,'Bond_m =',Bond_m,'Bond_ma=',Bond_ma,'gravity=',gravity
Print*,H0 =',H0,'epsilon0 = ',epsilon0,'graE =',graE

open(1,file='case.txt')
write(1,*) "LF=",LF,'ENS=',ENS,'ENL=',ENL
write(1,*) 'height0=',height0
write(1,*) "taofs_t=",taofs_t,"taos_t=",taos_t
write(1,*) "lambda_i=",lambda_i,"lambda_w=",lambda_w,"lambda_v=",lambda_v,"lambda_su=",lambda_su
write(1,*) "diff_ice_p=",diff_ice_p,"diff_w_p=",diff_w_p,"diff_v_p=",diff_v_p,"diff_su_p=",diff_su_p
write(1,*) "rhocp_w=",rhocp_w,"rhocp_i=",rhocp_i,"rhocp_v=",rhocp_v,"rhocp_su=",rhocp_su
write(1,*) 'phydx=',phydx,'phydt=',phydt,'radius=',Ri*phydy
write(1,*) 'Hm=',Hm,'Bond_m =',Bond_m,'Fm_L=',Fm_L,'Bond_ma =',Bond_ma
close(1)

END SUBROUTINE

!=====

SUBROUTINE Main_T

USE START_L
CALL MELT_FRONT
CALL COLLISION
CALL STREAM
CALL LBM_BOUNDARY

END SUBROUTINE

!=====

SUBROUTINE MICROSTRUCTURE
USE START_L

s=0
height=4
s(:,1:height)=1

open(10,file="InitialZone.dat")
write(10,*)"VARIABLES="X" "Y" "S" '
write(10,*)"ZONE I=',NX,'J=',NY,'T=POINTS'
do J=1,NY
do I=1,NX
write(10,*) I, J, s(I,J)

```

```

enddo
enddo
close(10)
RETURN

```

END SUBROUTINE

```

!*****

```

SUBROUTINE COLLISION

USE START_L

implicit none

double precision::diff_fs

CALL SOURCE

```

do j=1,NY
do i=1,NX
do k=0,4
!  Z1=CX(K)*UP(I,J)+CY(K)*VP(I,J)
!  Z2=UP(I,J)*UP(I,J)+VP(I,J)*VP(I,J)
    heq=Temperature(I,J)*WIT(K) !*(1.d0+3.d0*Z1+4.5d0*Z1**2.d0-1.5d0*Z2)
if(s(I,J).eq.0) then
if(FR(I,J)<0.001d0) then
if (RHO(I,J)>(deng+denl)/2d0) diff_fs= diff_l
if (RHO(I,J)<(deng+denl)/2d0) diff_fs= diff_v
taof_t = diff_fs*3d0 + 0.5d0
hh(k,I,J)=h(k,I,J)-1.d0/taof_t*(h(k,I,J)-heq) + (LF/cp_ice*(FR(I,J)-FRF(I,J)))*WIT(k) !+ tsor(I,J)*WIT(k)*phydt
else
hh(k,I,J)=h(k,I,J)-1.d0/taofs_t*(h(k,I,J)-heq)+ LF/cp_ice*(FR(I,J)-FRF(I,J))*WIT(k) !+ tsor(I,J)*WI(k)*phydt
endif

elseif(s(I,J).eq.1) then
hh(k,I,J)=h(k,I,J)-1.d0/taos_t*(h(k,I,J)-heq) !+dt*tsor(I,J)*WI(k)
endif
enddo
enddo
enddo

DO I=1,NX
DO J=1,NY
    FRF(I,J)=FR(I,J)
END DO
END DO

```

END SUBROUTINE

```

!*****

```

SUBROUTINE SOURCE

USE START_L

implicit none

double precision,DIMENSION(0:NX+1,0:NY+1)::consor,pcsor !=== consor is the source term of conjugate, pcsor is the source tem for phase change

double precision:: XdU,YdV ! calculate partial derivative and Laplace

double precision,dimension(0:NX+1,0:NY+1)::lamda

double precision px1,py1,Dpt0,Dpt1,Dpt2,sadd_y,sadd_x,saddu_x,saddv_y,rho_avg_y,rho_avg_x

do j=0,NY+1

do i=0,NX+1

if(s(I,J).eq.0) then

if(RHO(I,J)>(deng+denl)/2d0) then

rhocp(I,J) = rhocp_w !*abs(RHO(I,J)-deng)/(denl-deng) + rhocp_v*abs(denl-RHO(i,j))/(denl-deng)

lamda(I,J) = lamda_w !*abs(RHO(I,J)-deng)/(denl-deng)+ lamda_v*abs(denl-RHO(i,j))/(denl-deng)

else

rhocp(I,J) = rhocp_v

lamda(I,J) = lamda_v

endif

```

        if(FR(I,J)>=0.001d0) then
            rhocp(I,J) = rhocp_i
            lamda(I,J) = lambda_i
        endif
    else
        rhocp(I,J) = rhocp_su
        lamda(I,J)= lambda_su
    endif
enddo
enddo

! ----- (Calculation of fluid-solid coupled heat transfer problems, variable density problems) -----
-----
! consor=0.d0
! do j=height+1,NY-1
! do i=1,(NX+1)/2-1
!     rho_avg_y = (rhocp(i,j+1)+rhocp(I,J))/2.0d0
!     rho_avg_x = (rhocp(I+1,J)+rhocp(I,J))/2.0d0
!     sadd_y= (1.0d0/rho_avg_y-1.0d0/rhocp(I,J))*2.0d0/phydy
!     sadd_x= (1.0d0/rho_avg_x-1.0d0/rhocp(I,J))*2.0d0/phydx
!     px1=(-lamda(I,J)*(GRAD(Temperature,I,J,0)))*sadd_x
!     py1=(-lamda(I,J)*(GRAD(Temperature,I,J,1)))*sadd_y
!     tsor(I,J)=px1+py1
! enddo
! enddo
!
! do j=height+1,NY-1
! do i=(NX+1)/2+1,NX
!     rho_avg_y = (rhocp(i,j+1)+rhocp(I,J))/2.0d0
!     rho_avg_x = (rhocp(I-1,J)+rhocp(I,J))/2.0d0
!     sadd_y= (1.0d0/rho_avg_y-1.0d0/rhocp(I,J))*2.0d0/phydy
!     sadd_x= (1.0d0/rhocp(I,J)-1.0d0/rho_avg_x)*2.0d0/phydx
!     px1=(-lamda(I,J)*(GRAD(Temperature,I,J,0)))* sadd_x
!     py1=(-lamda(I,J)*(GRAD(Temperature,I,J,1)))* sadd_y
!     tsor(I,J)=px1+py1
! enddo
! enddo
!
! I=(NX+1)/2
! do j=height+1,NY-1
!     rho_avg_y = (rhocp(i,j+1)+rhocp(I,J))/2.0d0
!     sadd_y= (1.0d0/rho_avg_y-1.0d0/rhocp(I,J))*2.0d0/phydy
!     py1=(-lamda(I,J)*(GRAD(Temperature,I,J,1)))* sadd_y
!     tsor(I,J)=py1
! enddo
!
!=====calculate PpPT=Dpt0+Dpt1*Dpt2 =====!
! do J=1,NY
! do I=1,NX
!     XdU=GRAD(UP,I,J,0)
!     YdV=GRAD(VP,I,J,1)
!     if(s(I,J).eq.0) then
!         Dpt0=RHO(I,J)*RR/(1.0d0-b*RHO(I,J))
!         Dpt1=-A*RHO(I,J)*RHO(I,J)/(1.0d0+2.0d0*B*RHO(I,J)-B*B*RHO(I,J)*RHO(I,J))
!         Dpt2=-omega*(1.0d0+omega*(1.0d0-sqrt(Temperature(I,J)/tc)))/sqrt(Temperature(I,J)*tc)
!         pcsor(I,J)=(1.0d0-(Dpt0+Dpt1*Dpt2)/rhocp(I,J))*Temperature(I,J)*(XdU+YdV)
!     else
!         consor(I,J)=0
!         pcsor(I,J)=0.d0      !===== No phase change source term in the solid region =====
!     endif
! enddo
! enddo
! tsor=consor

```

CONTAINS

```

Double precision function GRAD(VAR,TTI,TTJ,DMARK)
  double precision,DIMENSION(0:NX+1,0:NY+1)::VAR
  INTEGER*4::TTI,TTJ
  INTEGER::DMARK
  DOUBLE PRECISION::TEMPGRAD
  INTEGER::KK

  SELECT CASE(DMARK)
  CASE (0)
    IF(TTI/=1.AND.TTI/=NX) THEN
      ! GRAD=(VAR(TTI+1,TTJ)-VAR(TTI-1,TTJ))/3.d0+(VAR(TTI+1,TTJ+1)-VAR(TTI-1,TTJ-
1))/12.d0+(VAR(TTI+1,TTJ-1)-VAR(TTI-1,TTJ+1))/12.d0
      GRAD=(VAR(TTI+1,TTJ)-VAR(TTI-1,TTJ))/phydx/2.d0
    ELSE IF (TTI==1) THEN
      GRAD=(var(2,ttj)-var(NX,ttj))/phydx/2.d0
    ELSE IF (TTI==NX) THEN
      GRAD=(var(1,ttj)-var(NX-1,ttj))/phydx/2.d0
    END IF
  CASE (1)
    IF (TTJ/=1.AND.TTJ/=NY) THEN
      ! GRAD=(VAR(TTI,TTJ+1)-VAR(TTI,TTJ-1))/3.d0+(VAR(TTI+1,TTJ+1)-VAR(TTI-1,TTJ-
1))/12.d0+(VAR(TTI-1,TTJ+1)-VAR(TTI+1,TTJ-1))/12.d0
      GRAD=(VAR(TTI,TTJ+1)-VAR(TTI,TTJ-1))/phydy/2.d0
    ELSE IF (TTJ==1) THEN
      GRAD=(VAR(TTI,TTJ+1)-VAR(TTI,TTJ))/phydy
    ELSE IF (TTJ==NY) THEN
      GRAD=(VAR(TTI,TTJ)-VAR(TTI,TTJ-1))/phydy
    END IF
  END SELECT
  RETURN
END FUNCTION

```

END SUBROUTINE

```

!=====
SUBROUTINE STREAM
  USE START_L

```

```

  hh(:,0,:)=hh(:,NX,:)
  hh(:,NX+1,:)=hh(:,1,:)

```

```

  do j=1,NY
  do i=1,NX
  do k=0,4
    h(k,I,J)=hh(k,i-CX(K),j-CY(K))
  enddo
  enddo
  enddo

```

```

  DO I=1,NX
  DO J=1,NY-1
    dratio= rhocp(I,J)/rhocp(I,J+1)

```

```

    h(2,I,J+1)=(1d0-dratio)/(1d0+dratio)*hh(4,I,J+1)+2d0*dratio/(1d0+dratio)*hh(2,I,J)
    ! h(5,I,J+1)=(1d0-dratio)/(1d0+dratio)*hh(7,I,J+1)+2d0*dratio/(1d0+dratio)*hh(5,I,J)
    ! h(6,I,J+1)=(1d0-dratio)/(1d0+dratio)*hh(8,I,J+1)+2d0*dratio/(1d0+dratio)*hh(6,I,J)

```

```

    h(4,I,J)=-(1d0-dratio)/(1d0+dratio)*hh(2,I,J)+2d0/(1d0+dratio)*hh(4,I,J+1)
    ! h(7,I,J)=-(1d0-dratio)/(1d0+dratio)*hh(5,I,J)+2d0/(1d0+dratio)*hh(7,I,J+1)
    ! h(8,I,J)=-(1d0-dratio)/(1d0+dratio)*hh(6,I,J)+2d0/(1d0+dratio)*hh(8,I,J+1)

```

```

    dratio= rhocp(I,J)/rhocp(I+1,J)
    h(1,I+1,J)=(1d0-dratio)/(1d0+dratio)*hh(3,I+1,J)+2d0*dratio/(1d0+dratio)*hh(1,I,J)
    ! h(5,I+1,J)=(1d0-dratio)/(1d0+dratio)*hh(7,I+1,J)+2d0*dratio/(1d0+dratio)*hh(5,I,J)
    ! h(8,I+1,J)=(1d0-dratio)/(1d0+dratio)*hh(6,I+1,J)+2d0*dratio/(1d0+dratio)*hh(8,I,J)

```

```

    h(3,I,J)=-(1d0-dratio)/(1d0+dratio)*hh(1,I,J)+2d0/(1d0+dratio)*hh(3,I+1,J)

```



```

!      h(6,I,J)=-(1d0-dratio)/(1d0+dratio)*hh(8,I,J)+2d0/(1d0+dratio)*hh(6,I+1,J)
!      h(7,I,J)=-(1d0-dratio)/(1d0+dratio)*hh(5,I,J)+2d0/(1d0+dratio)*hh(7,I+1,J)

ENDDO
ENDDO

RETURN
END SUBROUTINE

!=====

SUBROUTINE LBM_BOUNDARY
  USE START_L
  implicit none
  double precision heq1,heq2,dratio

!----- Lower boundary-----
  do i=1,NX
    Temperature(i,1)=Tbottom(i)
  enddo

  do i=1,NX
    Z1=0.d0
    Z2=0.d0
    heq1=Temperature(I,1)*WIT(2) !*(1.d0+3.d0*Z1+4.5d0*Z1**2.d0-1.5d0*Z2)
    h(2,i,1)=heq1 !-hh(4,i,2)
!    heq1=Temperature(I,1)*WIT(5) !*(1.d0+3.d0*Z1+4.5d0*Z1**2.d0-1.5d0*Z2)
!    h(5,i,1)=heq1 !-hh(7,i,2)
!    heq1=Temperature(I,1)*WIT(6) !*(1.d0+3.d0*Z1+4.5d0*Z1**2.d0-1.5d0*Z2)
!    h(6,i,1)=heq1 !-hh(8,i,2)
  enddo

!----- Upper boundary -----
  DO I=1,NX
    Temperature(i,NY)= Tup
!    Z1=CX(4)*UP(I,NY-1)+CY(4)*VP(I,NY-1)
!    Z2=UP(I,NY-1)**2.+VP(I,NY-1)**2.
    h(4,I,NY)=Temperature(i,NY)*WIT(4) !*(1.d0+3.d0*Z1+4.5d0*Z1**2.-1.5d0*Z2) !+h(4,I,NY-1)-Temperature(I,NY-1)*WI(4)*(1.d0+3.d0*Z1+4.5d0*Z1**2.-1.5d0*Z2)

!    Z1=CX(7)*UP(I,NY-1)+CY(7)*VP(I,NY-1)
!    Z2=UP(I,NY-1)**2.+VP(I,NY-1)**2.
!    h(7,I,NY)=Temperature(i,NY)*WIT(7) !*(1.d0+3.d0*Z1+4.5d0*Z1**2.-1.5d0*Z2) !+h(7,I,NY-1)-Temperature(I,NY-1)*WI(7)*(1.d0+3.d0*Z1+4.5d0*Z1**2.-1.5d0*Z2)

!    Z1=CX(8)*UP(I,NY-1)+CY(8)*VP(I,NY-1)
!    Z2=UP(I,NY-1)**2.+VP(I,NY-1)**2.
!    h(8,I,NY)=Temperature(i,NY)*WIT(8) !*(1.d0+3.d0*Z1+4.5d0*Z1**2.-1.5d0*Z2) !+h(8,I,NY-1)-Temperature(I,NY-1)*WI(8)*(1.d0+3.d0*Z1+4.5d0*Z1**2.-1.5d0*Z2)
  ENDDO

!=====conjugate heat transfer=====
! DO I=1,NX
!   if (FR(I,height+1)<0.5d0) then
!     dratio= rhocp_su/rhocp(I,height+1)
!   else
!     dratio= rhocp_su/rhocp_i
!   endif
!   h(2,I,height+1)=(1d0-dratio)/(1d0+dratio)*hh(4,I,height+1)+2d0*dratio/(1d0+dratio)*hh(2,I,height)
!   h(5,I,height+1)=(1d0-dratio)/(1d0+dratio)*hh(7,I,height+1)+2d0*dratio/(1d0+dratio)*hh(5,I,height)
!   h(6,I,height+1)=(1d0-dratio)/(1d0+dratio)*hh(8,I,height+1)+2d0*dratio/(1d0+dratio)*hh(6,I,height)
!
!   h(4,I,height)=-(1d0-dratio)/(1d0+dratio)*hh(2,I,height)+2d0/(1d0+dratio)*hh(4,I,height+1)
!   h(7,I,height)=-(1d0-dratio)/(1d0+dratio)*hh(5,I,height)+2d0/(1d0+dratio)*hh(7,I,height+1)
!   h(8,I,height)=-(1d0-dratio)/(1d0+dratio)*hh(6,I,height)+2d0/(1d0+dratio)*hh(8,I,height+1)
! ENDDO

```

```

do j=1,NY
do i=1,NX
    Temperature(I,J)=sum(h(:,I,J))
enddo
enddo

do i=1,NX
    Temperature(i,1)=Tbottom(i)
enddo

RETURN
END SUBROUTINE

!=====

SUBROUTINE MELT_FRONT
USE START_L
IMPLICIT NONE

DO I=1,NX
    DO J=1,NY
        IF(S(I,J)==0) THEN
            EN(I,J)= FRF(I,J)*cp_ice*Temperature(I,J)+ (1d0-FRF(I,J))*CP*Temperature(I,J)+ LF*(1d0-FRF(I,J)) ! enthalpy
        ENDIF
    END DO
END DO

DO I=1,NX
    DO J=1,NY
        IF(S(I,J)==0) THEN
            IF(RHO(I,J)>=(denl+deng)/2d0) THEN
                IF(EN(I,J)>ENL) FR(I,J)=0.d0 ! liquid phase
                IF(EN(I,J)>=ENS.AND.EN(I,J)<=ENL) FR(I,J)=(ENL-EN(I,J))/(ENL-ENS) ! solid,liquid phase coexist
                IF(EN(I,J)<ENS) FR(I,J)=1.d0 ! solid phase
            ENDIF
        ENDIF
    END DO
END DO

END SUBROUTINE

!=====

SUBROUTINE BINEX
USE START_L
BONDS=.FALSE.

DO J=2,ny-1
DO I=2,nx-1
    IF(RHO(I,J)<(deng+denl)/2) THEN
        IF( RHO(I+1,J)>=(deng+denl)/2 .OR. RHO(I-1,J)>=(deng+denl)/2 .OR. RHO(I,J-1)>=(deng+denl)/2 .OR.
        RHO(I,J+1)>=(deng+denl)/2 ) BONDS(I,J)=.TRUE.
    ENDIF
ENDDO
ENDDO

RETURN
END SUBROUTINE

!=====
SUBROUTINE BINEX2
USE START_L
BONDS2=.FALSE.

DO J=height+2,ny-1
DO I=2,nx-1

```

```
IF(RHO(I,J)>(deng+denl)/2) THEN
  IF( RHO(I+1,J)<=(deng+denl)/2 .OR. RHO(I-1,J)<=(deng+denl)/2 .OR. RHO(I,J-1)<=(deng+denl)/2 .OR.
RHO(I,J+1)<=(deng+denl)/2 ) BONDS2(I,J)=.TRUE.
  ENDIF
ENDDO
ENDDO

RETURN
END SUBROUTINE
```

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