



Real space study of pattern formation in freezing colloidal suspensions

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“My life amounts to no more than one drop in a limitless ocean. Yet what is any ocean, but a multitude of drops?”

Abstract

We investigate the interaction of colloidal particles with ice–water interfaces. To this end, the experimental setup we use consists of a directional solidification stage, a light microscope, and thin sample cells, which allows for the possibility of particles to be viewed at the single particle level, and thermally in two dimensions (2D). First, the interaction of single particles with a moving ice–water interface is studied. We show that speed, ice growth facets and grain boundaries are important parameters in determining the way in which particles are incorporated into the ice. Secondly, once a particle is trapped, as long as it is not too cold, it is still free to move. This is due to the presence of premelted liquid trapped within the ice, surrounding the particles in a thin layer. Particle movement is measured by use of tracking algorithms, and related to theoretical predictions, which use a balance between a thermomolecular and a viscous force to describe the motion. The extracted premelted layer thickness and its dependence on the undercooling implies that for the particle–ice system, non-retarded van der Waals interactions dominate. However, we find that the forces in the model should be modified for particles trapped in grain boundaries, and along cellular instabilities, or if impurities are present. Thirdly, the thermomolecular motion is also key to understanding how segregated ice, ice which is devoid of particles, can form in concentrated suspensions of particles, where the pore space between particles can also stay liquid below the bulk melting temperature. We study segregated ice growth both at the macroscopic scale and at the particle level. Regular ice lenses form in a regime defined by the temperature gradient and cooling rate, and these formations cause large structural changes in freezing colloidal suspensions. We explore how changing conditions such as the packing, size, shape and polydispersity of the particles, and the impurity concentration affect this process. Finally, due to the confinement of the system, the particles are in quasi 2D, whereas the ice–water system is in 3D. Consequently, we investigate the ice–water meniscus in 3D, both theoretically and experimentally using laser scanning confocal microscopy. The capillary length we measure is of the order of a colloidal particle.

Declaration

This thesis is submitted for the degree of Doctor of Philosophy in Physical and Theoretical Chemistry at the University of Oxford. No part of this thesis has been accepted or is currently being submitted for any degree, diploma, certificate or other qualification in this University or elsewhere. This thesis is wholly my own work, except where indicated.

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Chapter 1

Introduction

1.1 Motivation

The Earth’s current climate allows for ice, water and water vapour to coexist on the surface and in the atmosphere. Water surrounds the globe in its oceans, but this water freezes at its poles. On land, water also freezes, forming land masses covered by ice sheets (Antarctica and Greenland), or partially covered by ice, depending on weather and altitude (everywhere else). The ice on Earth plays a critical role in the climate system. In recent times, the decline of land-based ice is hypothesised to occur as a consequence of global warming; this contributes to sea level rise [1]. In the opposing climate extreme, glacial periods have seen ice covering much of the surface of the earth [2]. Extra-terrestrial ice also exists, and with advances in space travel, it has been sampled by tools on the ground, notably, recently on comet 67P by the Philae lander [3]. Last year, its journey captured the imaginations of many people, while social media documented its progress and discoveries [4]. On bodies in space, such as comets, which are described as “dirty snowballs” [5], and planets, for example Mars [6, 7], we may investigate the role these ice–water mixtures played in the early evolution of life, and explore planet habitability for extra-terrestrial life [8, 9].

The ice on Earth also holds the key to understanding past climates [10, 11]. It traps gas bubbles [12], particles of mineral dust [13–16] and dissolved impurities [17] such as organic molecules [18] in layers of snow which over the years get packed by the layers forming above

it. Scientists have looked back $\sim 130,000$ years in Greenland [19] and $\sim 800,000$ years in Antarctica [16], by drilling ice cores several kilometres deep. Bubbles and dust are preservations of the climate at a given depth, which is related to a given time in the past, and they contain information about the composition of the atmosphere, like the amounts of methane and carbon dioxide [12], desert dust [16], and species of micro-organisms [20]. Additionally, the reflectivity of surface ice decreases in the presence of dissolved particles, and consequently this has global warming effects [21].

Common, everyday experiences with ice may be the symmetry and pattern of snowflakes, as well as their stickiness and ability to form snowballs of ice. The hexagonal microscopic structure of water molecules arranged in a crystal lattice [22, 23], and their morphologically unstable, diffusion-limited and unpredictable growth [24, 25], explains why snowflakes are shaped the way they are, as well as causing their uniqueness [26]. The ability to combine snowflakes together has been attributed to a layer of water on the surface of ice, which has been found to exist at temperatures below the bulk melting temperature. These are what are called ‘premelted liquid layers’, and they are understood to have consequences for many physical processes [8, 27]. The energetic cost of forming liquid below the bulk melting temperature is paid for by a reduction in surface free energy of the system, and the review by Dash *et al.* [8] highlights experimental evidence that confirms its existence. An important feature is that the premelted layer thickness is a function of temperature below the bulk melting temperature. Overheating of crystals, above this temperature, is not possible as the crystal fully converts to the liquid state. The absence of this behaviour is explained by considering that melting occurs at free surfaces below the bulk melting temperature, and therefore the solid immediately becomes liquid at this temperature [28]. Experimental evidence backs up the theoretical concepts surrounding premelted layers. For example, by the detection of surface disorder on ice using direct methods (x-ray reflectivity) [29], or the application of the concept to describe segregated ice growth (pure ice formed after having rejected particles) [30]. The latter effect depends on surface premelting occurring not at the interface between ice and its vapour phase, but between ice and a foreign substrate (the particle).

The thesis deals with the behaviour of systems of particles, suspended in water and ice, and held at a temperature close to the melting point, where premelting against particle surfaces occurs. The relevance of this system is clear, by the comparison we can make with it and what we find in the environment and in technology. Hence, particles synthesised in the laboratory

may be used as a model system, and their behaviour related to processes in the wider world.

Below, we break down the title of this thesis into two parts, ‘freezing colloidal suspensions’ and ‘pattern formation’, explaining first what they are, then how they are relevant to our investigation.

1.1.1 Freezing colloidal suspensions

Colloidal particles have lengthscales from nanometres (10^{-9} m) to several micrometres (10^{-6} m), and they can be made of many different materials and in a huge diversity of shapes [31]. They are dispersed in a solvent, such as water, where they are subject to thermal fluctuations, leading to Brownian motion, which was originally described in [32]. Colloidal dispersions have a wide range of applications, they are: directly contained in materials such as paints, food and personal care products; used as a model system for atomic or molecular systems to study the fundamental physics of phase transitions [33]. The specific system of freezing colloidal suspensions refers to the solidification of the solvent in which the particles are dispersed, or suspended. Solid–liquid interfaces interact with colloidal particles in many interesting ways. In this thesis, we only deal with solvents of water, or water containing other dissolved impurities, besides the particles.

Applications of this model system span as broadly as natural processes such as heaving ground, to the refrigerating of edible materials [34–36]. The mechanism of ground heave, specifically named ‘frost heave’, is caused by the suction of water along a temperature gradient, from warm to cold, where the coldest region, at surface layer, is frozen, but liquid water is present underneath in soils and rocks. Damage caused by this process results in pot holes in roads, bent ‘drunken’ forests, and many ground shapes and patterns [37, 38]. The frost heave process has inspired a host of physicists, engineers and mathematicians to try to explain the phenomenon [37, 39–44]. The damage is mainly as a result of the formation of regularly spaced ‘ice lenses’, macroscopic regions of nearly pure, segregated ice that are formed from the displaced water, moved by cryosuction, as depicted in figure 1.1. Two distinct frozen regions occur, the ice in the ice lenses, which is free of particles, and the ice between the particles, which are left between the ice lenses. When and where this interstitial water freezes is one of our topics of examination.

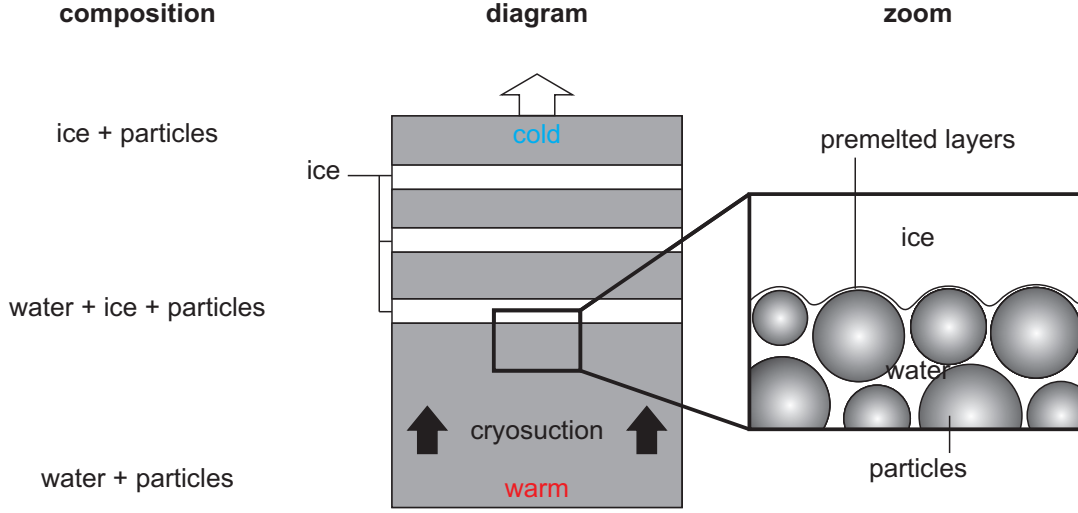


Figure 1.1: Schematic diagram showing the process of frost heave. Ice lenses (pure ice) form in a particle suspension where a temperature gradient acts. It is cooled by removing heat in the direction shown by the white arrow, and cryosuction occurs in the direction shown by the black arrows, while ice lenses grow in the opposite direction. The left hand side shows the changing composition of the grey phase, though the exact boundaries are debated. The right hand side shows a zoom of the interfacial area.

The interfaces formed in a freezing colloidal suspension are ubiquitous. Between particles and the bulk ice–water interface, a close up of the interfacial region, as depicted in figure 1.1, will show that layers of water prevent the particle from actually touching the ice. This thesis will study the consequences of these interfacial layers. A description of the flow in the water layer leads to predictions for single particle rejection, and for segregated ice growth in concentrated particle suspensions, such as in frost heave. Up to a given strength of undercooling, these interfaces between the particle, water, and surrounding ice, still exist when the particle is totally engulfed by the ice. Flow can still occur in the film, provided a temperature gradient acts to induce it. This is called ‘temperature gradient migration’, or ‘regelation’ of particles [45, 46], but the term regelation can also be used to describe ice crystal sintering [47]. Here, we will use it for the former.

1.1.2 Pattern formation: looking in real space

We define pattern formation as the phenomena of a systematic repeat of spacial elements. This occurs in our system as a consequence of the physical processes involved. The patterns referred to could be the positions of trapped particles within the ice after a degree of rejection and then engulfment, or macroscopic regions of ice formed during frost heave. Segregated ice can be of

the form of ice lenses during slow cooling in frost heave, or the unstable growth which occurs during fast cooling, leading to segregation of particles from cellular ice [48].

In this thesis, we observe these patterns by looking in real space. This term refers to accessibility of the technique of optical microscopy to observe colloidal particles. As well as this, the ice–water interface itself can be seen using a normal light microscope for dilute systems. The opportunity to use microscopy to probe a model system offers several advantages. The forces on a particle can be directly measured by measuring resultant velocities of both ice and particles. This is crucial to understanding regelation, the motion of particles through ice, or the critical speed of ice before particles stop being rejected by the ice–water interface, and start being incorporated into the ice. By the use of image analysis techniques to track particles, and track the ice–water interface, the premelted layer thickness can also be estimated. The final thickness and spacing of ice lenses can also be measured, as well as their growth rates.

1.2 Scope of the thesis

The theoretical background and experimental methods used in this work are presented in chapter 2. Premelting in its various forms is the main theoretical topic for discussion. We also show how instabilities in the ice–water interface can grow, after ice nucleation, as well as introducing the thermomolecular pressure gradient, caused by a reduction in temperature. The experimental setup revolves around cooling a sample in a controlled way. We describe the stage, with thermal components, the microscope, and the colloidal particle systems. The temperature gradient between the plates is an important parameter, and we show how we calibrate the instrument, and calculate the limitations on the thermal properties. We describe how sample cells, capable of confining the particles in 2D, are created, in order to be able to see colloidal particles in real space.

We start by studying the simplest model system in chapter 3, in which single particles interact with ice close to the melting temperature. Current theoretical understanding, with regards to engulfment and regelation, is discussed in greater detail, by considering the two opposing forces involved. Experimentally, we start by observing just the ice growth in the system, before moving on to looking at the single particle level. The interactions with colloidal particles in suspension with a moving ice–water interface are described. Some quantitative

measurements are taken. We then explore how the movement of particles can occur within the ice in the process called ‘regelation’. Particle velocities are measured, and these will be used to estimate the premelted layer thickness between the particle in the ice. We note that some different engulfment conditions, such as trapping in grain boundaries, and the addition of impurities, change the motion of particles, so we distinguish between these situations during the discussion.

In chapter 4, we take a different approach, observing model concentrated colloidal suspensions, where single particle resolution is not possible, but macroscopic regions of segregated ice form. In concentrated suspensions, premelting occurs widely, and we observe the regime where ice lenses form at regular intervals. This has relevance in particular to frost heave, and other technological applications. We first investigate the process of lens formation in detail, for example by taking temperature measurements inside a cell, while viewing it in real space. We attempt to understand the microscopic behaviour by changing the macroscopic conditions, such as the temperature gradient and speed of pulling.

Following on from chapter 4, chapter 5 deals with the same system, but varying three key parameters: particle packing, particle size and shape, and impurity concentration. All have significant effects on the growth rate and real space properties of segregated ice. We relate these changes to properties of the suspension such as the compressibility, permeability and interfacial resistance in premelted layers.

In chapter 6, concentrated particle suspensions are observed at the particle level, while freezing. Ice segregation occurs when freezing is slow enough, and we measure particle build up ahead of the interface. Lower critical engulfment velocities than in dilute particle suspensions are explained by considering a particle force, acting in the direction opposite to the ice growth. Particle configuration is found to affect the eventual pattern of engulfed particles within the ice. Segregated ice in the form of ice-lenses is also found to occur in temperature gradient dependent growth modes.

Finally, in chapter 7, we study the ice–water interface in a plane perpendicular to the sample cell glass wall and parallel to the temperature gradient, using confocal microscopy. Fluorescent dye which is insoluble in the ice phase allows for distinction between the water and ice phases. Image analysis techniques are used to find the interface between the dye rich region (water) and

dye poor region (ice). We use the analogy of capillary rise of a gas–liquid interface under gravity to derive an expression for the relevant capillary lengthscale in this application.

Chapter 2

Theoretical background and experimental methods

ABSTRACT

In this chapter we derive and explain the theoretical expressions underlying physical behaviour in the freezing colloidal suspensions, such as regelation, particle engulfment, cryosuction and ice lens formation. Then, the experimental setup used is presented in detail. This includes the temperature gradient system, microscope to view the system, and the colloidal model system including sample holder. Finally, we present some results in order to characterise the thermal properties of the system.

2.1 Introduction

In this chapter we explain the various physical processes happening in a freezing colloidal suspension. To assist the reader we introduce the setup at the earliest possible point, because of the role it plays in the theory section. The setup consists of a thermally two dimensional system, in which a temperature gradient, ∇T , acts in only one direction along the sample. To unidirectionally solidify (freeze) the sample, the sample must be pulled in parallel to this gradient, moving at a velocity V in the direction of the cold side of the gradient, which is inherently at a temperature below the bulk melting point, T_m . To study the interaction of a ice–water interface with colloidal particles, the position of T_m must be within a field of view of a microscope. A diagram of unidirectional solidification is shown in figure 2.1.

The simplest way of achieving this system experimentally is by using two plates, with temperatures independently controlled, and a motor connected to the sample, which can drag it across the gradient at a fixed speed. A microscope can then be used to observe the sample between the two plates, where ∇T has been designed so that T_m is between the plates, and therefore in the field of view, and the behaviour close to the melting point can be observed. This chapter is organised as follows; we begin by exploring some of the main physical principles involved in the system, in a theoretical outline (section 2.2). Then, the experimental setup is described in detail (section 2.3). Finally, we characterise the system by the use of thermocouple measurements and theoretical models (section 2.4).

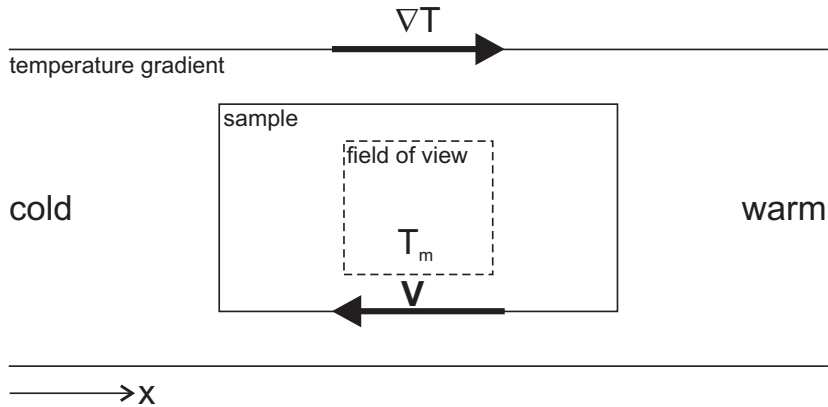


Figure 2.1: Diagram of the unidirectional solidification of a sample moved at a velocity, V , in an independently controlled temperature gradient, ∇T , which is constructed so that the melting temperature, T_m , is in the field of view.

2.2 Theoretical outline

In this thesis, interpreting the results often relies on the assumption that water exists below the bulk melting temperature in suspensions of colloidal particles. This water is described as ‘premelted’, due to the fact that it is present at lower temperatures than expected from the normal phase diagram of water [27]. A huge body of theoretical work on this subject exists, e.g. [45, 49–56], supported by experimental evidence, e.g. [29, 49, 57–59]. Three ways in which premelting can occur in particle suspensions, are as follows:

- I. curvature induced premelting in the pore space,
- II. interfacial premelting on the surface of a particle, or in a grain boundary between two grains of ice,
- III. impurity induced premelting.

In section 2.2.1 we will explain the above in greater detail. Figure 2.2 depicts all three forms of premelting, in a schematic picture of a colloidal suspension containing ice, where a temperature gradient is acting across it.

Another main theoretical concept is the flow of water along a temperature gradient, towards colder temperatures. In section 2.2.2, we outline this behaviour. This flow occurs due to a thermomolecular pressure gradient; the changes in pressure can be caused by the intermolecular forces between particles and ice which result in premelting (as in section 2.2.1 II). This force also causes the phenomenon of regelation, and is crucial in explaining how particles are rejected from an ice interface and may concentrate next to the interface. It also explains how the flow of water towards an ice lens is maintained during frost heave.

In section 2.2.3, we will then discuss ice growth instabilities. When ice nucleates in super-cooled water, it is unstable to perturbations of the interface. Perturbations with wavelengths above a critical size can grow, as dictated by the ice–water surface energy, but a particular wavelength will dominate [24]. This leads to cellular (linear) and dendritic (non-linear) growth of ice. If the ice–water interface pushes the particles, instead of capturing them, the particle configuration is shaped by this growth morphology. This effect has given rise to a whole field of materials science, where materials are moulded by ice growth [48]. When impurities are present,

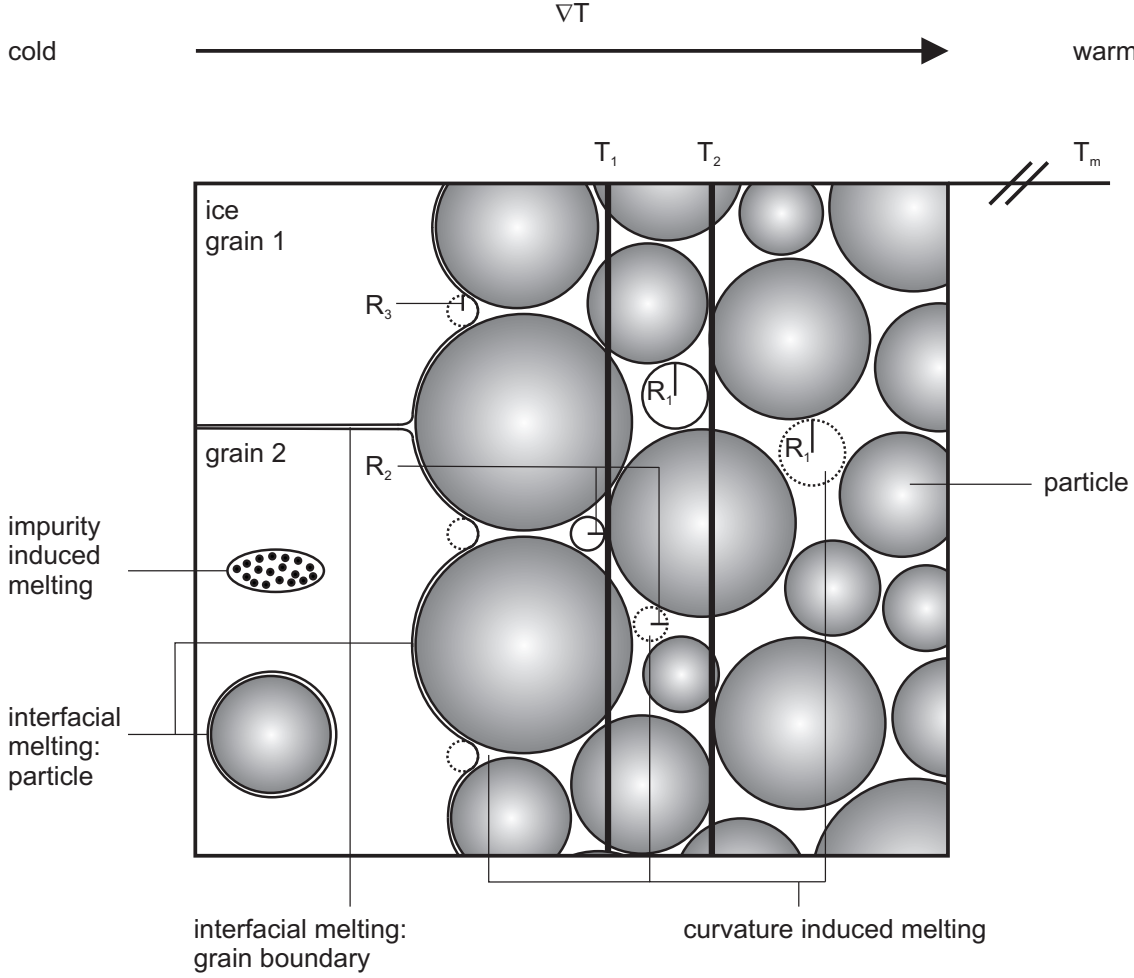


Figure 2.2: A polydisperse colloidal suspension in contact with ice under a temperature gradient, ∇T . In this diagram, several forms of premelting are depicted (not-to-scale), which are described in section 2.2.1. Temperatures T_1 and T_2 represent the maximum temperature at which a pore ice sphere of radius R_1 and R_2 is thermodynamically stable: $T_1 < T_2$ and $R_1 > R_2$. For a temperature T , where $T_1 < T < T_2$, pores of radius R_1 contain ice, whereas pores of radius $\leq R_1$ contain water. Pores filled with ice are depicted as circle with its circumference as a solid line; pores filled with water are depicted as circle with its circumference as a dotted line. Pore throats, with a smaller radius of curvature, all approximately R_3 (depending on the exact particle configuration), are also depicted, and occur at a temperature below T_1 . Interfacial melting occurs at both particle surfaces and grain boundaries. Impurity induced melting is depicted as a pocket of water, which contains impurities.

this instability is enhanced due to constitutional supercooling, where the rate of diffusion of the impurities is comparable to the diffusion of heat along a gradient. Unstable ice growth in both forms can lead to pockets of fluid (containing impurities or particles) contained within the ice. These pockets can move along a temperature gradient in a similar way to the regelation of particles, causing structural changes in the ice. The final concept we will discuss is the ice nucleation process, in section 2.2.4.

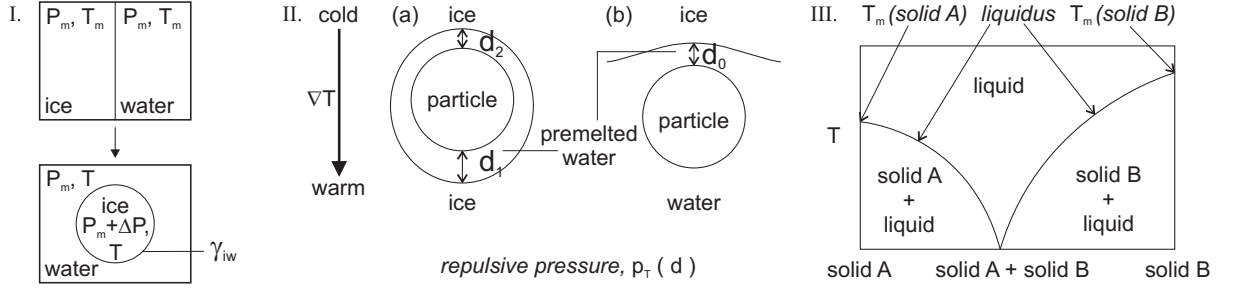


Figure 2.3: State changes in premelted systems: I. schematic representation of the components in the derivation of the Gibbs–Thomson equation; II. experiencing a temperature gradient of ∇T , (a) a particle trapped in ice and surrounded by a premelted water layer of thickness d_1 and d_2 , and (b) a particle at a warmer temperature separated from an advancing ice front by a premelted water layer of thickness d_0 , where $d_0 > d_1 > d_2$ (not to scale); III. equilibrium phase diagram in terms of T vs the composition of A + B, which are two immiscible solids, e.g. ice and salt.

2.2.1 Premelting behaviour

Here, we discuss premelting behaviour in ice–particle suspensions, at temperatures close to, but below the equilibrium melting temperature, T_m . Figure 2.3, shows the state changes schematically, and is referred to throughout.

I. Curvature induced premelting: the Gibbs–Thomson effect

Water in the suspension may remain below the equilibrium melting temperature, T_m , due to the Gibbs–Thomson effect, i.e. curvature induced melting, as shown in figure 2.2. Here, ice cannot grow into pores which are smaller than a critical size, at a certain temperature. We will now derive the Gibbs–Thomson equation. At the reference point, ice at chemical potential μ_i , is in equilibrium with water at chemical potential μ_w , and the phases are both at the melting temperature and pressure, T_m and P_m . Hence we have,

$$\mu_i(P_m, T_m) = \mu_w(P_m, T_m). \quad (2.1)$$

If the ice–water interface becomes curved, then we can find the new temperature, T , where $T < T_m$, at which the ice and water are in equilibrium by equating the new chemical potentials. Here, the pressure in the ice has increased by an amount ΔP , as depicted in figure 2.3 I. This pressure difference is due to the Laplace pressure, which depends on the surface energy at the

interface between the ice and water, γ_{iw} , and the curvature, κ , and is given by,

$$\Delta P = \gamma_{iw}\kappa. \quad (2.2)$$

If we assume that the densities of the two phases are equal so that the pressure in the water remains the same as at the reference point, the condition for equilibrium becomes,

$$\mu_i(P_m + \Delta P, T) = \mu_w(P_m, T). \quad (2.3)$$

For the changes in chemical potentials relative to the reference point we have,

$$\mu_i(P_m + \Delta P, T) = \mu_i(P_m, T_m) + \int_{T_m}^T \left(\frac{\partial \mu_i}{\partial T} \right)_P dT + \int_{P_m}^{P_m + \Delta P} \left(\frac{\partial \mu_i}{\partial P} \right)_T dP, \quad (2.4)$$

and

$$\mu_w(P_m, T) = \mu_w(P_m, T_m) + \int_{T_m}^T \left(\frac{\partial \mu_w}{\partial T} \right)_P dT. \quad (2.5)$$

When we apply equations 2.1 and 2.3, and use the Gibbs–Duhem equation, $Nd\mu = -SdT + VdP$, which gives the change in chemical potentials as a function of pressure and temperature, we have,

$$-S_m^i(T - T_m) + V_m^i(P_m + \Delta P - P_m) = -S_m^w(T - T_m), \quad (2.6)$$

in which we assume that the molar entropy, $S_m^a (= S^a/N)$, and molar volume, $V_m^a (= V^a/N)$, are constant with respect to temperature and pressure over this range. Using $\Delta S = S_m^w - S_m^i$ and introducing the latent heat of solidification per unit mass of water $L_m = T_m \Delta S / M$, M being the molar mass, the undercooling, ΔT_{GT} , can be defined as,

$$\Delta T_{GT} = T_m - T = \frac{T_m}{L_m M} V_m^i \Delta P. \quad (2.7)$$

Here, the subscript GT refers to Gibbs–Thomson. Finally if we substitute ΔP for equation 2.2 and the density of ice, $\rho_i = M/V_m^i$ we get the Gibbs–Thomson equation,

$$\Delta T_{GT} = \frac{T_m}{L_m \rho_i} \gamma_{iw} \kappa. \quad (2.8)$$

This equation gives the undercooling required for ice of radius R and curvature $\kappa = 2/R$ to exist at a given pressure. This means that if we have a porous material such as a colloidal suspension with pores of radius R in equilibrium with an ice interface, pores remain filled with water below T_m down to the temperature T , before ice nucleates into the pores. This in turn means that the water in the pores is supercooled.

II. Premelting due to the presence of another surface

Interfacial premelting occurs in ice when it comes into contact with another phase besides water. This phase could be water vapour (called surface premelting), another ice surface with a different grain orientation (called grain boundary premelting), or the surface of another solid, such as a particle. Intermolecular forces between the phases act to shift the freezing point to lower temperatures, and subsequently premelted water can exist in very thin layers, of thickness d , below the bulk freezing point, T_m . The interfacial undercooling is defined as,

$$\Delta T_{int} = \frac{T_m}{L_m \rho_i} p_T(d), \quad (2.9)$$

where p_T is the ‘disjoining pressure’, also called the thermomolecular pressure, arising from these intermolecular forces. This relationship is found by substituting ΔP with the disjoining pressure, rather than the Laplace pressure, in equation 2.7. The disjoining pressure depends on the thickness of the premelted layer, d , and the type and the strength of the intermolecular forces in the system [60, 61].

If dispersion forces are considered, the interaction energy between two molecules in the separate phases, separated by a distance r is,

$$U = -C/r^6, \quad (2.10)$$

where C is a constant. If the interactions between all the molecules in two semi-infinite phases, or slabs, of densities ρ_1 and ρ_2 , are considered, the interaction energy is [62]

$$U = - \int_D^\infty \frac{\pi C \rho_1 \rho_2 A}{6x^3} dx = - \frac{\pi C \rho_1 \rho_2 A}{12D^2}, \quad (2.11)$$

where $\rho_1 A dx$ is the number of molecules in a slice of thickness dx , of part of the slab 1 which is

a distance x apart from slab 2, A is the area of the slab, and D is the distance of the vacuum between the two slabs. We can define the Hamaker constant, A_{12} , by redefining the interaction energy per unit area as,

$$U/A = -\frac{A_{12}}{12\pi D^2} \quad (2.12)$$

so that $A_{12} = \pi^2 C \rho_1 \rho_2$. We note, that a negative Hamaker constant corresponds to a repulsive force, as the force is defined as $F = -\partial U / \partial D$.

If we now reconsider the force between ice and particle surfaces, separated by a premelted film, the disjoining pressure, based on the dispersion (van der Waals) interactions is

$$p_T = -\frac{A_{iwp}}{6\pi d^3}. \quad (2.13)$$

The new Hamaker constant, A_{iwp} , for the ice, water and particle system, is defined as $A_{iwp} \equiv A_{ip} + A_{ww} - A_{iw} - A_{pw}$. Premelting can result as long as A_{iwp} is negative, giving a positive pressure in the film (see [63] for a list of relevant values). Other intermolecular forces give rise to different pressures: for example, double layer repulsions due to charges dissolved in the water [56, 63–65]. Combining equations 2.9 and 2.13 the premelted layer thickness becomes,

$$d = \left(-\frac{T_m}{L_m \rho_i} \frac{A_{iwp}}{6\pi} \right)^{\frac{1}{3}} (\Delta T_{int})^{-\frac{1}{3}}. \quad (2.14)$$

The layer thickness decreases as the temperature is reduced, i.e. ΔT_{int} increases, and this is depicted schematically in figure 2.3 II. (a), where $d_2 > d_1$. In chapter 3 we discuss how this changing layer thickness because of the temperature change over the diameter of a particle can cause the particle to move along the temperature gradient, in a phenomenon known as regelation.

During ice growth, particles can be ‘rejected’ from the ice, leaving it nearly pure, or they can be ‘engulfed’ by the ice, where they end up trapped inside the ice. The layer of premelted water of thickness d which separates the particle from the ice acts as a lubricant and prevents the engulfment of the particle by the ice, as shown in figure 2.3 II. (b). A particle is trapped by the ice if this layer of water cannot be replenished at a high enough rate. The fluid flow through the film depends on the particle size and the speed of the freezing front, making them important variables [66]. This basic principle is of significant importance when considering the interaction

between a particle and an ice surface, which in turn determines the final particle pattern within the ice.

III. Impurity induced premelting

This colligative effect is a bulk phenomenon, whereby the equilibrium melting temperature of water is lowered by the presence of another component in the mixture, defined here as an impurity. The size of an impurity can range across many lengthscales, from ionic, molecular species to, the more recently proposed nanoparticles [67]. The most common example of the use of the colligative effect in the world is adding salt to ice on roads and pavements. The ice is dissolved in a mixture of water and salt, until the equilibrium composition is reached. An important point to note is that the segregation coefficient, the ratio between the impurity concentrations in ice and water is close to zero. This is because the solubility of impurities in ice is negligible. This means that in a closed system, during solidification, the concentration of impurities in the water phase increases.

Figure 2.3 III shows a schematic temperature – composition phase diagram of two immiscible solids, which could be for example ice + an impurity such as salt. The liquidus reduces from the value of T_m in the pure solid A, to a point which is met by the other liquidus, which is called the eutectic temperature. This ‘freezing point depression’ can be predicted [68], and the undercooling is defined as,

$$\Delta T_{col} = \frac{R_g T_m^2 c}{L_m \rho_i}, \quad (2.15)$$

at a molar concentration of impurity, c (in units of mol m^{-3}), where R_g is the gas constant. In this derivation, ideality, such that the undercooling does not depend on the type of impurity, is assumed.

If we include the presence of a particle, it is found that the effects of impurities on premelting behaviour, i.e. melting against the particle surface, are complex [56, 64]. The complexity is enhanced by the dependency of the premelted layer thickness, d , on the impurity concentration, because of the zero segregation coefficient. The thickness of the layer at a given temperature is found to depend on the particular particle substrate, due to intermolecular forces (which could be attractive or repulsive), and surface charge: the concentration of impurity determines the

relative strength of the contributions of the forces. However, for large impurity concentrations, which we will deal with in experiments (ionic, molecular or gaseous), the colligative effect dominates and increasing the impurity concentration will enhance the thickness of the premelted layer.

In figure 2.2, the impurity induced melting is depicted as an area of premelted water, not including a particle. This represents another form of impurity based premelting, whereby water pockets are trapped in ice. They are unstable, and move along a temperature gradient. These pockets are caused by the pinching phenomenon, which is discussed in more detail in section 2.2.3.

2.2.2 Thermomolecular pressure gradients: flow of water along a temperature gradient

The flow of water along a temperature gradient from warm to cold has some important consequences. It forms the most basic explanation for frost heave [49, 69], whereby water will be sucked towards a growing ice lens, which is a region of segregated ice, forming below the melting temperature in a porous medium. Consider again the pressure difference as,

$$\Delta P = P_i - P_w, \quad (2.16)$$

where P_i and P_w are the pressures of the ice and water, which are in local thermodynamic equilibrium. We can follow the same derivation as in section 2.2.1 I to conclude that

$$P_i - P_w = \frac{L_m \rho_i}{T_m} \Delta T, \quad (2.17)$$

where ΔT is the undercooling. This is the Clapeyron equation, and as in section 2.2.1 I, we assume here that the densities of the ice and water are the same. In mechanical equilibrium we can assume that the ice pressure is equal to the overburden pressure, which is P_0 . Therefore, equation 2.17 becomes

$$P_w = P_0 - \frac{L_m \rho_i}{T_m} \Delta T. \quad (2.18)$$

This equation demonstrates that if the undercooling changes, e.g. along a temperature gradient, provided the temperature is below T_m , then the pressure in the water will reduce, relative to the constant overburden pressure. This pressure gradient causes water to flow from warm to cold.

Another thermomolecular pressure gradient is set up in thin liquid films, which wet surfaces at temperatures below the melting point (section 2.2.1 II). This pressure gradient explains the phenomena of regelation and particle rejection, which is shown in the schematic in figure 2.3 II. Moreover, in frozen fringe models of frost heave [55, 70], where temperatures are above the Gibbs–Thomson pore freezing limit and ice infiltrates the pores, water can still move along a pressure gradient towards an ice lens via the thin films that wet the particle surfaces. The disjoining pressure, p_T , in premelted layers such as the ones depicted in figure 2.3 II, can be integrated over the surface of a particle of volume v_p , giving the thermomolecular force which can drive a particle along a temperature gradient from cold to warm [45, 46],

$$F_T = \frac{L_m \rho_i}{T_m} v_p \nabla T. \quad (2.19)$$

This force is balanced by a viscous force, as water flows along the gradient, in the opposite direction to the particle, in order to replace the volume of the moved particle.

2.2.3 Instability

Instability during solidification is the process where the ice–water interface loses its planarity. This process causes the deformation of the surface into cellular (columnar) structures and dendritic (branched, tree like) structures. The interfacial free energy increases on forming a larger surface, however, an instability can grow favourably under certain conditions. A planar solidification front only occurs at the smallest undercoolings, where the diffusion of heat is fast in comparison to the rearrangement of the surface of the ice. Figure 2.4 (a) demonstrates the effect of the temperature gradient direction ∇T , on an interface perturbation (description taken from [71], lecture 3). Heat transfer is always from warm to cold and the rate of heat transfer depends on the temperature gradient: it is faster with a larger gradient. In the diagram, isotherms (lines at a constant temperature) next to a perturbation are compressed or dilated, meaning locally a large or small gradient is felt. Subsequently, the arrow sizes representing the direction and magnitude of the heat transfer show how the perturbation can grow or shrink. The first

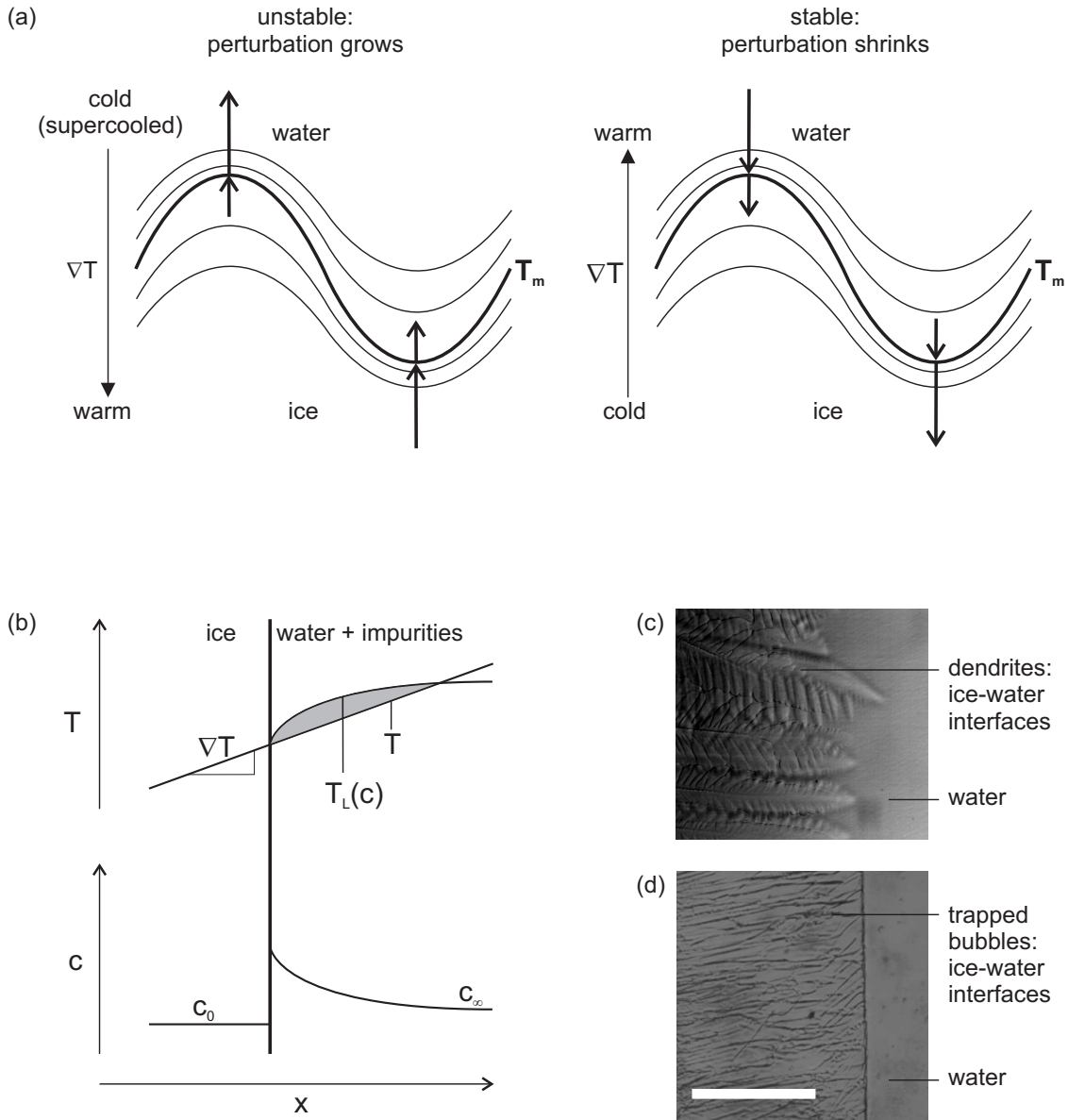


Figure 2.4: (a) Heat transfer response to a perturbation in a ice-water interface (thick black line) under different conditions: temperature isotherms are shown as thin black lines, arrows show the direction and magnitude of heat transfer. Under supercooled conditions, the interface is unstable; with the temperature gradient the other way, the interface is stable [71]. (b) Schematic graphs of temperature, T , and concentration, c , vs position, x , showing pure ice growing into impure water, of concentration c ; T_L , the liquidus temperature is inversely proportional to the concentration of solute, which builds up against the interface. If a linear gradient is applied, constitutional supercooling may occur (grey area). (c) Dendritic growth of ice into supercooled pure water. (d) Pinching instability in a system containing an impurity. Ice, which has grown unstably, has trapped pockets of water + impurities inside it. The scale bar denotes 500 μm .

situation represents the growth of the ice into supercooled water, such as after a crystal has nucleated, whereas the second situation is commonly experienced during unidirectional solidification, where the undercooling is low. Small wavelength perturbations are stable due to the Gibbs–Thomson curvature effect. The wavelength mode that grows fastest can be calculated by

the use of a linear Stefan model, and it is of the order of 0.1 mm for typical experimental temperature gradients [71]. However, growth of these instabilities can quickly become non-linear, when the cellular instabilities become unstable themselves and form dendrites. Computer simulations are required to model dendrites and tip splitting [72]. Under the solidification conditions used in this thesis, for pure water we almost always experience the stable situation, as the temperature gradient acts in the direction shown in figure 2.1, with ice already nucleated on the left hand side. However, before the nucleation of ice, water must be supercooled, so we see unstable growth of the ice, as shown in the image in figure 2.4 (c).

Furthermore, if we add an additional component to the system, an impurity, the situation may be influenced by the impurity concentration gradient as well as the temperature gradient. In figure 2.4 (b), ice is forming under a gradient of ∇T . As the ice forms, assuming the diffusion of the impurity is slow, it may build up against the interface, forming a concentration profile as depicted in the bottom graph. If we approximate the liquidus (see figure 2.3 III) as linear, then,

$$T_L = T_m - mc, \quad (2.20)$$

where m is a constant. The liquidus temperature, T_L , is plotted in the top graph in figure 2.4 (b), and if the gradient next to the ice–water interface is large enough, then constitutional supercooling can occur in the grey box. In this region, the temperature of the water, T , is lower than the liquidus temperature. Any random perturbation of the interface puts ice into the supercooled water phase. The ice at the tip of the perturbation is surrounded by water with a higher T_L , so the tip has a greater drive for solidification, so it grows. Recently, Peppin *et al.* extended the theory on instability during solidification caused by soluble impurities, to impurities in the form of nanoparticles [67]. Under certain conditions, constitutional supercooling can occur, leading to instability of the interface, and the possibility of nucleating ice between the particles themselves. However, we expect that the colloidal lengthscales used in our experiments produce supercoolings too small for this kind of instability to occur.

During the non-linear growth of unstable ice, a phenomenon known as ‘pinching’ can occur, whereby pockets of water, containing a concentrated impurity, can be trapped in the ice, as shown in figure 2.4 (d). These pockets of fluid can have an effect on the structure of particles trapped in the ice. This will be investigated in chapter 3 of this thesis.

2.2.4 Nucleation of ice

Ice growth does not occur spontaneously when pure water is cooled to below the bulk melting temperature. Instead, the water becomes supercooled, until a critical nucleus of water molecules arranged in an ordered state resembling an ice crystal forms during random molecular motion. Phase change of the surrounding water of this large enough nucleated crystal then becomes spontaneous, as the nucleation barrier is overcome. This critical nucleus size can be determined from classical nucleation theory, which balances the effect of free energy increase on forming a new ice–water surface, $\Delta G_{surface} = \frac{1}{N}4\pi r^2\gamma_{iw}$, against the free energy decrease upon bulk phase change below T_m , $\Delta G_{bulk} = \frac{1}{N}\frac{4}{3}\pi r^3\rho_i\Delta\mu_{iw}$, where r is the radius of a nucleus, and the chemical potential difference between the ice–water phases is $\Delta\mu_{iw} = \frac{L_m}{T_m}\Delta T$. The maximum in $\Delta G_{tot} = \Delta G_{surface} - \Delta G_{bulk}$ as a function of r is at r_c , the critical nucleus radius. Here, $r_c = \frac{2\gamma_{iw}T_m}{\rho_i L_m \Delta T}$, and for $r > r_c$ the barrier to spontaneous nucleation is overcome. This mechanism is called homogeneous nucleation. With increasing undercooling, ΔT , r_c decreases, so ice nucleation is more probable at lower temperatures. Supercooled water may survive for temperatures as low as -40°C , at which point r_c is only a few molecular radii, which is a fairly probable random nucleus size. However, if external surfaces that ‘wet’ ice are present in the system, the arrangement of water molecules into the structure of ice may be aided, and therefore the free energy barrier to nucleation will be significantly lowered. This process is called heterogeneous nucleation, and will occur at smaller undercoolings relative to homogeneous nucleation. At the point of nucleation of one or more nuclei by either method, the water will be highly supercooled, and the ice surface becomes unstable, as discussed in section 2.2.3. Dendritic tips will break off as a result of latent heat convection. A tip will likely be much larger than r_c , therefore it will grow spontaneously into another orientation of ice grain. Hence it is highly probable that many different grains of ice will form from a single nucleated crystal.

2.3 Experimental methods

2.3.1 Freezing setup

As stated in section 2.1, freezing with a constant cooling rate was achieved as follows: a sample containing nucleated ice was pulled across a gradient, ∇T , at a fixed speed, V , where both the

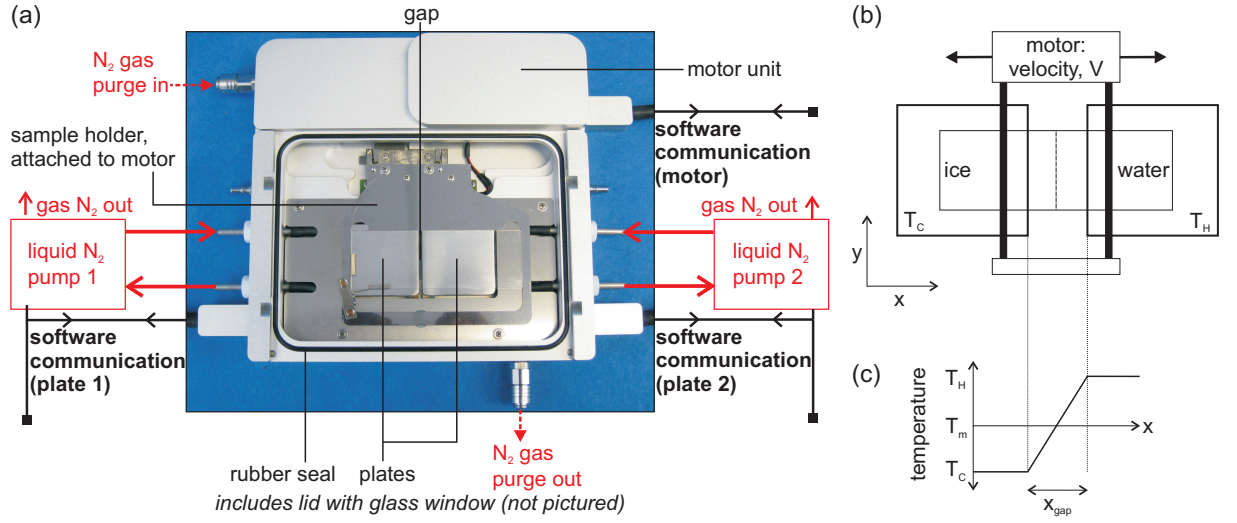


Figure 2.5: (a) A labelled photograph of the Linkam GS350 freezing stage. The nitrogen (N_2) liquid/gas input/outputs are shown, and the pumps shown schematically. The software communication wires are also shown schematically, and the computer is represented by three small black boxes, which connects to all three wires. (b) A schematic picture of the plates and motor, which is attached to a sample cell by two strips (thick black lines). These represent the tape which holds the sample cell firmly against the plates. The sample cell contains both ice and water, as the temperature of the plates which they are in contact with, are both above (T_H) and below (T_C) the melting point of water, T_m . In (c) the theoretical temperature profile is shown, with temperature *vs* x , where the dotted lines connect the plate edges to their equivalent positions along x as in the schematic picture in (b) above.

gradient and the speed were controlled independently. A photograph and schematic diagram of the setup used is shown in figure 2.5. A Linkam GS350 stage was employed, along with Linksys32 software which controlled the temperature of the two plates and the motor speed. The plates could be cooled to a minimum temperature of approximately -196°C (limited by the boiling temperature of nitrogen, N_2), and heated to a maximum temperature of 350°C . The temperature of the plates could be controlled with an accuracy of 0.1°C . Cooling was achieved by the use of a pump, which sucked liquid nitrogen from a dewar, through the plates, where it condensed and evaporated and nitrogen gas was released to the surroundings. Heating was achieved by the use of electrical resistance heaters embedded within the plates. The plates and sample were contained within a sealed box, where the air could be replaced by N_2 via the purge tubing in order to remove water vapour, which could condense on the sample. The plate temperatures were measured by a thermocouple contained within the plate (0.6 mm below the surface, and 3.7 mm in from the gap between the plates). We note that the temperature within the sample cell was not equal to the values measured by these thermocouples, since perfect thermal contact was not made, and there was likely to be a small temperature gradient in the z

direction, between the plate and the surroundings. The theoretical temperature gradient across the gap, $\nabla T_{theory} = \frac{(T_H - T_C)}{x_{gap}}$, where x_{gap} is the distance between the two plates, and T_C and T_H are the temperatures of the cold and hot plates, is the slope of the curve in figure 2.5 (c). This theoretical temperature gradient is a guide, however, as the temperature at the edge of a plate is not expected to be equal to the set temperature T_C or T_H , due to the presence of the other plate. This results in a lower gradient than predicted. The actual temperature gradient inside a sample cell was measured (see section 2.4.1).

The nucleation temperature of ice in an experimental system is notoriously hard to predict [73], and it lies outside the focus of this thesis. The fact that ice does not wet the particle surfaces suggests that they are not good heterogeneous nucleators. Often it was observed that a particle suspension could remain ice free up to a cold plate temperature of $T_C = -35^\circ\text{C}$. However, it is likely that some surface (e.g. impurities, glass walls) in our system will act as a heterogeneous nucleator. When performing an experiment, the ice nucleation temperature was not generally noted: the cold plate was cooled until ice nucleated, while the hot plate was left at room temperature. Subsequently, the gradient of the experiment was set up by heating or cooling both plates, and the ice grew to a stable volume. After the gradient was set up, a fixed rate of cooling was maintained by moving the motor at a constant speed. The motor was a stepper motor, with a minimum step of $1\text{ }\mu\text{m}$, and which the software could control at rates between $1\text{ }\mu\text{m s}^{-1}$ and $2000\text{ }\mu\text{m s}^{-1}$.

Some recent research concluded that particles may irreversibly aggregate during the initial fast growth of ice [74]. Particles experience a separation dependent force as a consequence of van der Waals attractions and electrostatic repulsions. These forces are described by Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [62]. At longer ranges the repulsive force felt by charges between the two surfaces dominates, while at short range the van der Waals force wins. When ice pushes the particles close enough, this close ranged attractive force binds the particles irreversibly. Therefore, the area in which this happened was generally ignored when interpreting the data. The length of this ‘pre-frozen’ section depended on the temperature gradient, which was defined by the nucleation temperature. In some circumstances, it was useful to use the nucleation process to standardise the history of samples, because the trapping of particles and pockets of fluid (through pinching) was consistent.

2.3.2 Microscopy

An upright bright field microscope was constructed from component parts, purchased mainly from Thorlabs. The components were contained within a cage system and external light was blocked by using black tubes. The diagram in figure 2.6 shows the schematic of the microscope, and table 2.1 lists the parts. The sample is illuminated by focusing a multiple LED light source onto P2, and consequently this image of the light source is collimated onto the sample by L3. An image of the sample is magnified by an objective lens and focused by a tube lens on to a camera. The imaging objective must have a working distance of at least 4.6 mm, which is the distance between the top of the Linkam GS350 stage lid and the plates. The movable x , y , z translation components were stiff, which ensured the stage had sufficient stability.

Name	Type	Details
LEDs		Matrix of multiple cold white LEDs
L1	Plano convex lens	Frosted for blurring the matrix of LEDs at the source
L2	Achromatic lens	
L3	Achromatic lens	Small focal length to reduce the depth of field
L4	Tube lens	Imaging sample onto camera
P1	Pinhole	Controls the field of view
P2		Controls the depth of field
M	Mirror	Birefringent so place PF 1 after this
O	Olympus imaging objectives	
	PLN 4 $\times$, NA= 0.10	working distance 18.5 mm
	SLMPLN 20 $\times$, NA= 0.25	working distance 25 mm
	SLMPLN 50 $\times$, NA= 0.35	working distance 18 mm
PF 1+2	Polarising filters	Placed above and below the sample
R	Retardation plate	Made of birefringent material which looks purple between crossed polarisers; birefringent ice crystals of different orientations will be visualised as a wider range of colour
camera	PixeLINK PL-B741U or PixeLINK PL-B742U	CMOS, 1280 $\times$ 1024 pixels, USB 2.0 CMOS, 1280 $\times$ 1024 pixels, USB 2.0 (colour)
x and y motion	2 $\times$ LNR50DD/M micrometer travel stages	placed on top of, and perpendicular to, each other for motion in 2D
z motion	Edmund Optics vertical translation stage	
Homebuilt adapter	PTCL workshop	For connecting the x , y , z translation to the Linkam GS350 freezing stage

Table 2.1: Components of the microscope setup; purchased from Thorlabs unless stated otherwise in column 2.

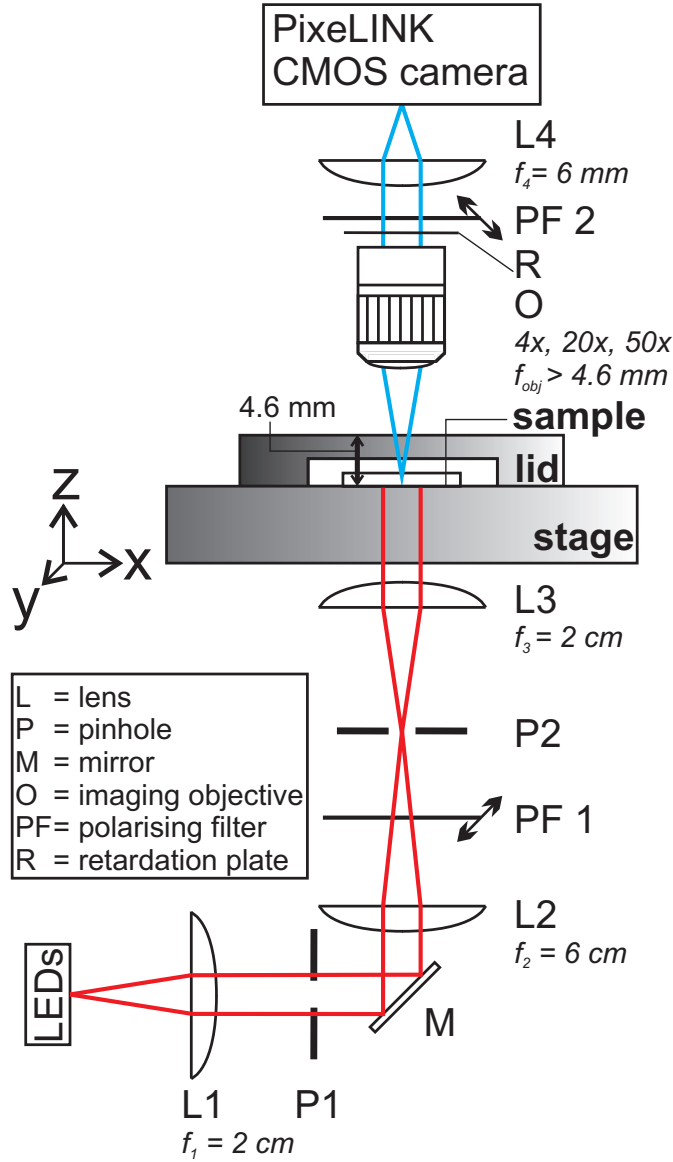


Figure 2.6: Diagram of the microscope setup. Köhler lens setup (L1 – 3) is below the sample, and is a source of uniform illumination of the sample (red). An image of the sample is transmitted through the imaging objective, magnified and focused on to the camera by L4. The sample can be moved into focus by moving the stage in z , and different areas of the sample can be viewed by moving the stage in the x and y directions.

Crossed polarisers were used to differentiate between water, and different grains of ice which have different crystal orientations. Distinguishing between grains is important in our experiments since two grains will be separated by a grain boundary, in which interfacially premelted liquid may be present (section 2.2.1 II). The birefringence of a material is defined as $\Delta n = n_e - n_o$, where n_e and n_o are the refractive indices of the substance for the extraordinary and ordinary rays. These correspond to rays entering the crystal perpendicular (extraordinary) or in parallel (ordinary) to the optical axis of the crystal, which is the crystallographic c -axis in

ice. As n_e and n_o are different in ice, the birefringence is non-zero.

The system is set up so that the ice sample is placed between two polarisers at 90 degrees to each other (crossed). The ice crystal orientation with respect to the polarisers will determine the amount of light transmitted through. When the direction of light propagation is tilted with respect to the optical axis, the incident wave is resolved into ordinary and extraordinary components. If the optical axis of the crystal is orientated in parallel to either polariser, then it appears dark, since only an extraordinary component propagates through the crystal, and this will not pass through both polarisers. Similarly, if the optical axis is orientated perpendicular to both polarisers, only the ordinary component propagates through the crystal, and it also appears dark (independent of the angle of the crossed polarisers). The maximum brightness is observed when the optical axis is at 45° to both polarisers. Here, the contribution of light from the e and o rays together is at a maximum. The two ray components travel at different speeds through the ice, and a phase difference results, $\delta = (2\pi/\lambda)\Delta n l_p$, where l_p is the path length through the material and λ is the wavelength of light entering the material. As white light contains a spectrum of wavelengths, the different phase shifts produce an interference colour scale as a function of $\Delta n l_p$, which is known as the retardation [75]. For ice, $\Delta n_{ice} = 0.001$ [76], which is fairly small, so that with a thickness l_p on the colloidal scale, i.e. of the order of 10 μm , the range of colours available due to this interference is limited to shades of grey [75]. To bring the colour range into a wider spectrum, a retardation plate, made of strongly birefringent material, of birefringence Δn_{ret} , was also placed between the crossed polarisers. This displaces the colour scale by a fixed amount, and the retardation caused by the ice is either added or subtracted, depending on the orientation of the retardation plate. This orientation is always with the retardation plate optical axis at 45° to both polarisers, to obtain its maximum birefringence (with the addition/subtraction of Δn_{ret} to/from Δn_{ice}). This wider spectrum allowed us to distinguish between more grains of ice. Also, water no longer appeared dark between crossed polarisers – it was the colour caused by the birefringence of the retardation plate, which in our case corresponded to purple.

2.3.3 Colloidal model systems

Solvent: Colloidal particles were dispersed in ultra pure water. The ultra pure water (Type I) has a resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$, which means that a very low number of ions are dissolved (of

the order of 10 ng dm^{-3}), however dissolved gases are still present. Dissolved gas acts the same as any impurity in causing instabilities (section 2.2.3). However, its removal is experimentally very difficult due to the high solubility of gases in the air, which surrounds the experimental setup, e.g. the solubilities of O_2 and CO_2 are 0.045 and 1.75 g gas/kg water at 20°C .

Colloids: The two types of particle systems used were: polydisperse silica particles and monodisperse melamine formaldehyde particles. A range of particle sizes were used, in order to study trends in size dependence. The melamine particles have a very low polydispersity ($<1.7\%$) so can be used to study effects such as regelation and particle trapping, where the size of the particle is an important parameter. The particles are charge stabilised by surface carboxylic acid groups, so when dispersed in water they have an anionic surface charge due to the partial dissolution of the $-\text{COOH}$ group. This leads to electrostatic repulsion between the particles, which prevents their aggregation, caused by attractive van der Waals forces. The silica particles were polydisperse, and obtained as a powder from JGC Catalysts and Chemicals with several different size distributions. They are also stabilised in water by anionic surface charges. They were used because of their availability in large volumes, which was required for the frost heave experiments (about $150 \text{ }\mu\text{l}$ at a volume fraction of 0.3 per cell), and they are also a well studied material in ice physics (e.g. [57, 77, 78]).

2.3.4 Sample cell

A sample cell was used to contain the suspension of particles. Sample cells were prepared by several different methods, depending on the required height, perpendicular to the direction of cooling (the z direction, out of the page, in figure 2.5 (b)). In this thesis we study both thermally two dimensional (2D) systems, which contain a three dimensional (3D) suspension of particles in a relatively thin layer, so that the temperature gradient in the z direction is minimal, and suspensions which are 2D at the particle level, containing a single layer of particles that can be tracked individually. In principle the observed phenomena should not depend on the height of the suspension (for a thermally 2D system). Figure 2.7 shows a schematic of the protocols for making each of the cells, which we describe below.

Thermally 2D cells: used for frost heave experiments, in which ice lenses form. The sample solution was inserted into the top, and this end was left open during an experiment. UV glue

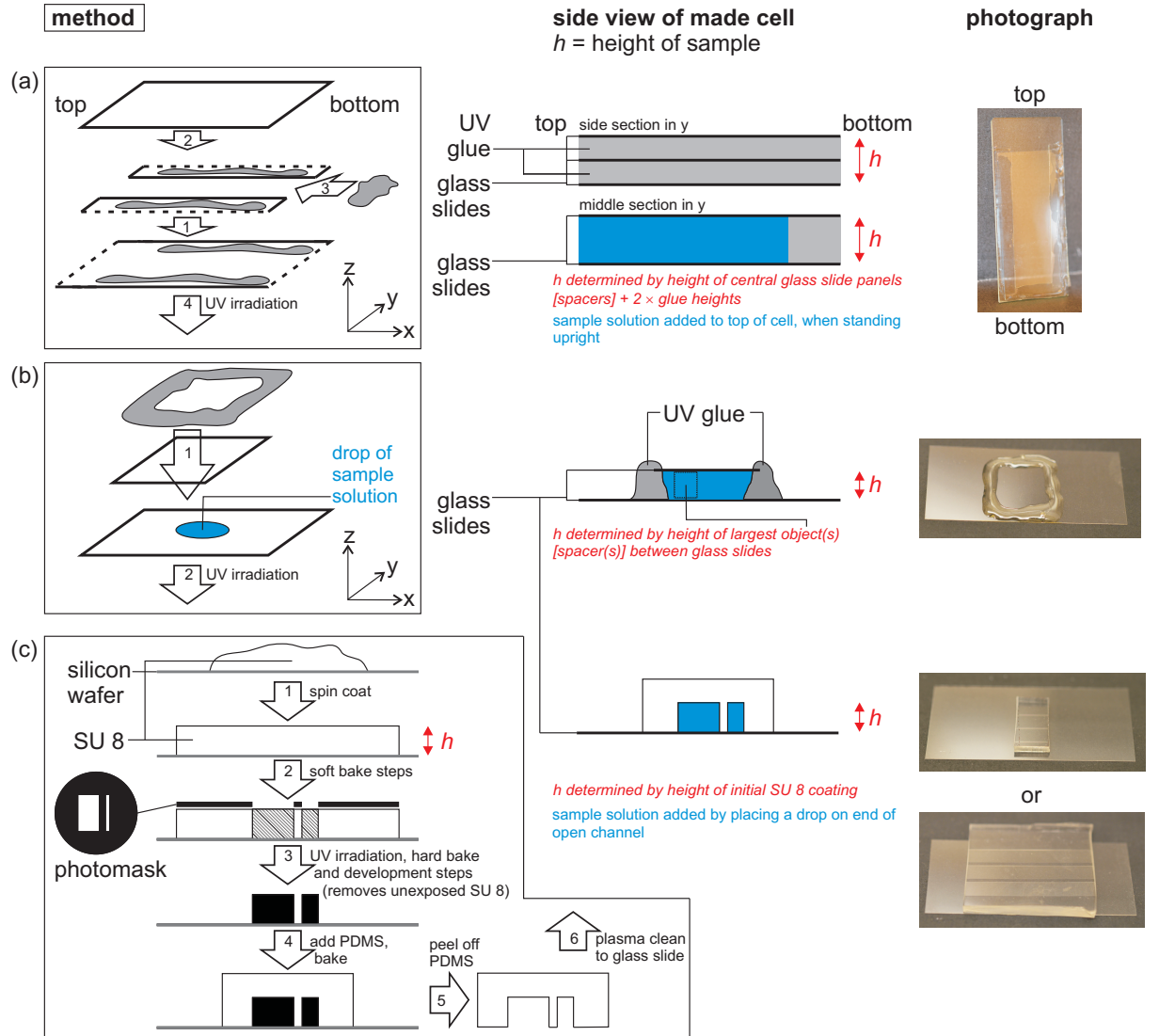


Figure 2.7: Diagram of the methods for making sample cells of varying heights, filled with sample solution (coloured blue). Consecutive steps are labelled (not to scale). (a) Thermally 2D cell: dashed lines represent cut glass edges. (b) Confined, closed cell. (c) PDMS cell. [Colour online]

(NOA 81) was used to create three cell walls, which was cured by 60 s of irradiation with UV light. For frost heave experiments, the internal height, $h = 0.28$ mm, but this could vary by up to 0.02 mm, depending on the amount of glue used.

Confined, closed cells: these cells had the advantage of being easy to fill with a well defined volume of suspension at a fixed concentration. However, they had the disadvantage of not being able to confine the cell height to a particle diameter, due to the inevitable dust particles present, which would act as spacers. Again, UV glue was used to seal the cell on all four sides of the top square glass coverslip. The internal height was estimated to be $h = 20$ μm .

PDMS cells: cell heights comparable to the diameter of the particle were made from polydimethylsiloxane (PDMS). Channels were constructed from a PDMS imprint of an SU-8 wafer, which was bound to a glass slide, as described in standard soft lithography protocols [79]. The glass and PDMS were plasma cleaned for 1 minute as part of the sealing process. The final height of the cell was well defined, as the spin coat step produced a layer of SU-8 with a fixed height covering the surface of the silicon wafer. The internal height, h , was between 6–10 μm . PDMS cells could also be used to form 3D suspensions of different, larger well defined heights, with $h = 50\text{--}100\ \mu\text{m}$. They had the disadvantage of being more difficult to fill with an even distribution of particles, as that depended on the speed of filling, which in turn depended on how clean the cell was. They also had the tendency to dry out if they were not saturated with water at the open end.

2.4 Characterisation of thermal properties

2.4.1 Thermocouple measurements

Figure 2.8 shows how two independent thermocouples, τ_1 and τ_2 (each accurate to 0.1°C), positioned at different initial positions in a sample cell, can be used to make temperature measurements. The thermocouples should measure the same temperature at the same position along x ; note that $x = 0$ is the centre between the plates. The top left hand panel in figure 2.8 explains how the motor position, which is what the Linksys software measures, is converted to the thermocouple position along x , by using $x = 0$ as the reference point. First, an image of the thermocouple, with the camera at a fixed x position, is taken. The distance between the left-hand edge of the image and the centre between the plates, α_c , is measured by finding the gap between the plates, x_{gap} , from the plate edge positions (marked by dashed lines). Note that α_c is the same for all subsequent images. Next, the position of the centre of the thermocouple relative to the left-hand edge of the image, α , is measured for at least three thermocouple positions, and for both thermocouples. At the same time, the motor position as measured by the software is recorded. The position α and the motor position from the software are linearly related, so they are fitted with a straight line (graph in top left hand panel in figure 2.8). Using this fit, α_c is used to find the motor position at the centre between the plates, where $x = 0$. This motor position is used to convert the motor position recorded by the software during the

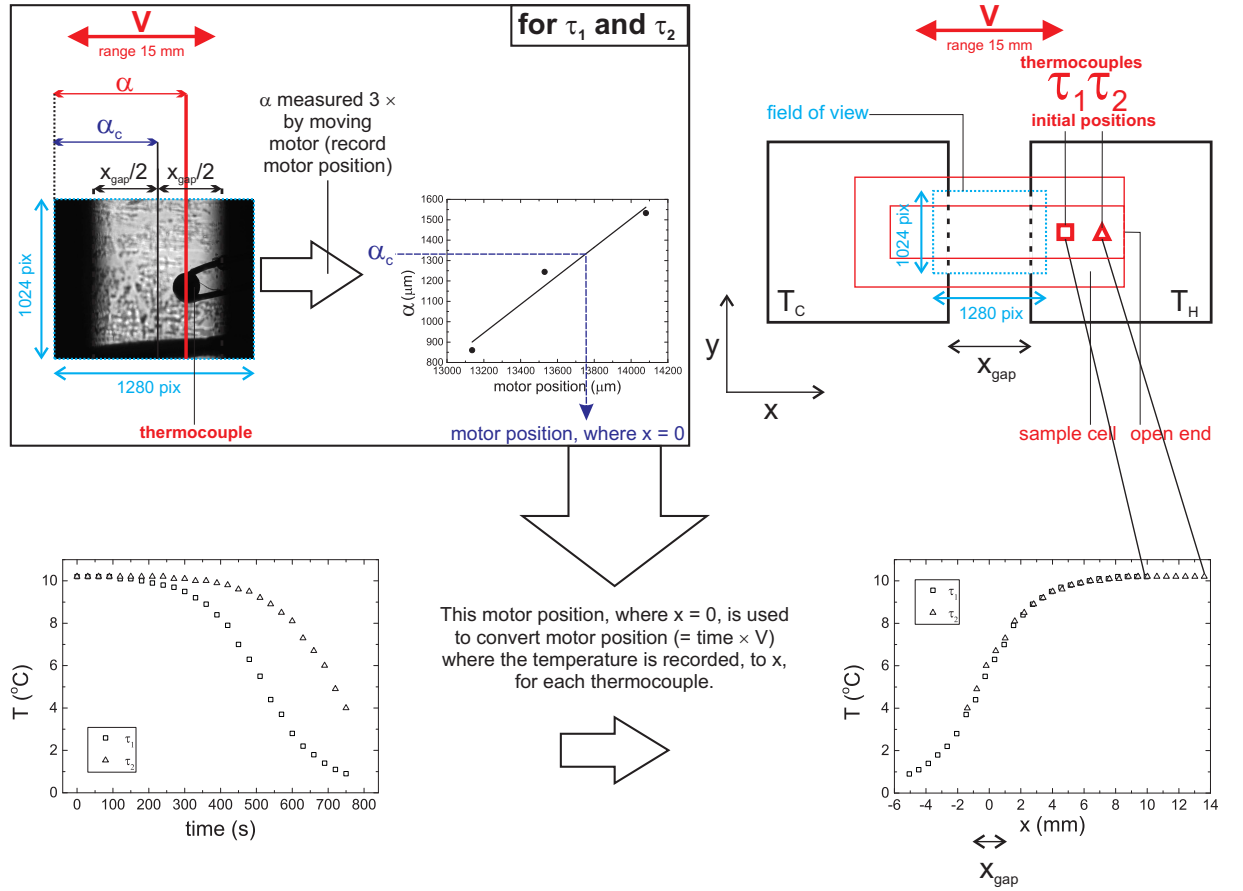


Figure 2.8: Diagram to show how the temperature, T , vs distance, x , where $x = 0$ is the centre between the plates, is measured by two independent thermocouples, τ_1 and τ_2 , starting at different initial positions (bottom right graph). Parts drawn in red are moved by the motor with velocity V and the position along the motor's range is measured externally by the Linksys software. An image recorded by the camera is marked out with blue dotted lines (both for an example image and in the schematic diagram). The value α is the position of the centre of the thermocouple from the left-hand edge of the image; α_c is the position of the centre between the plates from the left-hand edge of the image. The error in the temperature measurement by the thermocouple is equivalent to the height of a symbol. [Colour online]

temperature measurement to x .

The two independent thermocouples are used to verify each other's measurement, and to enhance the range of the sweep. A transient phase (with time), where the temperature gradient is changing, may lead to different temperatures as measured by the thermocouples at the same x . This effect is apparent in the system of Peppin *et al.* [80], where in their figure 2 (b) 30 minutes is taken before the thermocouples reach a steady state. However, as can be seen in the graph of T vs x (figure 2.8), our measurements of the temperature are within the error bounds, and we do not observe the transient phase. The reasons for this will be explained in the section below.

Experiment	V ($\mu\text{m s}^{-1}$)	T_C ($^{\circ}\text{C}$)	T_H ($^{\circ}\text{C}$)	ice present?
(a) 1	20	0	10	No
2	20	0	10	No
(b) 1	5	0	10	No
2	10	0	10	No
3	20	0	10	No
(c) 1	10	0	10	No
2	10	0	5	No
3	10	0	2.5	No
4	10	0	1	No
(f) 1	1.5	-2	0.5	Yes
2	10	-2	0.5	Yes

Table 2.2: Conditions for thermocouple experiments presented in figure 2.9.

Thermocouple measurements under different conditions, defined by V , T_C , T_H and the presence or non presence of nucleated ice, are presented in figure 2.9. The measurements were taken in a ‘thermally 2D cell’ (made as described in figure 2.7), where the central glass slide was thicker than normal, making the internal height $h = 1.1$ mm, in order to accommodate the thermocouples within the cell. In all experiments, the gradient was measured by moving the sample from warm to cold.

No ice: In figure 2.9 (a), the reproducibility of the measurements is checked by repeating the experiment under the same conditions. The two measurements are very close. It should also be noted that the temperature gradient experienced by the sample is not the theoretical gradient, $\nabla T_{theory} = \frac{(T_H - T_C)}{x_{gap}} = \frac{10-0}{2} = 5^{\circ}\text{C mm}^{-1}$. Instead, the plates experience an edge effect, whereby the temperature at the edges of both plates are warmed (T_C) or cooled (T_H), due to the presence of the other plate, and the actual gradient is lower than the theoretical gradient. The actual gradient between the plates, i.e. in field of view of the microscope, is fairly constant, as can be observed in the inset in (a). If the experiment is repeated with the same gradient, but at different pulling speeds, the gradient felt by the sample remains the same, as shown in (b). This shows that heat transfer is quick compared with the pulling velocity. Furthermore, in (c) we change the gradient and measure it at the same speed. The fits shown are linear fits to both thermocouple measurements between the plates. In graphs (d) and (e) we plot the gradient and intercept of these fits and find a linear relationship between the theoretical temperature gradient and the actual temperature gradient.

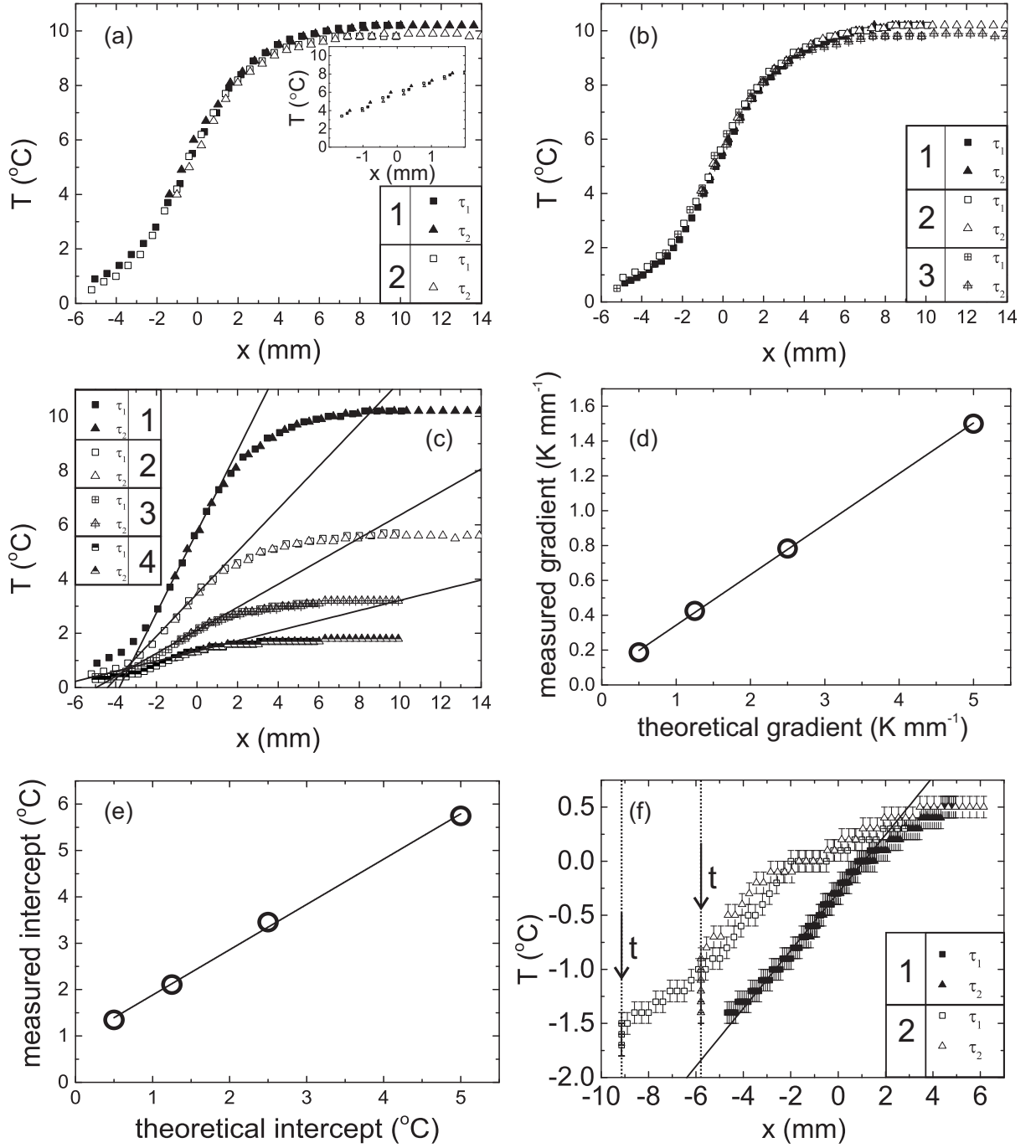


Figure 2.9: (a) – (c) and (f): temperature, T , *vs* distance relative to the centre of the plates, x , measured simultaneously by two thermocouples, τ_1 and τ_2 under different conditions, which are summarised in table 2.2. In (a), the inset is a zoom of the profile between the plates. In (c), the lines are the linear fits to the region between the plates. The graphs in (d) and (e) are the slopes and intercepts of the fit in (c), plotted against their theoretical slopes and intercepts, based on the values for T_C and T_H . In (f) the fit is also shown for experiment 1, and the dotted lines show the final positions of each of the thermocouples in experiment 2. The temperature is still measured by both thermocouples: x no longer changes, but time, t , increases as indicated.

Ice: Finally, as shown in figure 2.9 (f), we measured the temperature gradient experienced with the presence of ice, using the gradient common in frost heave experiments (chapters 4 and 5). It should be noted that because this cell was more than double the thickness of an actual frost heave cell (chapter 4), the measurements are more prone to the effects of latent heat (refer to number (3) in section 2.4.2 below). Ice was nucleated and the gradient was measured for two different pulling speeds, in two separate experiments. A stark contrast between the experiments was observed. For the low pulling speed ($1.5 \mu\text{m s}^{-1}$), which is the value at which the frost heave experiments were performed, the gradient is fairly linear, with 0°C measured between the plates, in agreement with the theoretical gradient. The linear fit to the data between the plates gives the equation $T(^{\circ}\text{C}) = 0.27x(\text{mm}) - 0.3$. The thermocouples measured 0°C when the ice–water interface crossed their centre, which is indicated by α in figure 2.8, which means they are well calibrated. For the higher pulling speed ($10 \mu\text{m s}^{-1}$), the temperature felt by the thermocouple is much higher than for the lower pulling speed, and there is a large discontinuity in the gradient around 0°C . The melting temperature, 0°C , and hence the ice–water interface, is beyond the field of view, and on the cold plate. This effect is explained by latent heat: as the ice freezes, latent heat is released. There is a finite time for this heat to dissipate from the sample cell to the surroundings. If the ice is formed faster than the heat can be released, the gradient felt within the cell will be affected by this. The effect is clear in the overall extra ‘warmness’ in the sample cell, i.e. the faster speed leads to a shift to higher temperatures. In addition, the melting temperature, T_m , is measured over a large distance. For experiment 2, the end position of each of the thermocouples is marked by a dotted line. The points on these lines now correspond to increasing time, as the temperature continues to be measured after the motor has stopped. The temperature decreases further, approaching the temperature tended to in experiment 1. Furthermore, this effect also explains the shift to higher temperatures for the warmer thermocouple, τ_2 .

2.4.2 Other analysis

Historically, dimensionless numbers have been a useful tool to realise the limitations of the thermal properties of the setup, including the properties of the sample cell [81,82]. As it was not possible to measure the temperature in a true cell, due to the thermocouple thickness being larger than the confining height of the sample cell, it is important to show by analysis of the thermal

Name	Symbol (unit)		Thermally 2D cell*	Confined, closed cell	PDMS cell
Height of sample	h (m)		1.1×10^{-3}	2.0×10^{-5}	1.0×10^{-5}
Height of cell bottom	h_b (m)		9.9×10^{-4}	1.1×10^{-4}	1.1×10^{-4}
Height of cell top	h_t (m)		1.1×10^{-4}	1.1×10^{-4}	3.0×10^{-3}
plate temperature difference	$T_H - T_C$ (K)	theo. act.	2.5 0.7**	20 5***	20 5***
velocity	V ($\mu\text{m s}^{-1}$)	min. max.	1.5 10	1 20	1 20
(1) Biot number	$\frac{\beta h_b}{k_g}$		8.7×10^{-3}	9.6×10^{-4}	9.6×10^{-4}
(2) E	$\frac{2\beta(T_{RT}-T_C)}{k_g} \frac{x_{gap}}{(T_H-T_C)}$	min. max.	3.1×10^{-1} 1.1	5.3×10^{-2} 2.1×10^{-1}	5.3×10^{-2} 2.1×10^{-1}
(3)	$\frac{h\rho L_m V}{h_b k_g} \frac{x_{gap}}{(T_H-T_C)}$	min. max.	3.5×10^{-1} 8.4	4.8×10^{-3} 3.8×10^{-1}	2.4×10^{-3} 1.9×10^{-1}
(4)	$\frac{k_i h}{k_g h_b}$		2.3	3.8×10^{-1}	1.9×10^{-1}
(5)	k_g or $k_{PDMS} \cdot \frac{h_t}{k_g h_b}$		1.1×10^{-1}	1.0	3.6

Table 2.3: Characteristics of typical experimental conditions, including dimensionless numbers (1)–(5). *height of sample as in thermocouple experiments, **based on figure 2.9 (f), ***based on figure 2.9 (d). Refer to table 2.4 for a list of system values.

properties that the range of conditions we study are suitable. Several dimensionless numbers are shown in table 2.3 using the thermophysical data values from table 2.4. They measure the relative contributions of heat transfers, and in a good model system, where temperatures inside the sample cell can be predicted accurately after calibration, the dimensionless numbers (1)–(5) should be < 1 .

Name	Symbol	Unit	Value
thermal conductivity of glass	k_g	$\text{W m}^{-1} \text{K}^{-1}$	1.14
thermal conductivity of ice	k_i	$\text{W m}^{-1} \text{K}^{-1}$	2.4
thermal conductivity of water	k_w	$\text{W m}^{-1} \text{K}^{-1}$	0.6
thermal conductivity of PDMS	k_{PDMS}	$\text{W m}^{-1} \text{K}^{-1}$	0.15
heat transfer coefficient in air	β	$\text{W m}^{-2} \text{K}^{-1}$	10
distance between plates	x_{gap}	m	2×10^{-3}
density of ice	ρ_i	kg m^{-3}	917
density of water	ρ_w	kg m^{-3}	1000
latent heat of fusion	L_m	J kg^{-1}	3.3×10^5
melting temperature	T_m	$^{\circ}\text{C (K)}$	0 (273.15)
room temperature	T_{RT}	$^{\circ}\text{C (K)}$	20 (293.15)
ice–water surface energy	γ_{iw}	J m^{-2}	3×10^{-2}
water viscosity at T_m	η	Pa s	2×10^{-3}

Table 2.4: Typical system values.

The implications for (1) – (5) < 1 , are as follows:

- (1) Heat transfer through the bottom glass slide is quick, by conduction, whereas heat transfer to the outside air is slow, by convection: it can be assumed that the temperature of the cell bottom is uniform, and equal to the temperature of the plate edge, when at a plate edge.
- (2) Heat transfer through the bottom glass slide, with thermal conductivity k_g , from the two plates is quick, whereas heat transfer to the outside air is slow: it can be assumed that the temperature distribution along the gap between the plates is determined by convection through the cell bottom.
- (3) Latent heat formed by solidification of the sample does not have an effect on the temperature gradient experienced by the sample. It is useful to note here that a higher pulling velocity (V) and lower gradient ($\frac{T_H - T_C}{x_{gap}}$) produce a larger number (3).
- (4) The substance being solidified in the cell will not have an effect on the temperature of the bottom glass slide as heat transfer through the bottom glass slide is fast compared to that through the sample.
- (5) Heat transfer through the top of the cell is less than through the bottom glass slide.

These conditions are met in almost all the cells. For the thermally 2D cell, in the maximum case for (2) and (3), and for (4), the condition is not met. This is because of the small temperature gradient used, as well as the large sample volume. The crossover between the min-

imum and maximum in (3) shows that the latent heat effect is important at the higher speed, as was observed, see figure 2.9 (e). In the PDMS cell, the thick layer of plastic will prevent heat from escaping, and therefore latent heat will not be removed as fast as in a glass walled cell, hence the condition is not met for (5).

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Chapter 3

Single particle engulfment and regelation

ABSTRACT

In this chapter we study some of the rich phenomena of single particles interacting with ice close to the melting temperature, in a well defined temperature gradient, at a resolution at the single particle level. First, we observe how ice grain growth influences the engulfment–rejection transition of particles by ice. Following this, we look at how particles that have been engulfed by ice move within and between ice grains, for example, in a process termed regelation. Finally, we look at the effect of doped impurities on regelation.

3.1 Introduction

The interaction of colloidal scale particles with ice is of special relevance to the sciences of climate, materials, food, biology and physics [17, 27, 48, 83, 84]. This problem has fascinated physicists for centuries: a weighted wire was observed to cut through a block of ice under gravity, leaving the ice intact (frozen) after its movement. This behaviour was originally attributed to pressure melting [47, 85]. However, pressures far too low to induce melting were also found to allow for this phenomenon, called ‘wire regelation’, therefore leading to a new physical interpretation [86]. It was suggested that a thin layer of water must exist between the solid wire and the ice to account for the motion of the wire. This thin film, existing at temperatures below the bulk melting point, was later attributed to the preferential wetting of the solid material (the wire) by water, rather than by ice. Because of the temperatures at which it can form, this film is often called a ‘premelted layer’. Premelted layers form between water vapour and other ice grains; this explains why snow is sticky, due to the joining and subsequent freezing of the premelted layers surrounding ice grains [87].

The premelted layer thickness is a function of temperature – it starts with a finite thickness at a given undercooling, gets larger as the temperature is increased, and diverges when the temperature is further increased to the bulk melting temperature. If a temperature gradient exists, the premelted layer thickness changes, and this results in a pressure gradient in the liquid. An elegant experiment by Wilen and Dash showed how water can flow along a temperature gradient in the premelted layer between ice and another material, in this case not a wire, but a flexible membrane [49]. The fact that the membrane was flexible allowed for the modelling of the membrane distortion after this flow had been set up [53]. The membrane changed shape because of the input of water, which subsequently froze, while maintaining the premelted layer at its equilibrium thickness. The final membrane shape was determined when the liquid pressure was equal everywhere in the film, so the pressure gradient was eliminated. This flow in premelted films plays an important role in many theories regarding the interaction of particles with the ice–water interface.

The first common interaction possible is one where a particle is rejected by an advancing ice–water interface. In order to reject a particle, water must be able to freeze onto the ice–water interface that lies between the particle and the ice. To do this, a premelted layer must exist

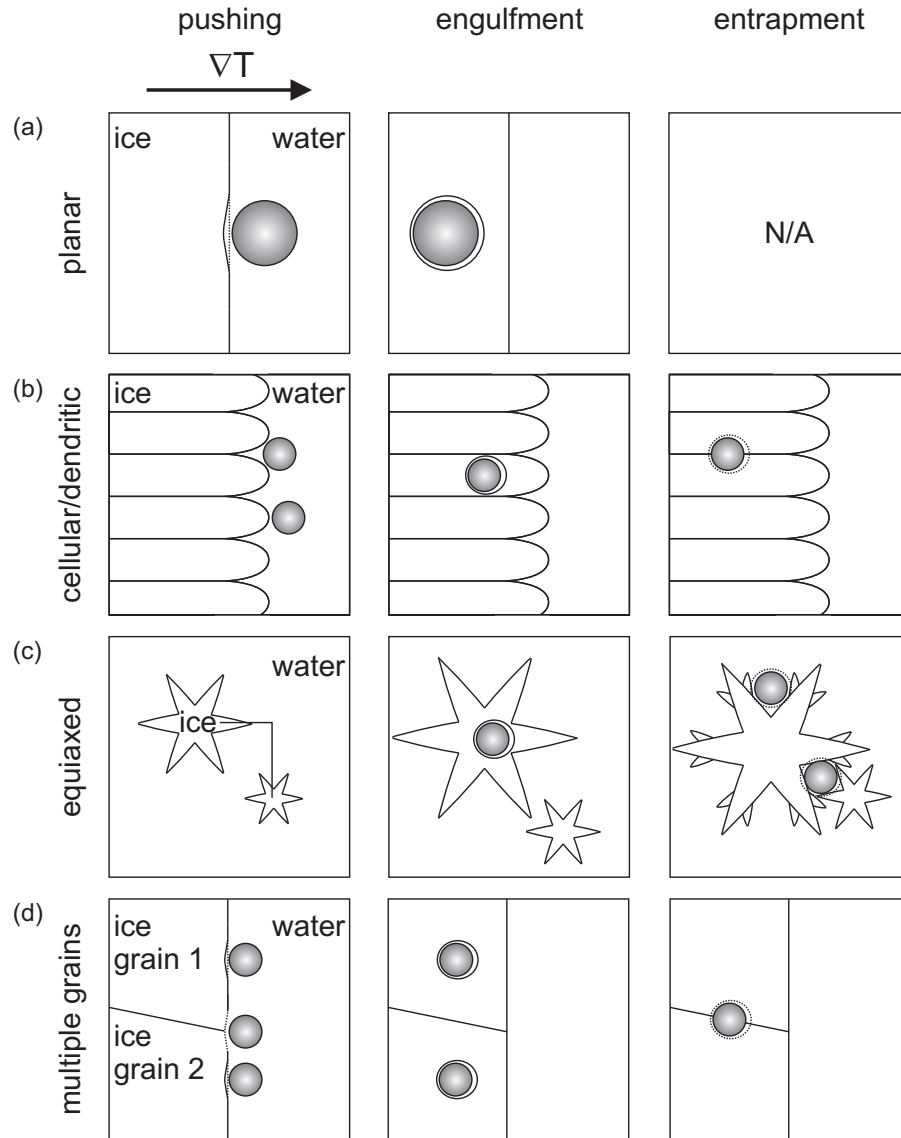


Figure 3.1: Schematic diagram showing pushing, engulfment and entrapment of particles by different ice–water interface morphologies: (a) planar, (b) cellular/dendritic (shown as cellular), (c) equiaxed, and (d) multiple grains, with the temperature gradient, ∇T , applied in the direction shown for the first picture. Also shown are premelted layers surrounding the particles within the ice; these are shown as dotted lines when the theoretical description of their shape is not known. Note that in reality, the ice–water interface is moving, but in the diagrams show a steady frame of reference.

between the ice and the particle, and water must flow along the layer from warm to cold, as described above. Over the last decades of the previous century, experimentalists have measured engulfment velocities of particles [84, 88–94]. There are issues around how to define particle engulfment away from the simplest model of a planar interface engulfing a particle [66, 95, 96], as shown in figure 3.1 (a). For example, if the ice surface morphology is cellular (linear instability) or dendritic (non-linear instability), engulfment becomes entrapment, where particles are pushed between an unstable interface, and then freeze in after jamming, see e.g. [97] and figure 3.1 (b).

Metallurgists are familiar with particle trapping [98]: part of their figure 1 is reproduced in figure 3.1, as applied to an ice–water system. Particles are either pushed, or incorporated into the solid by either engulfment or entrapment, and where the particle sits in the solid is dictated by this, and the interface morphology (a)–(d). Both planar and cellular interfaces may occur in a single ice grain, but equiaxed growth occurs when multiple ice grains nucleate simultaneously from a supercooled melt [25, 99]. Initially well dispersed particles will be evenly distributed in the solid for (a)–(d) engulfment, but for entrapment they will be arranged in lines in parallel to the temperature gradient for (b), in clumps between or within grains for (c), or along grain boundaries for (d).

Ice crystal shape variation as a function of additives is essential in the production of freeze cast porous materials, see e.g. [100–102]. Ice structuring proteins are thought to have a complementary surface to certain ice surfaces, therefore they are able to change the ice–water surface energy (as with a surfactant). This changes the grain growth of ice, for example, by causing fast growth along the hexagonal axis *c*-axis [76]. Particles in the suspension may be entrapped by these single or multiple grains (figure 3.1 (b) and (d)), therefore jammed together into a structure which is moulded by the ice grain. The crystal grain growth caused by the additives is usually down to trial and error [103]. The fully faceted equilibrium crystal shape of an ice crystal, predicted by Wulff [104] is only found under extremely well-controlled conditions [105], and otherwise ice crystal growth involves complications such as surface roughening, morphological instabilities and the formation of many grains [106]. Fundamental observations like the clear transitions between growth morphologies of snow crystals from plate- to column- like geometries and back again with increasing undercooling are currently not fully understood [26]. However, above a certain supersaturation, the diffusion limited growth, which causes unstable interfaces and dendritic growth, is predicted [107].

An engulfed or entrapped particle is not necessarily static within the ice. Premelted layers, by definition, still exist while ice surrounds a particle. The flow through this premelted layer may drive the particle out of the ice, after the system has thermally equilibrated, due to the temperature gradient induced flow, also called ‘regelation’. Additionally, molecular species trapped in the ice, by mechanisms such as pinching, are in a metastable ‘premelted’ state. These can also be transported along this temperature gradient.

In this chapter we will study both engulfment and regelation phenomena, and importantly

we will show that regelation cannot be understood without observing the proceeding engulfment. Our setup allows for the detection of grains (polarised light microscopy), the detection of crystal orientations (light microscopy), and basic control over the ice grain growth, by the use of thin channels (PDMS) and controlled cooling (temperature gradient stage). As a result, we can thus study the effects of ice growth on trapping and regelation of particles. This chapter is organised as follows: first, we discuss the theory of premelting as applied to particles, and the different aspects of ice growth (section 3.2). The description of the experimental methods is given in section 3.3, and the results follow in section 3.4. Finally we conclude our findings in section 3.5.

3.2 Theory

3.2.1 Premelting

We may recall from chapter 2 that there are two contributions to the pressure difference between ice and water in a particle suspension held below the bulk melting point of ice [45]. One is caused by the Gibbs–Thomson effect, or curvature induced melting (section 2.2.1 I), and the other is due to interfacial melting at the surface of a particle (section 2.2.1 II). The combined contribution is defined as,

$$\Delta P = P_i - P_w = \gamma_{iw}\kappa + p_T, \quad (3.1)$$

where the first term is due to the Laplace Pressure, with ice–water surface energy γ_{iw} and curvature κ , and the second term is the thermomolecular (‘disjoining’) pressure, p_T , in a premelted film. Figure 2.3 II is reproduced in figure 3.2, with appropriate labels.

Particle engulfment

The combined effects of the above pressure difference lead to a distinct interfacial structure between ice growing into a colloidal suspension, as shown in figure 2.2. First of all, the particles are separated from the ice by a premelted layer, see figure 3.2 (a). This forms because of the disjoining pressure, which arises due to the repulsive interactions between ice and the particle, and leads to the preferential wetting of the particle by water, and not ice. Secondly, if particles are closely packed, neighbouring spherical particles form a space between them in which ice

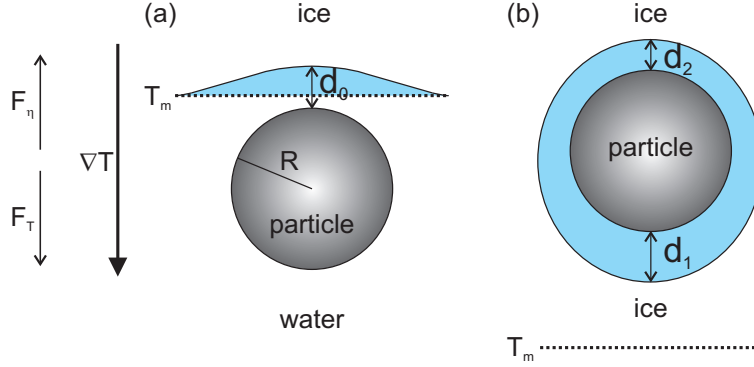


Figure 3.2: Schematic for particle (a) engulfment, (b) regelation (not to scale). The direction of the temperature gradient from cold to warm, ∇T , is indicated, as well as the directions of the thermomolecular and viscous forces, F_T and F_η , and the position of the bulk melting temperature, T_m (dotted line). Regions where premelted water is present are coloured blue, and the thickness of the premelted layers are labelled as d_0 , d_1 and d_2 . [Colour online]

with a positive curvature $\kappa \geq 0$ may form. In equilibrium, the chemical potentials of the ice and water phases are equal. As a consequence, this pressure difference can be calculated as a function of the temperature, T , below the equilibrium melting point, where the undercooling is defined as $\Delta T = T_m - T$, giving (section 2.2.1 I),

$$\Delta P = \frac{L_m \rho_i}{T_m} \Delta T, \quad (3.2)$$

where L_m is the latent heat of solidification per unit mass of water and ρ_i is the mass density of ice. For a stable premelted film, $p_T > 0$, and p_T increases as the premelted layer thickness, d , reduces (equation 2.13). The premelted film thickness is a function of temperature, and in general,

$$d = \lambda \left(\frac{\Delta T}{T_m} \right)^{-1/\nu}, \quad (3.3)$$

where the constants λ and ν are physical parameters determined by the type and range of interactions between the particle and the ice [51]. These effects combined result in the variation of P_w with temperature (equation 3.1). The pressure in the water, P_w , is lower where the film is colder and thinner, which drives a flow in the water from warm to cold. Once this water reaches the cold end of the particle, it pushes the particle forward, away from the ice, and freezes. The force driving the particle away from the ice is called the thermomolecular force, and is calculated by integrating the disjoining pressure, $p_T = -A/(6\pi d^3)$, where van der Waals interactions dominate (equation 2.13, where here A is the Hamaker constant), over the surface

of the particle. We here follow the derivation by Worster and Wettlaufer [45], having equated the expressions 3.1 and 3.2, and integrated to find this force,

$$F_T \approx \lambda^3 L_m \rho_i \frac{\pi R}{d_0^2} \left(1 + \frac{3l^4}{d_0^4} \right). \quad (3.4)$$

Here, R is the particle radius, and d_0 is the minimum thickness of the premelted layer, in the vicinity of the particle, which is its thickness directly above the top of the particle (shown in figure 3.2 (a)). The characteristic lengthscale, l , is the film thickness directly above the top of the particle, when the top of the particle is in line with the T_m isotherm. It is defined as $l^4 = \lambda^3 T_m / \nabla T$. The force acts in the direction of the temperature gradient from cold to warm, and results in a particle being ‘rejected’ from the ice, so it is an important interaction when considering ice segregation from a particle suspension. The thermomolecular force is balanced by the viscous force, which is derived from lubrication theory [45],

$$F_\eta \approx -\frac{6\pi\eta R^2}{d_0} V \left(1 + \frac{3l^4}{d_0^4} \right)^2, \quad (3.5)$$

where V is the flow velocity in the film, which is equal and opposite to the ice velocity. In equilibrium, the forces are balanced, so that $F_\eta + F_T = 0$, and an expression for V in terms of d_0 can be deduced. For an ice growth rate, V , this equation determines the distance d_0 where the van der Waals and hydrodynamic forces are balanced. By differentiating V with respect to d_0 , the only positive solution gives the maximum value of V , which corresponds to the critical engulfment velocity, V_c . Above this value, no steady equilibrium situation is possible. The minimum possible film thickness before engulfment is this solution, $d_0 = \sqrt{3}l$; the particle is always at a position warmer than the T_m isotherm, as $d_0(\text{min.}) > l$. This value of d_0 can be substituted back into the expression for V to give V_c , and after recalling the definition of l ,

$$V_c = \frac{\lambda^{\frac{9}{4}} L_m \rho_i}{8\sqrt{3}\eta T_m^{\frac{1}{4}}} \frac{\nabla T^{\frac{1}{4}}}{R}. \quad (3.6)$$

From this equation we can see that particles are more easily engulfed when they are larger, and under lower temperature gradients. Many experimentalists have measured V_c , e.g. [84, 88, 90–94, 108]. The latest theories all apply the above model to systems with increasing levels of detail, for example by including a buoyancy term accounting for the weight of the particles [66, 95], and for the case where the solidification rate is high and the system is out of equilibrium [96].

Particle regelation

After the particle has been trapped within ice, a special case exists where the disjoining pressure can be integrated over the whole particle surface to give the resultant thermomolecular force. Figure 3.2 (b) is a schematic diagram showing the premelted layers surrounding the particle. In the derivation it is assumed that the thermal conductivities and densities of the particle, ice and water are equal, and that no local heat changes occur due to the effect of latent heat. The temperature gradient causes a variation in the film thickness over the surface of the particle (equation 3.3). The resultant thermomolecular force is calculated as [45,46],

$$F_T = \frac{L_m \rho_i}{T_m} v_p \nabla T, \quad (3.7)$$

where v_p is the volume of a particle, and the force again acts in the direction of the temperature gradient from cold to warm. The lubrication force caused by flow in the premelted film is [45],

$$F_\eta = -v_p \frac{6\eta R}{d^3} |V|, \quad (3.8)$$

where η is the viscosity of the water in the film, and $|V|$ is the flow velocity, which is also equal to the velocity of the particle, that migrates along the temperature gradient, ∇T . This is a process called ‘regelation’, whereby a particle moves from cold to warm along a temperature gradient. Balancing the forces so that $F_T + F_\eta = 0$, leads to an expression for $|V|$ as a function of d ,

$$|V| = \frac{L_m \rho_i}{6\eta R T_m} \nabla T d^3. \quad (3.9)$$

This predicts that $|V|$ increases towards smaller undercoolings, where the film thickness gets larger, according to equation 3.3, suggesting that a particle will accelerate out of the ice. If $|V|$ is measured as a function of the undercooling, the premelted layer thickness can be measured. Premelted film thickness as a function of temperature have previously been measured using a huge variety of methods, as summarised by Dash *et al.* [27]. Additionally, the results of Romkens and Miller [109], where regelation of particles was observed, have since been analysed using the above method [54]. By fitting the velocity of the particle as a function of the undercooling, they found values for λ and ν , which were 3.6 Å and 2.

3.2.2 Ice growth

Crystals take on a fully faceted form at absolute zero. Above this temperature, surface roughening occurs, arising from the increasing disorder at the surface. Against a vapour phase, the structures formed during ice crystal roughening are complex, and depend on the vapour pressure and temperature, as depicted in the Nakaya diagrams in [23, 26]. Against supercooled water, we have seen in chapter 2, how the surface of ice can become unstable, as convincingly demonstrated in experiments by Koo *et al.* [110].

Under less ideal conditions, ice is much more complicated than this picture. First, ice is generally not made up of a single grain, unless very controlled growth is implemented (e.g. [105]). This results in the presence of grain boundaries between separate ice crystals, where the regelation problem changes due to additional premelting at grain boundaries [65]. In our experiments, we have little control over the crystallographic orientation of the crystals. Grain boundaries are active and may also move along a temperature gradient, analogous to the regelation of particles, due to flow in the premelted layers between grain boundaries. This motion may produce a resultant force on a trapped particle, dragging it along in the direction of motion of the grain boundary. Secondly, the effect of impurities, even in tiny amounts, has an effect on several physical properties: (i) the premelted layer thickness between ice and particles or at grain boundaries, (ii) instability in the ice interface, and (iii) the presence of impurity rich pockets formed after pinching due to these instabilities. In our model experimental system, we must analyse our results within the limitations of the system.

3.3 Experimental methods

Setup:

The experimental setup described in chapter 2 was used to study the interaction of particles with an ice–water interface. The sample cells were the ‘confined, closed’ and ‘PDMS’ cells (see section 2.3.4). Both of these allowed for a well controlled constant temperature gradient to be applied to a thin sample, where particles can be confined to a monolayer (section 2.4). In section 2.4.2 we show that the latent heat released by this small sample volume does not have an effect on the local temperature gradient. By comparing this analysis with direct measurements, taken

within a larger cell (where the effect is larger) with a low gradient and speed, it can be shown that this assumption is valid. The temperature gradient was measured using thermocouples, as explained in section 2.4.1. The theoretical temperature gradient is related to the actual temperature gradient by $\nabla T_{theory} = \frac{(T_H - T_C)}{x_{gap}} = 3.4 \nabla T$ (with the factor 3.4 from the linear fit in figure 2.9 (d)), where the set plate temperatures for the hot and cold plates are T_H and T_C , and the gap between the plates is x_{gap} . The particles used were melamine particles, which were stable in water, highly monodisperse, and available in a range of sizes, and silica particles, which were used in frost heave experiments in chapters 4 and 5.

Particle tracking:

Particles were located and tracked using standard protocols in Interactive Data Language (IDL) [111]. A bandpass filter was applied to the 8-bit image in order to minimise background noise, then bright spots with Gaussian intensity profiles were located. These included the particles (which have a central bright spot) as well as other features. Cut offs were applied to the features of the spots (brightness, radius, and ellipticity), by trial and error, so that only the particles remained. The particle location was given as a pixel value in x and y . These coordinates are plotted on top of two typical raw images in figure 3.3 (a). A tracking program was used, where a threshold maximum distance was set, up to which a particle could move from the position it was located in in the previous frame. Particles that fitted this criteria were given an ID, and individual particles' tracks (x_p, y_p, t) could be plotted, where the time, t , is the frame number $\times$ the time interval per frame, t_f .

Ice–water interface tracking:

Typical images of a suspension that contains ice, water and particles, is shown in figure 3.3 (top images). The ice and water do not look different optically, because the refractive indices of ice and water are almost the same. However, the interface between the two phases is easily located, due to scattering of light. In order to find its position (single valued along x and y), several stages were implemented using Mathematica. The stages are shown in figure 3.3 (b) for two cases, 1. where there were particles at the interface, and 2. where there were no particles at the interface. The stages are: (I) apply a Laplace Gaussian filter – finds edges of an object, showing the inside of the edge in darker tones and the outside in brighter tones; (II) convolve the image with a Sobel mask to in order to detect horizontal edges; (III) binarise the image to convert

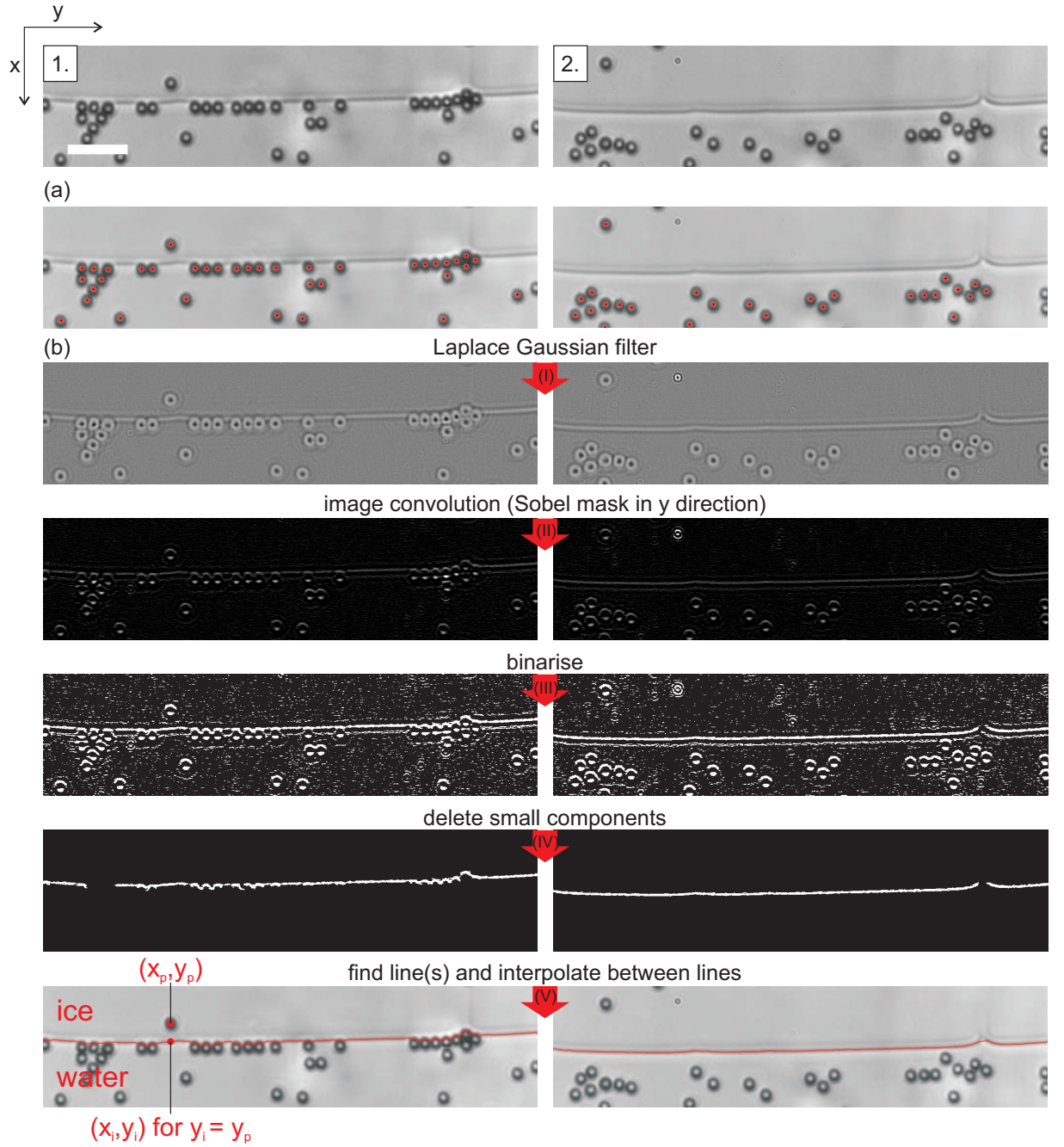


Figure 3.3: From the top raw images, with particles (1.) and no particles (2.) present next to the interface, features are located. (a) Particle tracking (red dots). (b) Ice-water interface tracking (red line) in stages (I)–(V). The scale bar denotes $20 \mu\text{m}$.

into components which are black and white; (IV) delete small components, in order to be left with just the interface; (V) find the line that is the interface (go along each column selecting first where the pixel value equals 1), and interpolate between two y values if none are detected, usually because a particle is there (example in 1.).

Motion of particles relative to the ice–water interface:

Generally, the x position of the ice–water interface, x_i , at the y position of a particle, y_p , was found. Next, the x position of the particle, x_p , was subtracted from x_i , giving $\Delta x = x_i - x_p$. The points (x_p, y_p) and (x_i, y_i) are labelled for one particle in figure 3.3. For a particle trapped in the ice, $\Delta x > 0$, and for a particle in suspension $\Delta x < 0$.

The velocity is measured by looking at an individual particle track. We plot Δx vs t , and fit this with the power law,

$$\Delta x = [a(t_e - t)]^b, \quad (3.10)$$

where t_e is the end time, when the particle reaches the ice–water interface and $\Delta x = 0$. By differentiation, a resultant expression for $|V|$ can be formed,

$$|V| = \left| \frac{d\Delta x}{dt} \right| = \frac{b\Delta x}{(t_e - t)}. \quad (3.11)$$

An expression for the velocity as a function of the undercooling is found by inserting equation 3.3 (with undercooling $\Delta T = \nabla T \Delta x$) into equation 3.9,

$$|V| = K \Delta x^n \quad (3.12)$$

where

$$K = \frac{L_m \rho_i}{6\eta R} \lambda^3 \left(\frac{\nabla T}{T_m} \right)^{(1-(3/\nu))} \quad (3.13)$$

and

$$n = -\frac{3}{\nu}. \quad (3.14)$$

Upon integration, equation 3.12 becomes,

$$\Delta x = [K(1 - n)(t_e - t)]^{(1/(1-n))}. \quad (3.15)$$

Hence, by finding a and b from the power law fit, and comparing the expressions for Δx (equations 3.10 and 3.15) we can find K and n , which lead to a determination of the physical constants

λ and ν . Hence, we have an expression for the film thickness as a function of the undercooling (equation 3.3).

Ice growth velocity:

In this chapter, relatively high temperature gradients were used (of the order $\nabla T_{theory} = 10 \text{ K mm}^{-1}$); for motor pulling speeds $\lesssim 20 \mu\text{m s}^{-1}$, the ice grew at the same rate as the pulling speed, V_m . First, in order to check that the velocity of the motor input by the software was equal to the actual motor pulling speed, V_m , a fixed point in the sample cell was tracked, and its position, $|x|$ is plotted in figure 3.4 (a). $|V_m|$ may be calculated by differentiating the position data with respect to time, or finding the gradient of a linear fit. We find that V_m is close to the set pulling speed (figure 3.4 (a)).

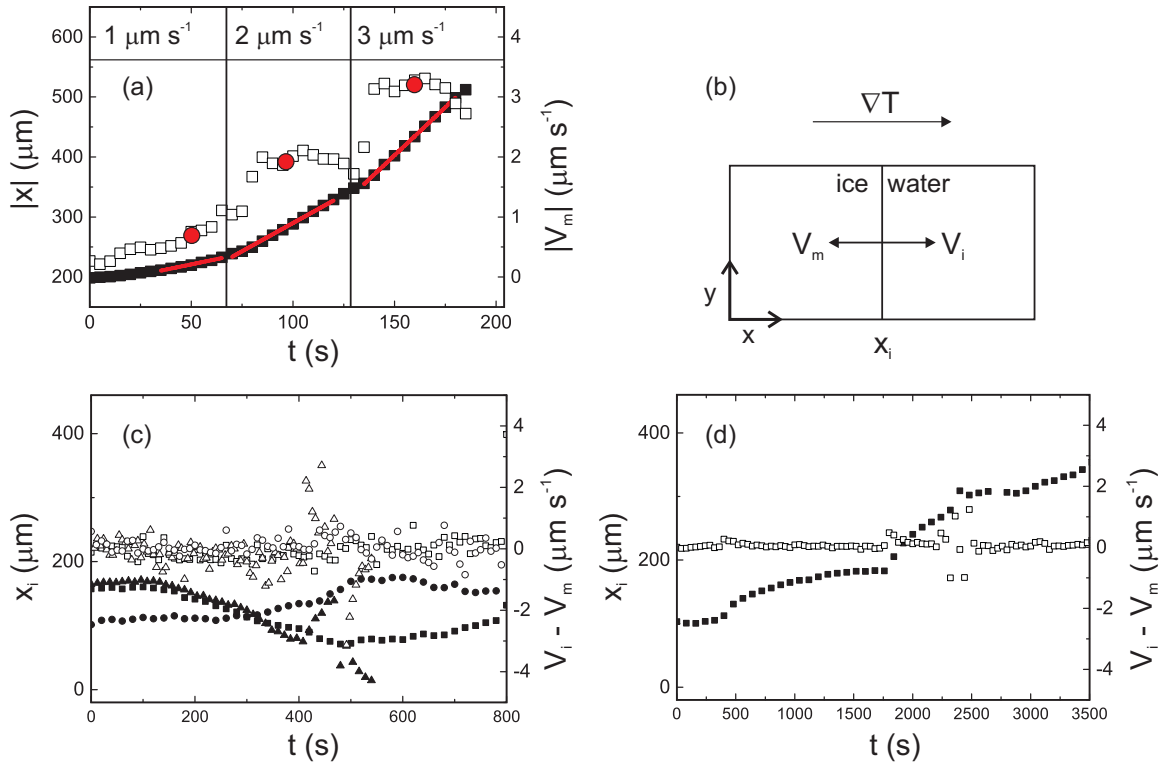


Figure 3.4: (a) Graph of the position of a fixed point in a cell, $|x|$ (filled squares), and its velocity ($d|x|/dt$), which is the measured pulling velocity $|V_m|$ (empty squares), *vs* time, t . At the times marked by the vertical black lines, the set pulling speed, indicated at the top of the plot, was changed. Linear fits to the data are also plotted (red lines), and the gradient is plotted as a red circle for each pulling speed. (b) Schematic diagram showing a sample which is pulled at motor velocity V_m across a fixed temperature gradient, ∇T . If the ice grows at a velocity $V_i = V_m$, then the ice–water interface, x_i , remains at a fixed position. (c) & (d) Graphs of the position of the ice interface, x_i (filled symbols), and $V_i - V_m$ (empty symbols), *vs* t , for (c) a rapidly changing (every ~ 30 seconds for 3 different experiments), and (d) slowing changing (every ~ 30 minutes) set pulling speed.

Under a constant applied temperature gradient, ∇T , the position of the ice–water interface, x_i , remains constant only when the ice growth velocity, V_i , is equal to V_m , as shown in the schematic diagram in figure 3.4 (b). We can track the interface, measuring x_i , and find $V_i - V_m$ by taking the derivative of the position with respect to time. Where $V_i - V_m = 0$, the ice grows at the same rate as the motor pulling speed, therefore, combined with figure 3.4 (a), we can assume that the input pulling speed is the ice growth velocity. Two experimental situations are shown in figure 3.4 (c) and (d), and in both cases $V_i - V_m \approx 0$. The ice moves slightly in the frame of reference (up to $\pm 1 \mu\text{m s}^{-1}$), due to local temperature variations, however, this is small compared to the V_m values used (which were up to $20 \mu\text{m s}^{-1}$). For this test case, $\nabla T = 2.9 \text{ K mm}^{-1}$.

3.4 Results and discussion

3.4.1 Ice growth

We have deduced that the ice interface structure during ice growth in our system depends on the temperature gradient. Polarised light microscopy images taken during ice growth under two different gradients are presented in figure 3.5. Many ice grains are present within the field of view for both conditions. In the high gradient case, the interface is smooth, and approximately perpendicular to the direction of the temperature gradient. This smoothness is caused by the roughening of the ice crystal facets, with the surface being freed from the ordering influence of the molecular crystal lattice [106]. However, in the low gradient case, the interfacial structure is much richer. Faceted grooves are more likely; these occur at the ice–water interface between two grains, where each grain takes a form dictated by its crystal orientation. The local temperature around the ice–water interface is closer to the melting point than it is for a higher temperature gradient. Therefore, coexistence may occur over a less well defined distance, meaning that the actual ice–water interface departs from being smooth. As well as the faceted growth and grooves, a single ice grain is more unstable to perturbations under a low gradient, assuming a constant gradient in impurity concentration. This situation is depicted schematically in figure 2.4 (b). In the zoom image in figure 3.5 (b), the grain on the right (darker blue coloured) has experienced unstable growth. Both these effects make particle interactions with the ice rich and complicated.

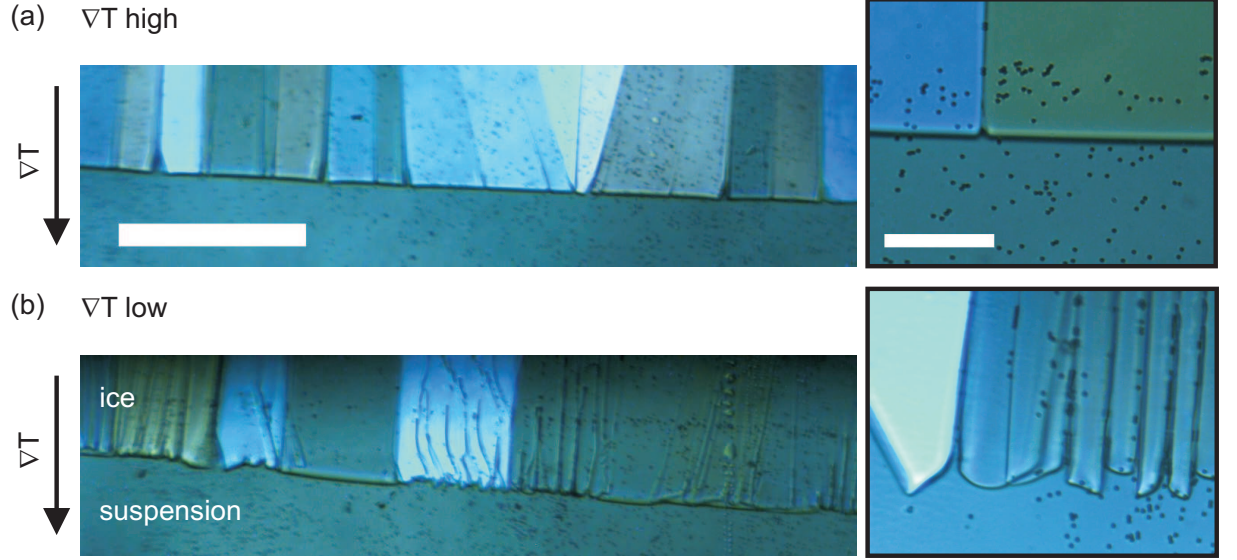


Figure 3.5: Images of the ice–suspension interface under two different gradients, where in (a) $\nabla T(\text{high}) = 7.3 \text{ K mm}^{-1}$ and in (b) $\nabla T(\text{low}) = 1.5 \text{ K mm}^{-1}$. The zooms (right hand side, boxed) are taken with a different objective at a later time. All samples were contained in PDMS channels of height = $50 \text{ }\mu\text{m}$. The left scale bar denotes $500 \text{ }\mu\text{m}$ and the right scale bar denotes $100 \text{ }\mu\text{m}$. [Colour online]

3.4.2 Ice interaction with particles

During ice growth – engulfment

Figure 3.6 shows representative examples illustrating the host of engulfment phenomena, with experimental details in table 3.1. In (a) and (b) time series of typical particle engulfments are shown. The ice–water interface the particle interacts with appears to be planar (roughened), and perpendicular to the direction of ∇T . The interface is deflected by the particle, as a premelted layer forms due to interfacial melting. In figure 3.6 (a), the particle is free to move along the interface (time between 20 – 39.5 s), before the premelted layer can no longer be maintained by the flow of water, and the viscous resistance force therefore causes the particle to be engulfed. The shape of the interface can be seen clearly in the images. When a second particle interacts with a particle that is already being pushed by the interface, as in figure 3.6 (b), one of the particles is more likely to be engulfed. The viscous force is larger in the presence of two particles. One of the particles is engulfed, but the force is not great enough under these conditions to cause the engulfment of the second particle. Note, at $t = 5 \text{ s}$ there is some water present between the particle being encapsulated by the ice, and the particle which will eventually be pushed. Some particles which have built up in a layer are engulfed in figure 3.6 (c). A perturbation

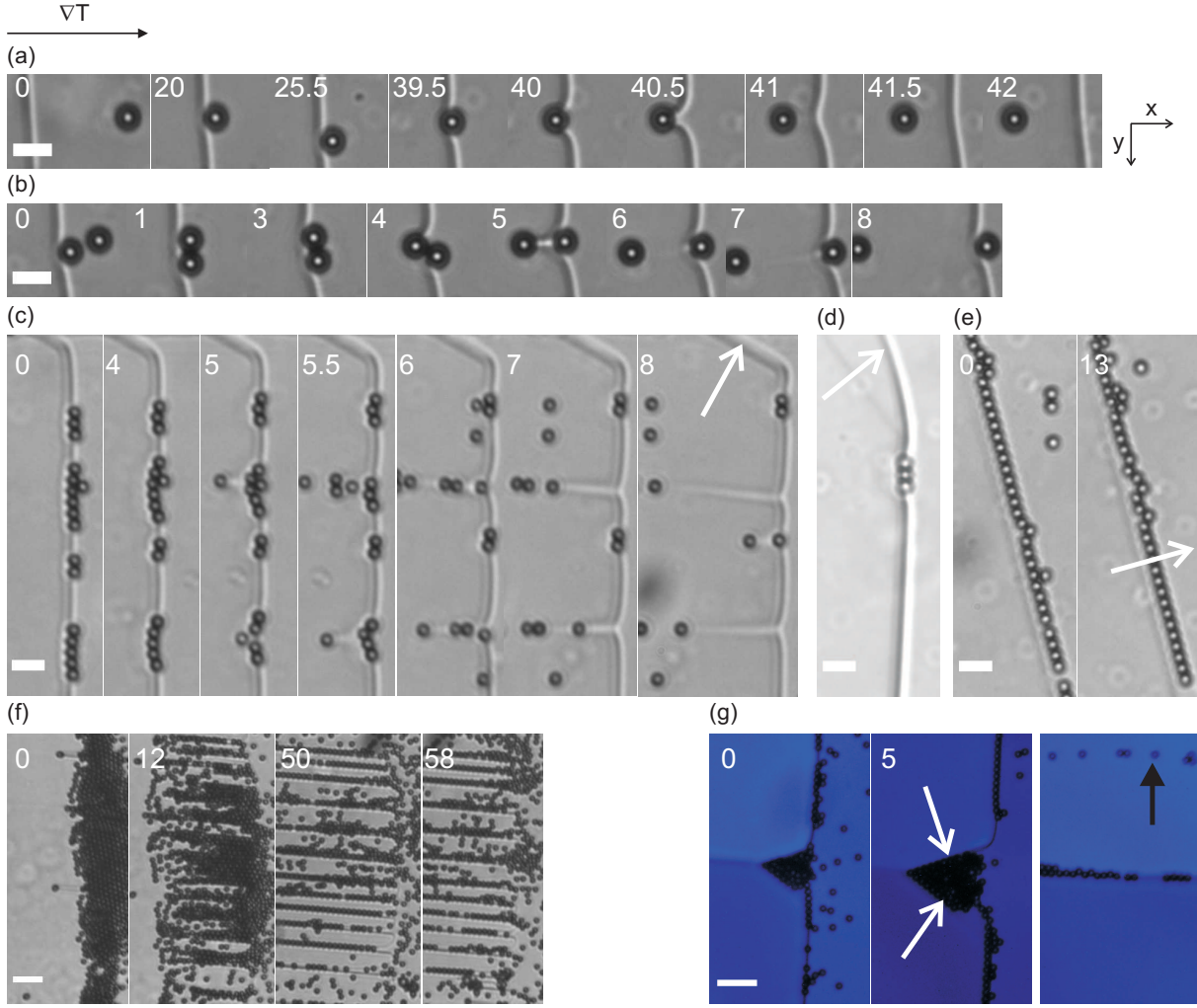


Figure 3.6: Particle trapping in dilute suspensions. (a) The engulfment of a single particle by a moving ice–water interface; (b) the engulfment of a particle after interacting with another particle at the interface; (c) the trapping of a layer of particles; (d) particles resistant to engulfment at a grain edge; (e) a particular grain edge that is resistant to particle engulfment; (f) entrapment of particles by an unstable interface; (g) particle collection in front of a grain boundary, and their subsequent entrapment (final image), particles engulfed within a single grain are indicated by the black arrow. Conditions for each experiment are tabulated in table 3.1. Times (in s) are shown in the top left of each image. White arrows show the direction of growth of the engulfment resistant facet. All samples were contained in PDMS channels of height = 8 μm , with a temperature gradient, ∇T , acting along the direction shown at the top. The scale bars in (a)–(e) denote 10 μm , and in (f) and (g) denote 20 μm . [Colour online]

in the interface, caused by an engulfment event (e.g. $t = 5$ s), makes it easier to engulf more particles at the same position, therefore lines of particles form in the ice. In figure 3.6 (c)–(e) the images show how some facets of ice can be more repellent to particles. The white arrows show the direction of growth of the non-roughened facet. The surface facets depend on the orientation of the nucleated ice crystal. As this facet becomes increasingly perpendicular to ∇T , the particles are forced to interact with it, and they resist being engulfed up to a much higher

Experiment	∇T (K mm ⁻¹)	R (μm)	V_i ($\mu\text{m s}^{-1}$)	particle concentration
(a)	2.9	3.1	10	dilute
(b)	2.9	3.1	10	dilute
(c)	5.9	1.8	20	dilute, single layer
(d)	5.9	1.8	5	dilute
(e)	2.9	1.8	20	dilute, single layer
(f)	7.4	1.8	5	concentrated at the interface
(g)	2.2	1.8	10	dilute, single layer

Table 3.1: Conditions for trapping experiments presented in figure 3.6.

particle concentration at the interface, even at this relatively lower gradient. An explanation for this changing behaviour may be because different crystal facets experience different degrees of premelting (see e.g. [112]). In figure 3.6 (f), the interface has become unstable, likely because of the sample history (since the gradient is relatively high), and particles are entrapped along the walls of the cellular projections, as they grow. The ‘sample history’ refers to the consideration of effects such as how much of the sample cell has already been frozen. As any impurity in the suspension is not soluble in the ice which freezes from it, towards the end of an experiment, the impurity concentration gradient next to the interface will be different from at the start. For clarity, this impurity is not added, but would be already present with the particles. In figure 3.6 (g), particles build up inside a grain boundary groove, which subsequently increases in size. The grain boundary is confirmed by use of polarised light microscopy, showing that the line parallel to ∇T , which stems from the groove, is indeed between crystals of different colours and therefore different grains with different orientations. Once the viscous resistance is too high to support the growth of ice behind the particles, they are eventually entrapped along the grain boundary, as shown in the final image. This image also shows that particles may also be engulfed by the planar interface of a single grain (see top of image).

Measuring critical particle engulfment velocities is difficult, because of the complexity of the ice–water interface. Generally, as explained in the above section, surface facets and grooves are more likely under a low gradient, whereas planar interfaces are more common at high gradients, though both types of interface may occur under both conditions, depending on the history of the sample.

Once a planar ice–water interface has been formed in a dilute suspension of particles, the critical engulfment velocity may be measured. In our experiments here, we can directly control

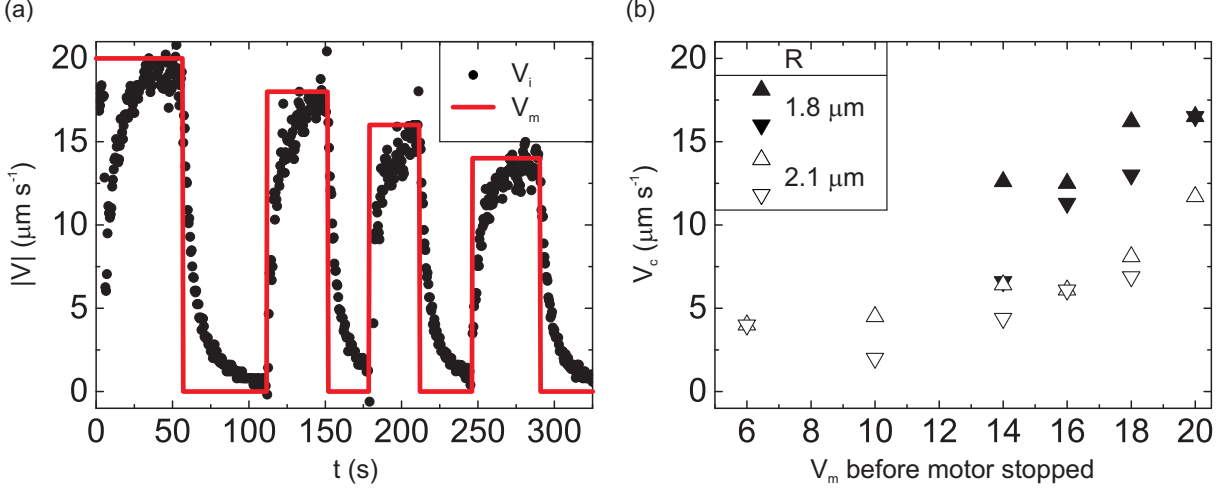


Figure 3.7: (a) Graph of the motor speed, $|V_m|$ and $|V_i|$ vs time, t . (b) Graph of the critical engulfment velocity, V_c , for two different particle sizes, $R = 1.8 \mu\text{m}$ and $R = 2.1 \mu\text{m}$ (closed and open symbols), where the maximum and minimum threshold (up and down triangles) are found by the change in V_i between the frames where particles are engulfed and when they are rejected from the ice.

the speed of the motor, V_m . We have shown in section 3.3 that $V_m = V_i$. Ideally, the speed is increased incrementally until the particle is engulfed, thus obtaining V_c . However, as figure 3.6 (c) shows, V_c is still difficult to define. From a time of 5 s, one particle is engulfed, however, the engulfment process does not happen instantaneously. Between the images, the interface is moving, but some particles continue to be pushed out. Even if the suspension is made so dilute that the continuing growth of ice under the critical engulfment velocity does not build up a layer of particles, there continues to be some hysteresis in the system. Therefore, we developed a new method, where the ice was grown at a speed above V_c , then the motor was stopped, and the interface decelerated until it came to a standstill. When the motor was stopped, V_i can be accurately measured by tracking. At some point during the interface deceleration, the sampled particles in the suspension transition from being engulfed to being pushed out, therefore V_c is directly measured. The maximum and minimum V_c is taken by looking at a graph of V_i , and reading off the value of V_i when t is between engulfing and rejecting particles. There is a dependence on the value of V_m before the motor stops, which shows the complexity of the problem, as this is probably caused by the history of the sample. For example, an impurity build up in the system may cause easier trapping later on in the experiment. Nevertheless, our results clearly demonstrate the dependence of V_c on R , for a larger particle is more easily engulfed. The average value for V_c is $\sim 13 \mu\text{m s}^{-1}$ for $R = 1.8 \mu\text{m}$ and $\sim 6 \mu\text{m s}^{-1}$ for $R = 2.1 \mu\text{m}$, and here

$\nabla T = 7.3 \text{ K mm}^{-1}$. From equation 3.6 and using the values in table 2.4, the viscosity of water at T_m , $\eta = 2 \times 10^{-3} \text{ Pa s}$, and $\lambda = 5 \text{ \AA}$ (see later in the chapter for typical values), we find that the theoretical V_c are 16 and $14 \text{ \mu m s}^{-1}$, which are close to the experimental values.

After ice growth – regelation

Particles which move in parallel to the applied temperature gradient from cold to warm, and accelerate out of the ice, are observed in our system. These are defined as ‘regelating’ particles, and they move because of the thermomolecular force, defined in equation 3.7. In figure 3.8 (a), a time series showing a particle moving relative to the ice–water interface is shown. The deflections in the ice–water interface are similar to that observed in 3.6 (a), but occurring in reverse. In figure 3.8 (b), a time series of a larger area of ice is shown. The images were taken under polarised light microscopy, meaning that grains within the ice could be distinguished by colour. Some particles, which show representative behaviour, are boxed and labelled 1–5.

A description of them is as follows:

- P1. moves out of the ice, in a direction nearly parallel to ∇T ,
- P2. held in a triple junction grain boundary, which moves, dragging the particle with it,
- P3. (initially top particle) starts in a grain, moves into a grain boundary, and moves out of the ice following grain boundaries, rather than exactly parallel to ∇T ,
- P4. (initially bottom particle) starts in a grain boundary, and moves out of the ice following grain boundaries, rather than exactly parallel to ∇T ,
- P5. stuck particle, which does not move over course of experiment.

From these observations, the redistribution of particles by the application of a temperature gradient is clear. Furthermore, the influence of grain boundaries on the motion of particles is also demonstrated.

For a given experiment, the distance between a particle and the ice–water interface, Δx , is found, as described in section 3.3. A plot of particle trajectories over an image of the suspension at the initial time, $t = 0 \text{ s}$, is shown in figure 3.9 (a), while the power law fits (equation 3.10)

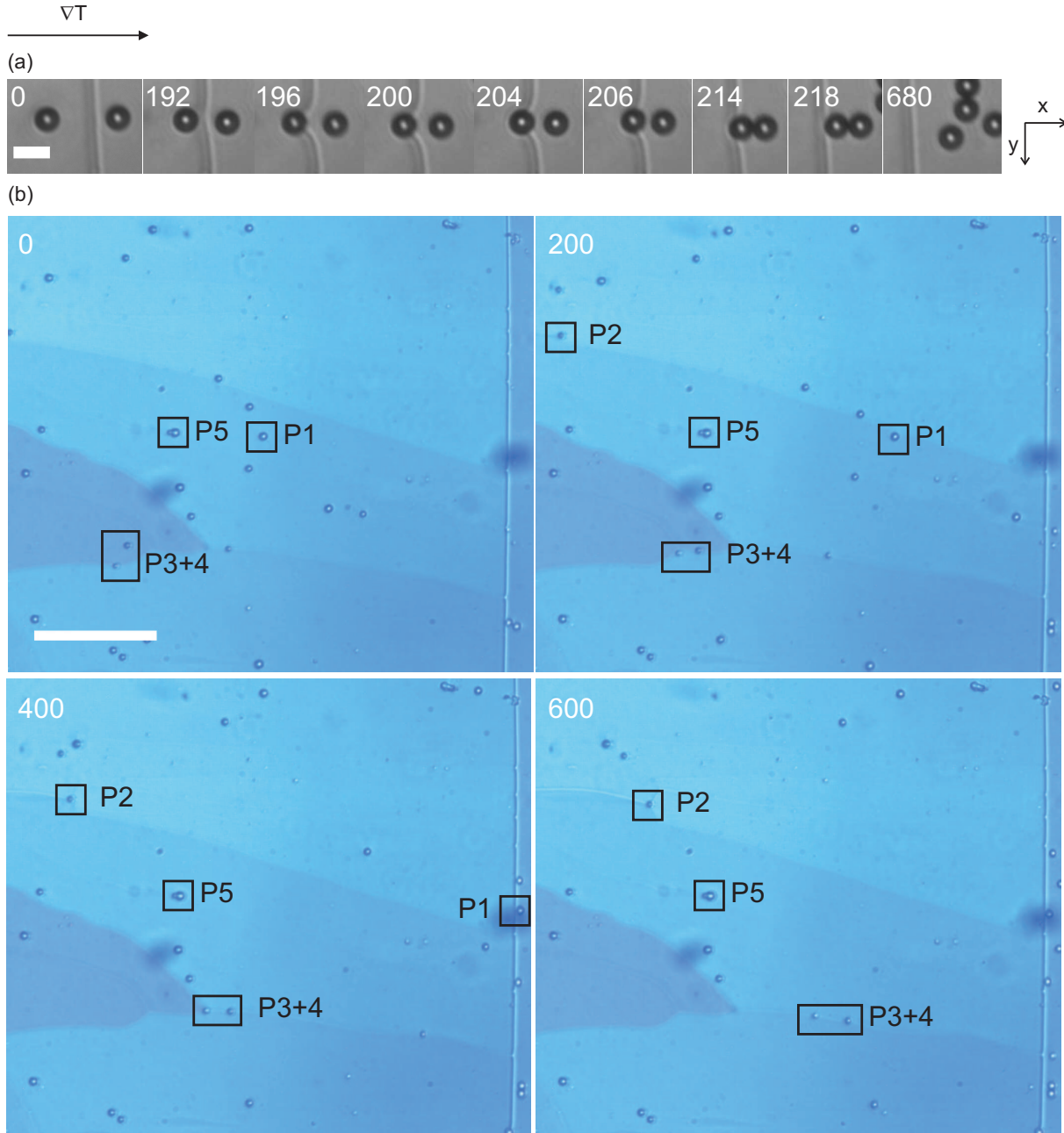


Figure 3.8: Regelation in dilute suspensions. (a) The regelation of a single melamine particle ($\nabla T = 2.9 \text{ K mm}^{-1}$); (b) the regelation of many silica particles, some particles are boxed and labelled 1–5, and are discussed in the text ($\nabla T = 7.4 \text{ K mm}^{-1}$). Times (in s) are shown in the top left of each image. All samples were contained in PDMS channels of height = $8 \text{ }\mu\text{m}$, with a temperature gradient, ∇T , acting along the direction shown at the top. The scale bar denotes $10 \text{ }\mu\text{m}$ in (a), and $100 \text{ }\mu\text{m}$ in (b). [Colour online]

to the Δx vs t data for five particles are shown in (b). These five particles, which are boxed in figure 3.9 (a), are separated into four particles which were trapped within an ice grain, that moved parallel to the temperature gradient, ∇T , and a particle that was trapped between two

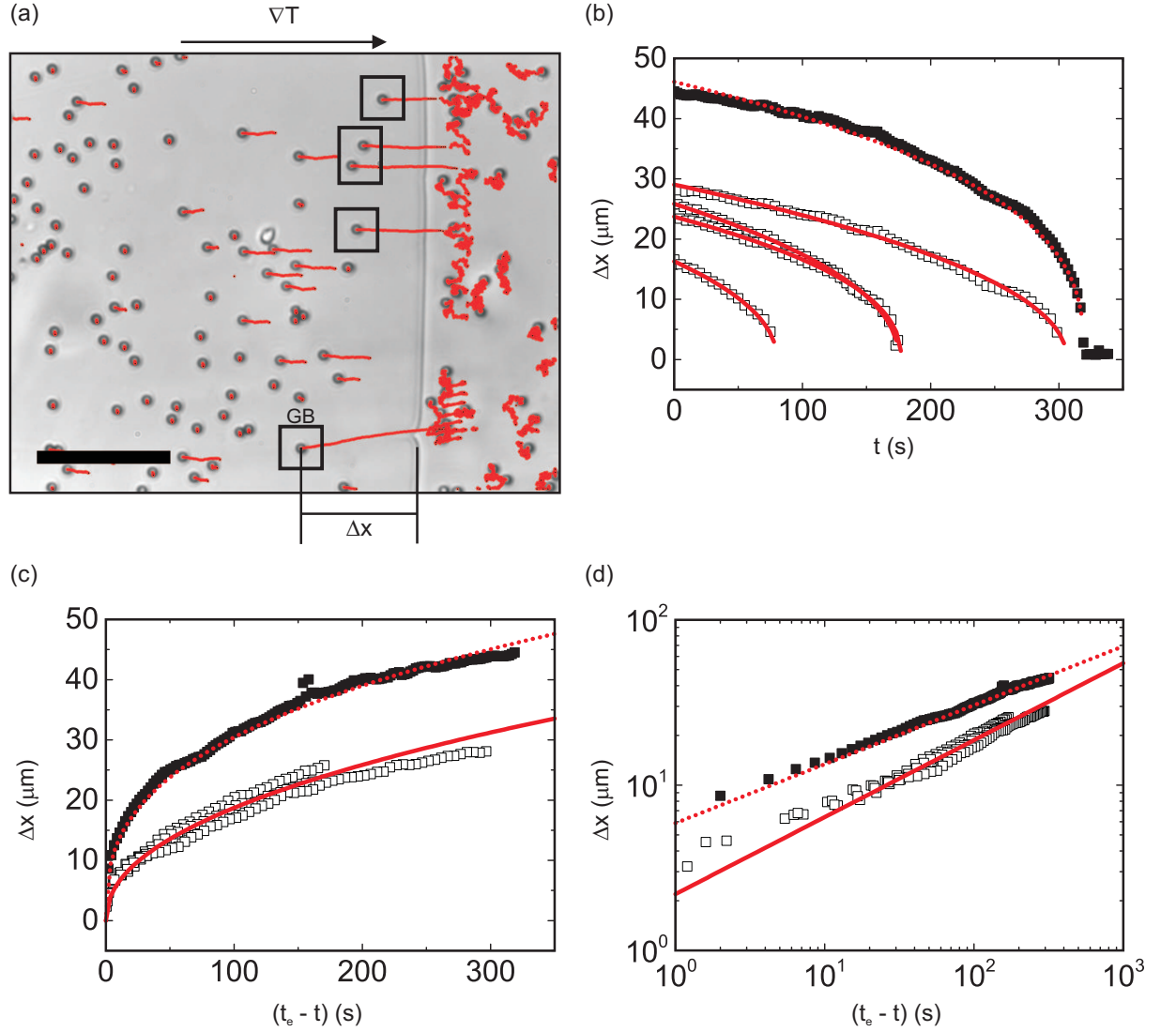


Figure 3.9: (a) Overplot of tracks of particles over an image of the suspension at the initial time. The position of the particle relative to the interface, Δx , is shown for the grain boundary (GB) particle. This particular particle is a special case, as it is trapped in a grain boundary – the grain boundary groove can be seen at the ice–water interface. The scale bar denotes $50 \mu\text{m}$, and the direction of the temperature gradient, ∇T , is also shown. (b) Δx vs time, t for the five boxed particles in (a) (open symbols – non-grain boundary, closed symbols – grain boundary), fitted with a power law of the form $\Delta x = [a(t_e - t)]^b$, as described in the text (solid lines – non-grain boundary, dotted lines – grain boundary). (c) & (d) Plots (linear and log scales) of Δx vs $(t_e - t)$, with power law fits.

separate grains, moving along a grain boundary, at a slight angle to ∇T . The same data are shown in figure 3.9 (c) and (d), but here Δx is plotted against the time relative to the time at which the particles are released from the ice, $(t_e - t)$. From the fit parameters, λ and ν are calculated for each particle, and the average and standard deviation, taken over similar particles. The power law fit shown in figure 3.9 (c) and (d) for the equivalent particles uses the average a

Experiment	Notes	R (μm)	∇T (K mm^{-1})	λ ($\text{\AA}$)	S.D. ($\text{\AA}$)	ν	S.D.
1 (a)	figure 3.9	1.8	2.9	3.17	0.93	2.61	0.26
(b)	figure 3.9 (grain boundary)	1.8	2.9	0.71	—	1.66	—
2		1.8	2.9	2.88	1.01	2.77	0.33
3	figure 3.6 (f) (in cellular grooves)	1.8	7.3	7.21	0.91	3.28	0.23
4		2.1	1.5	3.77	2.85	3.08	0.90
5		3.1	2.9	3.52	2.59	2.93	0.67

Table 3.2: Conditions for regelation experiments presented in figure 3.10. Here, λ and ν are averaged over a number of fits, where possible. ‘S.D.’ stands for Standard Deviation.

and b values, as calculated from these average values of λ and ν .

A series of experiments were performed, in order to test the method, and study the relative importance of the radius of the particle, engulfment history, temperature gradient and concentration of impurities. The first two topics will be discussed in this section (experiments 1–5), and the second two topics will be discussed in the following section, which specifically deals with impurities (experiments 6–8). The details of the first 5 experiments are summarised in the table below (table 3.2). Note that experiment 1 corresponds to the data presented in figure 3.9, with the grain boundary particle separated from the rest of the data, and experiment 3 corresponds to the particles that were trapped by a cellular instability as shown in figure 3.6 (f).

By comparing the expressions for Δx in equations 3.10 and 3.15, free fitting parameters a and b can be used to determine the physical constants λ and ν , which together determine the premelted layer thickness, d , as a function of the undercooling, ΔT . The average values of λ and ν for each experiment are tabulated in table 3.2. In figure 3.10 (a), Δx is plotted as a function of $(t_e - t)$ for each of the experiments. The power law fits, $\Delta x = [a(t_e - t)]^b$, for the data of figure 3.9 are shown as examples, and lines which correspond to $\nu = 2$ and 4 are also shown for comparison. According to equation 3.11, the magnitude of Δx is proportional to the velocity of the particle, if b is constant. Comparing the particles with similar b (or similar ν since from equations 3.10, 3.14 and 3.15 we find $\nu = 3b/(1 - b)$), the particles with the highest velocity are in experiment 3, which we note, have unusual engulfment conditions. Although V does in theory depend on ∇T (equations 3.12 and 3.13), which for experiment 3 is different, it is possible to compare the data because for $\nu = 3$, $(\nabla T/T_m)^{(1-(3/\nu))} = 1$. We will see in the

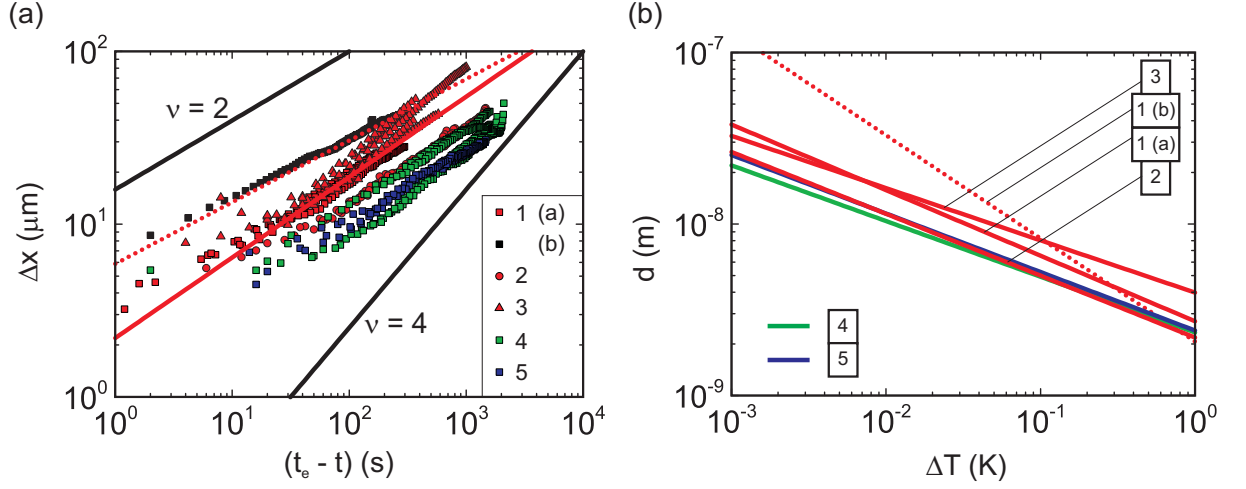


Figure 3.10: (a) Graph showing Δx vs $(t_e - t)$ for experiments 1–5 with conditions shown in table 3.2. The lines $\Delta x = [a(t_e - t)]^b$ are plotted for experiment 1 (a) (red solid) and (b) (red dotted) as examples, where a and b were found from the power law fits. Also shown are examples of lines which correspond to $\nu = 2$ and 4 for comparison. (b) Graph showing the premelted layer thickness, d , vs the undercooling, ΔT (equation 3.3), where λ and ν are calculated using the method described in section 3.3. The experiment names, as shown in table 3.2 label the red $1.8 \mu\text{m}$ particle lines.

next section that the particle velocity is fairly independent of ∇T .

In figure 3.10 (b), the premelted layer thickness d vs the undercooling, ΔT , is plotted for all the experiments, where d is defined by equation 3.3. For all particles ν is close to a value of 3, which implies that non-retarded van der Waals interactions are acting as the dominant interfacial interaction controlling the premelted layer thickness. However, the grain boundary particle has a much lower effective ν , where we interpret the data assuming the definitions of F_T and F_η are still valid for this case. This suggests another mechanism is involved in forming the premelted layer which separates the particle from the ice. This makes physical sense, if we consider that the particle is not only surrounded by a layer separating it from surrounding ice grains, but it also touches a channel, formed by a premelted layer in the grain boundary. A sketch of a possible situation is shown in figure 3.11, though we hope that future theoretical work will investigate this effect. ν seems to be unaffected by the engulfment mechanism, though the value of λ is significantly higher for particles which were trapped along the cellular instabilities. This results in a thicker premelted layer for all undercoolings.

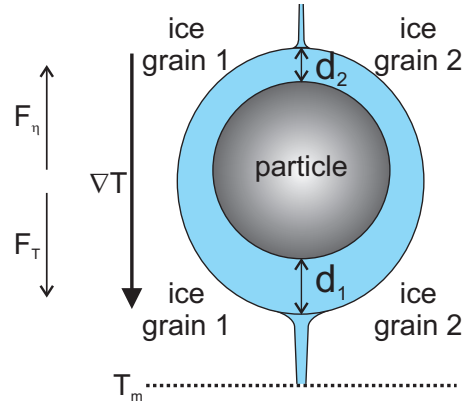


Figure 3.11: Schematic for particle regelation (not to scale), where the particle is trapped between two ice grains, along a grain boundary. The direction of the temperature gradient, ∇T , is indicated, as well as the directions of the thermomolecular and viscous forces, F_T and F_η . Regions where premelted water is present are coloured blue.

3.4.3 Impurity effect

In a further series of experiments, the effect of doping the solution with impurities on regelation was investigated. First, an ethanol solution, at concentration 1 M containing no particles was observed after ice had been nucleated and a temperature gradient set up. Then, suspensions of silica particles, used because of their relevance in the frost heave experiments in chapters 4 and 5, of average radius $\sim 2.3 \mu\text{m}$, were made up in solutions at different concentrations of ethanol.

The instability in the ice interface is clearly visible in the presence of impurities. This instability during ice growth, either at the point of nucleation (mainly equiaxed growth), or during directional growth, where the sample is pulled across the temperature gradient, results in pockets of water being trapped in the ice. This phenomena is known as pinching, and the ice–water interfaces formed as a result of this can be seen in figure 3.12 (a). After the liquid has been trapped in the ice, there is a drive for the pocket to move along the temperature

Experiment	Ethanol concentration (M)	∇T (K mm ⁻¹)	λ (Å)	ν
6 (a)	0.30	7.3	27	3.6
(b)	0.30	10.2	21	3.3
7 (a)	0.45	7.3	25	3.3
(b)	0.45	10.2	23	3.2
8 (a)	0.87	7.3	21	3.3
(b)	0.87	10.2	30	3.9

Table 3.3: Conditions for regelation experiments presented in 3.13.

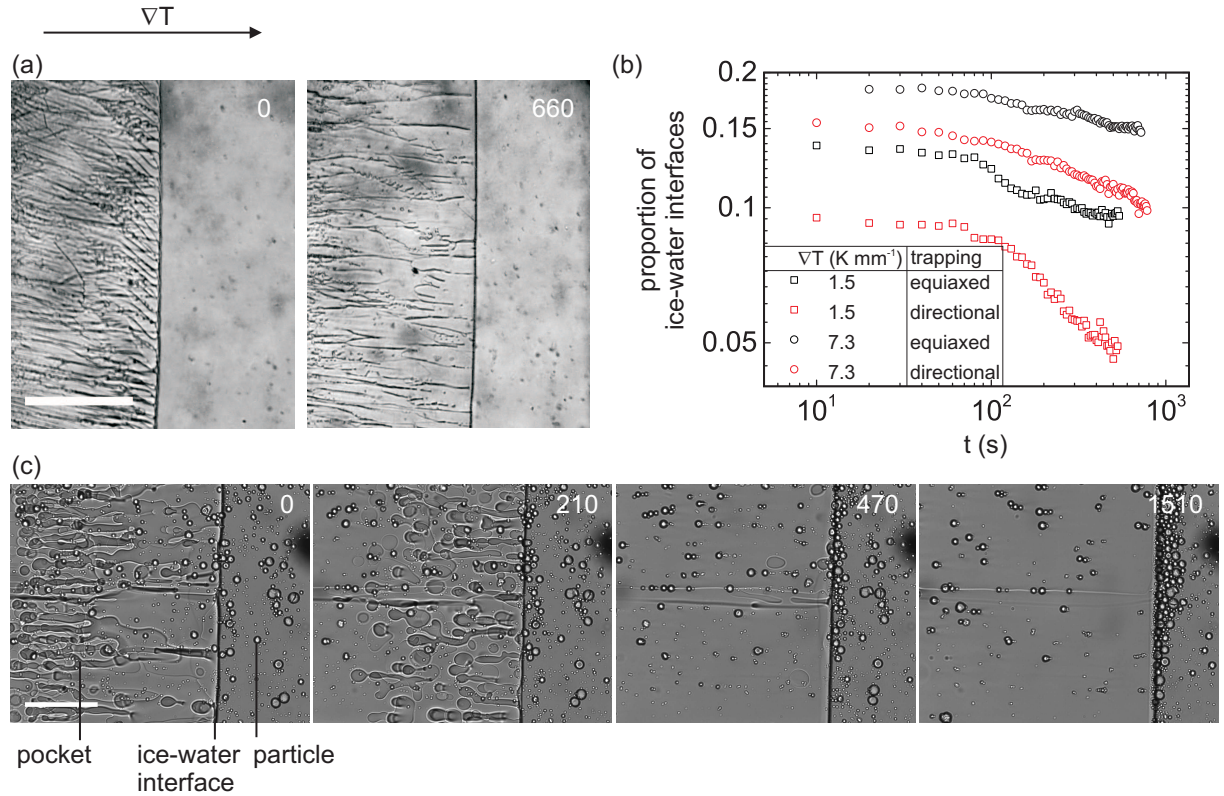


Figure 3.12: (a) Ice–water interfaces (right hand side of images) formed after pinching instabilities during ice growth; the scale bar denotes 500 μm . (b) Ice–water interfaces as a function of time for four separate experiments, where the temperature gradient and trapping mechanism is varied. (c) Images of pockets of premelted solution moving out of the ice, along a temperature gradient, and dragging particles; the scale bar denotes 50 μm . Times (in s) are shown in the top right of each image and the temperature gradient, ∇T , acts along the direction shown at the top.

gradient and out of the ice. This causes the proportion of interfaces in the images to decrease, as it tends towards a situation where only the ice–water interface, which is perpendicular to the temperature gradient, is present. A graph showing how the proportion of these interfaces change over time, under different conditions, is shown in figure 3.12 (b). This instability may have a strong effect on the particles which are trapped in the ice region. Bubbles of premelted solution may drag particles out of the ice. An example of this behaviour is shown in figure 3.12 (c); the ethanol concentration here is 0.45 M. Those particles surrounded by only ice, and not moved by the initial pocket motion, are likely to have a higher impurity concentration in this premelted liquid layer. These particles were observed to regelate, and analysed in the same way as in the previous section; the conditions are summarised in table 3.3.

In figure 3.13, the results of the above experiments are plotted, as well as some of experiments 1–3, for comparison. The particles move with a much greater velocity, as compared to all

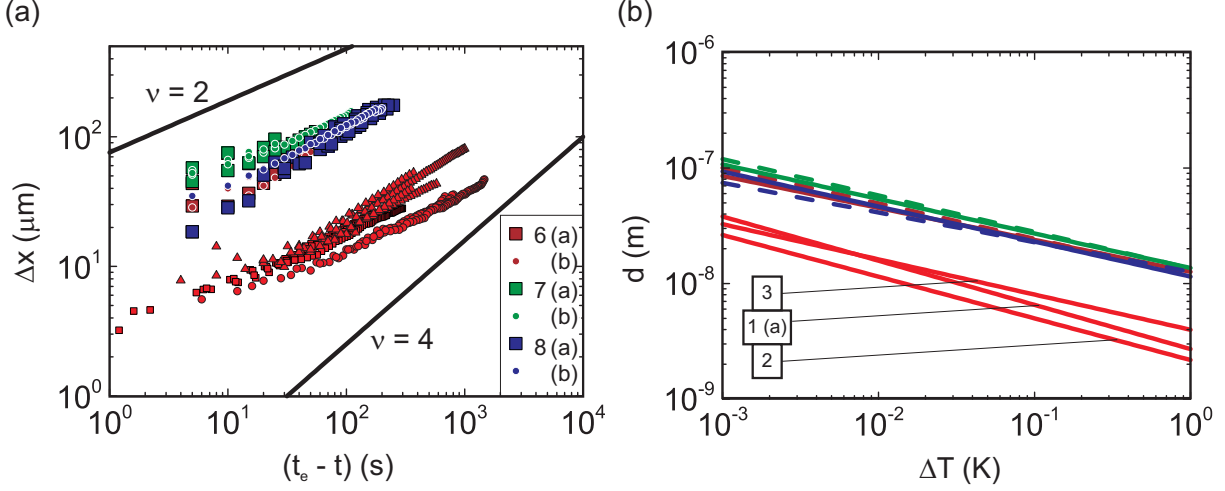


Figure 3.13: (a) Graph showing Δx vs $(t_e - t)$ for experiments 6–8 with conditions shown in table 3.3. Also shown are experiments 1 (a), 2 and 3 (symbols as defined in figure 3.10) for comparison. Examples of lines which correspond to $\nu = 2$ and 4 are shown for comparison. (b) Graph showing the premelted layer thickness, d , vs the undercooling, ΔT (equation 3.3), where λ and ν are calculated using the method described in section 3.3. Line colours are the same as the symbols in (a); solid lines represent (a) and dashed lines represent (b). The experiment names, as shown in table 3.2, label experiments 1–3 (the red 1.8 μm particle lines), shown for comparison.

the previous experiments. The premelted layer thickness is greater in all the samples containing impurities, over all undercoolings. λ is greater because of changes to the interfacial interactions. The change of temperature gradient has very little effect on d . The fits give slightly larger values for ν , which might suggest that the behaviour is being affected by the van der Waals retarded forces, which come into play when the layer thickens.

3.5 Conclusions

Colloidal scale particles interact with ice in many interesting ways. By directly observing the ice–water interface, we have shown that both engulfment and regelation can be observed at the particle scale. Particle inclusion in the ice is strongly affected by the ice grain structure, for example facets, cellular instabilities and grain boundaries. In fact, the term engulfment is replaced by another term, entrapment, when a particle is not trapped by a planar ice–water interface perpendicular to the temperature gradient. We have shown that this planar interface is possible, and more likely under larger temperature gradients in our system, as the gradient causes the grain to ‘roughen’. However, temperature gradient control does not exclude other effects

coming into play, such as the effect of impurities. A simple method of measuring the critical engulfment velocity at this planar interface was employed, to find that the results followed theoretical trends for the particle radii effect, where the larger particles were engulfed more easily.

We have found that regelation causes trapped particles to move within ice. The motion of a particle in relation to the bulk ice–water interface can be measured using our setup. Using this technique, premelted layer thicknesses can be measured as a function of the undercooling, by simply measuring the speed the particle moves through the ice as a function of the particle’s position relative to the ice–water interface. This was repeated under a number of different conditions. Particles moved at speeds typically of the order of $0.01 \mu\text{m s}^{-1}$ for 0.1 K below bulk melting and $1 \mu\text{m s}^{-1}$ for 0.01 K. With the addition of impurities, particles already move at $0.1 \mu\text{m s}^{-1}$ at 1 K below bulk melting. This translates to a typical premelted layer thickness of between ~ 1 nm and 50 nm and between 10 and 100 nm for suspensions with impurities. The value ν was typically around 3, which corresponds to non-retarded van der Waals interactions. The particle radius had little effect on the layer thickness, but the addition of impurities caused the layer to thicken significantly, meaning that particles were able to move relatively fast. This is an important observation as impurity is common in most settings outside the laboratory, such as in nature, and in industry. There are also clear differences in premelted layer thicknesses given a particles’ position in the ice, which is mainly determined by its engulfment history. These effects play an important role and require further exploration.

Acknowledgements

Rob Style, Stephen Peppin, John Wettlaufer and Timea Thorpe are thanked for many useful discussions.

Chapter 4

Segregated ice growth in a colloidal model system

ABSTRACT

In this chapter, we study the freezing of a dispersion of colloidal silica particles in water, focusing on the formation of segregated ice in the form of ice lenses. Local temperature measurements in combination with video microscopy lead to insights into the rich variety of factors that control ice lens formation. We observe the initiation of the lenses, their growth morphology and their final thickness and spacing. Surprisingly, we find that the growth rate of a lens does not depend on its undercooling. We consider the mixed phase in front of the warmest ice lens; when the cooling rate is brought to zero, a newly formed lens does not completely block the growth of a previously formed lens.

4.1 Introduction

Ice segregation is of key importance in determining the microstructure and bulk properties of materials in a wide range of different fields. Notably, it occurs in cold regions where soils and rocks are often damaged by the formation of bands of segregated (particle-free) ice lenses – a process called ‘frost heave’. Processes that involve faster cooling rates also experience ice segregation. Freeze casting uses ice growth in particle suspensions to form porous ceramics, with controlled, anisotropic microstructure [96, 113–116]. In biology, ice segregation can cause disruption during the cryopreservation of biological matter [117, 118] or in protein crystal annealing [119].

Segregated ice growth is complicated, as evidenced by the large community actively working to understand the physics that underlies this process (see e.g. [120, 121] for reviews specifically on frost heave). This is compounded by the fact that experiments on soils and engineering materials are hard to interpret, due to their heterogeneity and polydispersity. Thus it is necessary to work with model systems, such as suspensions of colloidal particles, to carefully control the freezing process.

Previous experimental work has in particular been divided about the composition of the region ahead of the warmest growing ice lens under slow freezing conditions. Based on experimental evidence, theories have been developed, which crucially, either require the presence or absence of pore ice in this region, these have been elegantly summarised by Peppin and Style [121]. A direct way of probing the presence of pore ice is by the use of microscopy; an indirect method is through measuring the temperature. The final structures of ice lenses formed under different conditions, which would in theory change the composition of this region, can be used as another indirect probe. In particular, control factors are: the particle size and polydispersity (determining local pore size and consequently the extent of frozen pores) and the cooling rate (determining relative temperatures).

Here, we systematically study the process of ice lens growth in a simple model system, using a directional solidification method (adapted from [82, 122]), which gives a fixed, well defined rate of cooling. We uniaxially freeze a suspension of colloidal silica particles in water. Our setup allows for microscopic inspection of the freezing process, measuring the initiation and evolution of the lenses under a range of conditions. We measure the effect of cooling rate and sample cell

conditions on lens formation and growth.

This chapter is organised as follows: first, a short overview of the theories of ice lens formation is given (section 4.2), followed by a description of the experimental methods (section 4.3). Then, the results are presented and discussed in sections 4.4 and 4.5. Finally we summarise our findings in a conclusion (section 4.6).

4.2 Theoretical background

Ice segregation is the separation of pure ice from a freezing particle suspension. Thermally two dimensional freezing occurs in a system where a temperature gradient, ∇T , with limits below and above T_m , the equilibrium melting temperature of ice, is applied to a thin sample, and material is moved parallel to the gradient at a velocity V in the direction of the cold limit. The mechanism for growing segregated ice requires the existence of water below its freezing point. This ‘premelted’ water can exist both due to a repulsive interaction between a particle and ice, or via the Gibbs-Thompson effect, or due to the presence of impurities. These forms of premelting are described in detail in section 2.2.1. The thermomolecular pressure gradient, as described in section 2.2.2, causes the suction of water towards an ice lens, allowing it to grow. In figure 4.1 (a) we show the pressures acting in a system of a lens adjacent to a suspension under a temperature gradient. Here, the water pressure adjacent to the lens, P_w , can be linked to the Darcy pressure, p , for flow through the porous suspension, as described in Appendix A of [123]. Given the pressure balance shown in figure 4.1 (a), equation 2.17, which gives $P_i - P_w$, the difference in the pressures of water and ice in a lens, can be used to find the Darcy pressure in terms of the undercooling, $\Delta T = T_m - T$,

$$p = P_0 - \frac{L_m \rho_i}{T_m} \Delta T. \quad (4.1)$$

Here, L_m is the latent heat of solidification per unit mass of water and ρ_i is the density of ice. The deficit between the pressure of water in the suspension or the Darcy pressure, p , and the pressure in the ice, P_i , is carried by the porous suspension itself, with mechanical equilibrium dictating that $P_i = P_0$.

Experimental observations have started questioning this model: (i) sufficient temperatures

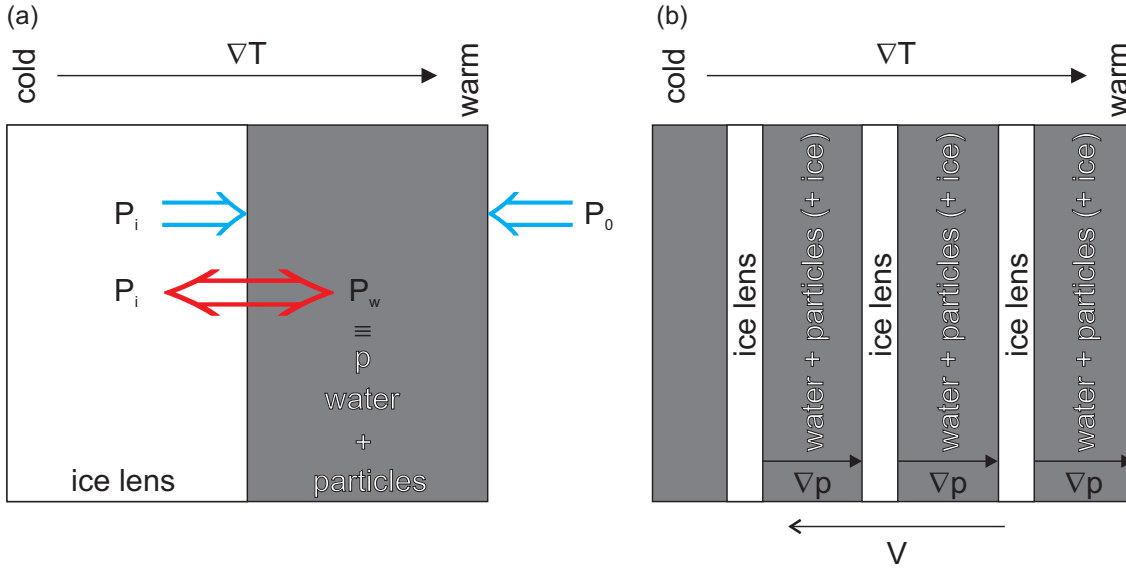


Figure 4.1: (a) Diagram showing pressures acting in a system containing an ice lens adjacent to a partially frozen particle suspension, and which are at thermal (red) and mechanical (blue) equilibrium. (b) Diagram showing the Darcy pressure gradient in the water, ∇p , acting through particle suspensions, containing periodic lenses, which could be partially or fully frozen.

were reached to allow for ice to be contained in the pore space between the particles, based on pore size predictions; (ii) the measured growth rates of ice lenses are too low, based on Darcy’s prediction of the flow rate of water; and (iii) new lenses are able to nucleate ahead of the growing lens, resulting in the observation of series of periodic lenses [121]. The ‘Frozen Fringe’ model resolves all of these problems, by allowing ice to enter the pores between the particles ahead of the warmest lens, in a “frozen fringe” [42, 55, 124–127]. Water can still flow, at a reduced rate, towards a growing lens via the network of premelted layers around the particles. Furthermore, a new lens may nucleate from the ice within the frozen fringe. The role of the frozen fringe is still an ongoing debate in literature [44].

However, some experiments suggest that this ‘frozen fringe’ region does not exist. For example, in the region which is the supposed fringe, Watanabe *et al.* detected no ice by using Raman spectroscopy [128], Beskow noticed that particles could move [129], and the thermal properties measured by Akagawa were most similar to the unfrozen suspension [130]. Other theories have emerged to account for the three observations ((i)–(iii)) described in the previous paragraph, that seemed to require ice to exist in the region. These include a rethink into the pore size predictions, allowing the pores to be smaller and therefore less likely to contain ice (Gibbs–Thomson effect) [41, 131]. Style and Peppin [132] use an effective Darcy pressure, to account for lower than predicted experimental measurements of the growth rate of ice lenses. Thus, the

new Darcy pressure in the water is higher, provided the growth rate is significant, which means that the pressure gradient is lower. Finally, a model which uses a situation analogous to the constitutional supercooling depicted in figure 2.4 (c), but with air or compacted particles ahead of the lens acting like impurities, allows new lenses to nucleate without a frozen fringe [123,133].

It is therefore paramount to look closely at and take temperature measurements of the suspension next to the lens, to determine its composition. Furthermore, we may test the theories indirectly by looking how changing conditions such as the cooling rate affect lens growth rate. The thickness of a lens is determined by the water supply and is equal to $V_{lens}\Delta t$, where Δt is the time spent supplying the lens, and V_{lens} is the average lens growth rate. V_{lens} is given by Darcy's law, as follows. For regularly spaced periodic lenses, as shown in figure 4.1 (b), the Darcy pressure next to the lens is defined by equation 4.1. However, away from the lens surface, the Darcy pressure varies from the value at the lens (low) to the value at a higher temperature (high). Darcy's law predicts the flow rate of water through the porous medium towards the lens, which in turn is the lens growth rate,

$$V_{lens} = -\frac{K}{\eta}\nabla p, \quad (4.2)$$

where K and η are the permeability and the viscosity of the water respectively. The pressure gradient, ∇p is the change in pressure along the distance of the flow, i.e. through the porous particle suspension. For periodic lenses, the spacing between lenses is determined by the nucleation position of the warmer lens, relative to the colder one. The ease of nucleation determines the spacing. The Darcy pressure next to a lens, given by equation 4.1, is strictly proportional to the undercooling. Assuming equal spacings and a linear temperature gradient, the temperature difference between adjacent lenses is fixed. Consequently, ∇p should also be fixed between each pair of lenses, as shown in figure 4.1 (b). In this scenario, a constant water flux through the fringe occurs, meaning that V_{lens} is also constant. This also means that if the pulling speed, $V = 0$, then the pressure gradient causes water flow through the suspension towards all lenses, at equal rates, so that the colder lenses could theoretically still grow, and at the same rate as the warmest lens. However, if ice is present in pores, then the permeability of the particle suspension, therefore the lens growth rate, will be highly temperature dependent.

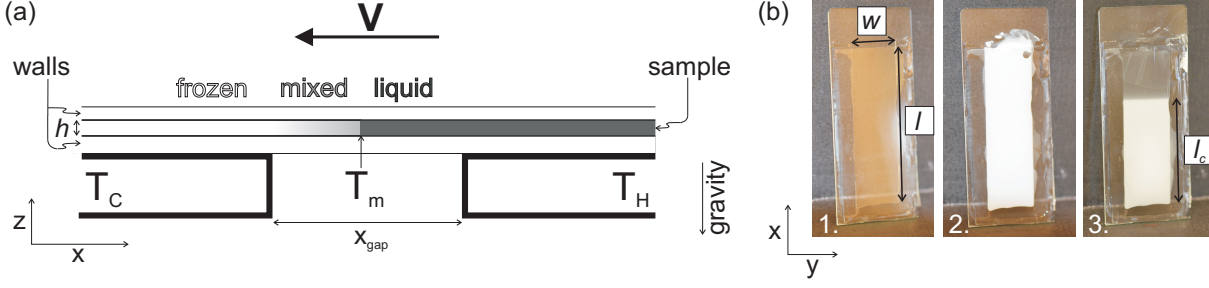


Figure 4.2: (a) A schematic of the experimental setup (not to scale), showing the sample contained within two glass walls. It is placed on two temperature controlled plates, at temperatures T_C and T_H , where T_m , the melting temperature of pure bulk water, is between the plates. The phases of the sample are shown above their corresponding x position. The positive direction of the velocity of the motor, V , the height of the sample, h , and the length of the gap between the plates, x_{gap} are also shown. l , w and h are in the x , y and z directions. (b) Photographs of: 1. an empty sample cell, where the length, l , and width, w , dimensions are marked; 2. a filled sample cell; 3. a sample cell after centrifugation, where the length of the suspension after centrifugation, l_c , is marked.

4.3 Experimental methods

A unidirectional solidification apparatus was used to observe the formation of segregated ice by freezing a thermally two-dimensional suspension of silica particles. A sample was pulled across a gradient, ∇T , at a fixed speed, V , where both the gradient and the speed could be independently controlled. A diagram of the setup is shown in figure 4.2 (a), and is described in more detail in section 2.3.

4.3.1 Sample cell

The thermally 2D cell was prepared by gluing two glass slides together with two glass slide spacers in between (see section 2.3.4 and figure 2.7 (a) for method of preparation). All glass was washed with ethanol, then plasma cleaned for at least 1 minute. The internal volume of the cell was $45 \times 12 \times 0.28 \text{ mm}^3$ (length $l \times$ width $w \times$ height h). The l and w dimensions of the cells could vary by a few mm, and h by up to 0.02 mm. The area $l \times w$ was not thought to affect the ice lens formation, as $l, w \gg h$. The effect of varying h was tested in one experiment by adding an extra spacer half way along l in one sample cell, so that $h = 0.39 \text{ mm}$.

A thinner cell, made from PDMS (polydimethylsiloxane), was also used to gain further insight into the segregation of ice. The internal volume of the cell was $30 \times 5 \times 0.1 \text{ mm}^3$. The l and w dimensions were the same order of magnitude as the glass walled cell, but h was halved.

4.3.2 Colloidal model system

The silica particles were obtained as a powder from JGC Catalysts and Chemicals. They were fairly polydisperse, with documented particle diameters ranging from 1 – 3 μm , and an average size of 1.5 μm . Particle suspensions were made up with solutions of ultra pure water at initial particle volume fraction $\phi_{p,i} = 0.31$. The particles were washed with water 3 times, by repeated centrifugation and redispersion. This step reduced the ionic impurity level, though there would likely be gaseous impurities present. The suspension was dispersed by ultra-sonic pulsation before being pipetted into the sample cell. The particles were packed by centrifugation for 30 minutes at a relative centrifugal force, ‘rcf’, of 156, with gravity acting along the $-x$ direction of the cell. The centrifugation step determined the initial packing of the particle suspension – the effects of this step are discussed in chapter 5. The top of the cell was left open. No evaporation occurred during the course of the experiment, due to the low temperatures inside the cell.

4.3.3 Directional freezing

A constant cooling rate was applied by pulling the sample across a fixed temperature gradient at a constant velocity. A Linkam GS350 stage was employed, which uses heating elements and a pump-controlled flow of liquid nitrogen to control the temperature of two plates, as shown in figure 2.5. The temperature gradient was created by independently fixing the temperature of the plates, which were separated by a gap of length $x_{gap} \approx 2$ mm. The temperatures of the cold and hot plates, T_C and T_H , were held such that $T_C < T_m < T_H$, where T_m is the melting temperature of pure bulk water. The sample was observed between the gap. A stepper motor held the sample cell in contact with the plates and moved it along the gradient, ∇T , at a velocity, V , with 1 μm increments. The plates had an area of 32×32 mm², which was large in comparison to the sample cell internal area, meaning that a gradient in the y direction was minimal. The sample height was also small so a constant temperature along the z direction was assumed. Heat transfer conditions within the sample cell have already been discussed in section 2.4.2. The whole setup depicted in figure 4.2 was contained within a sealed box to prevent the condensation of water vapour.

First, ice was nucleated by setting $T_C = -30^\circ\text{C}$, and holding T_H at room temperature. After the nucleation event, a temperature gradient was established by setting the plate tem-

peratures: $T_C = -2^\circ\text{C}$ and $T_H = 0.5^\circ\text{C}$. The gradient was left to stabilise for a minimum of 15 minutes before the motor was started. The motor speed was $V = 1.5\mu\text{m s}^{-1}$ unless stated otherwise. The duration of the directional freezing step was about 3 hours.

4.3.4 Microscopy and image analysis

The sample was illuminated from below using a Köhler lens setup, as depicted in figure 2.6. An image of the sample was projected onto a CCD camera using a simple microscope setup above, which had a field of view spanning the entire length of the gap between the two plates. The suspension could be observed at temperatures close to and including T_m , where a mixed ice–water–particle phase existed. Movies were recorded for the duration of sample freezing, typically at one frame per five seconds. After the experiment, the whole frozen sample was imaged to see the final structure, post freezing. To do this, the plates were both held at a temperature of -5°C , after which no melting within the suspension was observed. Moving the motor along the whole range in x , and the stage along y produced about 100 overlapping images. The images were then read in by the Microsoft Image Composite Editor (ICE), and the program stitched the images together, using the overlapping segments, in order to create an image of the whole sample.

The contrast between the areas of ice and the areas of particle suspension (frozen and unfrozen) was large, therefore a simple image analysis technique was employed, where a threshold brightness was set, above which it was determined that a lens was present. In all images presented, segregated ice is light in colour, as light is transmitted from the source below, and the frozen particle suspension is dark. The average thickness of lenses was calculated by measuring the thickness of a lens along its width, then taking the mean thickness of all the lenses along the length of the cell. A threshold was set, whereby if two lenses were measured within a certain distance of each other, they were deemed to be the same lens. The growth of a single lens was also measured, by finding the mean thickness per frame. Programs were written in Mathematica.

4.3.5 Standpipe

A method used to ascribe a temperature to a fixed point in the cell, is by the use of a ‘standpipe’. A standpipe is a cell containing pure water, which is built in parallel to the sample cell that

contains the suspension [134]. The standpipe cell experiences to the best approximation the same conditions as the sample cell, therefore the position of the ice–water interface, which is at the temperature of bulk melting, T_m , can be compared to the positions of interfaces in the parallel suspension–containing cell. The standpipe cell was made by a modification of the method described in section 4.3.1, by placing an extra glass slide spacer along the centre of a cell, to divide it into two discrete sections. To determine the effect of non particulate impurities on the bulk melting temperature (section 2.2.1 III), a sample cell containing the supernatant of the suspension can be frozen under the same conditions.

4.4 Results and discussion

Regions of segregated ice were formed during the directional freezing process in most samples. A typical example of the macroscopic view of the patterns formed is shown in figure 4.3 (a). All samples were frozen from left to right. The process of formation of ice lenses is presented in section 4.4.1, followed by an analysis of the ice lenses using polarised light microscopy in section 4.4.2. In section 4.4.3, temperature measurements taken inside the cell are presented. The final structure of the frozen suspension is shown in section 4.4.4. Finally in sections 4.4.5 and 4.4.6 the effect of changing the rate of cooling and the sample cell walls is demonstrated.

4.4.1 Growth of segregated ice

The formation of segregated ice lenses perpendicular to the temperature gradient was observed. Movies recorded for the duration of the experiment were analysed in order to determine physical properties such as the growth rate of a lens, and the position of relevant interfaces along x . The interface positions can then be related to the temperature by use of the thermocouple measurement, which was introduced in section 2.4.1, or by the standpipe, explained in section 4.3.5. The scale along x is standardised between measurements by taking $x = 0$ as the centre between the plates, and for an image $x = 0$ is estimated from the position of the plate edges.

We will now give a full description of the experiment in successive stages, referring to figure 4.4 for an overview, and to figures 4.3 and 4.5 for further results and analysis.

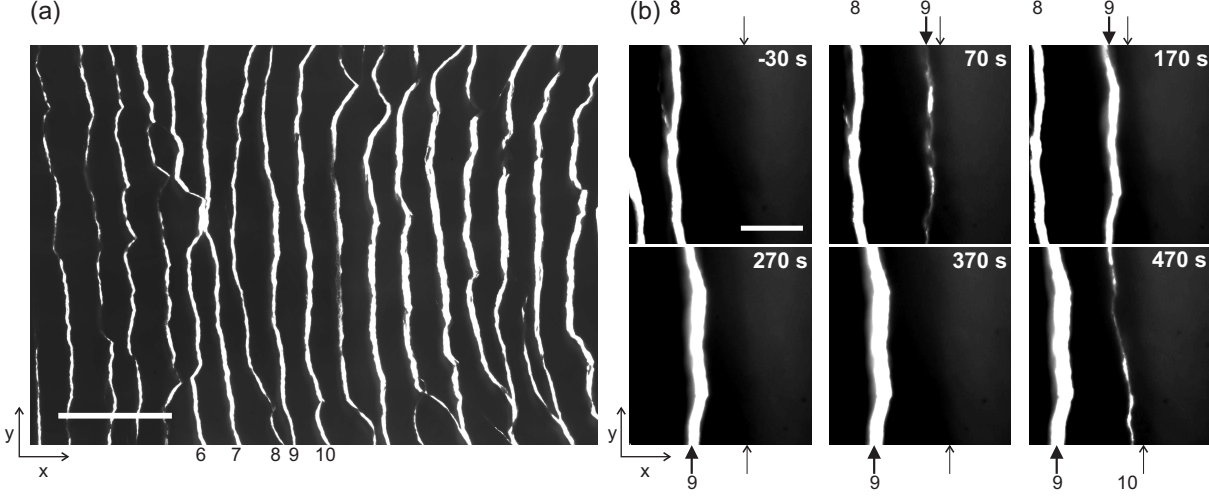


Figure 4.3: (a) Typical image of segregated ice in the form of ice lenses (labelled 6 – 10); segregated ice appears light, and frozen suspension appears dark. The scale bar denotes 2 mm. (b) A time series showing the nucleation of a lens. The sample has moved across a distance of ($V \times \text{time}$) in each subsequent frame. Thick arrows point towards the growing lens (9), and the surrounding lenses (8 and 10) are labelled. The thin arrows point towards the edge of the darker region of the suspension. The temperature range from the left to right of each image is $-0.8 \rightarrow -0.3^\circ\text{C}$. The scale bar denotes 500 μm ; times, with respect to the approximate nucleation time of lens 9 at $t = 0$ s, are shown within each image.

Stage 1. Nucleation: figure 4.4 (a)

The nucleation of ice results in unstable dendritic growth of large ice crystals. The ice can be observed in the image on the left hand side as a darker region, as compared the unfrozen lighter left hand side, beyond $x = x_{nuc}$. When water freezes, the refractive index (RI) changes from 1.33 to 1.31, while the silica particles have an RI of 1.54. The RI difference between the surrounding medium and the particles will therefore increase when ice is present. The enhanced refractive index difference on freezing (ice–particle) and also the new ice–water RI difference, will result in more scattering, and therefore less transmission of light. This initial rapid ice growth creates irreversible changes in ϕ_p [74], therefore causing different conditions for lens formation. Lenses forming in this ‘pre-frozen’ region were hence discarded during analysis. The position of x_{nuc} has little meaning, as it depends on the exact temperature gradient at the point of ice nucleation. The higher x_{nuc} , the more ‘pre-frozen’ suspension must be disregarded.

Stage 2. Gradient set, and nucleation and growth of first ice lens: figure 4.4 (b)

After ice nucleation, the intended gradient of the experiment is set. During this process, which involves heating and cooling the plates, the first ice lens nucleates at a position x_{LC} , and grows as its ‘hot’ side, at position x_{LH} , is moving towards the right, where the subscripts LC and LH

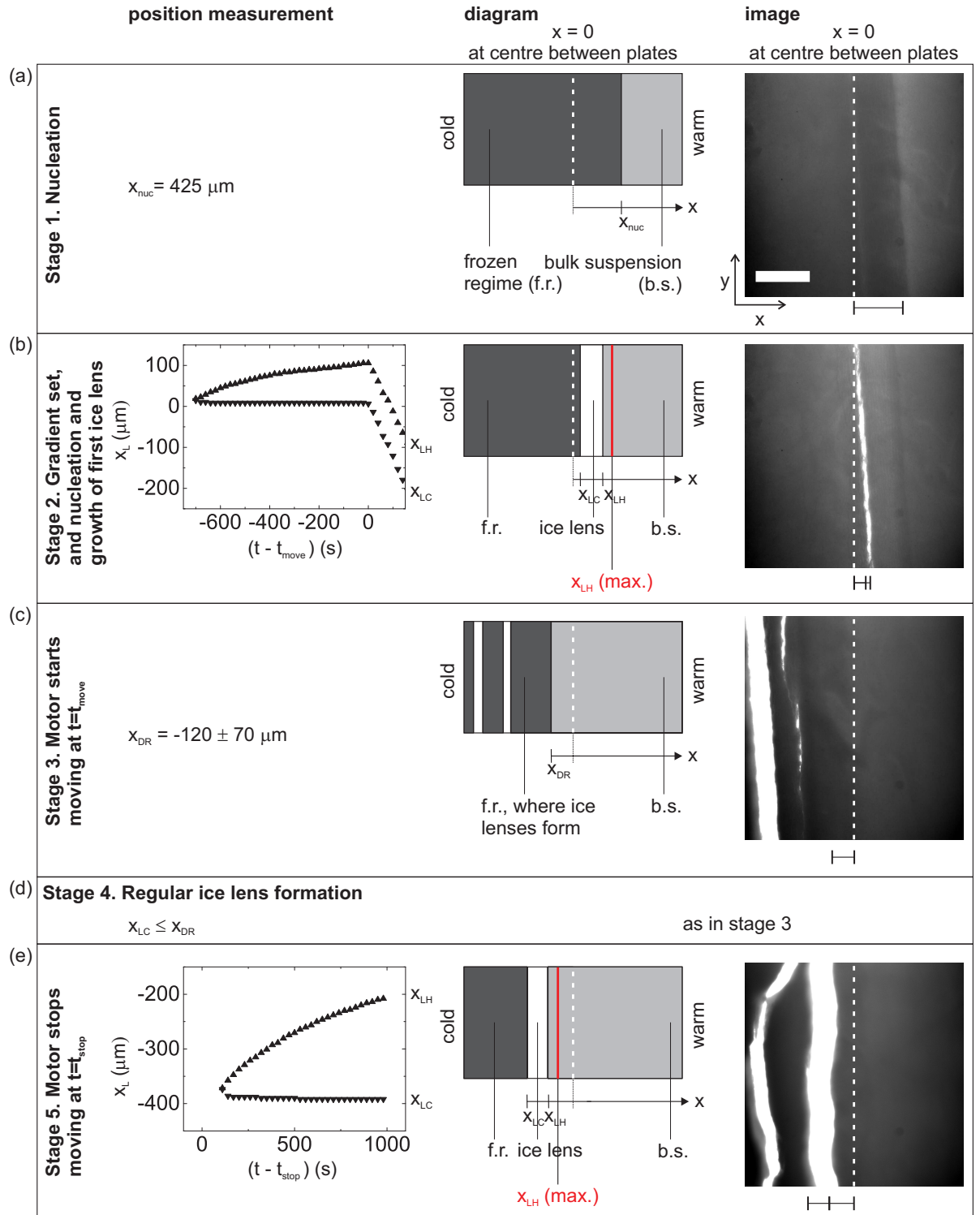


Figure 4.4: Stages of a typical experiment, as described in the text. Stage 4 is elaborated on in figure 4.3 (b). For each stage, a relevant position measurement is given, as well as a schematic diagram showing the different regions and interfaces. A corresponding microscopy image is shown next to the diagram, where the bar underneath marks the relevant interface(s), as shown in the related diagram. All images are the same size, and the scale bar in the first image denotes $500 \mu\text{m}$.

refer to the cold and hot sides of the lenses. A single ice lens can grow stably if the overburden pressure is low enough: according to the theory of Rempel *et al.* [55], a lens can nucleate as long as the overburden pressure is below a critical pressure, due to the fact that the nucleation site must be sufficiently cold,

$$P_0 \leq 2\gamma_{iw}\kappa(1 - \phi_p). \quad (4.3)$$

This means that the likelihood of being able to nucleate a lens increases if the particle packing is lower, and/or the pore radius, R_p , is small, where $\kappa = 2/R_p$. The ice rejects the particles from the interface, by balancing the flow to replenish the premelted layer, between it and the particle, with the thermomolecular force on the particle.

The maximum thickness was never normally reached as the growth of this lens did not come to a stop before the motor was started at $t = t_{move}$. The lens growth rate, V_{lens} , is set by the Darcy pressure gradient in the water, and this determines the position of $x_{LH}(\text{max.})$, while nucleation sets x_{LC} . Where a lens will nucleate first is determined by many factors, such as the cohesive strength of the suspension and temperature (which is constantly changing), whilst the gradient is set [55].

Stage 3. Motor starts moving – at $t = t_{move}$: figure 4.4 (c)

After the motor starts moving the sample cell towards the cold plate at a velocity of $V = 1.5 \mu\text{m s}^{-1}$, the growth rate of the first lens had slowed to $\sim 0.05 \mu\text{m s}^{-1}$. As a consequence of this relatively fast cooling, the pore space that surrounds the particles in front of the ice lens cools. It is likely that some of the pore spaces between particles freeze, as the temperature becomes low enough. This will be discussed in more detail in section 4.4.3. The edge of the dark region is at $x_{DR} \approx -120 \mu\text{m}$, over $200 \mu\text{m}$ behind the point $x_{LH}(\text{max.})$. This implies that there is ‘premelted’ water between x_{DR} and $x_{LH}(\text{max.})$, as long as the temperature gradient does not change upon moving the cell. This will be discussed further in section 4.4.3.

Stage 4. Regular ice lens formation: figures 4.4 (d), 4.3 (b) and 4.5 (a)

The nucleation position of an ice lens, x_{LC} , is always less than, but nearly equal to, the edge of the dark region. The time series in figure 4.3 (b) shows the process of the formation of regular lenses. Once a region of segregated ice is initiated within the suspension, it spreads

quickly along the width of the cell, in the y direction, to form the lens. This lens then grows in thickness, along x , due to flow of water through the suspension towards the freezing front. As the growth rate of the lens, V_{lens} , is slower than the motor speed, V , a new lens nucleates after the suspension ahead of the warmest lens is cooled to a critical temperature. In the final image in the time series in figure 4.3 (b), a new lens is nucleated at almost the same relative position as the previous lenses. This process repeats itself, with the colder lens at the same position relative to the nucleating lens, and as a consequence, regularly spaced lenses emerge. The lenses are occasionally connected, such as lenses 6 and 7 in figure 4.3. Lens 6 had propagated further into the suspension, but overall the spacing was unaffected. Such events may be caused by a change in the local structure of the packed suspension, which will affect the fracture process.

The lens must nucleate heterogeneously, as homogeneous nucleation of ice does not occur at the temperature inside the cell at this position [135]. It is therefore probable that ice already exists at the point where the warmest lens nucleates: in the optically darker region (DR) of the particle suspension ahead of the warmest lens (the edge of this region is pointed to by the thin arrows in figure 4.3 (b)). The presence of the DR was connected to the temperature, as it remained at the same position along the fixed gradient, and thus is consistent with the presence of ice. However, our setup does not allow us to measure the pore ice volume, i.e. extent to which the suspension is frozen.

Figure 4.5 (a) shows a plot of the mean thickness of lenses, τ vs time, t . The data is taken by focusing on one lens before it goes out of the field of view (on to the cold plate), and then moving back to the initial position again to focus on the next growing lens. The growth rate of a lens starts off being constant, then slows down as a new one begins to form, until it nearly stops, before going out of the field of view. This pattern is repeated for consecutive lenses in a similar fashion. During the constant growth period, $V_{lens} = 0.3 \pm 0.03 \mu\text{m s}^{-1}$, as calculated from linear fits to the constant growth region of many lenses (the first fit is shown on the graph in figure 4.5 (a)). Importantly, the final lens final thickness is determined by the growth rate and the time period for growth, so that,

$$\tau = V_{lens}\Delta t, \quad (4.4)$$

where the time taken to supply the lens is $\Delta t = s/V$, and s is the lens spacing. The lens spacing is defined as the distance between the centres of two consecutive lenses.

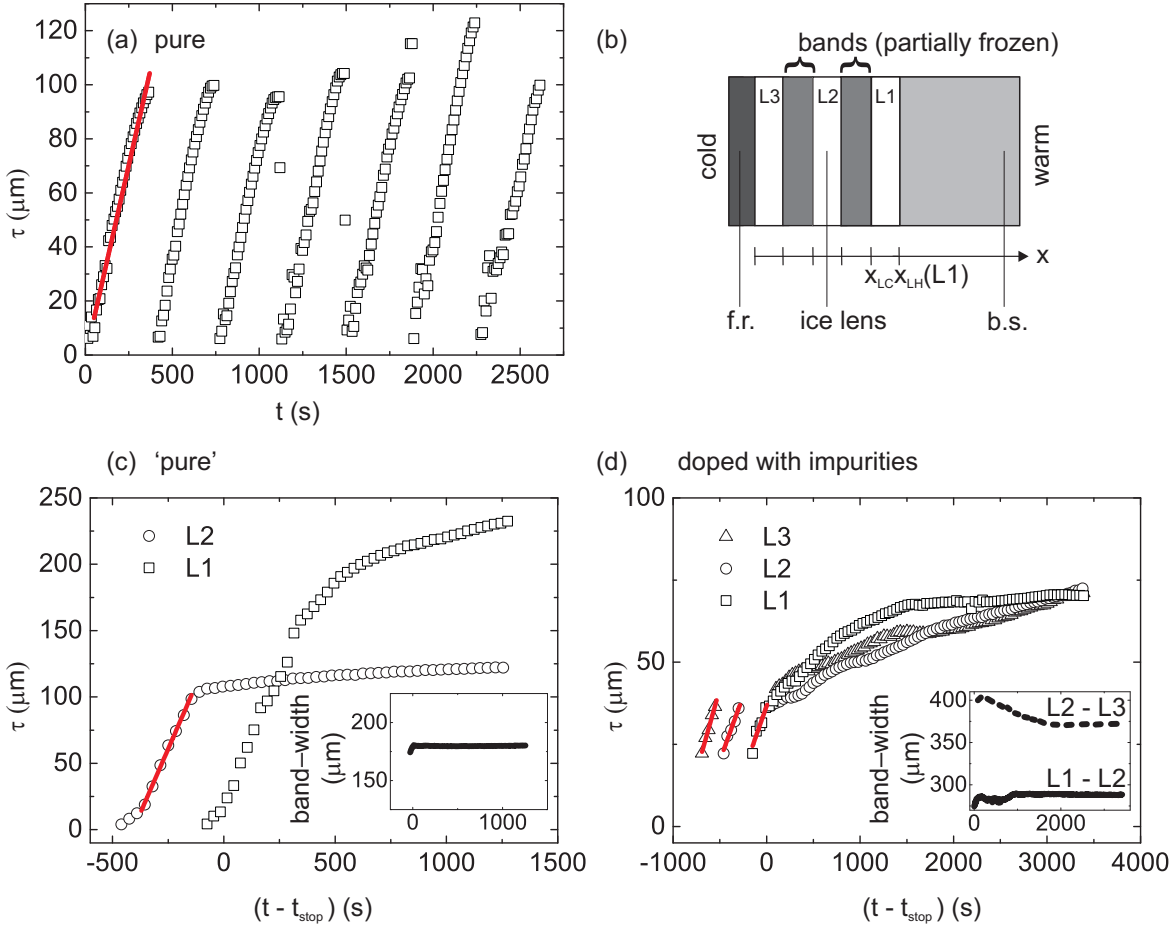


Figure 4.5: (a) The mean thickness, τ , of consecutive ice lenses plotted *vs* time, t ; (b) schematic diagram showing a possible final structure of an experiment; and (c) and (d) the mean thickness, τ , of two and three lenses plotted *vs* the time after the motor has stopped, $(t - t_{stop})$, in a pure and impure system. The insets show the width of the bands between lenses *vs* $(t - t_{stop})$. For (a), (c) and (d), before the motor stops, linear fits are used to measure the growth rate.

Stage 5. Motor stops moving – at $t = t_{stop}$: figures 4.4 (e) and 4.5 (b)–(d)

When the motor stops moving, ice lens nucleation and growth can still occur. In the case in figure 4.4, the final lens nucleates after the motor stops, at $t = t_{stop}$. As in stage 2, the position of the edges of the lens can be measured, as well as the thickness, τ .

In some experiments it was possible to observe the growth of lenses that were colder than the final lens. We could observe the growth of these lenses within the field of view, as shown schematically in figure 4.5 (b). In figure 4.5 (c) and (d), τ is plotted *vs* $(t - t_{stop})$, as t_{stop} is the reference point. In (c) lens 2 (L2), initiates and grows linearly and its growth then slows as the final lens, lens 1 (L1), nucleates. The motor is then stopped and L1 grows, its thickness eventually overtaking L2. The colder lens, L2, continues to grow, but at a much reduced rate.

The lenses grow from their hot edges, x_{LH} , but the final lens, L1, also experiences melting at the cold edge. This results in the band between the lenses being a constant width (inset).

In figure 4.5 (d), the system was doped with impurities, meaning that the lenses were thinner (see chapter 5 for further details), but also that there was a faster rate of growth in the colder lenses after the motor stopped. Interestingly lenses 1–3 grow at a similar rate, and again the bands between the lenses are of a fairly constant width (inset). This suggests that the impurities in the system is acting to increase the volume of water networks in the colder regions, in order for more lenses to grow at a higher rate. In both systems (c) and (d), the band between the lenses is not completely frozen, as there must be a network of water to feed the growing colder lens. The lenses that were colder than L2 in (c) and L3 in (d) did not grow after the motor stopped as it is likely that ice was blocking the pores, reducing the permeability, for water to flow through the suspension.

4.4.2 Polarised light microscopy observations

By placing crossed polarisers above and below the sample, we can distinguish the birefringent ice crystals within an ice lens. In figure 4.6 (a) we show the same lenses under different orientations of crossed polarisers and retardation plate. The lenses are multi-coloured, meaning that many grain orientations exist within a lens. Following rotation, all the grains change colour, indicating that none of the grains are orientated with their director, the c -axis, along the z axis. Between the lenses, where the particles are concentrated, the image appears black, even though pores between the particles are frozen at the low temperature that the images were taken. The particles prevent the transmittance of light at this intensity. Therefore, if a distinction between pore ice and pore water is to be observed, the light intensity must be increased. If it is increased to the same levels as in 4.3 (b), we cannot resolve a colour difference associated with the presence and non-presence of ice crystals in the pore space. We might expect to see pore ice in the dark region where new lenses nucleate (in figure 4.3 (b)). However, the lack of detection of pore ice by polarised light microscopy is likely due to the much smaller path length associated with pore ice crystals, which means the birefringence is too low to be resolved (section 2.3.2). Instead, the camera detects a slight colour change associated with the extra scattering, as discussed above (stage 1), and pore water appears purple, the colour associated with the birefringence of the retardation plate.

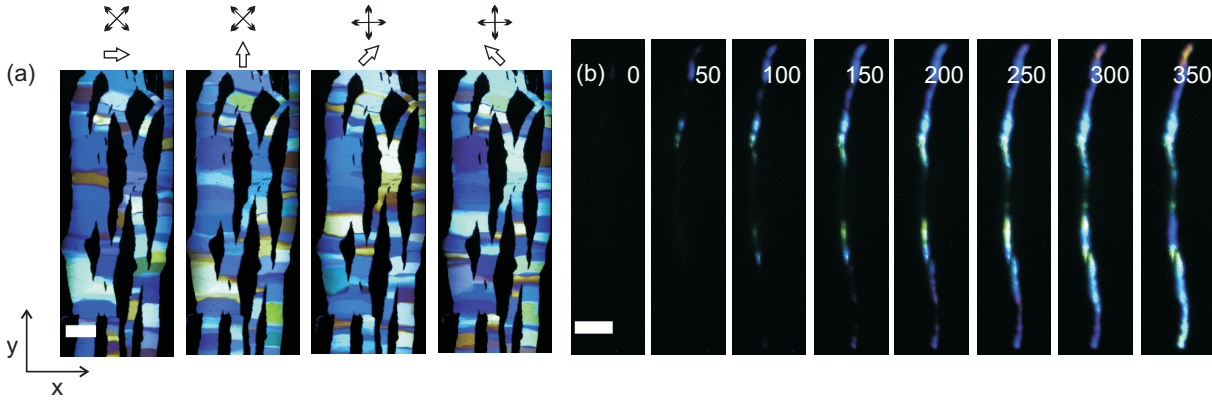


Figure 4.6: (a) Images of the same group of ice lenses between crossed polarisers at different orientations as indicated at the top. A retardation plate is also placed between the polarisers, at a 45° angle to the polarisers, as indicated by the large arrow. The scale bar denotes $500\ \mu\text{m}$. (b) Time series showing the growth of a lens in the y direction, where ice in the lens shows up between crossed polarisers. Images are not at the same position, x , along the gradient, as the lens is being displaced towards colder temperatures by the movement of the motor. The scale bar denotes $250\ \mu\text{m}$; times in s, with respect to the first image, are shown within each image.

Under low light intensities, the large contrast between the areas where a lens is observed and the area where particles are contained, presents the opportunity to study the opening of a lens in the y direction. In figure 4.6 (b) a time series of this process is shown. The growth in y is not quite instantaneous, but actually takes around 150 s to become large enough to resolve. Later on, it can also be seen that grain colours at a certain position are not constant. This is due to the nucleation of new crystals of a different orientation onto the lens: water flowing towards the lens forms new ice crystals by heterogeneous nucleation.

Style *et al.* [123] proposed a mechanism by which an ice-filled crack would propagate continuously along y , fracturing the suspension after its nucleation at the point with the largest geometrical supercooling. This supercooling would be caused by a region of low permeability ahead of the first lens. The low permeability region could be due to the growth of a lens which rejects particles, therefore concentrating them, and/or ice present in the pores. The lower part of the lens ‘nucleates’ the latest, but grows to a similar thickness as in higher regions. If we assume that the average growth rate is constant in time (see above), then this implies that the growth rate is inhomogeneous along y . This could be due to different local particle packings or ice fractions in the frozen fringe, causing different permeabilities.

4.4.3 Temperature measurements

The actual temperature gradient, ∇T , within a cell that closely resembled the sample cell, was measured using two thermocouples (accurate to 0.1°C), each fixed at different initial x inside a cell. The cell containing the thermocouples differed from a sample cell only in the height, h , which had to be increased from an internal height of $h = 0.28$ mm to $h = 1.1$ mm in order to accommodate the thermocouples. The temperature was measured as a function of position, x , as the cell travelled with velocity $V = 1.5 \mu\text{m s}^{-1}$, and the plates were set at temperatures $T_C = -2^\circ\text{C}$ and $T_H = 0.5^\circ\text{C}$, as in all of the experiments in chapters 4 and 5 (apart from in section 4.4.5). The results are shown in figure 4.7. One cell contained just pure water and ice, and another cell contained the silica particles as well. In the cell containing the silica particles, regular ice lenses formed. Both measured gradients are nearly constant between the plates, and the linear fits $T = \nabla T x + D$, where D is a constant, are shown on the graphs in (a) and (b). Figure 4.7 (b) is a zoom of the field of view of the microscope, between the plates, $-1 \lesssim x \lesssim 1$ mm. There is some heat transfer from the cell's warmer surroundings, since the plate temperatures are not constant, or not at the set temperatures. The two data sets overlap, and within error they are the same. However, the shift in the data can be explained by considering the change in thermal conductivity of the samples. Thermal conductivity of the particles is higher than that of water (table 2.4). The cell containing the particles can therefore conduct heat away from the stage faster and consequently the cell is relatively cooler. For the particle-containing cell, $\nabla T = 0.28 \text{ K mm}^{-1}$; this value is used in all subsequent calculations.

In figure 4.7 (b) images of freezing samples are placed below the graph, at the corresponding x values. The centre between the plates, at $x = 0$ (solid line), is found in the images by locating the edges of the two plates in a separate image, which is taken without a sample and without changing the x position of the stage. The position of the ice–water interface in the standpipe corresponds to $T = 0^\circ\text{C}$ on the graph. The ice–water interface in the normal cell containing the particle suspension supernatant is displaced to colder temperatures, $x_{T_m} - x_{T_m(c \neq 0)} = 200 \mu\text{m}$, which corresponds to an undercooling of 60 mK, using $\Delta T = \nabla T \Delta x$. Here, c is the impurity concentration, x_{T_m} is the position of the bulk melting temperature, and $x_{T_m(c \neq 0)}$ is the position of the bulk melting temperature in the supernatant sample. The interface is unstable, due to the presence of dissolved impurities. Dissolved air is also present: the bottom image shows that air rejected from the ice is nucleated into bubbles under the present freezing conditions. These

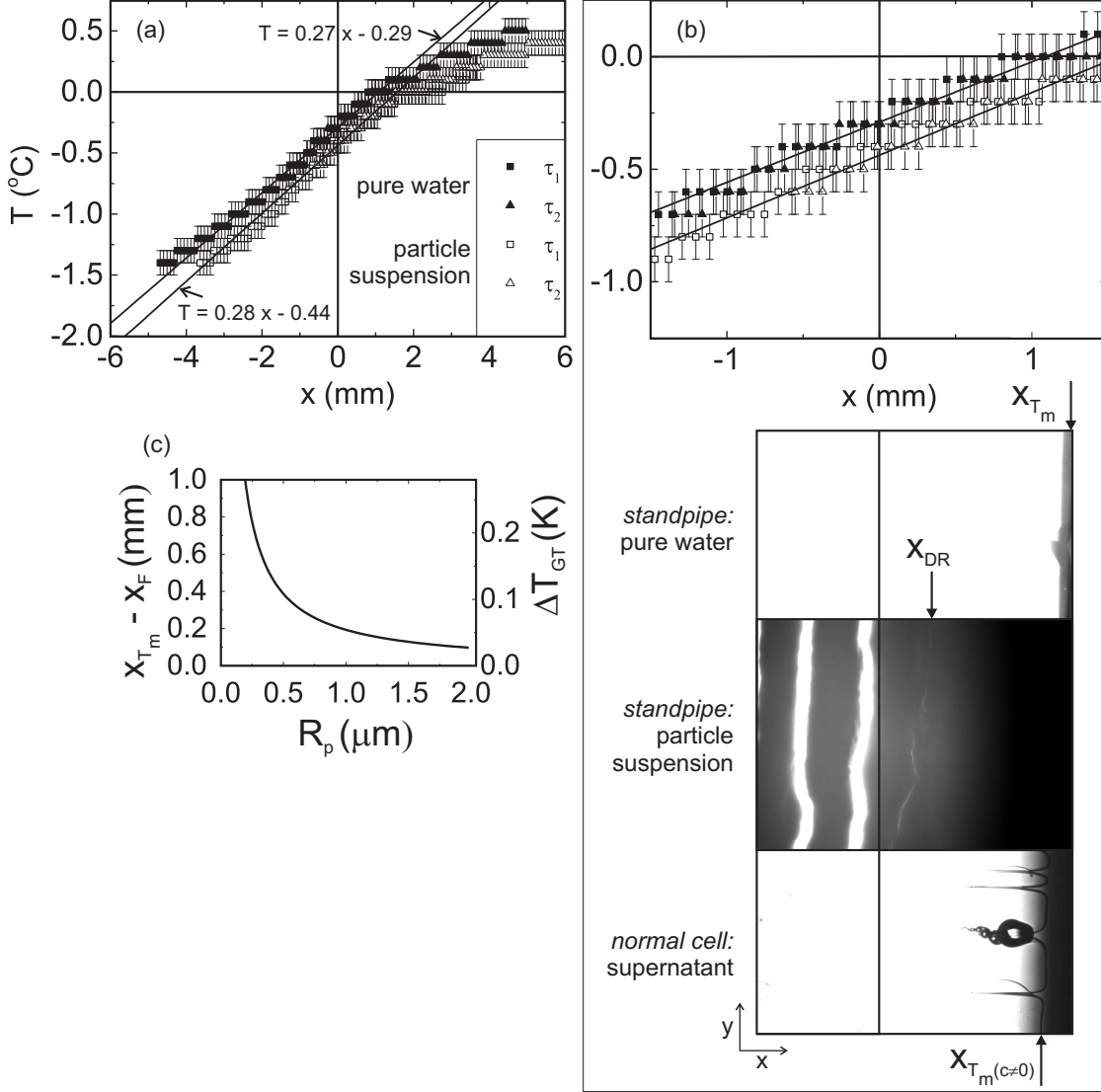


Figure 4.7: Methods of relating x positions to temperature. (a) Temperature, T , measured by the two thermocouples (τ_1 and τ_2) *vs* the distance along the cell, x , where $x = 0$ is the centre between the plates. Two data sets are plotted: pure water + ice; and water and silica particles + ice, in which ice lenses form. Linear fits are plotted and labelled. (b) A zoom in of the same data, and below it three images of the same scale as the graph, are placed at the corresponding x values to the graph, showing freezing in (top) pure water in a standpipe, (centre) the particle suspension sample in parallel to the standpipe, and (bottom) a separate cell containing the supernatant of the suspension. The ice–water interface, x_{T_m} , and the position of the edge of the dark region (also the lens nucleation position), x_{DR} , are marked by labelled arrows. (c) Plot of $x_p = x_{T_m} - x_F$ (left hand axis), which relates to the Gibbs–Thomson undercooling, ΔT_{GT} , by the temperature gradient $\nabla T = 0.28 \text{ K mm}^{-1}$ (right hand axis) *vs* the radius of the pores, R_p .

images are overexposed because a high light intensity was required to see the interface, which was beyond the cold plate edge. Considering the colligative effect, the undercooling of the supernatant relative to the pure water corresponds to an impurity concentration of $c \sim 25 \text{ mM}$ (equation 2.15, with $\Delta T_{col} = \nabla T \Delta x$). The particles must contribute some impurities to the suspension, but since they are washed to the same extent in each prepared batch, we expect

similar effects between experiments. However, the position of the dark region in the suspension contained in the standpipe cell, which was in parallel to the pure water cell, has a larger undercooling, at a displacement of $x_{T_m} - x_{DR} = 920 \text{ } \mu\text{m}$, which corresponds to an undercooling of 260 mK. Here, x_{DR} is the position of the edge of the dark region, which is also where the ice lenses appear to nucleate. A degree of undercooling is essential to the theory that water, existing at temperatures below T_m , flows along a temperature gradient towards an ice lens.

If we consider the Gibbs–Thomson effect, we can calculate the distance between the edge of a frozen fringe, x_F , and the position of bulk melting, x_{T_m} . The warmest edge of a frozen fringe is at the temperature above which pores of radius R_p are filled with water instead of ice due to equilibrium curvature effects. From equation 2.8, we find,

$$x_p = x_{T_m} - x_F = \frac{\Delta T_{GT}}{\nabla T} = \frac{T_m}{L_m \rho_i} \frac{1}{\nabla T} \frac{2\gamma_{sl}}{R_p}. \quad (4.5)$$

The plot in figure 4.7 (c) shows how x_p varies with R_p , taking ∇T from figure 4.7 (a). The experimental value of x_p is given by $x_{T_m(c \neq 0)} - x_{DR} = 720 \text{ } \mu\text{m}$, accounting for the supernatant shift: this corresponds to an undercooling of 200 mK. Assuming that the average radius of the pores scales with the radius of the particle, $R_p \sim R$, we have $R_p = 0.75 \text{ } \mu\text{m}$, giving $x_p = 260 \text{ } \mu\text{m}$. This suggests that the dark region may be the interface between pore water and pore ice, but it is at a lower temperature than expected. A possible explanation for this discrepancy is that the radius of the particle may not be a good estimate of the pore size in our suspension. In fact, as the suspension is polydisperse, we might expect a smaller average pore radius, a fraction β of the particle radius, as random close packing is denser for polydisperse spheres, leading to $R_p \sim \beta R$. For $0.2 \leq \beta \leq 0.6$, as given in [136, 137] for the range of pore sizes possible in the log-normal particle size distribution, the displacement is now between $430 \leq x_p \leq 1300 \text{ } \mu\text{m}$, and the experimental value of $x_p \sim 720 \text{ } \mu\text{m}$ is in the middle of this range. Furthermore, note there is some uncertainty in the measurement of x_{DR} .

Alternatively, the measured x_{DR} may not be the edge of pore ice. If the packing was loose we would expect some pores much greater than the particle size, and therefore a fraction of ice present up to the melting point (e.g. [123]). If this is the case, then we would not observe a well-defined pore ice–pore water interface. However, our observations are consistent with the idea of having a reasonably sharp distinction between pore ice and pore water, and this measured interface position fits with theoretical predictions.

4.4.4 Final structures

The structure of the suspension after freezing captures key features of frost heave, showing periodic spacing of ice lenses, with uniform thickness. From this, the average ‘total heave’, the area fraction of the lens *vs* the area fraction of the total suspension, can be calculated. The average total heave is equal to the ratio of the lens thickness and the lens spacing, τ/s , and is directly proportional to the ice lens growth rate. From equation 4.4 we have,

$$V_{lens} = \left(\frac{\tau}{s}\right) V, \quad (4.6)$$

where V is the pulling velocity. Therefore the heave is a good measure of the lens growth rate, and we can infer this from the final structures. Note that s is almost constant and can thus be interpreted as the periodicity of the ice lenses.

To analyse lens patterns like the one in figure 4.3 (a), we selected the region where lens growth had reached a steady state, in the centre of the cell. We discarded early growth where dendritic structures had formed during the initial, quick freezing stage (stage 1). We also discarded growth near the edges of the cell (in the y direction), where inflection of the lenses was probably caused by edge temperature gradients [80], and growth towards the end of the sample where changes in local particle packing may occur. The average thickness of the lenses in the case presented in figure 4.3 was $94 \pm 16 \mu\text{m}$, and the average spacing was $540 \pm 50 \mu\text{m}$, giving an average total heave of 0.17. It is useful to compare these parameters after a change in conditions, and we do this in sections 4.4.5 and 4.4.6, as well as in chapter 5.

The lens waviness, or the non linearity of the edges along the y direction has several possible causes. The first is the inhomogeneity in the particle packing, which will change the permeability of the suspension, and the ice fraction in the frozen fringe. The second is the process of propagation of the lens through the suspension. If it is a fracture-like process, where the lens grows almost instantaneously along y , and the suspension is torn apart, leaving a ragged edge.

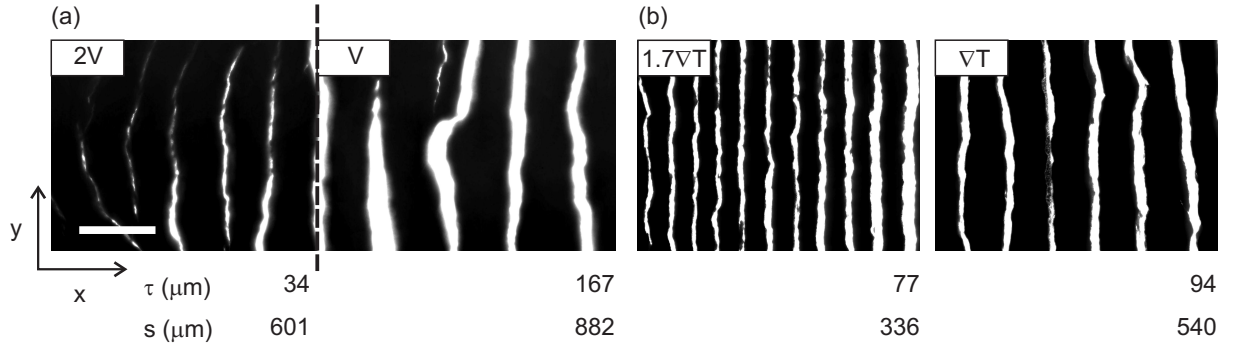


Figure 4.8: Final structures of ice lenses formed in: (a) a single experiment, where at the distance indicated by the dashed line, the speed of the motor, V , was halved, and in (b) separate experiments at different gradients, ∇T . The scale bar denotes 1 mm. Average values of the thickness, τ , and the spacing, s , are shown below each image.

4.4.5 Changing the freezing rate

The rate of cooling is an important parameter in ice lens formation and frost heave, since it can have a pronounced effect on the total heave of the soil. It can be varied in our experimental setup by changing either the motor speed, V , or the temperature gradient, ∇T . In a single experiment, the effect of changing V under a constant ∇T was investigated ($\nabla T = 0.28^\circ\text{C mm}^{-1}$), and in separate experiments, ∇T was varied, while V remained the same ($V = 1.5 \mu\text{m s}^{-1}$). The results are shown in figure 4.8. When V was reduced, the average thickness of lenses increased greatly, and there was a slight increase in the spacing. The average total heave also increased from 0.06 to 0.19. Similarly, when ∇T was reduced, the thickness increased slightly, and the spacing increased greatly, but the average total heave decreased from 0.23 to 0.17. The total heave was affected more significantly by the change in V .

The observed changes are qualitatively consistent with the frozen fringe theory of Rempel *et al.* [55], and the experiments of Taber on clay [39], where soil was frozen in an undefined temperature gradient, but the gradient could be inferred. A reduction in V in our experiment meant that each lens had more growth time, $\Delta t = s/V$, and additionally s increased by a factor of 1.5. The lens thickness τ increases by a factor of 5, therefore implying that the lens growth rate, V_{lens} , increased by a factor of 1.7. The width of the band between the lenses, $(s - \tau)$, does not change as significantly as the spacing does. The band-width only depends on the nucleation position of a new lens, relative to the edge of the previous one, and theory suggests this to be independent of V [55]. Therefore the change in s can be accounted for mainly by the large change in τ .

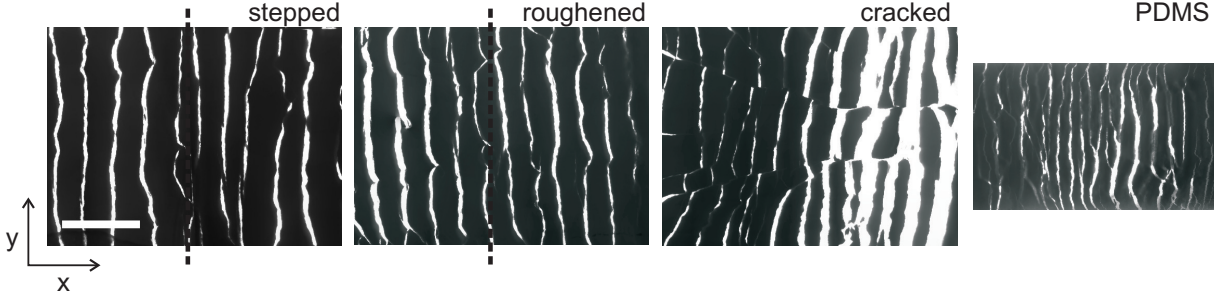


Figure 4.9: Final structures of ice lenses formed under different conditions: in a stepped cell (where the step, moving from $h_{low} \rightarrow h_{high}$, is at the dashed line), in a roughened cell (where roughening is to the right of the dashed line), in a cell that cracked, and in a PDMS cell of height $100\mu\text{m}$. The scale bar denotes 2 mm; all images are the same scale.

A reduction in ∇T allowed for the distance to the critical undercooling required to nucleate a lens to increase. This causes the lens spacing to increase. The change in V_{lens} by a factor of 0.7 is also not currently explained by this simple model, and other factors need to be considered, such its dependence on the frozen fringe thickness.

4.4.6 Changing the cell wall

The cell walls contain the freezing particle suspension, and it is important to check if their properties affect ice segregation behaviour. Final structures of ice lenses formed contained by different cell walls are presented in figure 4.9. To explore this effect, the experiment was repeated with a stepped cell, where the cell changed in height half way along the x region that was frozen. Since h could vary depending on the glue height in the cell preparation process (section 2.3.4), in order to cover all possibilities, a stepped cell where h was more than double was made. It is clear from the resulting final structure that the effect of cell height on lens thickness and spacing is minimal. This is consistent with the minimum value for dimensionless number (3) in table 2.3, corresponding to the conditions of our experiment, but using a thermally 2D cell of height $\gg h$. The fact that the number is < 1 implies that thermal conditions will be unaffected by latent heat at these two lower heights, so the thermal gradient, and therefore lens properties will be unchanged, assuming there are no geometric restrictions on the sizes of lenses.

Another cell was created in order to test the effect of roughened cell walls, which could resist the opening of a lens by increasing the friction on the suspension. The bottom glass wall was roughened by sandpaper half way along the cell, and a very small effect on lens thickness was observed.

In addition, we explored the effect of a crack in the confining walls. Here the effect was pronounced, since we see much thicker lenses. The overburden pressure is propagated through the cell by the walls. If the walls are not intact then the overburden pressure is significantly reduced, meaning that flow of water towards the lens increases according to the change in pressure gradient.

Furthermore, we changed the wall material. PDMS walls will conduct less heat away from the cell, as shown by number (5) in table 2.3, therefore the temperature gradient inside the cell may be affected. Lenses form inside the PDMS cell, but their final structure is significantly different to those formed in glass walled cells: the spacing is smaller and the lenses are thinner. It is possible that lenses nucleate via a different mechanism, with a lower energy barrier, and therefore leading to a significant reduction in the spacing. We thus note that the cell walls play an important role, but mainly through the material, and not the spacing or smoothness.

4.5 Discussion

Our system demonstrates the appearance of multiple lenses within a slowly freezing, closely packed porous suspension of colloidal particles. We have shown that it provides a good model system for frost heave. Predictions from previous theories are observed in our system, and we will discuss our results in light of them below.

The ice lenses appear to nucleate at an undercooling of $\Delta T = 0.26$ K, and the lenses continue to grow at undercoolings still greater than this. This nucleation temperature is one where you would expect to find pore ice if the pore radius was larger than $0.2\text{ }\mu\text{m}$ (figure 4.7 (c)). Since the radius of particles is larger than this, approximately $0.75\text{ }\mu\text{m}$, we would consequently expect at least some of the pores to be frozen. There is some evidence to suggest that a frozen fringe does exist in our system. However, experimentalists have found evidence that a stronger undercooling is required for ice in pores; by measuring heaving pressures in soils with different sized particulates, Penner [41] found that the ice entry temperature should be $\sim 6.6\times$ that predicted by the Gibbs–Thomson effect (equation 2.8), leading to unfrozen pores at much colder temperatures. This is in agreement with Watanabe’s experiments, where Raman spectroscopy detected that pore ice was absent down to an undercooling of 0.45 K, for a similar particle radius to that used in our experiments [128]. This suggests that there is still a possibility that

we observe an only partially frozen suspension.

The water fraction of the pore space in the suspension ahead of a growing ice lens has many contributions, as discussed by Hansen-Goos and Wettlaufer [56]. These include the Gibbs-Thomson effect, discussed above, and also the impurity concentration. This has important implications on the growth speed on ice, V_{lens} . We find that the growth rate is constant as a function of undercooling, until a new lens starts to grow. The explanation for this observation lies in considering the composition of the mixed phase region, where water suction occurs. The likely scenario is that the proportion of ice within the pores is temperature dependent. The permeability decrease caused by the decrease in water fraction as the lens moves towards colder temperatures, prevents V_{lens} from increasing as ∇p increases with the lens undercooling. Other experiments have found a relationship between the lens growth rate, V_{lens} , and the undercooling, ΔT , which reflects the change in pressure associated with the undercooling of the lens: equations 4.1 and 4.2 combined [77]. The growth rate increases with undercooling, as the pressure in the water at the ice lens become lower, and the pressure difference increases. Style *et al.* [132] improve the fit to the data by considering an interfacial resistance term, which reduces the growth rate to the measured values. Our observation that colder lenses continue to grow after a warmer one has nucleated (figure 4.5 (c) and (d)) shows that a water network must still exist within the frozen region between the lenses. The bandwidth remains the same, but moves across the gradient, suggesting that freezing and melting at its interfaces occur at the same rate.

4.6 Conclusions

In conclusion, we have performed a series of experiments to observe segregated ice growth in the freezing of particle suspensions, as a model system for frost heave. Regularly spaced ice lenses nucleate within a region which contains ice, and they grow at a rate which is independent of the undercooling. The linear growth rate observed here would be a useful empirical approximation for the modelling of frost heave. We have confirmed several factors that are important in determining lens structures. The composition of the region ahead of the ice lens determines many properties, such as lens thickness and spacing. We have furthermore shown that suspensions containing colder ice lenses are not completely frozen, and water can still flow through it. This raises the possibility that a particle suspension need not be progressively cooled for it to be

developed by ice lens growth. Our model system also demonstrates some theoretically expected properties of lens formation, such as the thickness and spacing changes on cooling rate decrease, and the crack-like initiation of a lens. This indicates a strong practical need to control these effects for industrial process that include a particle suspension freezing step, such as in materials industries. Current theories do not encompass all the factors in play when considering frost heave and ice lens formation, and we hope our experimental data may change that situation.. Our results are relevant to many fields in which ice segregation is a significant issue: from the preservation of biotissue, to freezing soils.

Acknowledgements

This work was a collaboration with Rob Style, Arran Curran, John Wettlaufer and Eric Dufresne. We thank Lia Verhoeff for help with experiments, and Stephen Peppin for useful discussions.

Chapter 5

Segregated ice growth: effect of changing conditions

ABSTRACT

In this chapter we discuss the effect of (i) particle packing, (ii) particle size and (iii) impurities on the formation of ice lenses, using the same techniques as in chapter 4. We observe that (i) ice lenses decrease in thickness with particle volume fraction, (ii) ice lens thickness and spacing decreases with increasing particle size, and (iii) ice lens thickness and regularity decreases with concentration of certain doped impurities. We interpret these trends in light of existing theories.

5.1 Introduction

The growth of ice in a colloidal particle suspension is relevant in a wide range of settings, from the natural world [27], to technology [116]. Particles are, for example, pieces of broken up rock in soils [37], dust in ice cores [13], cells in cryopreservation [117,118], and ceramic solids in freeze cast materials [48]. Ice segregation refers to the process of separation of these particles from ice, so will depend inherently on the structure of ice that forms. This will depend on a range of factors, such as the cooling rate and particle concentration. In this chapter, we will study a particular geometry of ice, called ice lenses, which are regions of ice which form in a ‘lens’ shape, perpendicular to a linear temperature gradient in a slowly freezing dense suspension of particles. It is an extension of chapter 4, using the same model system, in order to see the effect of system parameters: particle packing, particle size, and doped impurity concentration, on the structure of ice lenses. In nature, and in technological conditions, these effects are important, as an ‘ideal’ system that is impurity free, or at a consistent particle density or particle size, is unlikely.

We focus on varying several factors, which are thought to affect ice lens formation, but which have not yet been fully scrutinized in experiments in the multiple lensing regime: (i) the particle packing, by varying the particle volume fraction, in the colloidal suspension, (ii) the particle size, and (iii) the doped impurity concentration. The effects on the system are complicated, so it is important to work with a model system in which regular ice lens formation has been observed (chapter 4). The factors can then be varied systematically to look for any trends. As we have seen in chapter 4, the most important consequences of the properties of ice lenses are the nucleation and growth rate of the lens, which is coupled to the ice lens spacing and thickness, and therefore the total ‘heave’.

This chapter is organised as follows: we begin by presenting some theoretical concepts (section 5.2), then the experimental methods are described (chapter 5.3). The results are presented in section 5.4, and a discussion follows in section 5.5. Finally, we conclude in section 5.6. Sections 5.2 – 5.5 are split into the factors (i)–(iii).

5.2 Theoretical background

5.2.1 Particle packing

We recall from chapter 4 that an undercooled suspension forms ice lenses by the flow of water along a temperature gradient through the porous medium, where the water then freezes, and ‘heaves’ the particle suspension. We found that it is likely that inside the porous medium some of the pores ahead of the growing ice lens contain ice. The layer which contains this pore ice is called a ‘frozen fringe’, see e.g. [55, 126]. A new ice lens nucleates where particles at a critical temperature are separated from the surrounding ice by a thermomolecular force, which overcomes the overburden force of the suspension. The particles move out of the ice that surrounds them, along a temperature gradient, as we have observed in chapter 3, leaving behind a new layer of segregated ice. It should be noted here that the nucleation of ice lenses with no frozen fringe is also possible, due to geometrical supercooling [123].

The pore ice volume fraction, ϕ_i , is affected by the pore space radius, R_p , which is inherently configuration and particle volume fraction, ϕ_p , dependent. As more particles are contained within a given volume (larger ϕ_p), the volume of the pore space left between the particles reduces (smaller R_p). The dependence of R_p on ϕ_i comes from the effect of curvature induced melting. The Gibbs–Thomson equation defines the undercooling, ΔT_{GT} , up to where curvature induced melting occurs in pores,

$$\Delta T_{GT} = \frac{2T_m\gamma_{iw}}{L_m\rho_i R_p}, \quad (5.1)$$

where T_m is the bulk melting temperature, γ_{iw} is the ice–water surface energy, L_m is the latent heat of melting per unit mass and ρ_i is the density of ice. Figure 5.1 (a) depicts a schematic where the particle volume fraction is increased progressively. Between the first two volume fractions, $\phi_{p,1}$ and $\phi_{p,2}$, the average R_p reduces and pores are no longer filled with ice at this temperature, due to the Gibbs–Thomson effect.

Repulsive intermolecular interactions enable premelted water to exist in a thin film between ice and a single particle, exerting a thermomolecular pressure. It is this pressure that prevents the particle from being engulfed by a moving ice interface when it is cooled, thus being responsible

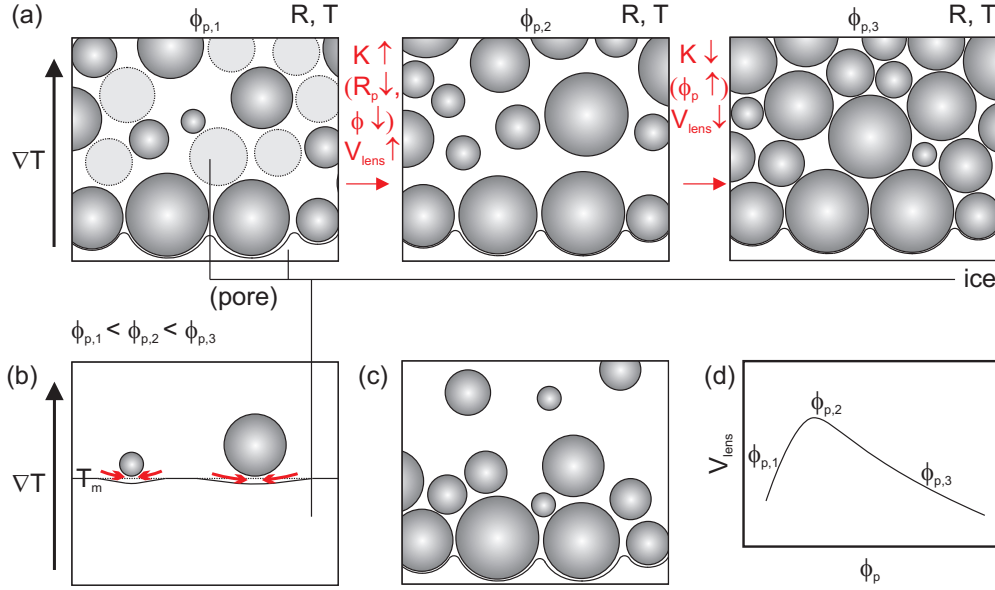


Figure 5.1: (a) Schematic diagrams showing suspensions of particles of average radius, R , in contact with ice under a temperature gradient, ∇T , and at a temperature T , in order to show the effects of the particle volume fraction, ϕ_p , on the growth rate of the segregated ice, V_{lens} , shown at the bottom of each picture. A simplistic picture of pore ice is shown, where a piece is approximated by a sphere. The changes in the average pore radius, R_p , the total volume fraction, ϕ , and the permeability, K , are also shown, and the trends are described in the text. (b) Schematic diagram illustrating the deformation of the ice interface at the surface of two different sized particles, as result of interfacial premelting. The position of the bulk melting point, T_m is indicated. (c) Schematic diagram showing a possible change in local particle volume fraction at the ice–water interface. (d) Schematic graph showing V_{lens} vs ϕ_p , with the particle volume fractions in (a) indicated.

for ice segregation [17, 66, 88–91, 93, 94, 96, 138]. This occurs below a critical cooling rate, where the ice grows slow enough for water flow to occur in the film, in order to deposit ice behind the particle. At large ice growth rates, where water cannot replenish the film before it becomes cold enough to freeze around the particle, the particle is trapped in the ice without being moved by it. Here, ice segregation does not occur: the particles' configuration is effectively just frozen in. Flow in the premelted film is depicted by the red arrows in figure 5.1 (b).

In dense particle suspensions, the particle–particle interactions must also be considered. This determines their structure in the suspension phase. The unfrozen suspension can be treated as a porous medium where flow is described by a Darcy pressure. The resistance to flow changes are attributed to the permeability of the suspension, K , which decreases with particle volume fraction, ϕ_p , according to the Kozeny-Carman equation [139–141]. Hence, a more dense particle suspension will not be able to sustain flow of water through it to deposit ice at the same cooling rate as for individual particles. Furthermore, if ice segregation occurs, there will be a local

change in particle packing, as long as the diffusivity of the particles is slower than the ice velocity. This concept is discussed further in chapter 6. There is therefore a time dependence in the permeability, as this build up of particles occurs, as depicted in figure 5.1 (c). At an intermediate cooling rate, or during this build up, segregation and changes in permeability start to interfere. Ice can both reject particles for a period, allowing them to concentrate ahead of the interface, and then engulf the particles, resulting in regular layers of particle rich and particle free ice. This leads to seemingly similar patterns as observed during ice lens formation, and we term this concept the ‘engulfment model’.

Both in the frozen fringe and engulfment model, the permeability of the suspension plays an important role. The total non-water volume fraction of the suspension is $\phi = \phi_p + \phi_i(R_p)$, and is termed total volume fraction henceforth; inserting this into the Kozeny–Carman equation [139–141], we obtain,

$$K = \frac{(1 - \phi)^3}{c_0 S^2} \quad (5.2)$$

where c_0 is a constant, which is typically equal to 5 [140, 141], and S is the surface area to volume ratio for a suspension at a total volume fraction ϕ , where the particles contributing (ice or solid) have radius R and sphericity s , $S = 3\phi/Rs$. On the assumption that particles are spherical with $s = 1$, we have,

$$K = \frac{R^2(1 - \phi)^3}{45\phi^2}. \quad (5.3)$$

This expression is used to find the flow rate towards a lens,

$$V_{lens} = -\frac{K}{\eta} \nabla p, \quad (5.4)$$

where η is the viscosity of the liquid in the pores, and ∇p is the pressure gradient in the liquid. This hydraulic flow rate may determine the total heave, or fraction of segregated ice in the suspension. Figure 5.1 (a) shows how the changes in ϕ and ϕ_p affect K and V_{lens} , while (d) schematically shows the resulting V_{lens} as a function of ϕ_p . Recently, Style *et al.* [132] have shown that if the pores are warm enough to be unfrozen, then at a critical particle size, the hydraulic resistance is not the rate determining factor, but the interfacial resistance in the premelted films becomes important. We will discuss this in the next section.

5.2.2 Particle size and shape

Particle size affects the rejection–engulfment transition as a result of the flow in the premelted film between a particle and ice. The simplest picture attributes the particle size dependence on the distance over which water needs to be transported, with a longer distance for a larger particle e.g. [45]. In figure 5.1 (b), the arrows show the magnitude and direction of the lubrication force, which is proportional to the particle radius squared, R^2 [45], and the flow rate. As the balancing thermomolecular force, which acts to push the particle ahead of the solidification front is proportional to R [45], then upon balancing the forces a critical engulfment velocity is proportional to $1/R$ (equation 3.6).

For a packed particle system, Style *et al.* [132] give the mathematical solution to the problem as applied to platelet particles in a porous medium. They calculate the ice segregation rate, including the effects of interfacial resistance in the premelted films, and show that this resistance is a dominant effect when looking at micrometre sized particles or larger. The other resistance effect is caused by the particles themselves: the hydraulic resistance of the porous suspension, as described in the previous section. This causes a low permeability for smaller particles (equation 5.3) and controls the lens growth rate for particles of the order of $0.1\ \mu\text{m}$ [132]. There is an intermediate size of particle that gives the largest ice lens growth rate, where the interfacial and hydraulic resistance combined is at its minimum [132]. Diagrams illustrating these effects are shown in figure 5.2 (a). However, as soon as ice invades the pore space, this “simple” interfacial resistance model needs to be modified. We must therefore also take into account how much the pores are frozen. The Gibbs–Thomson equation (equation 5.1) shows that smaller pores can stay unfrozen for larger undercoolings. When the porous medium can stay unfrozen for a longer period during cooling, ϕ_i is low and consequently the permeability is larger and ice segregation growth rates will be higher. The balance between the effect of interfacial resistance *vs* hydraulic resistance (only with unfrozen pores), and the hydraulic resistance when pore ice is present, will determine the ice segregation rate, and therefore ice lens thickness. This picture is shown schematically in figure 5.2 (b), where for T_2 the undercooling ΔT_{GT} (equation 5.1) is reached for most of the pores of radius R_p where $R = R_2$. In figure 5.2 (c), the growth rate of the segregated ice, V_{lens} , *vs* R is shown for the situations in (a) and (b).

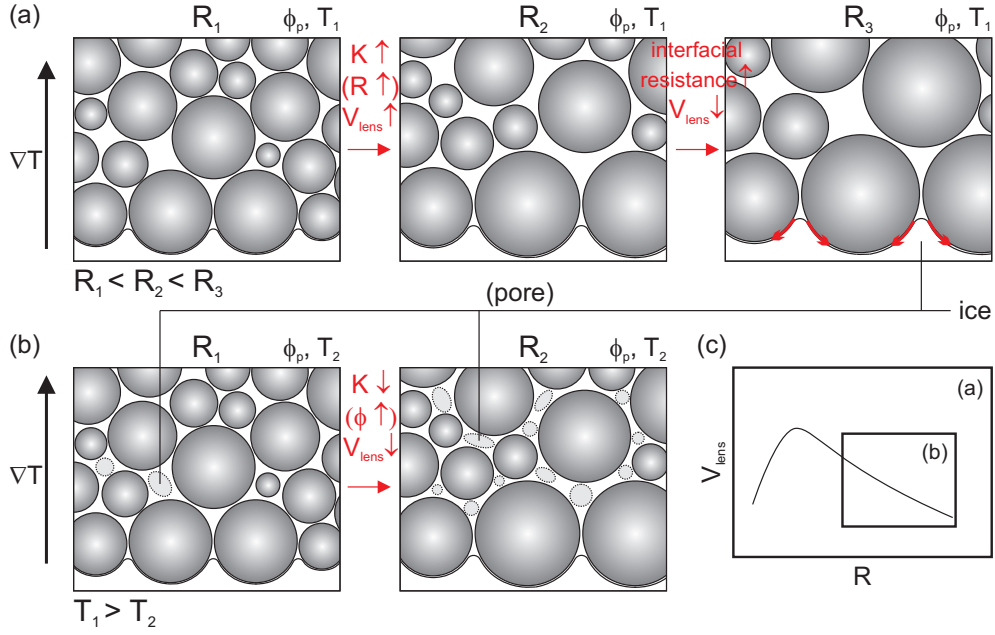


Figure 5.2: Schematic diagrams showing suspensions of particles in contact with ice under a temperature gradient, ∇T , in order to show the effects of the average particle radius, R , on the growth rate of the segregated ice, V_{lens} , which is shown at the bottom of each picture. In (a) R is increasing, while the temperature, T , and average particle volume fraction, ϕ_p , are constant, and in (b) T has been lowered so that some pores are filled with ice. K is the permeability of the suspension and ϕ is the total volume fraction. (c) Schematic graph showing V_{lens} vs R for (a) and (b)

5.2.3 Impurities

An additional component dissolved in water reduces its equilibrium freezing temperature. The undercooling, the temperature below the bulk melting temperature, required for freezing is given by (equation 2.15),

$$\Delta T_{col} = \frac{R_g T_m^2 c}{L_m \rho_i}. \quad (5.5)$$

The undercooling increases with the impurity concentration, c : for a system in which a temperature gradient is applied, ice exists up to a colder temperature, below T_m , in the presence of impurities. Additional factors come into play when the system is moving. Under directional solidification conditions, the sample is progressively cooled by movement along the temperature gradient towards the cold side. If the impurities cannot diffuse at the same rate as heat is transferred, causing the sample to freeze, then a concentration gradient will build up against the ice–water interface. Consequently the interface is unstable to perturbations, and ice growth is

no longer planar (section 2.2.3). Both particles and pockets of solution can be trapped by this unstable ice growth, as discussed in chapter 3.

The presence of impurities can also affect the interactions between the particles. If the impurity species is a charged ion, the DLVO potential between the particles is affected by the change in ionic strength of the solution. The repulsive force between the particles, caused by overlapping double layers, may become screened more strongly if additional ions are present within the solution. The electrostatic potential from the surface of a particle drops off exponentially with a decay length equal to the Debye Length. This quantity depends inversely on the square root of the ionic strength, I , of the solution containing ions of number density n_i and charge z_i , $I = \frac{1}{2} \sum_i n_i z_i^2$. If the salt concentration is high enough, the particles can fall into the van der Waals minimum and be irreversibly aggregated.

Using different species of impurity can test the relative importance of these effects. Non-ionic impurities do not have an effect on the double layer repulsion, but will have the equivalent effect on the bulk melting temperature, as long as they behave as ideal solutions. The comparison between non-ionic and ionic impurities can be used to directly probe this effect.

5.3 Experimental methods

The experimental system is identical to that in chapter 4, apart from the amendments to change the conditions in the colloidal model system (section 4.3.2). Here, we will discuss the ways in which the considered variables are altered in experiments. First, the particle packing is discussed, followed by different particle sizes, and finally the impurity concentration.

5.3.1 Particle packing

The simplest way of changing the particle packing is to start with a different initial particle volume fraction. In section 4.3.2, we describe how the particles are packed into the cell by a centrifugation step. This step was incorporated into the procedure because it achieved better consistency between experiments. Consequently, this step allows for another way to achieve a range of packing fractions, without varying the initial concentration of particles, but by simply changing the centrifugal force applied. We used relative centrifugal forces, ‘rcf’, expressed in

terms of g , Earth's acceleration, of 1, 39, 156 (in chapter 4), 278, 435; the force was applied for 30 minutes in all experiments. The rcf is calculated by,

$$\text{rcf} = \frac{r_{rev}\omega^2}{g}, \quad (5.6)$$

where r_{rev} is the radius of revolution, g is the acceleration due to gravity, and ω is the angular velocity. Here, $\omega = (2\pi/60) \times \text{rpm}$, where rpm is the revolutions per minute, input to the centrifuge machine, and we take values of $r_{rev} = 0.1725$ m and $g = 9.81$ m s⁻². The length of the suspension before (l) and after (l_c) centrifugation was recorded.

5.3.2 Particle size and shape

Suspensions of particles with different sizes were prepared as summarised in table 5.1. The silica particles (1) and (2) were obtained from JGC Catalysts and Chemicals as a powder [142], and were dispersed at volume fractions 0.31 and 0.41, after washing 3 times with ultra pure water. The mixture in (3) was also made up at these volume fractions. The silica nanoparticles (4) and rods (5) were prepared by Dr Yongxiang Gao, by the methods described in [143–145]. They were washed and prepared at volume fractions of 0.31 and 0.41 (nanoparticles), and just 0.41 (rods). The higher volume fraction was used as a check for the centrifugation results. First, particle size effect on ice lens formation was tested using the usual method of a centrifugation step using a relative centrifugal force, ‘rcf’, of 156. However, the changing size meant l_c also varies, as the downward velocity of the particle is proportional to its size squared. In order to eliminate the effects of packing on the suspensions of different sized silica particles, and the silica rods, we started off with higher initial concentrations, and did not centrifuge the sample.

Description	How prepared	Average diameter, d (μm)	Size range (μm)
(1) silica spheres	JGC*	1.5	1 – 3**
(2) silica spheres	JGC*	4.5	2 – 8**
(3) silica spheres	JGC*	3.0	1 – 6**
50:50 mixture of (1) and (2)			
(4) silica spheres	in group	0.15	monodisperse
(5) silica rods	in group	2.9 (length) 0.6 (width)	monodisperse

Table 5.1: List of particles. *full name JGC Catalysts and Chemicals, **above a vol% of 5.

5.3.3 Impurities

Particle suspensions of different concentrations of impurity were prepared by washing the particle suspension with a solution at the desired concentration of impurity. The ionic impurities NaCl and Na₂SO₄, and molecular impurities glucose, ethanol and glycerol were used. Chemicals were purchased from Fisher Scientific (NaCl) and Sigma–Aldrich (all others).

5.4 Results

Significant variations in ice lens structure, thickness and spacing, as well as the total heave, were observed under different conditions. Below we present results where trends in particle packing, particle size and shape, and impurities on ice lens formation are examined. In all the final structure images of the ice lenses presented, the samples were frozen from left to right.

5.4.1 Particle packing

During the centrifugation step, silica particles (1) (table 5.1), prepared at an initial volume fraction $\phi_{p,i}$ and contained in a sample cell of length l , were compacted. A sharp interface was formed between a layer of colloidal suspension of length l_c , and a layer of supernatant containing few particles. The length l_c decreased with rcf, therefore implying that the particle volume fraction of the suspension phase also increased with rcf. In the appendix of this chapter, two methods are used to estimate the final volume fraction of particles, ϕ_p , after centrifugation. For the freezing step, the sample cell was placed flat on the stage, meaning that particles could not only diffuse into the supernatant, but also sediment in the z direction, the direction which gravity now acts (see figure 4.2). It is therefore important to consider this when looking at ice lens formation, as the particle packing may vary over the course of the experiment.

Final structures of ice lenses formed after unidirectional freezing in particle suspensions subjected to different rcf, are shown in figure 5.3 (a). Also shown in the figure is the final structure formed in a separate experiment performed without the centrifugation step, but at a higher initial overall particle volume fraction. For each of these images, the thickness, τ , and spacing, s , of ice lenses are measured, and the results are plotted *vs* rcf and $\phi_{p,i}$ in figure 5.3

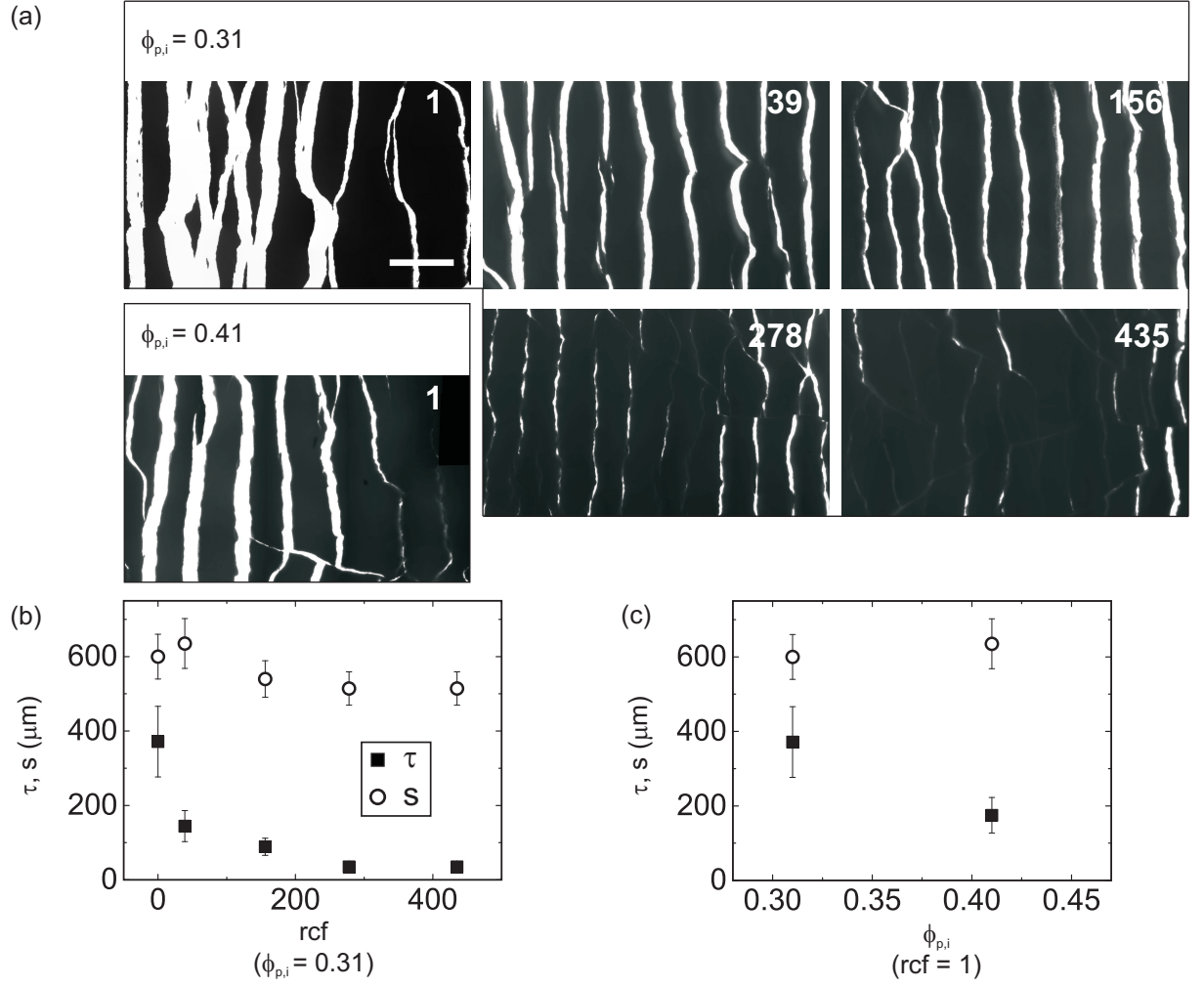


Figure 5.3: (a) Final structures of ice lenses formed under different particle packing conditions: initial particle volume fraction, $\phi_{p,i}$ (labelled within a box) and rcf (labelled within the image). The scale bar denotes 1 mm. The mean thickness, τ (closed), and spacing, s (open), of the lenses is plotted *vs* (b) rcf for $\phi_{p,i} = 0.31$ and (c) $\phi_{p,i}$ for rcf = 1.

(b) and (c). The spacing decreases slightly, but not very significantly, with rcf. However, the thickness of lenses decreases very significantly with rcf, so that the average total heave, τ/s , decreases. The check of changing the initial volume fraction produces data which fit the trend, assuming that a greater rcf produces a larger ϕ_p . Centrifuging the sample produces more regular lenses: when rcf = 1 the width of the lenses decreases significantly when moving along the length of the sample. This is likely due to the effect of sedimentation and diffusion on the particles, as the particles are not jammed into the cell by a centrifugation step.

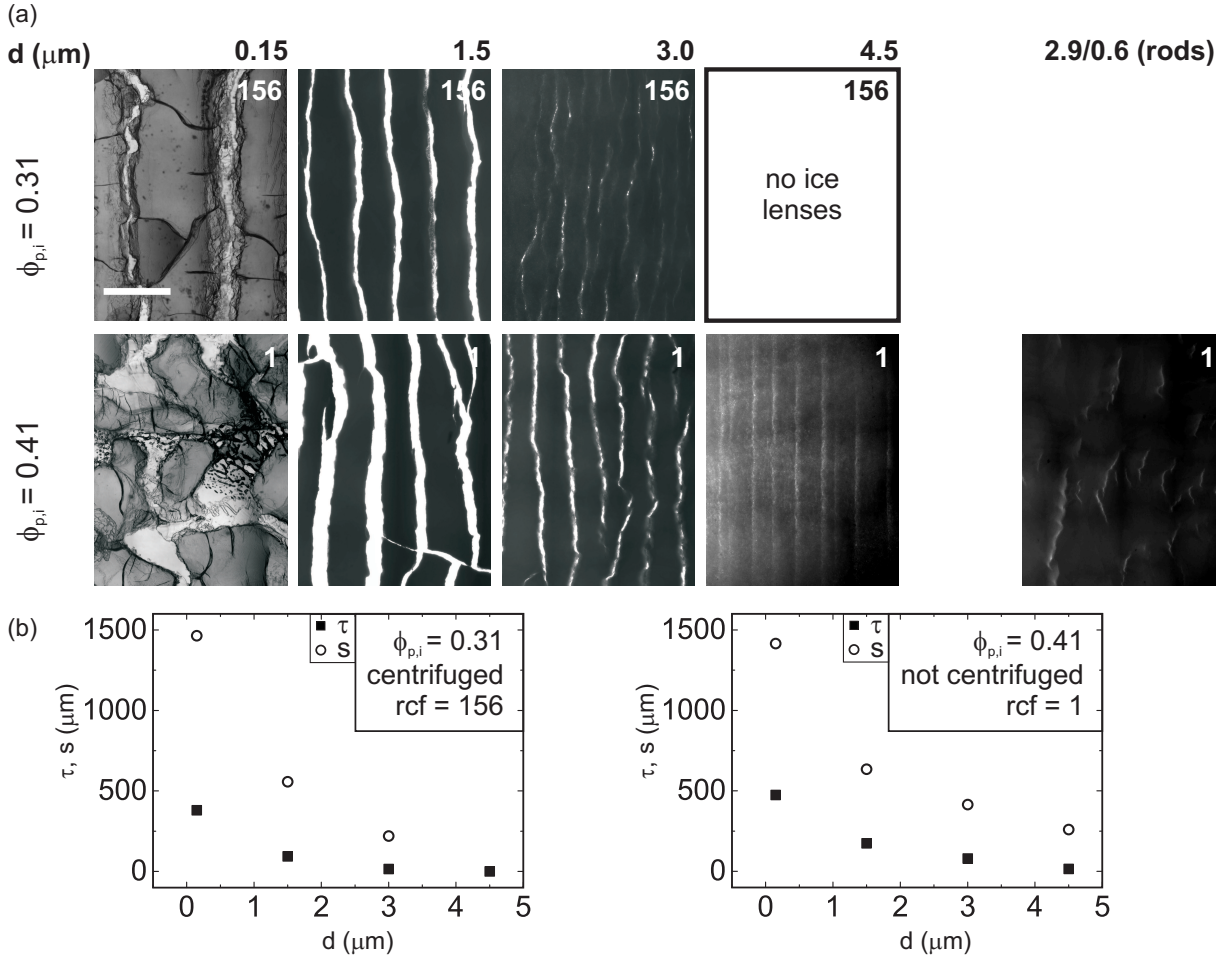


Figure 5.4: (a) Final structures of ice lenses formed in suspensions containing different sized particles: the diameter of the particle, d , is given above the images. Two different particle packing conditions were tested, one at $\phi_{p,i} = 0.31$ with $\text{rcf} = 156$, one at $\phi_{p,i} = 0.41$ with $\text{rcf} = 1$. Rods were only tested at $\text{rcf} = 1$. The scale bar denotes 1 mm. The two right most images have been adjusted in brightness and contrast in order to observe the ice lenses. (b) Graphs of τ and s vs d for the two particle packings.

5.4.2 Particle size and shape

Figure 5.4 shows the final structures after the freezing of suspensions made up of different sized particles, and the effect on the ice lens properties is clear. Focusing on the first row of final structures, where $\phi_{p,i} = 0.31$ and the particles were subjected to a rcf of 156, both the thickness, τ , and spacing, s , of ice lenses decrease as the particle size increases. The thickness goes from 250 μm to no ice lenses formed and the spacing goes from 1450 μm to no ice lenses formed. The average total heave, τ/s , is fairly constant, at ~ 0.17 for $d = 0.15, 1.5 \mu\text{m}$, before reducing to 0 for larger particles. In the second row, where $\phi_{p,i} = 0.41$, the final structures follow the same trends: the thickness and spacing decrease as the particle size increases, for spherical particles. As compared to the conditions in the first row, the lenses are slightly thicker, but the spacing

is similar, meaning that the average total heave is higher. For the particles of $d = 4.5 \text{ } \mu\text{m}$, we see (very thin) ice lenses form, as opposed to none at all, as in the first row. However, because of the dependence of the Pe number on d , where $d = 2R$ (equation 5.10), the centrifugation step performed on each of the samples in the first row does not give the same volume fraction of colloids, ϕ_p , in each sample. The interface position between the compacted colloidal suspension and supernatant, l_c , decreased with d . We know from section 5.4.1 that particle packing has a pronounced effect on ice lens formation, therefore to see the size effect, it is easier to look at the non centrifuged samples, where the packing fraction is constant for all particle sizes. It is still interesting to make comparisons between the two different conditions. In the non centrifuged samples of small particles, the lenses are less regular, however the regularity of lenses increases as the particle size increases. In the rods sample, lenses are very thin and take on non-uniform shapes at non-regular spacings. The rods are expected to be in the nematic phase at equilibrium at this volume fraction [146]. A non-freezing sample of the rods was observed and found to sediment after a few hours into a poly smectic phase, with increasing fluidity at larger h values, as the particle volume fraction decreased.

5.4.3 Impurities

Figure 5.5 shows the results of experiments using suspensions of different concentrations and species of doped impurities. There is a marked effect upon the additions of impurities for some of the species. The ionic species and glucose have similar effects on thickness, τ , and spacing, s , plotted in figure 5.6, *vs* ΔT_{col} , which is proportional to the molar concentration of solute (equation 5.5). The thickness of lenses decreases, and for the highest concentrations of glucose tested, those at 100 mM and above, the spacing dramatically reduces. The addition of glycerol and ethanol, on the other hand, had a minimal effect on τ and s .

To gain some insight into the behaviour of the suspensions, the particles were observed while they were unfrozen, and the solutions with no particles were observed during freezing. This separates the effects of the solute on the particles, and the solute on the freezing behaviour, which could both affect ice lens formation. The particles were not aggregated in 1 mM, but were aggregated in 50 mM Na_2SO_4 ; particles were not aggregated in 50 mM, but were aggregated in 100 mM NaCl ; particles were not aggregated in solutions of glucose, glycerol or ethanol up to concentrations of 500 mM.

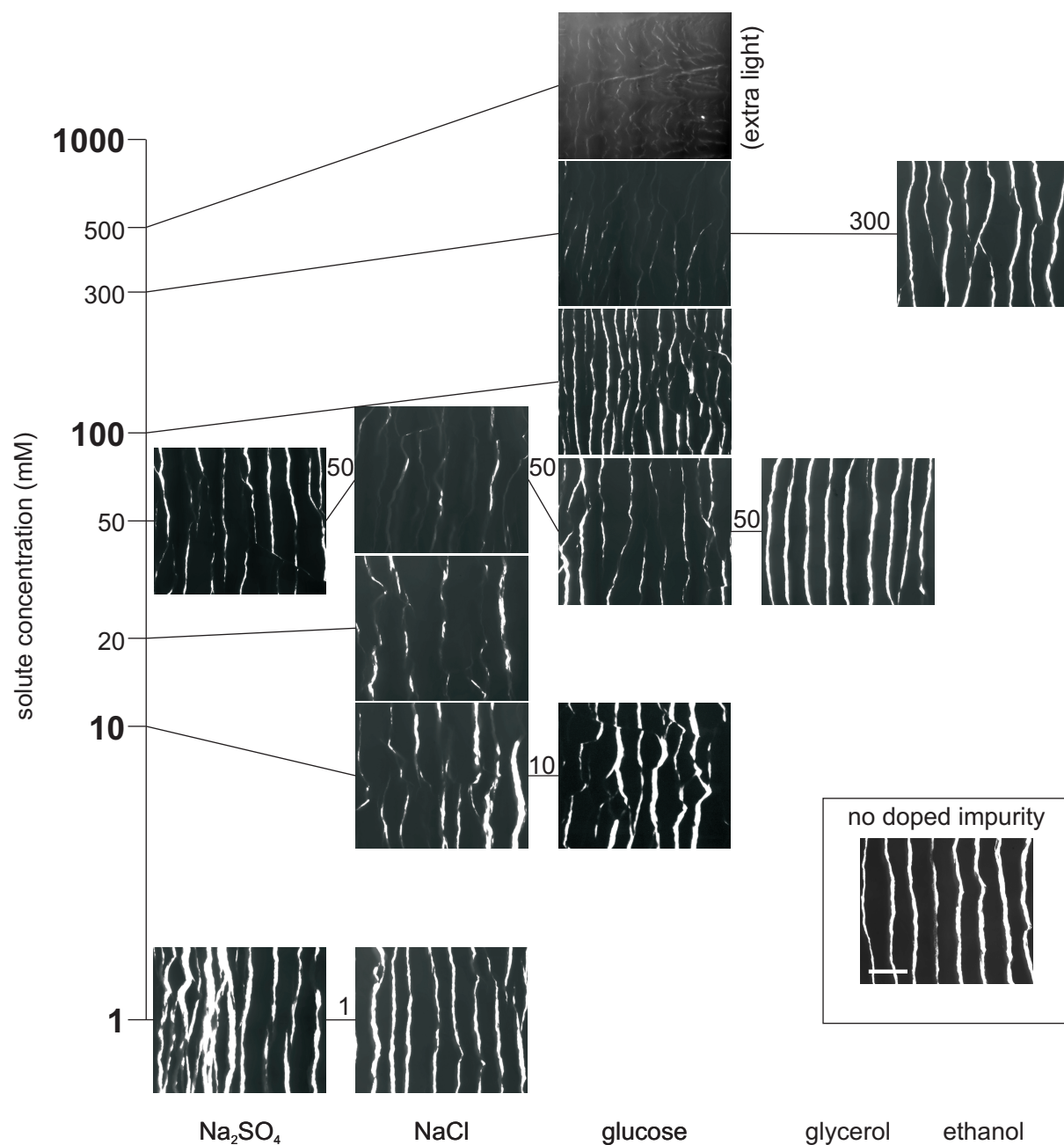


Figure 5.5: Final structures of ice lenses formed in suspensions containing different concentrations and species of impurity. The scale bar denotes 1 mm.

In figure 5.7, images of freezing solutions are shown, taken after freezing had stabilised, and with the sample between crossed polarisers, and with a retardation plate. It is observed that dominant grains grow, and these are distinguished by their different colours. The ice–solution interface is non planar, but the average position of the interface comes up to similar x positions between the samples, i.e. similar temperatures, which reflects the fact that freezing point depression is species independent for ideal solutions. The volume where water doped with

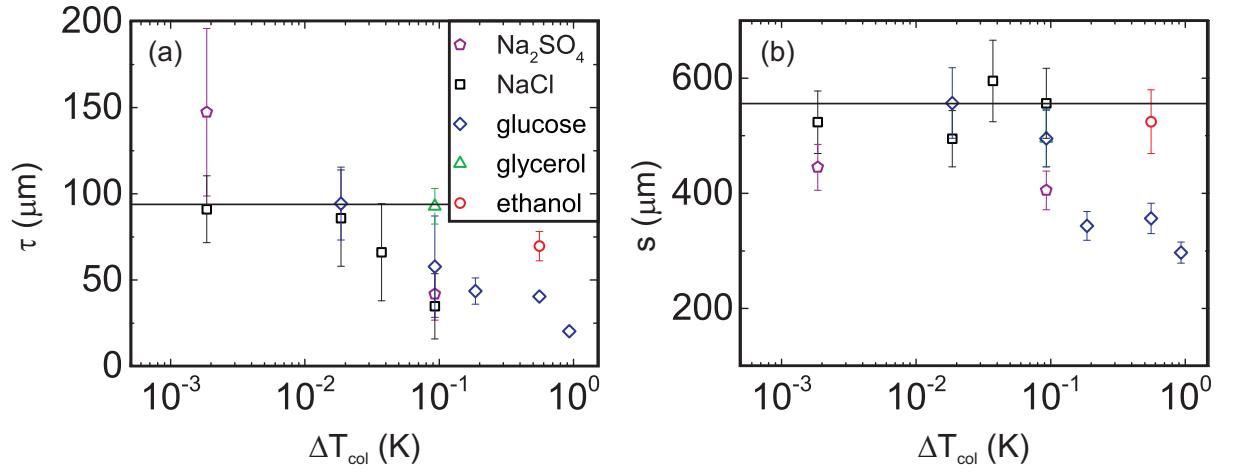


Figure 5.6: Graphs of (a) τ and (b) s vs ΔT_{col} for different species of impurity. The lines denote the values of τ and s for the sample with no doped impurities.

impurities and ice can coexist, the ‘mushy layer’ [147], is observed from the left hand side of each image, to the ice growth tips. The average grain size and shapes are similar in all the samples, however it is very difficult using this method to measure the exact ratio of water and ice in each of the samples.

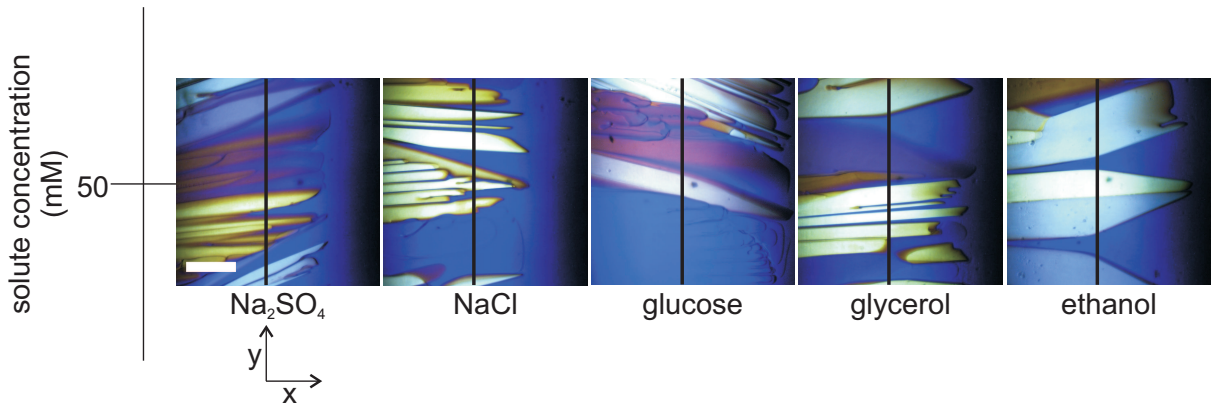


Figure 5.7: Freezing solution of different species of impurity, all at a concentration of 50 mM, under the same conditions as in the experiments described above, but with no particles. Images were taken after ~ 1 hour of progressive freezing, between crossed polarisers and with a retardation plate. Ice (left hand side) appears multi coloured as it is made up of many crystals, and water (right hand side) appears purple because a retardation plate was used. The centre between the plates, at $x = 0$, is approximately indicated by the black line. The scale bar denotes 500 μm .

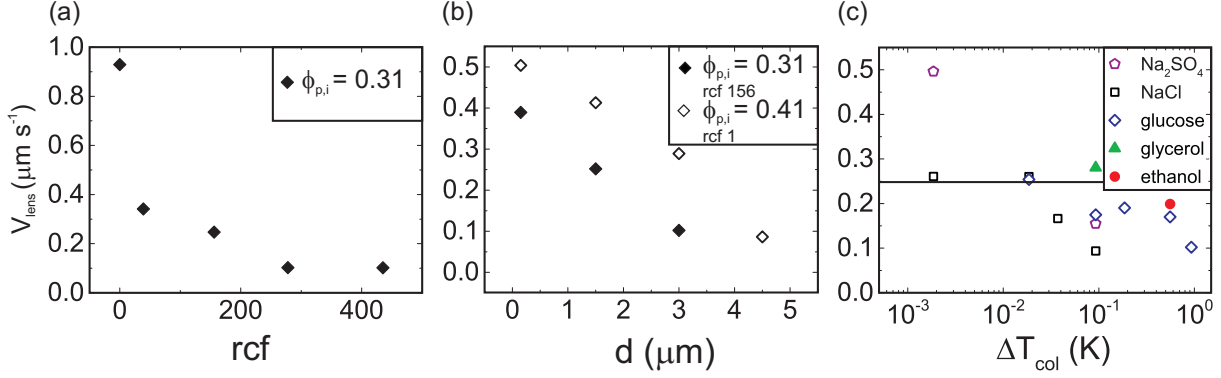


Figure 5.8: Graphs of the ice lens growth rate, V_{lens} , vs (a) rcf for $\phi_{p,i} = 0.31$; (b) particle diameter, d , for $\phi_{p,i} = 0.31$, which was centrifuged with rcf = 156 and 0.41, which was not centrifuged; and (c) ΔT_{col} for different species of impurity, the line denotes the values of V_{lens} for a similar sample with no doped impurity.

5.5 Discussion

We will discuss the ice lens property variation in light of the results presented above, and the conclusions made in chapter 4, and considering the current theories in frost heave. A key factor that is influenced is the ice lens growth rate, defined here as,

$$V_{lens} = \left(\frac{\tau}{s}\right) V, \quad (5.7)$$

where τ is the thickness, s is the spacing and V is the pulling velocity, and the average heave is equal to τ/s . V is held constant for all experiments in this chapter, but τ and s change significantly over the parameter range studied. The graphs in figure 5.8 show V_{lens} plotted vs rcf, d and ΔT_{col} .

5.5.1 Particle packing

Particles are a key component of the system, and the variation in their number density, or volume fraction, ϕ_p , can affect several properties important to ice lenses: the compressibility, the water fraction and the permeability of the suspension. First, comparing the data taken at different initial particle packing (and no centrifuging), $\phi_{p,i} = 0.31$ and 0.41, the thickness of lenses reduces for higher particle volume fraction, but the spacing is not affected (figure 5.3 (a) and (c)). Overall, V_{lens} decreases from $0.9 \mu\text{m s}^{-1}$ (figure 5.8 (a) where rcf= 1) to $0.4 \mu\text{m s}^{-1}$ (figure 5.8 (b) where $d = 1.5 \mu\text{m}$) with increasing $\phi_{p,i}$. Secondly, we find that the thickness

decreases and the spacing is fairly constant as the rcf during the centrifugation step is increased, and hence V_{lens} decreases from $0.9 \mu\text{m s}^{-1}$ to $0.1 \mu\text{m s}^{-1}$ (figure 5.8 (a)). As increasing the rcf is likely to also increase the particle volume fraction, these results corroborate the first finding.

Compressibility: If the particles are more closely packed, the suspension is less compressible [148], and the ice lens will not be able to open out to the same extent, given the same stress in the ice lens. The ice lens nucleation temperature is the same, since there is no change in the spacing.

Permeability: A alternative explanation for the change in V_{lens} lies in considering a permeability argument. It is clear from equation 5.3 that the permeability decreases with an increase in particle volume fraction. However, the effect is more subtle than this simple picture, as ice is likely to be present beyond the warmest ice lens (chapter 4), which will also affect the permeability of the suspension, since the total volume fraction is $\phi = \phi_p + \phi_i$. The extent to which the suspension is frozen could not be measured, but the first pores to freeze are the largest pores, due to the Gibbs–Thompson effect. If the variation in rcf does not change the frequency of the large pores significantly, then we can assume that there is similar amount of pore ice for all samples. The effect of the decreasing permeability with increasing particle volume fraction, ϕ_p , will then explain the decrease in V_{lens} . The small, non-frozen pores act as the main vehicle for water transport, so if these change in frequency considerably with rcf, they are unaffected by pore ice, but significantly affect the permeability.

Further experimental or theoretical work is required to determine the relative importance of these two effects in this system. We note that the lenses do not change in thickness significantly across each sample, except towards the later end of sampling along x . This suggests that the local packing density may be ‘evening out’ over time, by the rearrangement of particles during freezing, diffusion, sedimentation and heaving combined. These experimental results corroborate the idea that the particle packing is an important feature in frost heave. Often theories simplify the problem by assuming that the particles are at a single valued density ($\phi_p = 0.64$ in [132] and 0.5 in [55]). Our results show that the particle volume fraction affects the growth rate of a lens, and that lens formation can occur at lower particle volume fractions than is assumed in these theories.

5.5.2 Particle size and shape

The particle size effect on the structure of ice lenses is clear (figure 5.4). Focusing on the $\phi_{p,i} = 0.41$ data, where the particle packing does not vary, the thickness and the spacing of lenses both decrease with particle size. The ice lens growth rate, V_{lens} , is plotted *vs* the particle diameter d in figure 5.8 (b), showing that the flow rate towards the lens decreases with particle size. We have shown in section 5.2.2 how it is possible for V_{lens} to decrease with d in two ways. If the pores are filled with ice, the ice fraction increases as the pore radius increases (this is proportional to d), therefore the permeability decreases with d . Alternatively, if viscous resistance in the premelted layers at the ice–suspension interface is an important effect, then the larger particles will experience a larger resistance, which would also cause V_{lens} to decrease.

The fact that the viscous resistance is lowest for the smallest particles means that they are more easily rejected from the ice–water interface (chapter 3). V_{lens} is therefore dominated by the hydraulic resistance of the suspension. The permeability is dominated by ϕ_p as it is likely that $\phi_i = 0$ because of the Gibbs–Thomson effect. We observed that once the undercooled suspension layer, which grows as the ice lens is moved back towards the cold plate, reaches a critical thickness, it is engulfed suddenly by the ice and a new lens nucleates at a warmer temperature. This behaviour is described by the engulfment model (section 5.2.1), and although this is different from the pore ice model, ice lenses that follow the trend in heave and thickness and spacings are formed. However, it is questioned as to whether bands caused by pushing and then sudden engulfment are actually the same as ice lenses.

The reduction in spacing suggests that lenses are more easily nucleated in suspensions with larger particles. The critical engulfment velocity is now likely to be closer to the pulling speed than for the smaller particles, which are easily rejected from the ice. This leads to more lenses, as the likelihood of transitions between the two states is higher. The particles are caught between a state of being rejected and engulfed. If, however, a different mechanism occurs, we can consider other models to explain the change in lens spacing. Within the geometrical supercooling model [123], the undercooling required to nucleate a new lens is inversely proportional to the particle radius (their equation 12). This would also result in the observed smaller lens spacing for larger particles.

In figure 5.4, the $\phi_{p,i} = 0.31$ data is also presented, where each sample was centrifuged

for 30 minutes at an rcf of 156. The change in particle packing had an effect on the ice lenses, as the final structures look different from the $\phi_{p,i} = 0.41$ data. The final particle packing, ϕ_p , will increase as the particle size increases due the dependence of the sedimentation velocity on the particle radius. Therefore as well as a range in particle sizes, we are also looking at a range in ϕ_p . From the previous discussion, we note that increasing the particle packing causes a reduction in V_{lens} . Therefore the particle packing post centrifugation must be greater than $\phi_{p,i} = 0.41$ in all suspensions. Above a critical particle size, lenses do not nucleate at all, and the suspension freezes uniformly, with ice of thickness $\tau \sim 0$, but also $s \sim 0$, as it infiltrates all the pores. The velocity of the ice is greater than the engulfment transition, and the viscous drag of a more concentrated suspension of particles (*vs* the $\phi_{p,i} = 0.41$ data) is greater. With the combination of an increasing particle volume fraction, which also causes V_{lens} to decrease, as well as an increasing d , V_{lens} decreases with a greater rate in the $\phi_{p,i} = 0.31$ data.

In the suspension of rods, it is difficult to nucleate an ice lens. The rods are mainly engulfed by the ice, but occasionally ice can break apart the suspension. The rods generally align their long side parallel to the ice interface, but this configuration must cause interfacial resistance which does not allow for flow around a particle towards a lens. At this particle volume fraction, liquid crystalline phases exist [146], meaning that the suspension is more elastic and less compressible than the equivalent fluid phase in suspensions of spheres. This smaller compressibility results in lens not being able to open out both along x and y , resulting in thinner and shorter lenses.

5.5.3 Impurities

Increasing the concentration of solute in the suspension causes the lens structure to change dramatically (figures 5.5 and 5.6). We note from figure 5.7 that all species of impurity reduce the freezing temperature due to the colligative effect, and form a mushy layer where ice and water is present. This effect is not important in ice lens formation in particle suspensions, since despite there being a strong dependence on the water content caused by freezing point depression, the ice lenses formed in glycerol and ethanol solutions look like the pure case. In the NaCl and Na₂SO₄ samples the particles begin to aggregate above a certain salt concentration. As we have seen in chapter 4, the waviness of the lens is attributed to the changes in particle packings along y . If particles aggregate, these changes will be more dramatic, resulting in much

more wavy and irregular lenses, consistent with our observations. This particle packing variation also causes the total heave to decrease. The same effect also happens in glucose, which is a solute that does not destabilise the particles. Instead, glucose must have another effect on the particle suspension. An increase in the fluid viscosity with c could cause the change in V_{lens} . The variety of freeze cast materials [101–103] depends entirely on the modification of the ice morphology by solutes, to produce the porous composite materials. However, these depend on fast interface propagation. Kimizuka and Suzuki [149] have measured the change in homogeneous nucleation temperature *vs* that predicted by the colligative effect, and found a linear relationship. The constant of proportionality is different for different solutes, and they find a correlation with the amount of undercooling required to nucleate ice and the diffusivity of the solute, citing the viscosity of the solution as a possible cause. Although homogeneous nucleation does not occur in our system, the differences between the solutes could help to explain the change in ice lens formation we see.

5.6 Conclusions

We have shown that particle packing, particle size and impurity concentration of particle suspension all have a pronounced effect on the structure of ice lenses. The trends are explained in terms of the compressibility and permeability of the suspension, the interfacial resistance in the premelted films surrounding the particles, and the properties of the solution. The control of ice lens growth is of important consequence in many situations during the freezing of colloidal particle suspensions. These control factors must be taken into account when considering the freezing of soils, foodstuffs, biological matter and ceramics.

Appendix: quantifying the particle volume fraction

In order to quantify the effect the particle packing has on ice lens formation, we first need to find the particle volume fraction. The particle volume fraction experienced during freezing, $\phi_p(\text{sample})$, could be estimated by one of two methods, both shown in figure 5.9. First, in method 1, the particle suspension after centrifugation was assumed to be homogeneous, i.e. at a constant ϕ_p along l_c . To the naked eye, the concentration of the suspension did indeed look uniform. Here,

$$\phi_p(\text{sample}) = \left(\frac{l}{l_c} \right) \phi_{p,i}, \quad (5.8)$$

where $\phi_{p,i}$ is constant for each experiment, but l_c varies depending on the rcf.

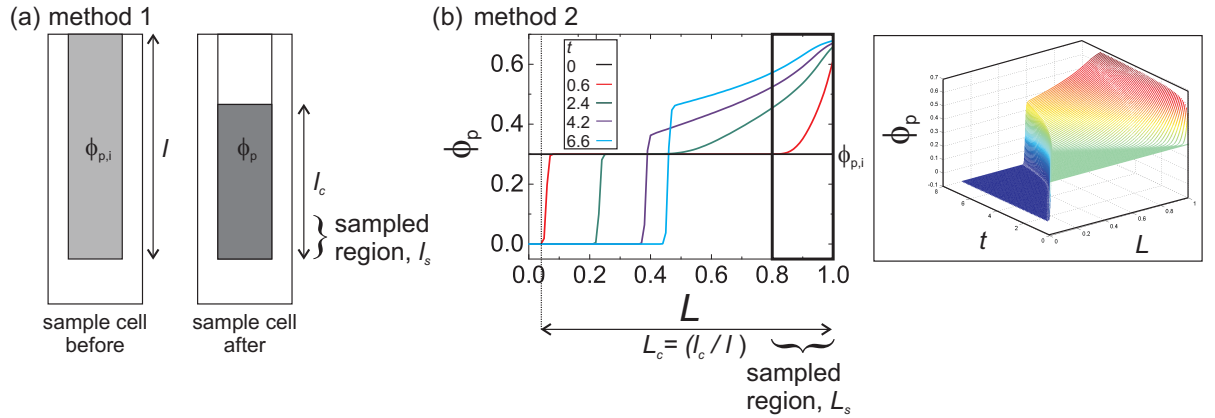


Figure 5.9: Methods of estimating the sample particle volume fraction, $\phi_p(\text{sample})$, after the centrifugation step. (a) Method 1 – $\phi_p(\text{sample})$ is assumed to be homogeneous, and found by the ratio of the length of the sample cell, l , to the length of the compacted colloid, l_c . (b) Method 2 – using L_c found in the four experiments, theoretical profiles of ϕ_p vs L were calculated using the method described in the text. L_c for the lowest rcf is shown. $\phi_p(\text{sample})$ is estimated by taking the normalised area under the curve for the sampled region (boxed within the plot). The graph in the box shows a 3D plot of the time dependence of ϕ_p vs L .

However, theoretical sedimentation profiles found in method 2 show how ϕ_p will indeed vary along l . These profiles were found using the equation of Auzerai, Jackson and Russel [150], which describes the time dependent steady state profile of particle concentration during sedimentation,

$$\frac{\partial \phi_p}{\partial t} + \frac{\partial}{\partial L} \left[(1 - \phi_p)^{6.55} \left(\phi_p - \frac{1}{Pe} \frac{1.85 \phi_{rcp}}{(\phi_{rcp} - \phi_p)^2} \frac{\partial \phi_p}{\partial L} \right) \right] = 0, \quad (5.9)$$

where ϕ_{rcp} is the random close packing particle concentration. The Peclet number is defined as,

$$Pe = \frac{4\pi R^3(\rho_p - \rho_w)gl}{3k_B T} \times \text{rcf}, \quad (5.10)$$

where R is the radius of the particle, g is the acceleration due to gravity, ρ_p and ρ_w are the densities of the particle and water, k_B is the Boltzmann constant, and T is the temperature. Here, we use the values $\phi_{rcp} = 0.7$, $R = 0.75 \times 10^{-6}$ m, $g = 9.81$ m s⁻², $\rho_p = 2200$ kg m⁻³, $\rho_w = 1000$ kg m⁻³, $T = 293.15$ K and $l = 4.5 \times 10^{-2}$ m. We can solve the partial differential equation in Matlab, and using the boundary condition $\frac{\partial \phi_p}{\partial L} = \frac{Pe\phi_p(\phi_{rcp}-\phi_p)^2}{1.85\phi_{rcp}}$, at $L = 0, 1$, since no particles can leave the cell. Values for Pe and the end time must be input. We note that the range of Pe numbers we use is between 9×10^6 and 9×10^7 , and the time of the centrifugation step is kept constant between runs, at 30 minutes. By trial and error we can find a set of solutions to the partial differential equation which fit our experimental results, where L_c is known. Either Pe is constant and t varies with the correct ratio of rcf, or the reverse. We found solutions with $Pe = 1000$ and $t = 0.6, 2.4, 4.2, 6.6$ fitted most closely with the measured values of L_c , and the profile observed by eye – a sharp interface, with the diffuseness increasing slightly at lower rcf. In figure 5.9 (b), the four profiles are plotted, and next to it, the variation of ϕ_p vs L over time, t , is plotted, to show how the profiles evolved. Using these profiles, the particle packing experienced during ice lensing can be estimated. The total area under all the curves is $\phi_{p,i} \times L$, since no material is lost during centrifugation, however, freezing only takes place in the region close to $L = 1$, for about 1/5 of the cell length l , which is denoted in the figure as L_s . Hence, we can estimate the particle packing experienced by the sample as,

$$\phi_p(\text{sample}) = \left(\frac{1}{L_s}\right) \int_{(1-L_s)}^1 \phi_p dL, \quad (5.11)$$

which varies with rcf. Because of the approximations used in finding $\phi_p(\text{sample})$ in both methods, it is useful to compare the results in light of the two calculations.

In figure 5.10 the mean ice lens thickness, τ , and spacing, s , are plotted vs the ϕ_p values found using methods 1 and 2. Method 2 of estimating ϕ_p produced values that fit better with the non centrifuged sample.

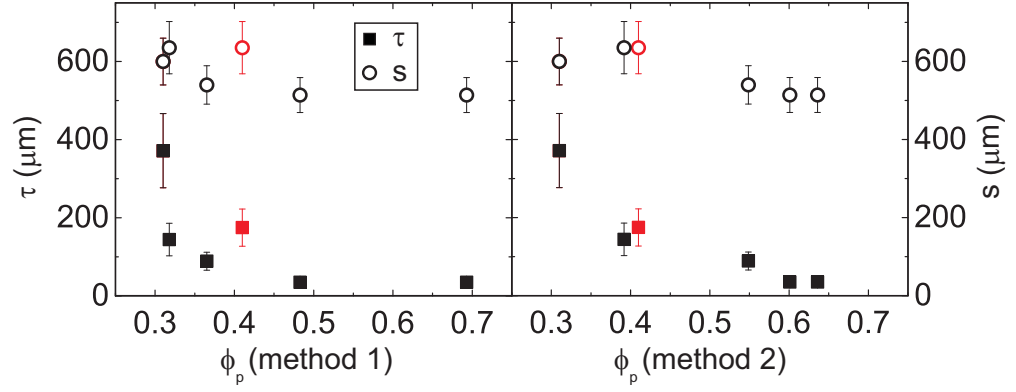


Figure 5.10: The mean thickness, τ , and spacing, s , of the ice lenses is plotted *vs* the estimated final volume fraction ϕ_p , calculated using both methods 1 and 2. The red symbols are the data where $\phi_{p,i} = 0.41$, with no centrifugation step.

Acknowledgements

This work was a collaboration with Rob Style, John Wettlaufer and Eric Dufresne. We thank Arran Curran and Lia Verhoeff for help with experiments, and Stephen Peppin for useful discussions.

Chapter 6

Freezing of concentrated particle suspensions, viewed at the particle level

ABSTRACT

In this chapter, we study, at the particle level, phenomena associated with the freezing of concentrated suspensions of particles. Model systems of monodisperse particles are used, and we observe how the process of ice segregation reacts to an increasing particle concentration at the interface, at ice growth rates well below the critical single particle engulfment velocity. New methods of trapping of the particles into the ice are observed, which differ from the trapping of single particles seen in chapter 3. The silica particles used in chapters 4 and 5 are also frozen in a thinner cell, and ice lenses form. We furthermore see a change in ice segregation patterns with temperature gradient. We observe ice lenses forming within a ‘frozen fringe’ region for the high gradient case, and ahead of the ‘frozen fringe’ for the low gradient case.

6.1 Introduction

Systems of concentrated particle suspensions in which the surrounding water is freezing, are very common. Soils are one such example [121], as well as industrial substances such as freeze cast materials [48]. The interaction of particles with growing ice is complicated due to the particle–particle interactions, and the change in viscous resistance. For the continued supply of water to the ice, when the suspension is cooled during directional solidification, water must flow through the particle suspension. A concentrated region of particles may be treated as a porous medium, where the particles themselves cause resistance to the flow of water around them. This is additional to the viscous resistance felt directly at the ice–water interface, in the premelted layers between individual particles and the ice. In chapter 3, it was found that phenomena attributed to the flow in premelted layers cause the motion of single particles through ice. Premelted layers are also an essential component of current theoretical understanding concerning the rejection of particles from the ice–water interface [95]. This layer must exist, in order to supply water to the growing ice behind the particle. In chapter 3, we also found that the mechanism of particle engulfment depends on other effects, such as the morphology of the interface. In the current chapter we study the complex interplay between these phenomena, with a focus on concentrated quasi–2D particle suspensions.

This chapter is organised as follows: we begin in section 6.2 by discussing the additional theory required to expand on chapter 3. In section 6.3, we describe the experimental methods, followed by results and discussion in section 6.4. Finally, in section 6.5, we present our conclusions.

6.2 Theory

The non–inclusion of colloidal particles by an ice–water interface is analogous to the problem of solute concentrating ahead of the interface. However, as particles have a significantly lower diffusivity to a molecule of solute such as salt, or ethanol, the concentration profile ahead of the interface is not the same. Peppin *et al.* [67] calculated concentration profiles for various particle diffusivities, with a view of explaining how a colloidal suspension might become morphologically unstable [151]. They focused theoretically on colloidal particles in the nanometer range. These

are different from our experimental conditions, where we observe micrometer sized colloidal particles by light microscopy. Nevertheless, we can apply the basic principles of particle build up to the problem of freezing colloidal particles. An important consideration for concentrated colloidal suspensions is the ice entry temperature, or the Gibbs–Thomson undercooling. This is the undercooling at which ice is thermodynamically stable in the pores between the closely packed particles. This undercooling is smaller for larger particles, where there are larger pores, as shown in section 2.2.1. Conversely, the trapping of particles by an ice–water interface, which is moving too fast for the premelted layer to be maintained, is a process that is out of equilibrium [66]. The process that eventually causes the particles to be encapsulated by the ice, i.e. either the freezing of the pores or particle encapsulation, is not easy to distinguish. However, predictions may be made about both mechanisms as follows: The Gibbs–Thomson undercooling is derived in section 2.2.1, and a plot of the undercooling as a function of pore radius is shown in figure 4.7 (c).

Here, we will discuss the second mechanism, as described in [152]. If the undercooling is small such that ice does not invade the pore space, and the velocity of the ice is low such that particles are not engulfed, then particles stay suspended in water, while ice continues to grow. The particles concentrate ahead of the interface, as shown in figure 6.1. The Gibbs–Thomson effect causes the water in the pores to stay in the liquid state. The suspension then forms a porous medium where the flow of water to the growing ice is dictated by Darcy’s law, as discussed in relation to frost heave in chapters 4 and 5. The thermomolecular and viscous forces acting on the particles are defined in section 3.2. They act in opposing directions, with the thermomolecular force preventing the ice from touching the surface of the particle and giving rise to a premelted layer of thickness d , and the viscous force acting on the liquid in this layer [45]. Another force must be defined, which describes how the presence of other particles in the liquid contribute to forcing the particles into the ice, i.e. this force is acting in the same direction as the viscous force. This ‘particle force’ is defined as,

$$F_P \sim R^2 \sigma_e, \tag{6.1}$$

where R is the radius of a particle, and σ_e is the effective stress, which is equivalent to the pressure, p , in the liquid next to the ice–water interface [152]. The length L is defined as the distance between the ice–water interface and the interface between the close packed particle

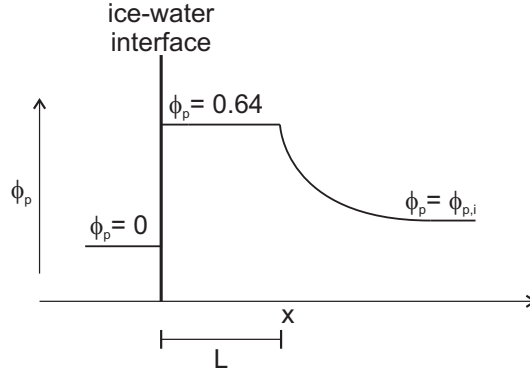


Figure 6.1: Schematic graph of the particle volume fraction, ϕ_p , vs position, x , showing pure ice growing into a suspension of particles of initial volume fraction $\phi_{p,i}$. The length of the close packed region, L , is shown.

suspension and the suspension at its initial concentration, as shown in figure 6.1. The stress, σ_e , or equivalently p , is negligible at a distance L from the ice–water interface, compared to its value at the interface. From Darcy’s law, the stress at the interface can be defined as,

$$\sigma_e = -\frac{L\eta V}{K}, \quad (6.2)$$

where η is the viscosity of the liquid, K is the permeability of the porous medium, defined by equation 5.3 and V is the velocity of flow. Therefore the final expression for the particle force is,

$$F_P \sim -\frac{R^2 L \eta V}{K}. \quad (6.3)$$

By balancing the forces, $F_T + F_\eta + F_P = 0$ (equations 3.4, 3.5 and 6.3), an expression for the velocity of the ice, which is equal and opposite to the flow velocity, as a function of d_0 , the premelted layer thickness where the particle is closest to the ice, which is along the direction of the temperature gradient, ∇T , can be found, as in section 3.2. The critical engulfment velocity is the maximum possible value of V , for a given film thickness, d_0 , since above this value, no film thickness can be maintained in a steady state.

The particle configuration in front of the ice–water interface may become an important factor when considering the pattern of particles within the ice, after they have been engulfed. In dilute suspensions, as we have seen in chapter 3, particles tend to be engulfed along lines parallel to the temperature gradient, following perturbations caused by other engulfment events.

Particles ahead of the interface are free to take up positions in crystal lattices, glassy states or random packings. This is concentration, size distribution and time-scale dependent, with the time-scale set by the ice growth speed and the diffusion time-scale. The Peclet number is a measure of the relative importance of these contributions

$$Pe = \frac{R\pi\eta}{k_B T} \cdot VL \quad (6.4)$$

where $k_B T$ is the thermal energy. For example, where $L = R$, Pe is > 1 for particles greater than a micrometer in radius, at ice speeds of $V = 1 \mu\text{m s}^{-1}$, meaning that the rate of ice growth is dominant. This makes it likely that an initially homogeneous particle suspension forms a layer of concentrated particles which are unable to disperse fast enough, so build up ahead of the interface (see figure 6.1).

6.3 Experimental methods

The experimental setup described in chapter 2 was used to study the interaction of concentrated particles suspensions with an ice interface. ‘PDMS’ cells were used to contain the suspensions, since the height of the sample cell could be well controlled (see section 2.3.4 for preparation method). The PDMS sample cells had a height between $h = 7\text{--}10 \mu\text{m}$. Confining the suspensions to close to a particle diameter meant that particles could only be concentrated into a monolayer, or close to a monolayer, therefore allowing for the close inspection of the behaviour, using light microscopy. A well controlled constant temperature gradient can be applied to the thin sample. The particles used were melamine particles, which were stable in water, highly monodisperse, and available in a range of sizes, and silica particles, which were used in frost heave experiments in chapters 4 and 5. Ice was nucleated in the sample, and then the temperature gradient was set.

6.4 Results and discussion

Following the nucleation of ice, particles are initially trapped in the ice by fast equiaxed, then directional growth, until the ice slows down, and stops at the position of the bulk melting temperature. The temperature gradient is set and the motor started at a speed which is much lower

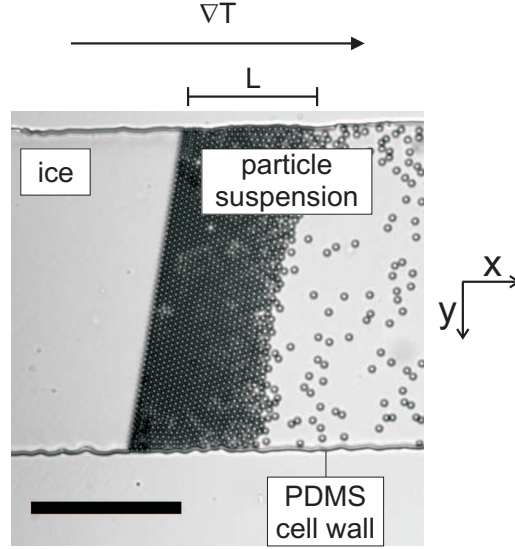


Figure 6.2: The build up of colloidal particles (radius, $R = 1.8 \mu\text{m}$) in front of a moving ice–water interface. The sample was contained in PDMS channels of height $7 \mu\text{m}$, with a temperature gradient, ∇T , acting along the direction shown at the top. The packed region length is denoted by L . The scale bar denotes $100 \mu\text{m}$.

than the critical engulfment velocity. The particles are rejected from the ice–water interface, and build up directly ahead of it. The ice therefore becomes segregated from the particle suspension. The layer of concentrated particles thickens, and as their diffusion is slow compared to the speed of the ice, particles build up with a sharp interface between the particle layer and the particle suspension at the initial concentration. We will now first discuss experiments using melamine particle suspensions, followed by silica particle suspensions.

6.4.1 Melamine spheres

Figure 6.2 shows the particle build up in a suspension of melamine particles, as well as the direction in which the temperature gradient acts (along x); this is the same in images in all subsequent figures. The approximate particle layer thickness, L , which is the distance between the ice interface, and the sharp boundary between particles at the initial concentration, $\phi_{p,i}$, and particles which are close packed, is also indicated in the figure.

An increase in $\phi_{p,i}$ leads to L increasing faster, see figure 6.3, with the experiment conditions in table 6.1. After a period of time, at just before 475 s, particles start to become engulfed. At this point, L is equal to the critical particle layer thickness, L_c . They are not all instantaneously engulfed, rather, the particles are stripped away from the suspension and into the ice. When

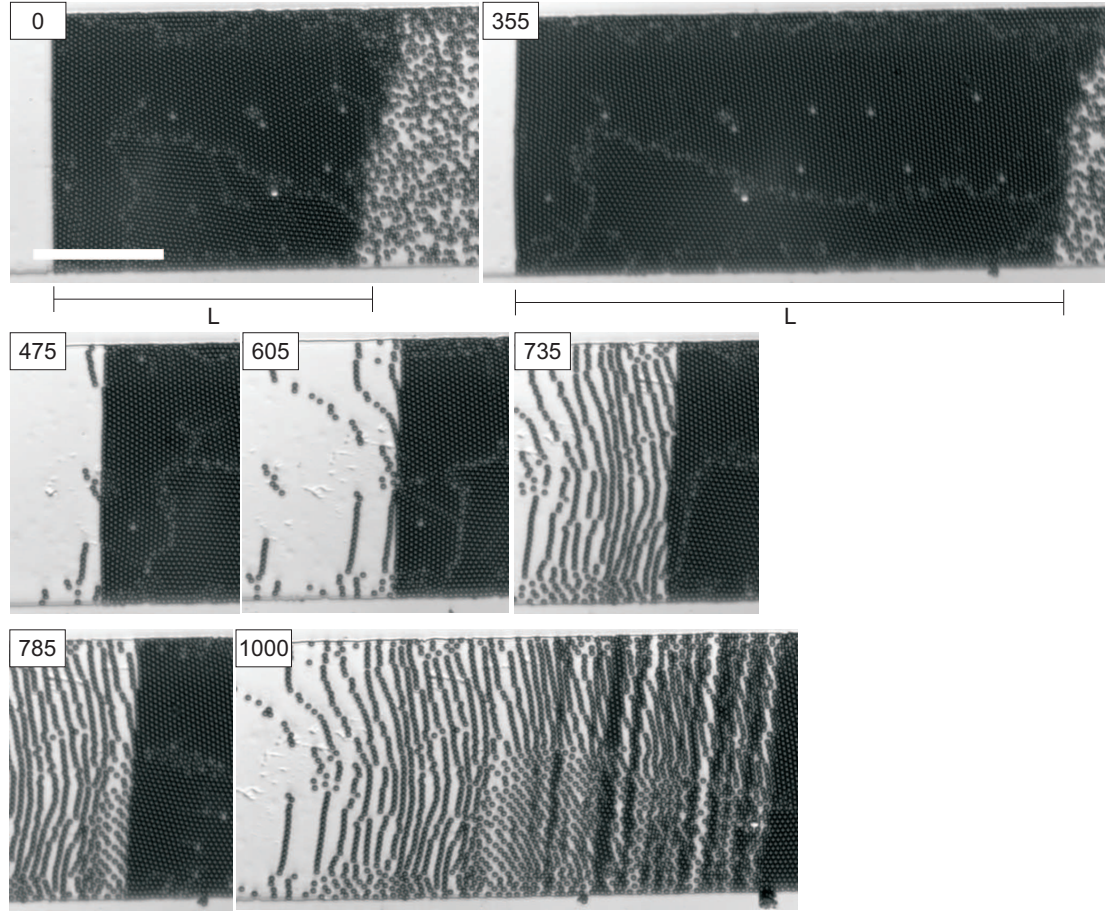


Figure 6.3: Part I (of II): particle trapping in concentrated suspensions of melamine spheres. Particle build up in a concentrated suspension, where the packed region length is denoted by L . Once L reaches a critical size, L_c , particles begin to be engulfed. The particle configuration in suspension is translated into the particles trapped in the ice. Conditions for the experiment are tabulated in table 6.1. Times (in s) are shown in the top left of each image. All samples were contained in PDMS channels of height $7\text{ }\mu\text{m}$, the scale bar denotes $100\text{ }\mu\text{m}$.

a different colloidal crystal orientation is met by the ice, the particles are trapped in lines orientated along the colloidal crystal axis, see e.g. the change in the bottom part of the image at 785 s in figure 6.3.

The ice does not grow at the same speed as the motor, like in experiments shown in chapter 3. Instead, the ice grows at a slower rate, and the sample is being continuously moved in the negative x direction, towards colder temperatures. The ice–water interface typically moves

Experiment	∇T (K mm^{-1})	R (μm)	V_i ($\mu\text{m s}^{-1}$)	L_c (μm)
Figure 6.3	0.7	2.1	1	470
Figure 6.5 (a)	0.5	3.0	1	350
Figure 6.5 (b)	0.5	3.0	1	230

Table 6.1: Conditions for trapping experiments on melamine spheres presented in figures 6.3 and 6.5.

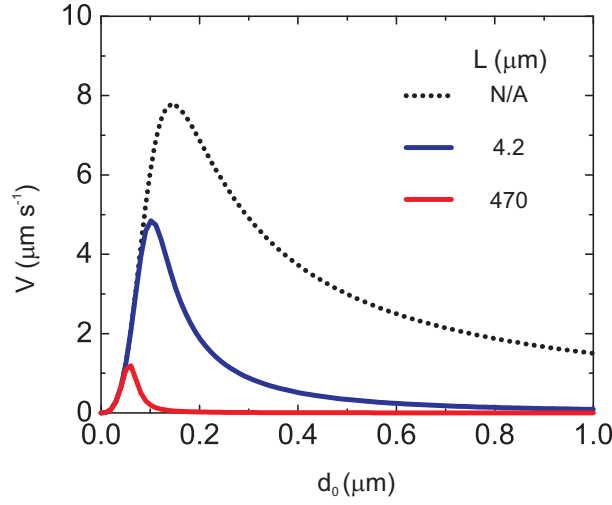


Figure 6.4: The ice growth velocity, V , plotted *vs* the minimum premelted layer thickness, d_0 , under various conditions, all with $R = 2.1 \mu\text{m}$. The dotted line represents the result without using the expression for F_P , which includes L , and the solid lines represent results including F_P . The value of L was chosen to present a single layer, $L = 2R \mu\text{m}$, and the critical layer thickness in the experiment in figure 6.3, $L_c = 470 \mu\text{m}$.

backwards at a rate of $\sim 0.25 \mu\text{m s}^{-1}$. After 500 s, a typical undercooling experienced by the interface is therefore $\sim 0.08 \text{ K}$. For a pore radius that scales with this particle size, the Gibbs–Thomson undercooling is close to this value (figure 4.7 (c)), which indicates that the cause of the ice growth delay is that pores of this size can be held in the liquid state. The non–homogeneous engulfment of the particles indicates a particle trapping process, rather than an invasion of the pore space by ice.

Particle engulfment velocities are typically lowered by the surrounding particles because of this extra ‘particle force’ (equation 6.3). In figure 6.4 the velocity of ice, V , is plotted as a function of the minimum premelted layer thickness, d_0 . This minimum thickness is the closest distance between the particle and the ice for a given V , which always occurs along the direction of the temperature gradient (see figure 3.2 (a)). The velocity, V , is calculated by solving the equation $F_T + F_\eta + F_P = 0$, with the forces defined in equations 3.4, 3.5 and 6.3 respectively. The dependency on d_0 is from both the thermomolecular and viscous forces, F_T and F_η . Here, we use the values given in the table 2.4, $\nabla T = 0.7 \text{ K mm}^{-1}$, $\eta = 2 \times 10^{-3} \text{ Pa s}$ and $\lambda = 5 \text{ \AA}$. A value of $\phi = 0.5$ was used to estimate the permeability, using the Kozeny–Carman equation (equation 5.3). Because the sample cell height is not an integer number of particle diameters, particles do not perfectly fit inside the cell, and we expect that $\phi < \phi_{rcp}$, where ϕ_{rcp} is the random close packing density. The maximum value of V corresponds to the critical engulfment

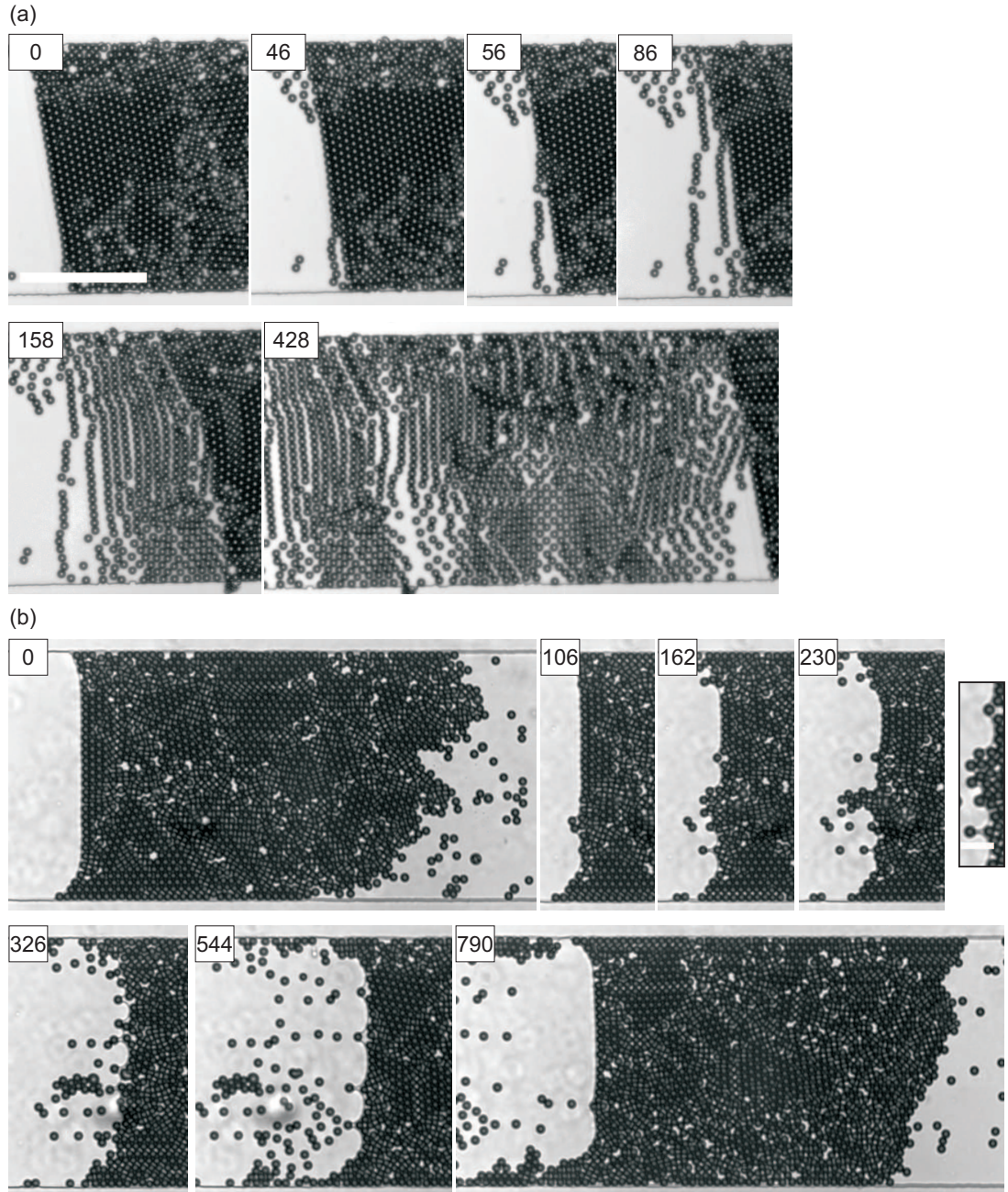


Figure 6.5: Part II (of II): particle trapping in concentrated suspensions of melamine spheres. (a) An example of particle trapping in a suspension containing larger particles, where bands are engulfed. (b) Another example of particle trapping, which is more similar to that seen in chapter 3, where particles are engulfed in lines parallel to the temperature gradient. Conditions for the experiments are tabulated in table 6.1. Times (in s) are shown in the top left of each image. All samples were contained in PDMS channels of height $7\text{ }\mu\text{m}$, the scale bar denotes $100\text{ }\mu\text{m}$. In (b) a zoom of the interfacial region at time 162 s is shown; the scale bar denotes $20\text{ }\mu\text{m}$.

velocity, V_c , above which a steady state cannot be maintained. The blue curve shows the solution including the particle force, where a layer thickness L of a particle diameter, $L = 4.2\text{ }\mu\text{m}$, is used. This significantly lowers the critical engulfment velocity, from the values obtained without

considering the particle force, F_P . Increasing the layer thickness to the experimental critical value, $L_c = 470 \text{ } \mu\text{m}$, causes the engulfment velocity to be lowered to a value close to that found for the experiment, $V_c = 1 \text{ } \mu\text{m s}^{-1}$ (red curve). For comparison, we also show the case of single particles, as studied in chapter 3, where the force due to the other particles, therefore the dependency on L , was not included (black curve).

Figure 6.5 (a) and (b) show different particle trapping behaviours, which take place under similar conditions. The first shows trapping in bands perpendicular to the temperature gradient, and the second along lines, parallel to it. These experiments show again the importance of the ice crystal morphology in this problem. As in chapter 3, we showed that different facets of ice were more prone to the engulfment of particles. In figure 6.5 (b), trapping began at a lower critical layer thickness because the ice was more unstable to the engulfment of particles. A similar pattern of trapping was observed in the experiment shown in figure 3.6 (c), and in both, layers of water can be seen between the particles being engulfed and the rest of the particle suspension (see the zoom in figure 6.5 (b)). In all the experiments summarised in table 6.1, particles are engulfed for a while, but as the trapping rate of particles exceeds the growth rate of the layer, the layer, of thickness L , becomes thin enough to support the pushing of particles again.

6.4.2 Silica spheres

For the experiments on silica particles, a high initial particle concentration was used. The particles are again concentrated at the interface by the growth of segregated ice. In figure 6.6, we show results from two different situations, with conditions shown in table 6.2. For the low temperature gradient case shown in figure 6.6 (a), the ice interface is less well defined, consistent with results from chapter 3. Darker areas appear in the suspension, ahead of the macroscopic ice–water interface. This is likely pore ice, meaning that some pores are large enough to contain ice at this temperature. Ahead of this region, a large macroscopic crystal of ice forms, and grows along x , as well as along y . New horizontal regions of segregated ice form ahead of the interface, nucleating from ice which propagates into regions at a warmer temperatures than the previous horizontal macroscopic region of ice. An interesting pattern of ice forms, which is similar to some results found in [67]. The segregated ice forming in large crystals is not necessary colder than the darker areas of pore ice.

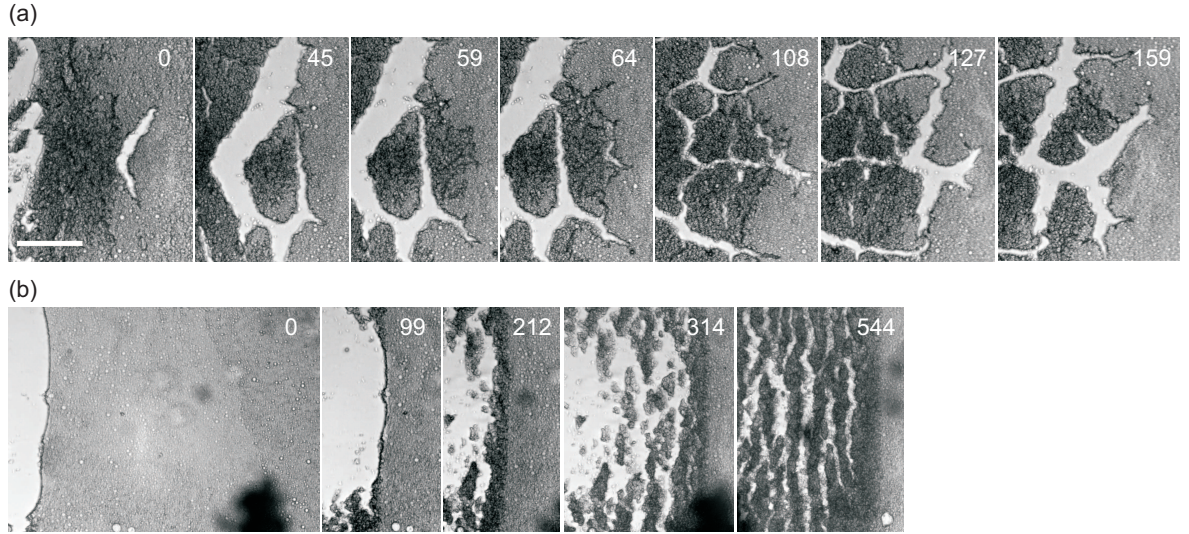


Figure 6.6: Particle trapping in concentrated suspensions of silica spheres. Times (in s) are shown in the top left of each image. All samples were contained in PDMS channels of height $7\text{ }\mu\text{m}$. The scale bar denotes $100\text{ }\mu\text{m}$.

In the high gradient case, shown in figure 6.6 (b), the particles are first engulfed by the ice–water interface in the region of the suspension which is held in a position colder (further to the left of the image) than the other particles (bottom part of image at time 0 s). As this variation in position along x represents a large change in temperature, due to the high gradient, it is possible that ice is able to invade the pores only here. They are then engulfed at the top part of the suspension too (time 99 s). The top and bottom parts of the suspension are probably held at a different position because of the ice–water meniscus at the wall of the sample cell, which is just outside the field of view. A darkening of the suspension phase occurs, in which the boundary is close to perpendicular to the temperature gradient, and has a sharp interface. Particles are able to segregate and layers of ice are formed, in regions that have the appearance of ice–lenses. These always appear behind the region which looks darker due to the probable invasion of the pores by ice, which is named a ‘frozen fringe’.

Experiment	∇T (K mm ⁻¹)	R (μm)	V_i ($\mu\text{m s}^{-1}$)
Figure 6.6 (a)	0.4	0.8 (polydisperse)	1
Figure 6.6 (b)	6.1	0.8 (polydisperse)	3

Table 6.2: Conditions for trapping experiments on silica spheres presented in figure 6.6.

6.5 Conclusions

Ice segregation can occur in suspensions of particles concentrated enough to immediately build up a layer of close packed particles ahead of the interface, during ice growth. While the ice grows at speeds below the critical engulfment velocity, this layer thickens, and builds up over time. Because the critical engulfment velocity is a function of this layer thickness, eventually this layer becomes large enough to reduce the critical engulfment velocity to the ice growth rate, and the layer is engulfed. The layer thickness dependence is due to the stress caused by this particle rich layer, which can be described by a consideration of Darcy's law. Experimentally, we find a difference in the critical engulfment velocity of melamine particles, as compared to the single particle engulfment velocity found in chapter 3. This is in agreement with theory, as the critical engulfment velocity decreases if a particle force is included. A non-equilibrium method of trapping of the particles was observed. Trapping may occur in bands perpendicular to the temperature gradient, or in lines along the temperature gradient; this behaviour is independent of R and ∇T , but likely due to the ice crystal orientation. The particle suspension crystallinity may also play a role, as the colloidal crystal orientation is observed to affect the pattern of the trapped particle bands.

A phase diagram of the ice velocity, V , *vs* the temperature gradient, ∇T , is possible to build, by using different gradients and gradually increasing the pulling velocity. However, consistency in building the layer thickness into a constant length and particle concentration is key to comparing results. As we have seen in the above section, a constant ice crystal orientation is also important.

Acknowledgements

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Chapter 7

The ice–water meniscus

ABSTRACT

In this chapter, we visualise the ice–water interface in a plane perpendicular to the glass wall and parallel to the temperature gradient, ∇T , by means of laser scanning confocal microscopy. The relevant capillary lengthscale is given by $\Lambda_c = \sqrt{\gamma_{iw}T_m/\nabla T L_m \rho_i}$, with γ_{iw} the ice–water surface energy, T_m the bulk melting temperature, L_m the latent heat of solidification, and ρ_i the mass density of the ice. This plays an analogous role as the capillary length in the well-known capillary rise problem of a fluid interface under gravity against a vertical wall. By using fluorescent dye, which is insoluble in the ice phase, the sample is placed on a conventional confocal microscope, and a three dimensional profile of the ice–water interface can be obtained. This profile is fitted to the Young–Laplace equation which allows for the determination of the relevant lengthscale of the problem. This lengthscale is of the correct order of magnitude, and we will discuss possible discrepancies.

7.1 Introduction

In chapter 3, we observed particle motion out of the ice and found a change in the particle speed after it gets closer than a distance of $\Delta x = 10 \text{ }\mu\text{m}$ from the ice–water interface at T_m (figure 3.9 (d)). If the ice–water interface is non–uniform in the direction perpendicular to the temperature gradient, this may be relevant to the observed change in particle speed in two dimensions. To determine the exact three dimensional shape of ice inside the sample cell, we use laser scanning confocal microscopy. The advantage of using confocal microscopy over light microscopy is that each focal plane can be scanned, in slices of sub micrometer thickness, in order to build up a three dimensional picture of the ice–water interface. The interface recognition can only occur if there is a distinct difference between the two phases, in the number of dye molecules the microscope detects. This is certainly possible in our system, because of the low impurity concentration in the ice phase, if it is grown slowly enough to reject the impurity, which in this case is the fluorescent dye.

This chapter is organised as follows: we begin in section 7.2 by deriving the theoretical expression for the curvature lengthscale, then presenting the Young–Laplace equation which will be used to fit the experimental profile. In section 7.3, we describe the experimental methods, followed by results and discussion in section 7.4. Finally, in section 7.5, we present our conclusions.

7.2 Theory

In this section, we present an expression for the meniscus profile formed by the ice–water interface at a single wall, where a temperature gradient acts in the direction along the wall. We first derive an expression for the lengthscale in the problem, Λ_c . The coordinate frame is shown in figure 7.1. In the derivation, we make the assumption that we only have a single wall at $z = 0$, and that the system is translationally invariant along y , the direction perpendicular to both z and x . This is a fair assumption because it turns out that the height and width of the experimental cell are of the order $10\times$ the characteristic lengthscale. Furthermore, we assume that the liquid water phase wets the glass completely [153].

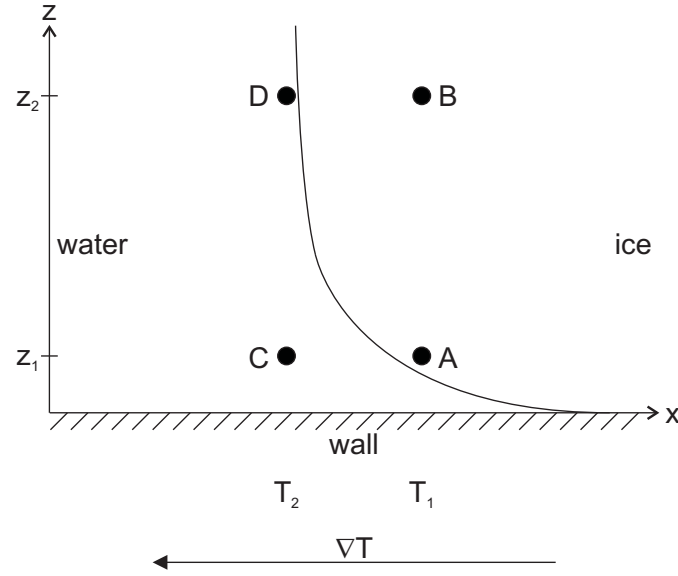


Figure 7.1: Diagram showing the curved ice–water interface next to a wall, under a temperature gradient, ∇T . The coordinate frame and points referred to in the derivation are also marked with black dots.

In mechanical equilibrium, there will be no flow between points in the same phase, and at the same temperature, that is, for points A and B (in the ice phase at temperature T_1) and points C and D (in the water phase at temperature T_2). This means that the pressure at A, p_A , and the pressure at B, p_B , are equal, and similarly, p_C and p_D are equal. At z_2 , points B and D are far away from the wall, and thus do not experience the effects of the curvature at the wall. The pressure at the point B is greater than at the point D because of the pressure difference in the ice,

$$p_B = p_D + \Delta P_i. \quad (7.1)$$

At z_1 however, the points A and C are close to the wall, and therefore experience the curvature effect, such that point A is next to the ice–water interface, and experiences a pressure difference due to the Laplace pressure, as well as due to the pressure difference in the water, hence,

$$p_A = p_C + \Delta P_w + \gamma_{iw}\kappa. \quad (7.2)$$

We can use the Gibbs–Duhem equation, $Nd\mu = -SdT + VdP$, to find the pressure differences in the ice or water phases, $\Delta P_a = (S_m^a/V_m^a)\Delta T$, where S_m and V_m are the molar entropy and volume for phase a . We can equate equations 7.1 and 7.2 due to mechanical equilibrium, and

as $p_C = p_D$, the expression becomes,

$$\gamma_{iw}\kappa = \left(\frac{S_m^i}{V_m^i} - \frac{S_m^w}{V_m^w} \right) \Delta T. \quad (7.3)$$

Assuming that the densities of the ice and water phases are equal, and using the relationship $L_m = T_m \Delta S / M$, where M is the molar mass, the right hand side of the equation can be simplified to

$$\gamma_{iw}\kappa = \frac{L_m \rho_i}{T_m} \Delta T. \quad (7.4)$$

The characteristic thermal capillary length Λ_c may be defined by $\Lambda_c^2 = x / \kappa$, while the undercooling is related to the temperature gradient, ∇T , by $\Delta T = \nabla T x$. Therefore the lengthscale is defined as,

$$\Lambda_c = \sqrt{\frac{\gamma_{iw} T_m}{\nabla T L_m \rho_i}}. \quad (7.5)$$

We can see from this expression that this lengthscale is inversely proportional to the temperature gradient, so we expect the curvature effect to be most prominent under low gradients.

The analogy with the shape of a colloidal gas–liquid [154, 155] leads to an equation relating Λ_c to the interface profile along z and x . The analytic solution to the Young–Laplace equation (linking capillary pressure with curvature and surface tension) is given by e.g. Batchelor [156],

$$z = \Lambda_c \left[\operatorname{arccosh} \left(\frac{2\Lambda_c}{x} \right) - \left(4 - \frac{x^2}{\Lambda_c^2} \right)^{\frac{1}{2}} + C \right], \quad (7.6)$$

where C is a constant depending on the contact angle, θ , between the ice–water interface and the wall. The constant C is given by,

$$C = \left(4 - \frac{h^2}{\Lambda_c^2} \right)^{\frac{1}{2}} - \operatorname{arccosh} \left(\frac{2\Lambda_c}{h} \right), \quad (7.7)$$

where h is the height of the curved interface along x , or $h \equiv x(0)$, and is given by,

$$h = \sqrt{2\Lambda_c^2(1 - \sin \theta)}. \quad (7.8)$$

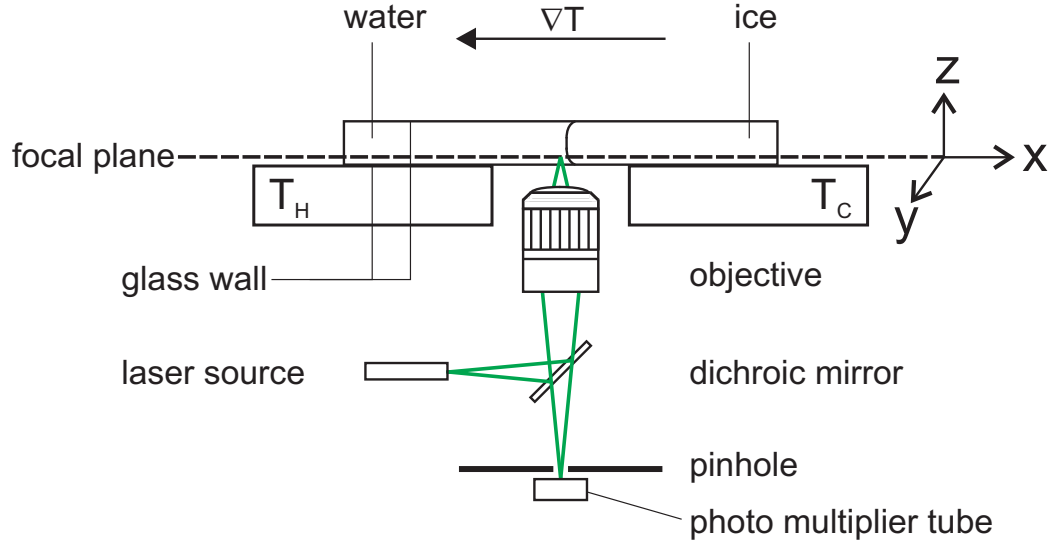


Figure 7.2: Diagram of the confocal microscope setup (not to scale), where the focal plane position in z , and focal point position in x and y is controlled by the scanning microscope. The temperature gradient, ∇T , acts in the direction shown, from cold to warm, and the sample cell (with glass walls) sits on hot and cold plates with temperatures T_H and T_C .

By fitting the experimentally determined ice–water interface profile with this expression, we can find the experimental value of Λ_c , and relate this to the theoretical value, given in equation 7.5. Alternatively, θ can be fixed (in our case to $\theta = 0^\circ$) such that the position of the wall can be treated as a fitting parameter, as explained in [154, 155]. This is the approach followed here.

7.3 Experimental methods

The freezing setup described in section 2.3.1 was used for directional freezing. The sample cell used was a thermally 2D cell, with an internal height of 0.28 mm, as described in section 2.3.4. In order to probe inside the sample cell, along z , laser scanning confocal microscopy (LSCM) was employed. LSCM detects fluorescent dye at points in the sample, and scans a 2D image in a single focal plane. This focal plane can be sub micrometer in thickness, therefore giving good resolution along z [157].

The optical setup, referring to the diagram in figure 7.2, is as follows:

- Light from a laser source reflects off a dichroic mirror, which sends the light through an objective lens, which focuses the light onto a point in the sample.
- If this point in the sample contains dye molecules, the light will interact with them, and

they will fluoresce, emitting photons of a different range of wavelengths (the emission spectrum).

- These photons follow the same optical path back through the objective, and are focused onto a detector, passing through the dichroic mirror. Photons from reflected and backscattered laser light are not allowed to pass through this filter.
- A pinhole placed before the detector ensures that light originating from outside the plane of focus is blocked from the detector – the ‘photo multiplier tube’.
- This results in a pixel (of adjustable area) being assigned a brightness based on the number of photons detected.
- The optical path is moved using rotating mirrors so that the whole focal plane is scanned, pixel by pixel, along x and y , for a given total area.
- Then, the other focal planes are each scanned, in set increments, in a process called a ‘ z -stack’.

A Thorlabs confocal scan head and laser source were used, with an Olympus IX73 microscope, and the $20\times$ objective listed in table 2.1. The laser light was at a wavelength of 532 nm, and a 538 nm longpass dichroic filter was used. The sample would ideally be just water and ice, meaning that there are no impurity effects (section 2.2.1 III). However, dye molecules must be added, in order to detect fluorescence. Rhodamine dye powder was dissolved in a small amount of ethanol first, as Rhodamine is not soluble in water. This solution was then dispersed in a large volume of water using ultrasonic pulsation, and then pipetted into a sample cell. In some experiments, silica particles were used to confirm the position of the bottom wall within the sample as the particles sediment to lie on the bottom of the cell. The particles scatter the laser light, so if a photo multiplier tube is placed so that the laser light coming from the sample does not go through the filter, the light can be detected, and the particles’ position identified.

The ice–water interface may be found using this method because the dye molecules are not soluble in the ice phase. Ice is nucleated in the solution by rapid cooling, then the sample is held, as shown in figure 2.3.4, on top of hot and cold plates, which form a temperature gradient between them. Since T_C is below the bulk melting point, and T_H is above it, the ice–water interface is between the two plates. After the temperature gradient is set, the ice is grown by

moving the sample across the gradient for ~ 10 minutes, at a speed of $\sim 1 \mu\text{m s}^{-1}$. This is to ensure the dye molecules are rejected from the ice, to form a pure ice phase. As we have seen in chapter 3, impurities cause pinching phenomena and regelation of bubbles out of the ice. During this motion, the ice–water interface develops over time, with bubbles moving through it (see figure 3.12), therefore after setting up the desired temperature gradient, the interface was left for over one hour for this to stabilise. The depth of measurement along z is limited by the amount of photons which can move through the sample. Since our system is not refractive index matched, the light which scatters from other dye molecules is lost. This means that only the ice–water interface in the region close to the bottom wall can be detected, although a similar ice–water interface is expected at the top of the cell.

7.4 Results and discussion

A 3D image of the ice–water interface is formed from a series of images in the x – y plane, taken at different z positions. An example of the 3D picture is shown in figure 7.3 (a). A slice along z and x is taken at a single value of y , as shown in figure 7.3 (b). Each row is fitted with the function, $y_i = a + b \tanh[(x_i - c)/d]$, where y_i is the intensity of the pixel, and x_i is the pixel along x , starting from a point in the ice. The free fitting parameters a , b , c and d are used, where c is the position of the ice–water interface in the image. Fits are shown with the data for the two rows marked in figure 7.3 (b), in figure 7.3 (c). For row A, which is above the sample cell wall, this is a good fit to the data, however for row B, the fit is not good because there is no ice–water interface below the wall. Repeating this for all the rows in z gives a profile of the interface in z and x , which is shown on top of the original image in figure 7.3 (d).

From these results, we can see already that the interface is curved. We fit this curve to the Young–Laplace equation (equation 7.6), leaving C a free fitting parameter. The data is converted into μm and shifted so that the wall is approximately at $z = 0$. The data shown in figure 7.4 are for an interface formed in a temperature gradient of 2.9 K mm^{-1} . The value of Λ_c found from the fit (red curve) is $12.4 \mu\text{m}$, while that predicted from theory (equation 7.5) is $3.0 \mu\text{m}$. The curve, using this theoretical value is also plotted on the graph (black curve). Using the experimental value of $\Lambda_c = 12.4 \mu\text{m}$, the expected surface energy is 0.5 J m^{-2} .

The differences between the experimental and the theoretical values of Λ_c may be the result

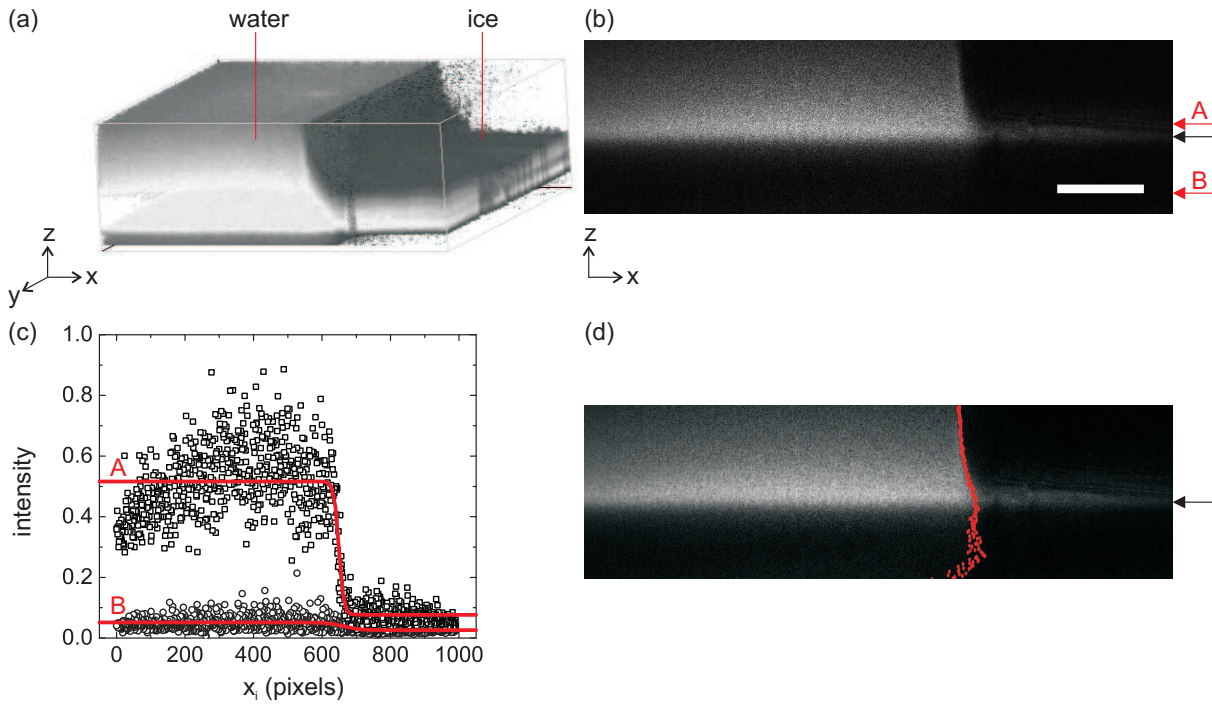


Figure 7.3: (a) A 3D representation of the confocal data; (b) a central slice cut along a single value of y , the scale bar denotes $50\ \mu\text{m}$ and the wall position is marked by a black arrow; (c) graph of pixel intensity $vs\ x_i$ for the two rows A (open squares) and B (open circles), as marked in (b), with hyperbolic tangent function fits; (d) the same image as in (b), with the ice–water interface position, c , shown in red for each row, marking out ice–water interface, the wall position is again marked by a black arrow.

of some possible scenarios. First, the error in the microscopy measurements. A long working distance objective needed to be used, due to the geometry of the stage and microscopy system. This had a relatively low numerical aperture objective, meaning that the resolution in z is not as good. If this is improved, the interface finding method could also be refined, by averaging the hyperbolic tangent fit parameter along a column and a row, to reflect the 2D nature of the curve. Secondly, the ethanol impurity added, which also contains dye molecules, may affect the interface profile; especially the value of γ_{iw} might change, resulting in a different theoretical Λ_c , though this alone is unlikely to change by the amount required.

Although the microscopy technique could be improved by perhaps moving the confocal scan head to above the cell, thus requiring shorter working distance objectives with a higher numerical aperture, the enhanced impurity concentration in the system is likely to be the strongest factor. We have already seen in chapter 3 the effect of the addition of impurities on ice growth and regelating pockets of liquid and particles. We would therefore use a different dye, in order to minimise the effect.

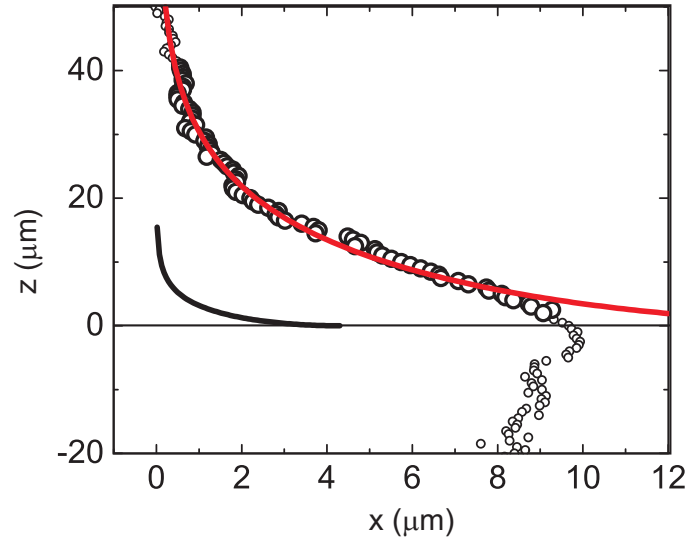


Figure 7.4: Graph of the ice–water interface position z vs x . The red curve is the fit, equation 7.6, to the data points deemed to be part of the ice–water interface (large circles); the data points outside the cell wall are also shown (small circles). The black curve is the curve if the theoretical value of Λ_c is used, plotted up to $h = \sqrt{2}\Lambda_c$.

7.5 Conclusions

A technique has successfully been employed to measure the ice–water meniscus in a glass walled sample cell. The ice–water interface curvature could explain how particles of $\sim \mu\text{m}$ radius use momentum from their motion along the temperature gradient in ice (regelation) to, once in the water phase, move at a greater speed. Here, we show that the water phase is at a distance of $\sim 10 \mu\text{m}$ before the measured ice–water interface. Further measurements could establish the effect of the temperature gradient on the capillary lengthscale.

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List of publications

To date the following publications based upon work in this thesis are in preparation:

Julia M. H. Schollick, Arran Curran, Timea Thorpe, Roel P. A. Dullens and Dirk G. A. L. Aarts. *Regelating particles viewed in real space, with consideration of the effect of grain boundaries*, in preparation (chapter 3).

Julia M. H. Schollick, Robert W. Style, Roel P. A. Dullens and Dirk G. A. L. Aarts. *Particle engulfment by an ice–water interface, viewed in a model system, in real space and at the single particle level*, in preparation (chapters 3 and 6).

Julia M. H. Schollick, Robert W. Style, Arran Curran, John S. Wettlaufer, Eric R. Dufresne, Patrick B. Warren, Krassimir P. Velikov, Roel P. A. Dullens and Dirk G. A. L. Aarts. *Segregated ice growth in a suspension of colloidal particles*, in preparation (chapters 4 and 5).

Julia M. H. Schollick, Robert W. Style, Timea Thorpe, Roel P. A. Dullens and Dirk G. A. L. Aarts. *The ice–water meniscus*, in preparation (chapter 7).

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