Thermal Regelation of a Single Particle

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Abstract

In this paper we study the process termed thermal regelation at single particle level. We experimentally extract the physical parameters that determine the interactions between ice and the silica particle for the regelation process. As the premelted layer around the particle plays a key role here, we use the extracted parameters to calculate the thickness of this thin premelted layer, at different given particle sizes.

1 Introduction

An advancing ice front interacts with foreign particles in the liquid water results in particle engulfment or rejection. However, an engulfed particle is not necessarily static within the ice. For example, dust particles that are trapped in the polar ice sheets are viewed as indicators of past climate conditions,[1] but this is not always an accurate indicator, as the particles can migrate into ice of a different age from their deposition due to ‘thermal regelation’.\cite{2,3}

A similar and closely related problem is pressure-induced regelation, wherein a weighted wire is pulled through a block of ice.\cite{4} Both thermal and pressure-induced regelation can be explained in terms of premelting, where a liquid film disjoins a solid surface from the ice surface, at temperatures below the bulk freezing point, as a result of the competition between
a reduction of interfacial free energy and the expense of maintaining a layer of undercooled
liquid.\textsuperscript{4,10}

In this paper we are interested in the thermal regelation process, where trapped particles
in ice migrate along the temperature gradient.\textsuperscript{6} Colloidal particles are particularly suited as
the model system for thermal regelation, as their size makes them observable and trackable
in real time using optical microscopy.\textsuperscript{7} Previously, experimentalists were more interested in
the phenomenon of the particle engulfment rather than the regelation event.\textsuperscript{8} Additionally,
polydisperse colloidal particles were typically used in these systems, making analysis more
difficult.\textsuperscript{6} Similarly, theoreticians have mainly focused on the forces on the particle in front
of the ice-water interface during the engulfment,\textsuperscript{3,9,10} rather than predicting the movement
of particles after they are engulfed in ice. Here, we carry out our experiments at single
particle resolution, which made observing and tracking individual particles and hence their
behaviour in the ice possible.

2 Theoretical backgrounds

2.1 Premelting

Premelting is controlled by the following three factors: curvature induced premelting (Gibbs-
Thomson effect), interfacial premelting and impurity induced premelting. For our experi-
mental set-up, premelting mainly arises from the interfacial premelting. Curvature induced
premelting is minimised by using a colloidal dispersion at very low particle concentration,
which eliminates the interstitial pores formed at high particle concentrations that contributes
most to the Gibbs-Thomson effect given the pores’ small radius. Impurity induced premelting
was minimised by using colloidal particles which were washed thoroughly before re-dispersing
them in deionised water in a very low concentration. The resulting colloidal suspension is
very pure, as the undercooling for this solution persists until $-40^\circ$C.
A repulsive intermolecular force acts between the ice and the particle, resulting in interfacial premelting. Premelted water exists at temperatures below the bulk melting temperature, $T_m$. This shift in the freezing temperature is known as the interfacial undercooling $\Delta T_{int}$:

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

(1)

where $L_m$ is the latent heat of water, $\rho_i$ is the density of ice, $P_T$ is the ‘disjoining pressure’, the intermolecular interaction per unit area, with which the solid and the substrate repel each other (also known as the ‘thermomolecular pressure’). The dependence of $P_T$ on the film thickness $d$ is determined by the type of intermolecular interactions of the system. When the distance between particle and solid phase is small compared to the particle radius, it is commonly related to the non-retarded Van der Waals forces, $U = -\frac{A_{iwp}}{12\pi d^2}$, where $A_{iwp}$ is the Hamaker constant $= \pi^2 C \rho_1 \rho_2$. Together, the pressure can be written as:

$$P_T = -\frac{A_{iwp}}{6\pi d^3}.$$  

(2)

We can see that as long as $A_{iwp}$ is negative, there is a repulsive disjoining pressure between the particle and the ice, which gives rise to a stable liquid film, i.e. interfacial premelting. Note that changing the conditions in the system may lead to other intermolecular forces, and therefore different types of disjoining pressures. For example, dissolved ionic impurities would cause double layer repulsion.

By combining Equations 1 and Equations 2, the premelted layer thickness becomes,

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

(3)

where $\lambda^3 = -\frac{A_{iwp}}{6\pi \rho_i L_m}$. Interfacial premelting is highly relevant in the interaction of particles with an advancing ice front, as illustrated in Figure 1. Equation 3 indicates that the layer thickness decreases as the temperature is reduced, shown schematically as $d_1 > d_2$. 


Figure 1: Schematic for a particle being engulfed by ice. The direction of the temperature gradient from cold to warm, $\nabla T$, is indicated, as well as the directions of the thermomolecular and viscous forces, $F_T$ and $F_\eta$, 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 $d_1$ and $d_2$.

in Figure 1. This has important consequences for particles immersed in ice as this results in a pressure difference in the premelted film via Equation 2, which causes the flow of water within the film, and thus movement of the particle.

Note that Equation 3 can be generalised for premelting resulted from other forces to the following equation:

$$d = \lambda \left(\frac{\Delta T_{\text{int}}}{T_m}\right)^{(-1/\nu)},$$

where the constants $\lambda$ and $\nu$ are physical parameters determined by the type and range of interactions between the particle and the ice.

### 2.2 Forces related to thermal regelation of particles in ice

The intermolecular forces that cause premelting also exist as a repulsive force between the solid and a foreign substrate. When the particle is fully engulfed by ice, the thermomolecular force on the particle can be calculated by integrating the disjoining pressure over the whole particle surface. Here we follow the approach of Worster and Wettlaufer.
Figure 1 is a schematic diagram showing a particle of radius $R$ surrounded by ice. We assume that the thermal conductivities of the particle, ice and water are equal, and the latent heat released and absorbed as the sphere migrates is negligible. The temperature is then given everywhere by:

$$T = T_0 + \nabla T x = T_0 - \nabla T R \cos \theta,$$

where $T_0$ is the temperature at the centre of the sphere, $x$ is measured from the centre towards the hot side, and $\theta$ is the polar angle measured from the horizontal. Therefore, if the dominant intermolecular interactions are van der Waals ($\nu = 3$), the thickness of the premelted film within this temperature field can be calculated from Equation 3 and 5 as:

$$d = \lambda T_{m}^{1/3} (T_m - T_0 + \nabla T R \cos \theta)^{-1/3}. \quad (6)$$

Together with Equation 2, the thermomolecular pressure within this film is

$$P_T = \frac{\rho_i L_m}{T_m} (T_m - T_0 + \nabla T R \cos \theta). \quad (7)$$

This gives a net thermomolecular force, acting in the direction of the temperature gradient, from cold to warm:

$$F_T = \frac{4\pi R^3}{3} \rho_i L_m \frac{T_m}{\nabla T}. \quad (8)$$

With the particle being pushed out of the ice by the thermomolecular force, there is a lubrication force acting in the opposite direction as the particle moving through the thin premelted film around it. Worster and Wettlaufer have concluded that the lubrication force is given by:

$$F_\eta = -\frac{4\pi R^3}{3} \frac{6\eta R |V| \Delta T_{int}}{\lambda^3} \frac{T_m}{T_m}. \quad (9)$$

Here $|V|$ is the flow velocity, which is numerically equal to the velocity of the particle which migrates along the temperature gradient, $\nabla T$, and $\eta$ is the viscosity of water. The rate at
which the particle is able to move depends on this viscous flow in the premelted film, which itself depends on the thickness and geometry of the premelted film.

As we assume there is no external force on the particle, the net thermomolecular force must be balanced solely by the lubrication forces, thus \( F_T + F_\eta = 0 \). From this, the regelation velocity can be calculated:

\[
|V| = \frac{L_m \rho_i}{6 \eta R} d^3 \frac{\nabla T}{T_m}.
\]

(10)

Using Equation (4) and \( \nu = 3 \), this can be generalised into the following form

\[
|V| = \frac{L_m \rho_i}{6 \eta R} \lambda^3 \left( \frac{\nabla T}{T_m} \right)^{1-3/\nu} \Delta x^{-3/\nu}.
\]

(11)

Hence, we find an expression for \( |V| \) as a function of \( d \). As the particle approaches the interface (moves up \( \nabla T \)), \( \Delta T \) decreases, which leads to an increase in \( d \) (Equation (4)). Here, in Equation (10) we also see the relationship where \( |V| \) is proportional to \( d^3 \), thus this increase of the premelted film thickness causes the particle to accelerate out of the ice.

In our experiment we can separately track the position of a particle and the interface, thus we can calculate \( |V| \) and \( \Delta T \) accordingly. This provides a method to determine the type of the interaction, and to measure the premelted film thickness using Equation (4). Wettlaufer et al. developed a theory covering premelting dynamics for all power law forces, suggesting that for \( \nu = 3, \lambda \approx 1.4 \, \text{Å} \), and for \( \nu = 2, \lambda \approx 0.2 \, \text{Å} \). More recently, Peppin et al. have analysed the regelation data of glass beads from Romkens and Miller, and found \( \nu \) and \( \lambda \) to be 2 and 3.6 Å respectively, indicating the force is a long range electrostatic interaction.

### 3 Experimental methods

Here we use the TPM particles at three different diameters: 1.8 \( \mu \text{m} \), 2.5 \( \mu \text{m} \) and 3.2 \( \mu \text{m} \), synthesized as described by Liu et al. A directional solidification apparatus is coupled with
a home-build bright-field microscope to record the movement of the particles. The freezing stage was the LinkamGS350 cooling stage, which provides a steady temperature gradient and a precise stepper motor that can move the sample along the gradient at given velocity. Hence we can (re-)disperse the particles in ice to achieve a good starting configuration of particle and interface for regelation to happen. The details of the experimental methods can be found in Supplemental materials.

4 Results and discussion

4.1 Qualitative observations of regelation

Figure 2 shows 9 sequential snapshots taken from a typical regelation experiment with one particle exiting the ice-water interface. The first thing one can observe is that the interface is curved toward the particle when they are sufficiently close to each other. Rempel and Worster have predicted that when the particle is more insulating than the environment, the temperature field is distorted near the particle and the bulk melting temperature isotherm will curve towards the particle. In our system, as TPM is a silica based particle, we assume it has a similar thermal conductivity to silica (1.2 W m\(^{-1}\) K\(^{-1}\)), while for bulk ice, the thermal conductivity is about 2 W m\(^{-1}\) K\(^{-1}\). The prediction based on the difference in thermal conductivities is thus consistent with our observation.
Particles in our system are also observed to accelerate out of the ice along the temperature gradient. The event of exiting itself happened within 3 seconds, during which the particle moves about 4 µm. In contrast, in the 10 seconds before the exiting event, the particle moved less than 1 µm. We can visualise this acceleration process clearly by plotting the difference between the position of the particle and the interface, which we will discuss next.

### 4.2 Motion of particles relative to the ice-water interface

The particle trajectory is recorded using standard particle tracking method in Mathmatica. The detected trajectory is plotted on an experimental snapshot in Figure 3 (a). Here we can clearly see that the particle movement is highly constrained in the \( x \)-direction (perpendicular to the interface) during the regelation process due to the unidirectional thermomolecular force. Once the particle has crossed the interface and entered the water phase, it starts to move in the \( y \)-direction as well due to Brownian motion. The characteristic unidirectional movement within ice enables us to simplify our velocity analysis of regelation by only considering the position difference in the \( x \)-direction, \( \Delta x = x_p - \bar{x}_i \), where \( x_p \) is the \( x \)-position of the particle, and \( \bar{x}_i \) is the averaged position of the interface throughout the whole experiment.

In Figure 3 (b) we plot the \( x \)-position of the interface, where we can see the interface first approaches its thermodynamically preferred equilibrium position quickly in response to the change of the temperature gradient, and then starts fluctuating around this equilibrium position. Unfortunately, these fluctuations are an intrinsic part of our experiments. We can use the instantaneous position of the interface to calculate \( \Delta x \), this gives a noisy trajectory in the \( x \)-direction as shown in Figure 3 (c). Alternatively, we choose to use the average position of the interface (\( \bar{x}_i \)) to calculate the \( \Delta x \). The positions of the interface used to calculate the average position are shown in red in Figure 3 (b). We do not have a set of rules to choose the exact position of the start-point and endpoint as the choice does not drastically affect the final outcome. Any choice is valid as long as the start-point is after the interface has reached equilibrium and the end-point is after the particle has exited the ice. The resulting
Figure 3: (a) Particle trajectory plotted on top of an experimental snapshot. The particle starts moving in $y$-direction after it enters the water phase and starts Brownian motion; (b) Plot of the fluctuation of the ice-water interface, the section in red was chosen to calculate the $\bar{x_i}$ and $\Delta x$; (c) The distance between the particle and the interface against time, calculated using the instantaneous interface position; (d) The distance between the particle and the interface against time, calculated using the averaged interface position.

$\Delta x$ vs $t$ data is plotted in Figure 3 (d).

Taking a closer look at Figure 3 (d), the first point to note is that the curvature of the line corroborates the theory detailed in Section 2.2, which predicts that the particle velocity will increase as the particle moves up the temperature gradient towards lower undercooling. Secondly, the Brownian motion of the particle can again be observed as reflected by the fluctuations in $\Delta x$.

Note that according to our definition, particles leave the ice only when $\Delta x$ become negative. As shown in Figure 2 $\Delta x < 0$ corresponds to the point where the particle leaves the ice completely and the interface flattens. According to a different definition, one might claim that the particle has already left the ice when the interface is still curved.
4.3 Quantitative analysis of regelation

An expression for the velocity as a function of the undercooling is found by inserting Equation 4 (with undercooling $\nabla T = \Delta T/\Delta x$) into Equation 10:

\[ |V| = K\Delta x^n, \]  
\[ K = \frac{L_m\rho_i}{6\eta R} \lambda^3 \left( \frac{\nabla T}{T_m} \right)^{1-3/\nu}, \]
\[ n = -\frac{3}{\nu}. \]

Upon integration, Equation 12 becomes:

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

This suggests that it could be fitted with a power law,

\[ \Delta x = [a(t_e - t)]^b, \]
where \( t_e \) is the fitting parameter for the time at which the particle exits the ice, \( a = K(1 - n) \) and \( b = 1/(1 - n) \). By fitting this exponential equation with our experimental data, we first determine the fitting parameters \( a \) and \( b \), from which we obtain \( K \) and \( n \) and are able to calculate the physical constants \( \nu \), which determines which type of force is acting between the particle and the ice, and \( \lambda \), the lengthscale that relates with \( \nu \), \( A_{iwp} \) and \( L_m \).

We set the fitting parameter \( t_e \) around the time where \( \Delta x \) changes from positive to negative. Together with the free fitting parameters \( a \) and \( b \), a best fit was found and plotted with the original data points in Figure 4 which shows excellent agreement, except for the few points right before the exiting event (for example the small kink at the end in Figure 4). This is due to the exponential nature, as we have fewer data points around this area, making this region seem more noisy. Furthermore, the exit point happens at an exact time which could be influenced by the noise in the interface position.

Using the value of \( a \) and \( b \) we have determined from the fit, we obtain the values of \( K \) and \( n \), which are then used to calculate the velocity as the particle approaching the interface using Equation 12. Here we first plot \( |V| \) as a function of \( \Delta x \) in Figure 5 (a). To help visualise the freezing environment, the \( x \)-axis can be replaced by undercooling using \( \Delta T = \Delta x \times \nabla T \), shown in Figure 5 (b). From this plot, we can see that far from the interface, at low undercooling, the 1.8\( \mu \)m spheres are only moving at approximately 0.03\( \mu \)m s\(^{-1} \). As they approach the interface, they accelerate up to velocities close to 0.8\( \mu \)m s\(^{-1} \).
4.4 The premelting layer and the related physical parameters

Finally, $\lambda$ and $\nu$ can be calculated from the $K$ and $n$ values using Equations 13 and Equations 14. Then the premelted layer thickness, $d$, can be calculated as a function of the undercooling, $\Delta T$ via Equation 4. The result is shown in Figure 6 (a). In this plot, we see the expected increase in the premelted film thickness as undercooling decreases (as the particle moves towards warmer temperatures). The values obtained for the thickness are at tens of Ångstroms in scale, which agrees with our expectation. Combining Figure 5 (a) and Figure 6 (a), we have also plotted the premelted layer thickness against the regelation velocity in Figure 6 (b). If we cube the premelted layer thickness, we can find a linear relationship between $|V|$ and $d^3$, which is expected as from Equation 10.

The analysis was repeated for 46 particles across all 3 sizes, 1.8 $\mu$m, 2.5 $\mu$m and 3.2 $\mu$m. The results are summarized in Table 1 with averages and standard deviations of $\lambda$ and $\nu$. From the table we see that $\nu$ is around 3 for all sizes. According to previous literature, the $\nu$ value for short and long range electrostatic, non-retarded, and retarded van der Waals interaction are $3/2$, 2, 3 and 4 respectively. Hence our result indicates the main force responsible for premelting are non-retarded van der Waals interactions, instead of the electrostatic force as...
has been previously suggested for glass beads. As for \( \lambda \), similarly the value is also only determined by the type of the interaction, therefore should not change for particles with different sizes. From the mean values of \( \lambda \) one can observe a positive correlation between the \( \lambda \) and the particle diameter. This could be a result of experimental error, or it could be a sign suggesting we might want to take in account the curvature induced premelting when calculating \( \lambda \) in the future studies.

Table 1: Conditions for regelation experiments presented in Figure 7. Here, \( \lambda \) and \( \nu \) are averaged over a number of fits (\( N \)) for each particle size. ‘S.D.’ stands for Standard Deviation.

| Particle diameter (\( \mu m \)) | \( N \) | \( \nu \) | S.D. (\( \nu \)) | \( \lambda \) (\( \AA \)) | S.D. (\( \lambda \)) |
|-------------------------------|--------|----------|------------------|------------------|------------------|
| 1.8                           | 19     | 3.05     | 0.16             | 2.55             | 0.35             |
| 2.5                           | 14     | 3.02     | 0.11             | 2.78             | 0.39             |
| 3.2                           | 13     | 2.93     | 0.17             | 3.11             | 0.77             |

The regelation velocities as a function of \( \Delta x \) are calculated for each particle size using the averaged \( \lambda \) and \( \nu \), and are plotted in Figure 7 (a). The result for \( d \) vs \( \Delta x \) is plotted in Figure 7 (b). Here we observed that particles of all sizes move at speeds typically on the order of 0.01\( \mu m s^{-1} \) when far from the interface, with a sharp increase around 5\( \mu m \) (2-3 particle diameters). The bigger the particle, the greater this acceleration. The premelted layer thickness when the particle is far from the interface is about 30 \( \AA \), then as it accelerates in approaching the interface, the thickness of the premelted layer increases accordingly, up to the order of 100 \( \AA \). The premelted layer thickness is similar across all three sizes, which is expected as it is purely determined by the interaction (\( \lambda \) and \( \nu \)) between the particle surface and ice.
Figure 7: (a) The $|V|$ vs $\Delta x$ plot and (b) the $d$ vs $\Delta x$ plot for all three particle sizes using the averaged value of the parameters.

5 Conclusions and outlook

We have observed thermal regelation of colloidal spheres at the single particle scale, and experimentally measured the motion of the particle with respect to the position of the bulk ice-water interface. We fitted the interfacial premelting theory with our experimental data to gain an indication of the origin of the thermal regelation behaviour for the silica particles. Here we found the value $\nu$ was typically around 3 for all particle sizes, which corresponds to non-retarded van der Waals interactions, instead of the electrostatic force ($\nu = 2$), which was predicted previously. We were then able to calculate the premelted layer thickness and regelation velocity as a function of the undercooling. They are on the order of 30 Å and 0.01 $\mu$m s$^{-1}$ respectively when far away from the interface, and subsequently experiencing an exponential growth as the particle approaches the interface. We have also confirmed that the particle radius has little effect on the premelted layer thickness.
Supplemental materials

1 Experimental methods

1.1 Experimental materials

1.1.1 Freezing Stage

We use a Linkam GS350 stage, which provides a fixed temperature gradient can be established and the sample can be translated at prescribed rates using the Linksys32 software. A photograph and schematic diagram of the set-up used is shown in Figure 1 In contrast to freezing from a cold boundary held at a fixed temperature (fixed chill), we use directional solidification which allows independent control of the freezing rate and temperature gradient. This configuration also has the advantages of similarity to industrial solidification techniques. The stage provides a temperature range of -196 °C (limited by the boiling temperature of nitrogen) to 350 °C, 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. Also, the air inside the box could be replaced by nitrogen via the purge tubing in order to remove water vapour, which could condense on the sample. Heating was achieved by the use of electrical resistance heaters embedded within the plates. The motor is a stepper motor that could move at rates between 1 µm s$^{-1}$, and 2000 µm s$^{-1}$ with a minimum step of 1 µm, which was controlled by the same software.

In a typical experiment, the sample is placed on top of the Peltier plates, thermal insulation is achieved by covering the sample with the metal lid. An observation window was made in the middle to let the light path come through. The desired temperature gradient $\nabla T$ is established by setting the temperatures of Peltier elements and the sample is then put in motion by the motor. The theoretical temperature gradient across the gap can be calculated by $\nabla T_{Theory} = (T_H - T_C)/x_{gap}$, where $T_C$ and $T_H$ are the set temperatures of the cold and
Figure 1: (a) A labelled photograph of the Linkam GS350 freezing stage. The nitrogen input/outputs and the pumps are shown schematically. Three software communication wires connect to the computer are present for the independent control of temperature and motor; (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 controlled separately, one above \( T_H \) and the other one below \( T_C \) the melting point of water, \( T_m \). The theoretical temperature profile is shown below, with temperature vs \( x \), where the dotted lines connect the plate edges to their equivalent positions along \( x \).

hot plates, and \( x_{gap} \) is the distance between the two plates, which is 2 mm here.

When performing an experiment, the cold plate was cooled until ice nucleated, while the hot plate was left at room temperature, thus the precise ice nucleation temperature was not generally noted. After nucleation of the ice was confirmed, the desired temperature gradient was set and the sample was left to stabilise. A fixed rate of cooling was maintained by controlling the motor to move the sample into the cold plate at a constant speed.

1.1.2 Bright-field optical 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 shows the schematic of the microscope, and Table 2 lists the parts. The sample is illuminated with a LED light source, magnified
with a 20× or 50× Olympus Long Working Distance M-Plan Fluorite objective according to the experiment, and the gray-scale images are recorded using a Ximea MQ013MG-E2 CMOS camera at desired capturing rate. We chose the long working distance objectives because in our set-up the imaging objective must have a working distance of at least 4.6 mm, which is the distance from the sample (Peltier plates) to the top of the Linkam GS350 stage (lid). The microscope stage can be manually translated in \( x, y, z \) directions to achieve a good field of view and sharp focusing using travel stage components.

Table 2: Building components for the microscope set-up and the sample stage. All components are purchased from Thorlabs unless otherwise stated.

| Name          | Type                  | Details                                           |
|---------------|-----------------------|---------------------------------------------------|
| LEDs          | Cold white LED        | Viewing angle of 140°                             |
| L1            | Plano convex lens     | Frosted for blurring the matrix of LEDs at the source |
| L2            | Achromatic lens       | Small focal length to reduce the depth of field   |
| L3            | Achromatic lens       |                                                   |
| L4            | Tube lens             | Imaging sample onto camera                        |
| P1            | Pinhole               | Controls the field of view                        |
| P2            | Pinhole               | Controls the depth of field                       |
| Motion in \( x, y \) | Manual Linear Translation Stages x 2 | Placed on top of, and perpendicular to, each other for motion in 2D |
| z motion      | Edmund Optics vertical translation stage | Controls the depth of field                       |
| Homebuilt mount | Mount                 | Mount the freezing set-up onto the translation stage |

1.1.3 Colloidal model systems

In this paper we chose TPM as our model particle for its higher-than-water density, and its simple synthesis procedures. Particles were synthesised according to the recipe\(^\text{[16]}\) and Pluronic\textsuperscript{®} F108 surfactant was added to the surface to reduce polydispersity and sterically stabilise the particles in solution.\(^\text{[7]}\) Here the polydispersity is the ratio of the standard deviation over the arithmetic mean. We have prepared highly monodisperse particles of three different sizes: 1.8 \(\mu\text{m} \), 2.5 \(\mu\text{m} \), 3.2 \(\mu\text{m} \), with polydispersities smaller than 5%. The
Figure 2: Diagram of the microscope set-up. Köhler lens set-up (L1 - 3) was placed below the sample to provide a source of uniform illumination (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.

Sizes and polydispersity were confirmed by using SEM. The particles are washed carefully with (Type I) deionized water with a resistivity of 18.2 Ω, which means that a very low number of ions are dissolved, to wash out the residual salt and minimise the salt concentration in the final solution. It is then redispersed in deionized water to form a suspension at required mass fraction. When dispersed in deionised water, fully crosslinked TPM particles have a fairly large anionic surface potential, zeta potential was measured using Malvern Nano Z to be $-34 \text{ mV}$. This leads to a short range repulsion between the particles, and between the particles and the wall of the cell, which strengthens the stability against aggregation and suppresses the tendency of particles to stick to the wall of the sample cell.
1.1.4 Sample cell

The sample cells were single-use UV glue cells with an internal height of $\sim 4 \mu m$. The SU-8 is a photosensitive polymer purchased from Chestech. Its formulation contains an epoxy oligomer with eight reactive acid-labile epoxy groups, which give a high degree of cross-linking under intense UV light. This provides a way to create various designs. Here a photomask was designed in CorelDraw and printed onto a sheet of acetate using a high resolution printer provided by Micro Lithography Services Ltd., this mask creates regions that are exposed to the UV light and regions that are not, thus we can selectively choose the regions for crosslinking. The defined height of our quasi-2D cell is achieved using the properties of SU-8 photoresist, as it can be spin-coated at a well defined thickness onto a blank silicon wafer. The thickness of SU-8 is controlled by spin-rate, baking times and temperatures, which is listed in the official MicroChem Processing Guidelines. To achieve an internal height of $4 \mu m$, the SU-8 was treated as follows. Note that all the steps are carried out at room temperature unless otherwise stated.

1. Centrifuge the SU-8 2005 photoresist polymer for 2 minutes at 2000 rpm to remove bubbles.

2. Preheat the wafer for 5 minutes at 65 $^\circ$C to remove any unwanted moisture from the surface of the blank silicon wafer.

3. Spin-coat the wafer with 5 ml of SU-8 2005 for 30 seconds at 500 rpm with an acceleration of 100 rpm/s, followed by 65 seconds at 4000 rpm with an acceleration of 300 rpm/s.

4. Leave the SU-8 to settle for 10 minutes before soft baking at 65 $^\circ$C for 2 minutes 30 seconds, then at 95 $^\circ$C for 3 minutes 30 seconds.

5. Cover the wafer with the photomask and a glass UV filter to minimise Fresnel diffraction which reduces resolution hold down the glass filter and photomask to avoid
unwanted diffraction caused by the presence of gaps.

6. The wafer was exposed under 2.7 Watts UV light for 30 seconds for the crosslinking of SU-8 to happen.

7. Photomask was removed and the wafer was baked at 65 °C for 2 minutes then at 95 °C for 3 minutes 30 seconds.

8. The wafer was washed in propylene glycol methyl ether acetate (developer) for 1 minute to dissolve any SU-8 that was not cross-linked. Any excess developer was then washed off by spraying with isopropanol for 10 seconds.

9. The isopropanol was dried off with nitrogen gas and the wafer is then hard baked at 150 °C for 40 minutes. This ensures the SU-8 is securely bound to the wafer.

This wafer now acts as a reusable template to produce the PDMS devices. The edge of the wafer was then taped up to a desired height for the PDMS to pour in from the above. PDMS was mixed with curing agents at the ratio of 10:1 so that the product has the desired flexibility. The mixture was first centrifuged to remove air bubbles and then poured onto the taped wafer. The device was left under vacuum suction for 30 minutes to remove any air bubbles formed during pouring, and the PDMS was then polymerised at 85 °C overnight. The polymerised PDMS layer was then peeled off and cut into individual PDMS stamps. These stamps with the designed channels is used as a reusable stamps to produce UV glue sample cells.

For each UV glue sample cells, 100 µl of NOA 81 UV glue (Norland optical adhesive 81) from Norland Products was placed in the middle of a microscope slide. The PDMS stamp was pushed in firmly, before irradiation with UV light to partially polymerise the glue (2.7 W, 30 seconds). Then the PDMS stamp was replaced by a square cover slip of similar size (15 mm x 15 mm), followed by further exposure to UV radiation (2.7 W, 1 minute) to produce a single-use UV glue stamp cell. The channels in the sample cells are with the internal height
predetermined by the SU-8. All glass components used in this step were rinsed with ethanol and plasma cleaned to minimise any contaminants from the surface of the cell.

1.2 Experimental methods

To achieve a good starting configuration of particle and interface, the following treatment was applied. As shown in Figure 3 (a), from a solution of particles, we first nucleate the ice by lowering the cold plate to $-40^\circ$C. After we have confirmed the formation of ice through bright-field images, the cold plate was heated to achieve a $\nabla T$ of 10 K mm$^{-1}$ while keeping the temperature of the hot plate constant. At the same time, the sample was moved towards the cold plate at a low translational velocity (1 $\mu$m s$^{-1}$) for 5 minutes to obtain a stable, flat interface (Figure 3 (b)). This step not only helps us to locate the position of the interface in the field of view at the same temperature gradient, but also collects multiple particles at the interface to improve the statistics. After this, the cold plate is rapidly lowered to a temperature of $-20^\circ$C at a rate of 30 $^\circ$C min$^{-1}$. This high freezing rate ensures rapid freezing which engulfs particles, and the change of the temperature gradient shifts the ice-water interface to a new equilibrium position, creating a space where regelation events can occur.

The growth of ice moves the particles for different distances before engulfing them (Figure 3 (c)), hence give them different starting positions for the regelation. The size of the regelation zone and the starting position of the particles were adjusted by translating the system slowly at 1 $\mu$m s$^{-1}$ towards the cold plate (Figure 3 (d)). Then the temperature of the cold plate was adjusted to reestablish $\nabla T = 10$ K mm$^{-1}$, but at a slower rate so that the interface can move back towards its equilibrium position at this temperature gradient slowly. Measurements begun just before the interface arrives in its original position to allow the whole regelation events to be recorded. After all the regelation events in the field of view had been recorded, we simply translated the sample slowly to move the interface until we achieve a new blank
Figure 3: (a) Unfrozen sample; (b) After initial nucleation and stabilisation, a planar interface was obtained at a $\nabla T = 10 \text{ K mm}^{-1}$; (c) Upon rapid freezing, the interface became unstable, and pushed the particles forward for a distance before engulfing them; (d) As the field of view was unchanged, when $\nabla T$ was adjusted back to $10 \text{ K mm}^{-1}$, the ice-water interface reappeared at the same position in (b) relative to the camera. The sample was translated towards the cold plate such that an ideal distance between the particles and the interface was achieved, before $\nabla T$ was adjusted and measurements began.

slate for the next experiment.

2 Image analysis

2.1 Particle tracking

For a typical image of colloidal particles where the particles have a central bright spot and a dark outer ring, a binary image was created by replacing all values above a globally determined threshold with 1 and others with 0, thus only leaving the dark ring in the image. Then the foreground image components were selected according to their sizes and elongation, ruling out potential noise from the binary image. This also gives particle locations as pixel coordinates in $x$ and $y$.

After the particle positions in each frame were determined, a tracking program based on the nearest locations was used. A threshold maximum distance, up to which a particle could
move from its position in the previous frame, was set. A trajectory required a minimum number of steps to be considered a valid particle. Particles that fit this criteria were given an ID, and an individual particle’s trajectory \((x_p, y_p, t)\) could be plotted, where the time, \(t\), is the frame number multiplied by the time interval per frame.

### 2.2 Interface identification

In optical microscopy, ice and water have nearly identical appearances because the refractive indices of ice and water are close in value. However, this difference, despite being small, still results in the scattering of light, which makes the interface easy to identify. The steps taken to find the position of the interface are shown in Figure 4. From the original image, a binary image was again created, but using a different threshold (usually higher than the threshold used for identifying the particle), to retain as much information about the interface as possible. This resulted in a binarised image in which the interface is black and background is white (Figure 4 (b)). From this, a negative image was created (Figure 4 (c)), making the foreground ‘objects’ white, thus suitable for the built-in ‘SelectComponents’ function in Mathematica. After this, the foreground image components were selected according to their ‘sizes’, ‘elongation’ and ‘orientation’. The resultant detected interface is shown in Figure 4 (d). Information about the interface might be lost during the processing, and the raw
detected interface is potentially noisy. Therefore a straight line was fitted to the detected interface (Figure 4(e)), and this line function was used for calculations.

**Acknowledgement**

S.C. thank the China Scholarship Council for financial support.

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