Objects Interacting with Solidification Fronts: Thermal and Solute Effects

Sidhanth Tyagi, Hélène Huynh, Cécile Monteux, Sylvain Deville

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In many materials processing routes, objects such as bubbles or particles interact with a moving solidification front. The output of this confrontation, from instantaneous encapsulation to complete rejection of objects, regulates the solidified microstructure and the spatial distribution of the objects, and thus the final properties of the materials. Here we investigate by in situ cryo-confocal microscopy how thermal conductivity and solute compete to control the interfacial curvature of the solidification front. We first validate the prediction of physical models in absence of solute, and then demonstrate the dominating effect of solute. In the case of cellular front morphology, we show that thermal effects depending on the particle conductivity induce a distortion of ice crystals thereby modifying the final microstructure of the solid. Overall our results show that to successfully predict and control solidification microstructure in the presence of objects, physical models that take into account both thermal and long-range solute effects are now required.

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Objects Interacting with Solidification Fronts:

Thermal and Solute Effects

Sidhanth Tyagi\textsuperscript{1,2}, Hélène Huynh\textsuperscript{1}, Cécile Monteux\textsuperscript{2,3}, and Sylvain Deville\textsuperscript{1,4,5}

\textsuperscript{1} LSFC, UMR 3080 CNRS/Saint-Gobain CREE, Saint-Gobain Research Provence, 84300 Cavaillon, France
\textsuperscript{2} Sciences et Ingénierie de la Matière Molle, ESPCI Paris, PSL Research University, CNRS, Sorbonne Universités, UPMC Univ Paris 06, 75005 Paris, France.
\textsuperscript{3} Global Station for Soft Matter, Global Institution for Collaborative Research and Education, Hokkaido University, Sapporo, Japan.
\textsuperscript{4} now with: Université de Lyon, Université Claude Bernard Lyon1, CNRS, Institut Lumière Matière, 69622 Villeurbanne, France.
\textsuperscript{5} Corresponding author. Email: sylvain.deville@univ-lyon1.fr.

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In many materials processing routes, objects such as bubbles or particles interact with a moving solidification front. The output of this confrontation, from instantaneous encapsulation to complete rejection of objects, regulates the solidified microstructure and the spatial distribution of the objects, and thus the final properties of the materials. Here we investigate by \textit{in situ} cryo-confocal microscopy how thermal conductivity and solute compete to control the interfacial curvature of the solidification front. We first validate the prediction of physical models in absence of solute, and then demonstrate the dominating effect of solute. In the case of cellular front morphol-
ogy, we show that thermal effects depending on the particle conductivity induce a distortion of ice crystals thereby modifying the final microstructure of the solid. Overall our results show that to successfully predict and control solidification microstructure in the presence of objects, physical models that take into account both thermal and long-range solute effects are now required.

**Keywords:** solidification, solutes, thermal conductivity, interfacial curvatures, microstructure

The interaction of solidification fronts with objects (droplets, bubbles, solid particles or cells) is a common phenomenon encountered in a plethora of situations, ranging from industrial to natural occurrences, such as the formation of sea ice, growth of single crystals, metallurgy, cryobiology, or food science. The objects (soft or hard) exhibit different types of behavior while interacting with a solidification front, from total rejection to complete or partial engulfment [2]. The dynamics of this interaction influences the solidified microstructure and the mechanical and functional properties of the materials. From homogeneous particle distribution in particle-reinforced metal matrix composites to complete rejection of inclusions or porosity management in castings and growth of single crystals, distinct outcomes may be desired depending on the application. The potential to actively govern the solidification microstructure is thus crucial.

The initial studies performed on encapsulation and/or rejection of particles by a freezing front, moving at a velocity $V_{sl}$, considered either the interplay of van der Waals and lubrication forces [5] or the change in chemical potential [25]. Most of these physical models established a criterion of critical velocity ($V_c$), for a given size of an insoluble object or *vice-versa* (critical radius), to predict whether the object will be encapsulated ($V_{sl} > V_c$) or rejected ($V_{sl} < V_c$) [2].

Subsequently, the studies performed showed that the curvature of the solidification front plays a major role in solidification dynamics, as it influences the magnitude of both viscous and van der Waals forces in the gap between the particle and the front. Theoretically, the critical velocity reduces drastically for
concave interfaces as opposed to ideal planar interfaces [11].

The disjoining pressure, arising in the gap between the growing solid and the particle, causes a deformation of the solidification front. However, it has been predicted that the thermal conductivity deforms the front $10^3$ times more than the other parameters [18]. If a particle has a lower thermal conductivity than the melt ($k_p/k_m < 1$), the solidification front bulges towards the object and repels it. In the opposite case ($k_p/k_m > 1$), the solidification front bends away from the particle and facilitates its encapsulation [27]. However, few experimental observations exist to ratify these numerical simulations, owing to the associated small time and space scales, as well as high temperatures of solidification, especially for metals [17,25].

The thermal conductivity ratio criterion is not extensive and has been contrary in certain experimental predictions of repulsion and engulfment of foreign particles [23]. The presence of solute in the melt may also influence the interaction between a particle and a solidification front, as solutes are rejected by the solid and segregate at the solid-melt interface, leading to a colligative depression of the melting temperature.

Here, we demonstrate in a systematic manner the influence of thermal conductivity on the front curvature using in situ cryo-confocal microscopy. We depict that solute segregation at the front overrides thermal conductivity effects and hence, not only controls the interfacial curvature but also the dynamics of particle capture. Furthermore, in the case of cellular front morphology, insulating particles, engulfed in the solid, induce a distortion of the surrounding ice crystals due to persisting local temperature gradients, thereby modifying the final microstructure of the solid.

**Thermal conductivity controls the interfacial curvature**

We perform solidification experiments with dilute aqueous dispersion of droplets, bubbles, and particles, of similar diameter $\approx 50 \mu m$, but varying thermal conductivity. We regulate the front velocity ($V_{sl}$) by translating a Hele-Shaw cell,
Figure 1: Objects interacting with a moving solidification front: principles and in situ confocal microscope imaging. (A) Model, sketch. (B) Experimental setup for in situ solidification experiments. A thin Hele-Shaw cell containing the suspension, emulsion or foam is pulled at a constant velocity ($V_{sl}$) through a constant temperature gradient ($G$) established by Peltier elements. In steady state, the solidification front is thus at a constant position under the microscope objective. (C) Typical time lapse for a freezing particle-in-water suspension with a Polystyrene (PS) particle. The solidification front develops a bump ($t \approx 17$ s) in the vicinity of the low thermal conductivity solid ($k_p/k_m < 1$). PS is in cyan, water in colormap viridis (fluorescence bar) while ice is in black. Scale bar = 50 $\mu$m. © (2020) S. Tyagi et al. (10.6084/m9.figshare.12046560) CC BY 4.0 license https://creativecommons.org/licenses/by/4.0/.

under a confocal laser scanning microscope, along a temperature gradient ($G$) imposed by two Peltier modules, as shown in Fig. 1. The independent selection of the two parameters ($V_{sl}$ & $G$) in our setup enables a uniform cooling rate and an improved control over the front morphology.

We observe a pronounced convex curvature (Fig. 2A) when the objects are thermally insulating compared to water ($k_p/k_m < 1$) and thus, the front tends to diverge towards them as they act as thermal shields causing the temperature in the gap behind them to be successively lowered. We used zirconia and stainless steel conducting particles and obtain a cusping of the front (Fig. 2A). The relatively higher thermal conductivity of the spheres ($k_p/k_m > 1$) enables a preferential heat flux from the melt to the front resulting in a concave depression.
Thus, the differing thermal conductivities result in a distortion of the isotherms away from the horizontal. The magnitude of the depression (convex or concave) depends on the thermal conductivity ratio of the particle to the melt ($k_p/k_m$) (Fig. 2B).

These observations are in agreement with the numerical model from Park et al. [18]. This model is based on the computation of the particle velocity when it is close to the front ($d << R$) and takes into account the balance of hydrodynamic and intermolecular forces, solidification front surface energy, contrast of the particle and melt thermal conductivities, and the flow caused by the density change upon solidification. It encompasses an asymptotic analysis in the lubrication approximation and theoretically predicts the curvature of the front as a function of $\gamma$ and $(k_p/k_m)$, shown in Fig. 2C, where $\gamma$ is a dimensionless surface energy parameter, $\gamma = (T_m \sigma_{sl})/(L_v G R^2)$, where $T_m$ is the bulk melting temperature at constant pressure, $G$ is the applied temperature gradient, $\sigma_{sl}$ is the interfacial tension between the solid and the melt, of the order $3 \times 10^{-2} Nm^{-1}$, and $R$ is the radius of the spherical object. Our solidification experiments correspond to $\gamma \approx 3.5 \times 10^{-3}$. We can see from Fig. 2C that when $k_p/k_m > 1$, the front is always concave and has a depression away from the object. While for $k_p/k_m < 1$, three curvatures are feasible corresponding to concave, concave-convex, and convex. The domain of concave-convex geometry is limited to higher $\gamma$ regions while it reduces to a confined zone when $k_p/k_m$ is close to 1 and $\gamma < 10^{-1}$. We could not investigate this region as it requires either the use of minute objects ($R < 5 \mu m$) or the application of a small temperature gradient ($G < 1 \times 10^2 Km^{-1}$), other parameters being constant for the particle-in-water system. While using minute objects is inconceivable as the interfacial curvature would be below the optical spatial resolution, using a smaller temperature gradient would render a planar front thermodynamically unstable owing to the supercooling [13].

Interestingly, there seems to be no conspicuous digression in the dynamics of objects with $k_p/k_m < 1$ or $k_p/k_m > 1$, which depict similar behaviour as can be
seen in the time-lapse figure (Fig. 1C). We do not observe repulsion of neither
the soft objects (oil droplet and air bubble) nor the insulating rigid particles in
the system investigated, which rather tend to be encapsulated instantaneously.
This trend is contrary to the previous studies [2], where a convex front tends
to increase the critical engulfment velocity ($V_c$) and facilitates repulsion of the
object through a reduction of lubrication drag forces in the gap between the
particle and the front [18].

All these predictions and results were obtained so far in pure systems. How-
ever, almost all real melt systems consist of solutes in some form or the other,
be it desired (for imparting better mechanical and/or physical properties) or
undesired (such as impurities, inclusions etc…). It has been shown recently
that the dynamics of interaction of an object with a solidification front and the
critical role of solutes have been highly underestimated in the studies so far [7].
We cannot use the existing models as they consider a dominant role of ther-
molecular forces, which are effective only at very short distances ($\sim 10^{-10}$
$m$) [2, 18, 21], while solute fields are long range ($\sim 10^{-4}$ $m$) [2, 7]. We therefore
investigate how solute impacts the interfacial curvature.

**Solute effects override thermal conductivity effects**

We carried out freezing experiments with the same set of objects (oil droplets,
gas bubbles, and particles) in the presence of 1wt.% TWEEN80 (acting as a
model solute) aqueous phase. This surfactant, needed to stabilize the bubbles
and drops, is used here as a model solute that decreases colligatively the freezing
point in all systems. We assume the thermal conductivity ratio of the objects
to melt remains the same as shown in Fig. 2C. Thermal conductivity is a ma-
terial property that depends primarily on temperature, and thus we expect no
significant changes to its value while adding small amounts of solute to water.
We observed only convex interfacial curvature in the absence of solute with
$k_p/k_m < 1$, however, in the presence of solute, solely concave curvatures are
observed (Fig. 3A). In the presence of conducting objects with $k_p/k_m > 1$, the
Figure 2: Thermal conductivity effects on interfacial curvature in absence of solute. (A) Insulating air-in-water bubble, polystyrene (PS) particle, propyl benzoate (PB) droplet, and Poly(methyl methacrylate) (PMMA) particle promote a convex curvature of the solidification front. Polyethylene (PE) particle does not affect the curvature. Conducting zirconia ($\text{ZrO}_2$) and stainless steel (SS) particles result in a concave depression. We added a very small amount (0.01 wt.%) of TWEEN80 to stabilise the foam and the emulsion, while no solute was present for the particle suspensions. PS, PB, and PE are in cyan, water in colormap viridis (fluorescence bar) while ice, air, PMMA, zirconia, and stainless steel are in black. Scale bar = 50 $\mu$m. (B) Plot of front deflection versus ($k_p/k_m$) for solidification of spherical objects in absence or at low concentration of solute. (C) Three distinct curvatures of the solidification front in the thermal conductivity ratio ($k_p/k_m$) versus $\gamma$ plane for a spherical particle, adapted from Park et al. [18]. © (2020) S. Tyagi et al. (10.6084/m9.figshare.12046560) CC BY 4.0 license https://creativecommons.org/licenses/by/4.0/.

front exhibits a much more pronounced concave depression as compared to the geometry observed in the absence of solutes (Fig. 4). Thus, the solute tends to play a dominant role and renders the solidification front concave regardless of the thermal conductivity ratio.
Figure 3: Impact of solute on the front curvature. (A) Concave depression of the solidification front with air bubble, polystyrene (PS), propyl benzoate (PB), poly(methyl methacrylate) (PMMA), polyethylene (PE), zirconia ($ZrO_2$), and stainless steel (SS) particles. PS, PB, and PE are in cyan, water in colormap viridis (fluorescence bar) while ice, air, PMMA, zirconia, and stainless steel are in black. Scale bar = 50 $\mu$m. (B) Typical time-lapse for a freezing particle-in-water suspension, with a PS particle, in the presence of solute: 1wt.% TWEEN 80. The solidification front bends away from the solid ($t \approx 41$ s) and eventually heals leaving a premelted film around the encapsulated particle. PS is in cyan, water in colormap viridis (fluorescence bar) while ice is in black. Scale bar = 50 $\mu$m. © (2020) S. Tyagi et al. (10.6084/m9.figshare.12046560) CC BY 4.0 license https://creativecommons.org/licenses/by/4.0/.

As an insoluble object approaches a solidification front, it obstructs the diffusion field, and leads to a build-up of solutes (rejected by ice) at the front. Since growth from solutions depends on the concentration gradient of solutes at the front, the liquidus temperature of the melt differs from the melting temperature of the bulk composition. The change in liquid composition alters its transformation temperature, referred to as constitutional supercooling [24]. Therefore, the solute-rich region colligatively depresses the freezing point of the aqueous phase. This distortion of the isotherm away from the horizontal manifests itself as the concave depression of the solidification front. The resulting thin film, visible in the high fluorescence crescent (Fig. 3) between the object and the
Figure 4: Maximum interfacial curvature depression with time observed before encapsulation, in absence (A) and presence (B) of solute; 1wt.\% TWEEN80, for a conducting zirconia particle \((k_p/k_m > 1)\). Scale bar = 20 µm © (2020) S. Tyagi et al. (10.6084/m9.figshare.12046560) CC BY 4.0 license https://creativecommons.org/licenses/by/4.0/.

Growing ice, is driven by the tendency to reduce the interfacial free energy and known as a premelted film [4, 20, 26]. The films are thermodynamically stable below their bulk melting temperature and are extremely sensitive to the presence of solutes (known as solute premelting). The solute premelted films are quite evident in these experiments (Fig. 3B), however, we do not observe any interfacial premelting in the absence or at low concentrations of solute (Fig. 1C).

The concave curvature of the front facilitates lateral solute diffusion causing the front to accelerate, while engulfing the object with a solute-rich premelted film around it.

These results depart from the behaviour predicted in most physical models, where thermal fields are expected to affect the curvature of the solidification front [2]. We believe the long-range solute field interactions (with a length scale of \(\sim D/V\)) dominate over the short-range thermomolecular forces. This enforces the importance of purely diffusive (solute) effects during solidification as they
not only alter the interfacial curvature but also the nature and equilibrium of forces on the particle. Solutes impact the premelted film thickness [26], viscosity, undercooling [21], and can induce phoresis of suspended objects [1, 7] during freezing. Therefore, the prediction of the object behaviour when it encounters a solidification front is not so trivial. We suggest that the criterion of thermal conductivity ratio ($k_p/k_m$), for concluding whether an object will undergo engulfment or rejection, needs to be modified to account for long-range solute field interactions. However, modelling of the solute effects is beyond the scope of this study.

Solute and thermal conductivity effects in cellular growth

We have discussed so far the interfacial geometry for an ideal planar front morphology preceding particle encapsulation. We will now focus on the breakdown of the planar front and the subsequent impact of thermal conductivity mismatch, when a particle is engulfed. Most realistic systems present a scenario where a planar shape is thermodynamically not stable. This can be attributed to a high freezing velocity, constitutional supercooling, and the complete rejection of solutes from the solid phase, which produces a severe concentration gradient at the front [16, 24]. The resulting perturbations destabilise a steady-state planar front into regularly spaced cells through the propagation of Mullins-Sekerka instability [15]. Although these instabilities have been investigated for a long time, we are not aware of any available quantitative models describing the capture of isolated single particles by a non-planar (cellular or dendritic) front morphology.

At high solidification velocity ($V_{sl} = 10 \times 10^{-6} \text{ms}^{-1}$) with 1wt.% TWEEN80 in the aqueous phase, we obtain a cellular front morphology with solute-rich grain boundaries (Fig. 5). For bubbles (Fig. 5A), the front tends to be moderately convex ($t \approx 3s$) with a deflection away from the horizontal, owing to the extremely low thermal conductivity of air, while it transforms into a concave depression in the proximity of the bubble ($t > 3s$). For the oil-in-water emulsion (Fig. 5B), the solidification front stays at the same ordinate before the
Figure 5: Deformation of the grain boundaries and blunting of the ice tip radius at the solidification front during encapsulation. (A, B, and C) Time-lapse of oil-in-water emulsion (A) with $G = 10 \text{ Kmm}^{-1}$, air-in-water foam (B) with $G = 15 \text{ Kmm}^{-1}$, and stainless steel sphere (SS) (C) with $G = 10 \text{ Kmm}^{-1}$, at $V_{sl} = 10 \times 10^{-6} \text{ ms}^{-1}$. Oil is in cyan, water in colormap viridis (fluorescence bar) and ice, air, and SS are in black. Scale bar = 50 $\mu$m. © (2020) S. Tyagi et al. (10.6084/m9.figshare.12046560) CC BY 4.0 license https://creativecommons.org/licenses/by/4.0/.

droplet impingement ($t < 3s$), contrary to the depression in planar morphology (Fig. 3A). The stainless steel particles (Fig. 5C), being highly conductive, induce a concave cusping of the front ($t \approx 3s$), which is further enhanced by the constitutional supercooling ($t \approx 6s$).

The solutes are partially segregated into the grain boundaries and hence, the effective concentration gradient at the ice-water front is considerably reduced compared to the previous planar front situations. Cellular fronts redistributes the rejected solutes parallel to the temperature gradient. This diminishes the extent of constitutional supercooling, thereby averting an extensive cusping of the front and preventing a dominant role of solutes before encapsulation. Thus,
the effective distance, between the object and the ice, at which solutes modify
the interfacial geometry of a cellular front is considerably smaller.

After encapsulation, the insulating particles \((k_p/k_m < 1)\) (Fig. 5A, 5B) de-
form the grain boundaries in their vicinity \((t > 10s)\) and alter the ice tip radius.
We believe the thinning of the grains around these particles is essentially related
to the local temperature gradients originating from the difference in thermal
conductivity ratio between the particle and the encircling crystal. The objects
remain at relatively higher temperatures for sufficient amount of time to mod-
ify the solidified microstructure. Indeed, the grain boundaries do not undergo
geometrical modifications (Fig. 5C) with stainless steel sphere, as it is highly
conductive \((k_p/k_m > 1)\), and therefore, homogenises its temperature with the
surrounding ice instantaneously.

The rapid cryo-confocal microscopy enables us to follow in situ the evolution
of the microstructure. The front eventually heals and recovers its original cellu-
lar spacing, which is a function of temperature gradient, solidification velocity,
and solute concentration gradient \([15, 24]\). The freezing of suspensions with
a cellular front is an attractive route for processing porous ceramics, metals,
and even composites \([8]\). An improved understanding of the critical param-
ters is thus desired to regulate the front morphology and the resulting material
properties \([9]\). The size and spacing of grains is an indispensable attribute
controlling the mechanical properties of a polycrystalline material (Hall-Petch
relationship) \([12, 19]\). Consequently, the heterogeneous microstructure can be
detrimental to an otherwise homogeneous finished product. Thus, solutes play
a key role in solidification and an in-depth understanding of their redistribution
mechanism is required.

**Conclusions**

Cryo-confocal microscopy \([7]\) exhibits great promise for the in situ analysis of
solidification mechanisms with foreign objects. We have demonstrated the role
of thermal conductivity mismatch on the distortion of solidification fronts in
the absence of solutes. Furthermore, our results show that both insulating and conducting particles get engulfed by the front in contrast to previous theoretical and numerical studies. In the presence of solute, the long-range solute field interactions play a critical role on the front curvature and the evolution of the solidification microstructure. With cellular front morphology, local temperature gradients around the engulfed particles distort grain growth and further work is required to correlate these observations to analogous real life systems. We hope our extensive research with ceramics, metals, and polymers serves for the formulation of a robust physical model with the incorporation of solute effects.

**Experimental section**

**Materials**

Propyl Benzoate, Tween80, Difluoro2-[1-(3,5-dimethyl-2H-pyrrol-2-ylidene-N)ethyl]-3,5-dimethyl-1H-pyrrolato-Nboron (BODIPY), and Sulforhodamine B (SRhB) were obtained from Sigma-Aldrich. Zirconia (ZrO$_2$) spheres (Zirmil Y from Saint-Gobain ZirPro, 50 – 63 µm) were provided by Saint-Gobain Research Provence. We purchased fluorescent green Polyethylene (1 g cm$^{-3}$, 45 – 53 µm) and Stainless Steel (7 g cm$^{-3}$, 48 – 57 µm) microspheres from Cospheric LLC. We ordered monodisperse green-fluorescent Polystyrene (48.1 µm) and Poly(methyl methacrylate) (PMMA) (50.3 µm) from Micro Particles GmbH. Deionized water, filtered with 0.45 µm Nylon membrane filters (VWR International), was used for the aqueous phase. The thermal and geometrical parameters which were important for our study are given in table 1 below. The material properties have values based on their typical conditions at 25°C and 1 atm.

**Sample Preparation**

The oil-in-water emulsions were prepared by using a microfluidic setup (microfluidic starter kit, Micronit Microfluidics, Netherlands) with pressure-controlled flow pumps (Fluiqent LineUP Flow EZ) and uncoated focused flow
droplet generator chips (FF\_DROP), with a nozzle diameter of 50 $\mu m$. The flow rate of oil and aqueous phases were controlled using Fluigent Flow Unit S (0 – 7 $\mu L/min$). The oil phase consisted of propyl benzoate with $10^{-4} M$ BODIPY, and the aqueous phase was a $10^{-5} M$ SRhB solution. The air-in-water foams were prepared by using the double syringe technique [10], with a luer adapter as connective, and a liquid fraction of 50 %. For the foams, we bubbled air through liquid perfluorohexane ($C_{6}F_{14} 98+\%$, Alfa Aesar) to obtain a gas composed of air and perfluorohexane vapour. Thus, we could delay coarsening [3] and ensure the bubbles remained stable during the experimental time-scales, typically varying from 4 to 6 hours at $V_{sl} = 10^{-6} ms^{-1}$. TWEEN80 was used as a non-ionic surfactant and solute to avoid long-range electrostatic interactions. We used the same surfactant for stabilising both the oil-in-water emulsions and the air-in-water foams. The particle suspensions were thoroughly sonicated (30 – 40 min) to ensure a homogeneous dispersion. The experiments in the presence of solute were carried out by adding 1wt.% TWEEN80 to the aqueous phase. We used the same solute and concentration for all systems to ensure comparable results. The solutions were frozen in a rectangular Hele-Shaw cell ($h = 100 \mu m$ and $V = 100 \mu l$), fabricated using two glass slides (Menzel, $24 \times 60 mm$, thickness 0.13 – 0.16 mm), and sealed with nail-polish at one end to avoid evaporation.
Freezing Stage

We performed directional freezing experiments, translating the sample along a constant linear temperature gradient of $10 \text{K mm}^{-1}$, using the cryo-confocal stage described previously [6]. We carried out all the experiments at $V_{sl} = 10^{-6} \text{ ms}^{-1}$, unless stated otherwise. The solidification front tends to appear immobile in the frame of observation, however, in the sample frame, it is the ice solidifying (along $\vec{x}$) at the velocity imposed by the pulling rate of the motor (MicosPollux Drive VT-80 translation stage PI, USA). We modified the stage by substituting the aluminium plate with a copper serpentine sheet and discarding the silicon carbide honeycomb interface. This led to an improved stability and a more robust cooling setup. The temperature gradient was imposed with two Peltier modules and controlled using TEC-1122 Dual Thermo Electric Cooling Temperature Controller from Meerstetter Engineering, Switzerland. We can thus decouple and control independently the solidification velocity ($V_{sl}$) and the temperature gradient ($G$).

Imaging & Analysis

The images were acquired through a Leica TCS SP8 confocal laser scanning microscope (Leica Microsystems SAS, Germany), equipped with 488 nm (blue) and 552 nm (green) lasers. We utilised the microscope at a scanning speed of 600 Hertz, with $1024 \times 1024$ pixels for imaging $775 \times 775 \mu\text{m}$, resulting in 1.7 seconds per frame. The high spatial resolution, coupled with rapid screening, enabled us to observe the dynamics of objects interacting with solidification fronts in situ. We used two photodetectors (PMT) to simultaneously image three phases:

1. BODIPY ($\lambda_{ex} 493 \text{ nm} ; \lambda_{em} 504 \text{ nm}$), the dye incorporated into the oil droplets. The same emission spectrum was utilised to image the fluorescent colloids.

2. SRhB ($\lambda_{ex} 565 \text{ nm} ; \lambda_{em} 586 \text{ nm}$), dissolved in water, to image the aqueous
phase and the grain boundaries in ice.

3. Ice, does not fluoresce, as it has very low solubility for solutes [14] and hence, appears black.

The emission spectra of the excited fluorophores was captured using a non-immersive objective (Leica HCX PL APO CS 20×). The working distance of 590 µm and an insulating foam cover facilitates the minimization of thermal perturbations on the freezing substrate. We used Fiji [22] and Python for image processing and data analysis.

Typical solidification parameters

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Table 2: Typical solidification parameters for an object in front of an ice-water solidification front. Lv, σsl, and λ adapted from Park et al. [18]

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Author contributions

S.D. and C.M. designed and supervised the project, S.D., C.M. and S.T. designed the experiments, S.T. and H.H. carried out the confocal microscopy, S.T. wrote the code to analyze the data, S.T., C.M. and S.D. analyzed the data. All
authors discussed the results and implications. S.T., C.M. and S.D. wrote the manuscript.

Conflict of interest

The authors declare no conflict of interest.

References


