

NORTHWESTERN UNIVERSITY

Effects of Gravity-Driven Convection on Microstructural Development during
Directional Solidification of Particle Suspensions

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Abstract

Directional freeze-casting is a porous materials fabrication technique that is used to create materials with complex, three-dimensional pore structures. Particle suspensions are solidified under a thermal gradient, promoting anisotropic growth of dendrites and incorporation of particles within interdendritic space. A fully-solidified directional freeze-cast structure is composed of dendrites that are separated by particle-packed walls and arranged in colonies. After solidification, the solidified fluid is removed *via* sublimation and the resulting particle scaffold is sintered to densify particle-packed walls. As microstructures are templated during the freezing process, microstructural parameters can be tuned *via* modifications to solidification conditions and suspension characteristics. However, the interdependency of these relationships is not well-understood; thus, predictive control over microstructural development during solidification is currently limited. Here, the effects of gravity-driven convective fluid motion, that arises during solidification, are studied to better understand processing-structure relationships in these materials.

First, a systematic investigation on the effect of solidification direction (with respect to gravity) on microstructures templated during the freeze-casting solidification process is conducted using aqueous particle suspensions. Solidifying in a buoyancy-unstable configuration is found to promote defects in resulting materials which can be avoided by solidifying in the buoyancy-stable configuration; defects observed include microstructural tilting, asymmetric dendritic features on particle walls, and lensing (cracking, in sintered materials). Next, the same aqueous suspensions are used to test the effect of initial suspension temperature on microstructural development. Radial segregation (variation in pore and wall width as a function of radial distance) is observed for all sample types, but the magnitude is greatest for samples that are solidified using an initial suspension temperature that is expected to produce a double fluid density gradient in the liquid.

That is, the double-fluid density gradient scenario is correlated with greatest degree of inhomogeneity in pore width distribution across the diameter of these samples, while samples solidified under conditions that promote the smallest gradient in fluid density exhibit lesser variations in pore width.

Subsequent work tests the suitability of using naphthalene as a suspending fluid for freeze-casting suspensions and the viability of resulting suspensions for microgravity flight testing on the International Space Station. It is shown that naphthalene can be used as a suspending fluid for freeze-casting suspensions and the resulting structures are primarily lamellar. While solidified in a buoyancy-stable (with respect to fluid density), radial microstructural segregation is still observed and attributed to radial temperature gradients during solidification, a driver for buoyancy driven convective fluid motion. Asymmetric dendritic features on particle walls are also observed and are attributed to interdendritic convection. Next, a naphthalene particle suspension that is electrosterically stabilized is tested and compared to results obtained with a sterically-stabilized suspension. Electrosterically-stabilized suspensions show increased stability relative to sterically stabilized naphthalene/particle suspensions.

Finally, freeze-thaw stability tests are conducted for naphthalene/particle suspensions stabilized *via* steric and electrosteric mechanisms. Freeze-thaw suspensions (subjected to an initial freeze in an ultrasonic bath, with temperatures held at either 10 or 50°C) are directionally solidified, particle sedimentation during solidification is quantified, and microstructures of solidified structures are investigated. It is found that electrosterically stabilized suspensions perform better under freeze-thaw testing relative to sterically stabilized suspensions. Sterically-stabilized suspensions subjected to freeze-thaw exhibit increased particle sedimentation relative to no-freeze-thaw suspensions and microstructural images show that earlier-to-solidify regions are

particle enriched relative to later regions for freeze-thaw suspensions. For electrosterically stabilized suspensions, sedimentation is found to be negligible and microstructural parameters (including lamellae thickness and particle fraction) do not change significantly for structures solidified using freeze-thaw suspensions relative to the no-freeze thaw condition.

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Chapter 1. Introduction

1.1. Overview

Directional solidification of particle suspensions is relevant to a variety of fields, including earth and planetary science [1], biology [2], food engineering [3], and chromatography [4]. In materials engineering, directional solidification of particle suspensions followed by sublimation of the suspending fluid is known as “freeze-casting;” this process has been used to fabricate porous metal [5-7], ceramic [8-10], polymer [11, 12], food [13, 14], pharmaceutical [15, 16], and composite [17, 18] materials with diverse intended applications [19-21]. A major advantage of this technique is the ability to adjust microstructural parameters by manipulating suspension characteristics and solidification conditions. In turn, this offers the potential to tailor mechanical and physical properties to suit desired applications, further enhancing the cross-cutting nature of the freeze-casting process [19-25].

Although freeze-casting has the potential to produce application-specific microstructures, solidification conditions must be properly controlled for precise microstructural control to be achieved. The underlying principles that govern microstructure formation during solidification are not well understood, making a priori predictions difficult. A major impediment to the study of these processes is gravity-driven convection that arises in the liquid due to the combination of temperature and particle and/or solute (e.g., binders, dispersants, surfactants) density/concentration gradients. Current theoretical models describing the freeze-casting solidification process are based on diffusive growth conditions [26-29]; gravity-driven convective effects are ignored.

The focus of this work is closely coupled with a microgravity directional solidification investigation, Microstructural Evolution in Freeze-Cast Materials (MEFC), intended for the

International Space Station (NASA MaterialsLab Open Science Campaign). The overarching goal of the ISS work is to utilize the ISS-microgravity environment to study freeze-cast microstructural development during directional solidification of particle suspensions under a predominantly diffusive growth regime (in the relative absence of gravity-driven convection), and to utilize knowledge gained to develop improved processing techniques that enable better predictive control over materials design for terrestrially-based processing. The following research objectives (RO) were defined to facilitate that work:

- RO-1. Establish the microgravity justification for freeze-casting solidification experiments to be carried out on the ISS.
- RO-2. Identify a viable suspension system for flight testing and run preliminary ground tests demonstrating that the system is capable of achieving flight objectives within platform, equipment, and science-related constraints.
- RO-3. Develop a test plan for the MEFC investigation, including designing flight experiments, establishing success criteria, and defining science requirements.

The MEFC microgravity solidification experiments are intended for processing on the Pore Formation Mobility Investigation (PFMI) furnace [\[30-39\]](#) on the ISS. Use of this furnace dictates many of the equipment constraints generally referenced in RO-2; the furnace is described in Appendix 2.

1.2. Thesis organization

Chapter 2 provides general background information on the freeze-casting technique as well as more detailed information related to freeze-cast microstructural development during solidification, including presentation of the You *et al.* [\[29\]](#) model for predicting freeze-cast

microstructures based on solidification conditions and suspension characteristics, which has been selected for testing as part of the intended ISS investigation.

Chapter 3 provides experimental methods; procedures both related to aqueous and non-aqueous freeze-casting suspension preparation and solidification procedures are discussed as well as various characterization methods. Greater detail and justification are provided for methods directly related to the selected flight system.

Chapter 4 and 5 provide experimental results related to directional freeze-casting of an aqueous system. Chapter 4 investigates solidification orientation with respect to gravity on microstructural development and Chapter 5 investigates the effect of the initial suspension temperature, where the initial temperatures selected are expected to produce categorically different fluid density profiles in the bulk suspension during the initial solidification phase. Results provided in these chapters provide partial microgravity justification in accordance with RO-1.

Chapter 6 and 7 provide experimental results for two naphthalene/Cu particle suspension systems; in Chapter 6, suspensions are sterically stabilized, whereas in Chapter 7, electrosteric stabilization is used. These results, coupled with results provided in Chapter 8, which assesses freeze/thaw stability for both suspension types, show that electrostatically stabilized naphthalene/Cu suspensions are more appropriate for flight testing relative to suspensions employing steric stabilization alone. Further microgravity justification is also provided within Chapter 6 and 7; thus, these chapters address both RO-1 and RO-2.

Lastly, Chapter 9 provides a summary of this work and suggestions for future directions, which includes a summary of the experimental design for intended flight experiments. This chapter partially addresses RO-3; that research objective is addressed more completely within the Science

Requirements Document that was submitted to NASA and is attached here as Appendix 1.

Additional suggestions for future work, outside of the ISS investigation, are also provided.

Chapter 2. Background

2.1. Overview of the freeze-casting technique

Directional freeze-casting is a solidification technique that produces materials with complex, three-dimensional pore structures [19, 21, 40]. The typical directional freeze-casting process is depicted in Fig. 2.1. First, a suspension of particles is put into a mold (Fig. 2.1-a). The thermally conductive base of the mold is cooled, promoting nucleation and directional propagation of a solidification front (Fig. 2.1-b). Initially, the solidification velocity is high and suspended particles are engulfed by the solid/liquid interface (often observed as a dense particle layer at the base of resulting materials [41]). Latent heat release from the initial solidification event reduces the velocity of the solid/liquid interface and particles are subsequently pushed by the solidification front (comprised of lamellae here, which, under ideal conditions, are aligned parallel to the imposed thermal gradient). A particle accumulation region forms ahead of the solidification front [41, 42] (Fig. 2.1-c); as solidification progresses, particles within the accumulation region are incorporated within interdendritic space (Fig. 2.1-d). A fully-solidified directional freeze-cast structure is composed of dendrites that are separated by particle-packed walls and arranged in colonies. After solidification, the solidified fluid is removed *via* sublimation (Fig. 2.1-e) and, in the case of ceramic and metallic material processing, the resulting scaffold is sintered to densify particle-packed walls (Fig. 2.1-f) [20, 21, 23, 25].

Freeze-casting has broad applicability in that it has been utilized as a processing method for porous metal [5-7], ceramic [8-10], polymer [11, 12], food [13, 14], pharmaceutical [15, 16], and composite [17, 18] materials. A major advantage of the technique is the ability to adjust microstructural parameters by manipulating solidification conditions [21, 43]. In turn, this offers the opportunity to tailor mechanical and physical properties to suit desired applications, which

further enhances the cross-cutting nature of the freeze-casting technology. This tunability is, arguably, the largest advantage of the freeze-casting technique. However, this freedom also adds significant complexity in attempting to understand the complex behavior of the system [21]. As a result of interdependent relationships in the freeze-casting process, material properties can vary widely even within seemingly similar systems, making predictive control over microstructural parameters difficult [21-23, 44]. A sound theoretical understanding of the principles that govern microstructural evolution for freeze-cast materials is necessary to improve predictive control over microstructural parameters templated during the solidification process (and, by consequence, functional and mechanical properties of resulting materials).

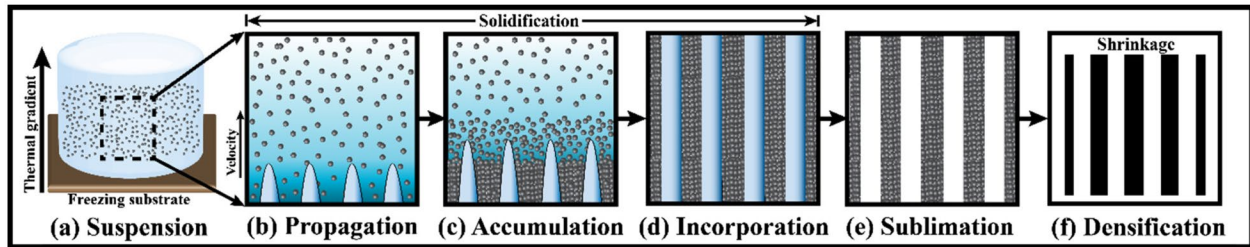


Fig. 2.1. Diagram that describes the directional freeze-casting process. The drawing in (a) shows a suspension consisting of particles (grey) dispersed in a liquid (dark blue) on a freezing substrate, which introduces a vertical thermal gradient from the base of the mold to the top of the suspension. After nucleation, (b) lamellae (light blue) propagate in the direction of the thermal gradient while rejecting/pushing particles away from the moving solid/liquid interface. In (c), an accumulation region of rejected particles develops ahead of the solid/liquid interface; this induces particle packing within interdendritic space. After (d) complete solidification, the (e) solidified fluid is removed *via* sublimation; this leaves elongated pores (white) which were templated by the lamellae during freezing. In the case of ceramic and metallic materials, (f) the remaining particle scaffold is sintered to densify particle-packed walls. Figure extracted without modification; ref. [21].

2.2. Particle interactions with an advancing solidification front

What is currently understood about microstructural evolution during solidification of freeze-cast materials is largely derived by considering an aqueous suspension of particles as a binary system, analogous to dilute alloy solidification [43, 45, 46], or otherwise employing theoretical models that describe the behavior of a single particle in the presence of an advancing solid/liquid interface. Microstructural development in these systems depends primarily on interactions between particles (and/or rejected solute) and the solid liquid interface, which defines, in large part, the morphology of the solidification front. As a result, extensive attention (long before freeze-casting technologies emerged) has been paid to controlling solidification behavior in the presence of particles [47-50].

Experimentally, it has been shown that particles are rejected (or, “pushed”) by an advancing solid/liquid interface if the velocity of the interface is below a critical value; above this value, particles are engulfed by the interface [47, 50-57]. Theoretical models help to determine whether a particle in the vicinity of the solid-liquid interface will be engulfed or rejected by the interface by balancing forces exercised on a particle at the interface [48, 56, 58-61]; some of the forces considered are depicted in Fig. 2.2. In dilute particle suspensions, these models are fairly effective for predicting behavior, but for higher volume fraction suspensions (as are typically employed for freeze-casting), the impact of multiple-particle interactions needs to be considered. An additional complexity is present in that freeze-casting systems typically employ both particles and solute (*e.g.*, binder, dispersant, surfactant); the combined effects of particles and solute are often not considered.

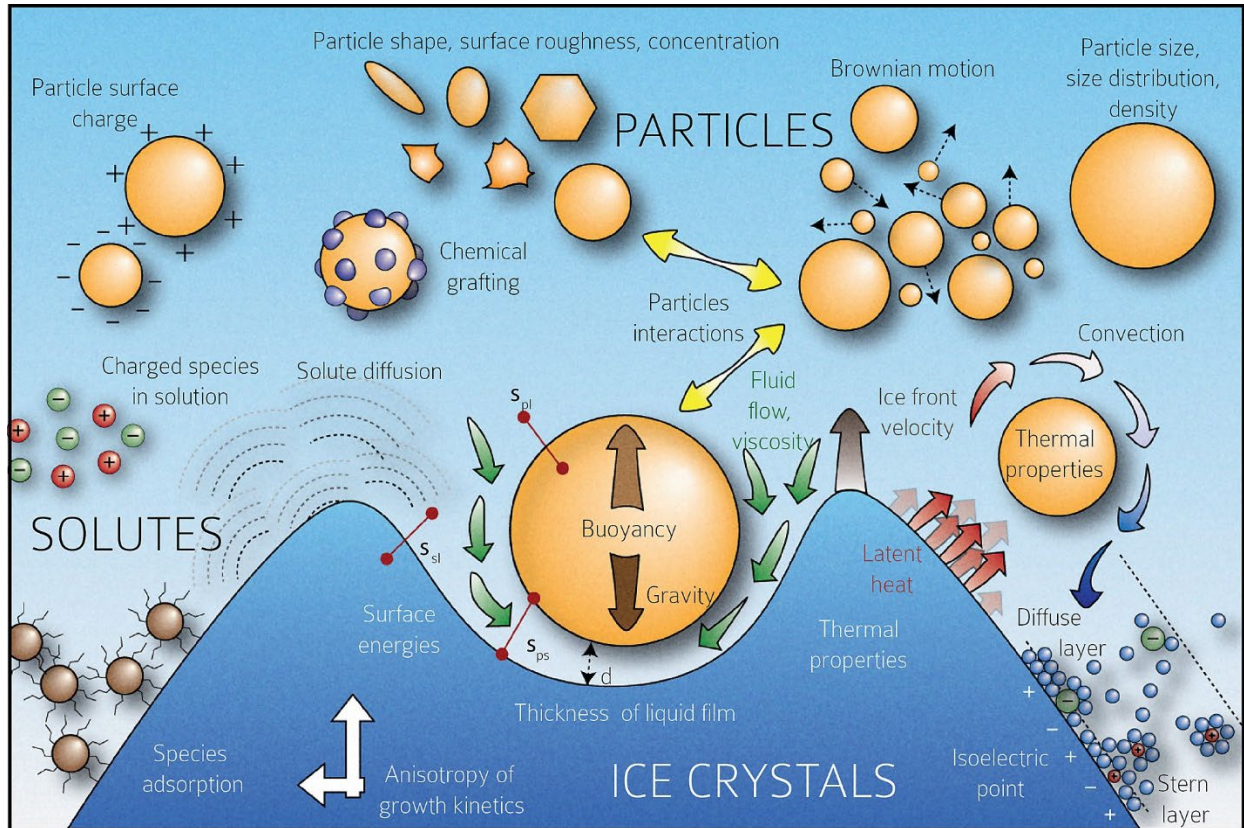


Fig. 2.2. Diagram showing many of the interactions between a particle and the solid/liquid interface that determine whether the particle will be pushed or engulfed by the solidification front. Figure extracted without modification from ref. [62].

2.3. Morphological instability of the solid/liquid interface

As microstructures of freeze-cast materials are templated during solidification, understanding the breakdown and morphological evolution of the solid/liquid interface (from planar to cells, dendrites, *etc.* [63-65]) is crucial for obtaining predictive control over material parameters. While the directional solidification of colloidal suspensions is often compared to the solidification of binary alloys [22, 29, 42, 43, 45, 46, 66, 67] (with particles taking the role of the solute, the suspending fluid as solvent), freeze-casting systems are often more complex than this because, as described above, suspensions contain both particles and additives (actual solute, where

dispersant is often used to achieve stable particle suspensions and binder is used to improve green strength of sublimated materials), both of which can impact (independently and interactively) the morphological evolution of the solidification front [68-71]. The breakdown of a planar solidification front in the presence of solute can be described in terms of a Mullins-Sekerka [72-76] instability. For particles, the breakdown of a planar solidification front is described in terms of particle-induced undercooling (which is generally small) [27, 67, 71, 77] and fluid flow; specifically, flow within the liquid separating a particle from an advancing solidification front and flow within the particle accumulation region (the enriched particle region that forms directly ahead of the solid/liquid interface, Fig. 2.1-c) [29].

While theoretical models considering how these two destabilization mechanisms interact are not presently available, some experimental work has been done [68, 70, 71, 78-80]; these studies have demonstrated that various factors (*e.g.*, particle size [70, 81], solidification velocity [70, 81, 82], and particle volume fraction [83]) promote one destabilization mechanism relative to the other. As Mullins-Sekerka [72] instabilities are largely diffusion-controlled, it has been suggested that the dynamics within the particle accumulation region (Fig. 2.1-c) are particularly important in determining whether a Mullins-Sekerka instability will dominate [70]. For example, during directional solidification of nanometric particle suspensions, diffusion of solute through the particle accumulation region becomes more easily obstructed relative to particle accumulation regions that form during solidification of larger particle suspensions. Accordingly, nanometric particle suspensions are thought to promote particle-induced instabilities at the solid/liquid interface [70, 81]. The nature of the solute is likely an important factor as well given that typical freeze-casting additives have relatively low diffusion rates and high propensities for entanglement [70, 84].

Characteristics of the particle accumulation region, including length [70] and particle volume fraction [78], have been used to better understand the transition between the destabilization/morphological evolution mechanisms. As the size of the accumulation region increases, the diffusion path for solute increases, eventually favoring particle-induced destabilization over Mullins-Sekerka-type mechanisms [70]. Lower particle volume fractions within the accumulation region (that is, the effective volume fraction near the solid/liquid interface, not the initial or bulk suspension volume fraction) promote destabilization mechanisms that are more representative of Mullins-Sekerka relative to particle-induced destabilization [78]. Importantly, particle volume fraction within the accumulation region has been shown to be impacted by suspension stability [41, 85], sedimentation, solidification velocity [86-88], and solidification orientation with respect to gravity (*i.e.*, buoyancy-driven convection) [89]. As gravity-induced convection induces fluid flow that can interact directly with the solidification front [90], causes macroscopic curvature to the solidification front [91, 92], and likely redistributes particles from the bulk suspension into the particle accumulation region [89], solidification studies conducted under 1g that are intended to investigate the relative roles of solute *vs.* particles on these destabilization mechanisms are likely complicated by the presence of gravity.

2.4. Typical microstructures and common defects

In directional freeze-cast materials, the structure of macropores is largely dictated by the morphology of the solidified fluid, which is governed by the nature of the fluid and solidification conditions. If highly anisotropic materials are desired, fluids with highly anisotropic growth kinetics should be prioritized. The overwhelming majority of published freeze-casting studies have employed water as the suspending fluid [21] (when water is used, the freeze-casting technique may also be referred to as “ice-templating”). As the growth kinetics of ice are highly anisotropic, the

resulting structure is lamellar (plate-like, Fig. 2.3-a) [93, 94]; growth of dendritic side arms is largely suppressed (though, dendritic structures can be produced with water, especially at relatively high solidification velocities [95], high initial particle volume fractions [96], and with the addition of relatively high concentrations of polymeric additives [97, 98] or cryoprotectants [99] in suspensions). Camphene is the second most commonly employed fluid, and the growth kinetics are less anisotropic relative to water; resulting structures are dendritic (Fig. 2.3-b); after sublimation and sintering, wall interconnectivity is generally quite high [100, 101] and the pore aspect ratio is low relative to materials fabricated using water [21]. Lastly, a relatively large number of studies have also been published demonstrating *tert*-butyl alcohol (TBA) as the suspending fluid; in these cases, resulting pore structures are often described as elongated honeycombs [102, 103] (or tubular, Fig. 2.3-c).

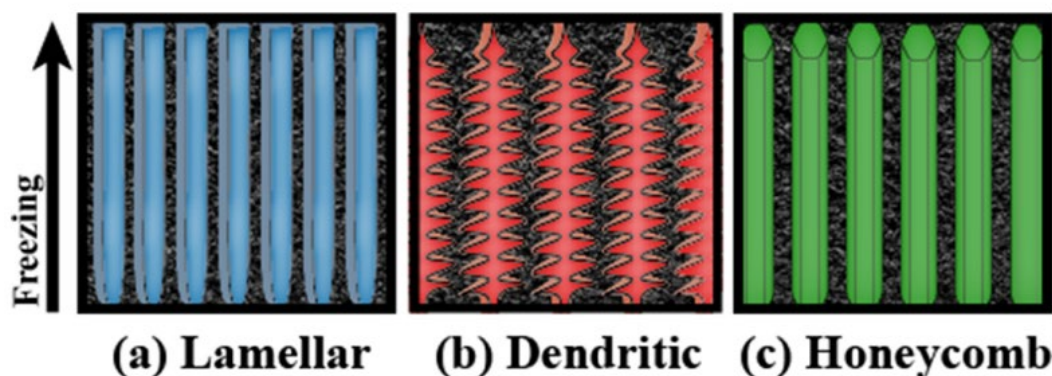


Fig. 2.3. Drawing showing the most common pore structures observed in directional freeze-cast materials. Lamellar structures are commonly observed *via* aqueous processing techniques; dendritic and elongated honeycomb (or tubular) structures can be achieved using camphene and *tert*-butyl alcohol, respectively. Figure extracted with modification, ref. [21].

While it is often assumed that use of a fluid exhibiting anisotropic growth kinetics coupled with directional freezing approaches produces anisotropic structures, microstructural transitions can occur, and are based on suspension characteristics and solidification conditions [29, 104]. Fig. 2.4 depicts (a) lamellar and (b) dendritic structures transitioning to (c) spears, and (d) bands. In all cases, lamellar and/or dendritic structures are desired, whereas spearing and banding structures belong to the lensing regime [29]; these are considered defects in freeze-cast materials because their presence significantly compromises mechanical properties in resulting materials [44]. While the lensing microstructures shown in Fig. 2.4 (c, d) are most often observed in freeze-cast materials obtained using aqueous suspensions [44], the transition from unidirectional structures, oriented parallel to the direction of the imposed thermal gradient (*i.e.*, ideal structures, Fig. 2.4-a, b) to lensing regimes (*i.e.*, defects, Fig. 2.4-c, d) is not unique to aqueous-based processing [29, 105, 106].

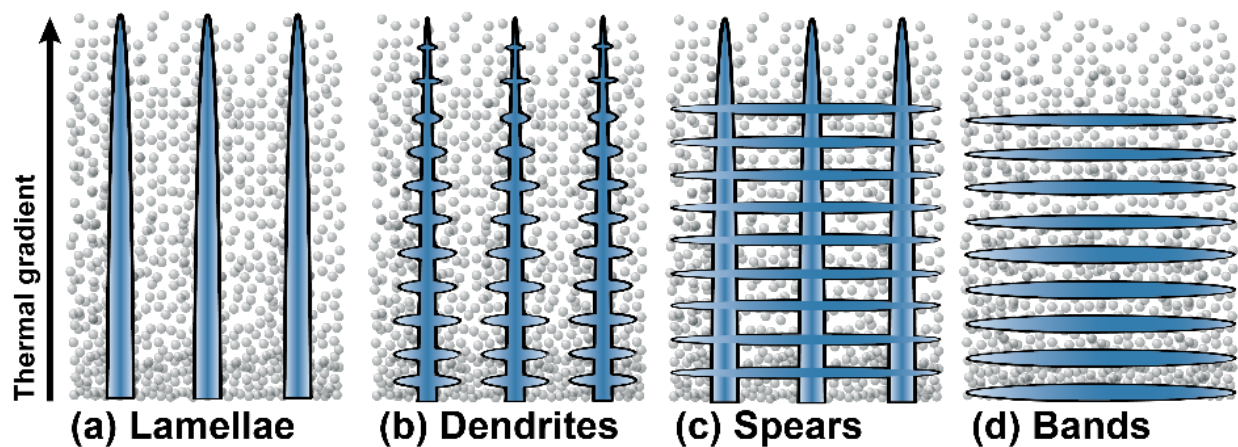


Fig. 2.4. Diagram showing the microstructural transition between anisotropic and lensing structures. The drawings in (a) and (b) depict solidification morphologies that result in anisotropic freeze-cast structures, including lamellae and dendrites, whereas the solidified structures, (c) spears and (d) bands, result in lensing defects in freeze-cast materials. Figure extracted without modification, ref. [89].

Banding defects arise during solidification as fluid-filled platelets, oriented perpendicular to the freezing direction, which are templated into cracks after sublimation. Banding is studied in a variety of fields, *e.g.*, geology (frost heaves [107-114]), food engineering [115], and cryobiology [116], as well as colloidal solidification [117-119]. Although various hypotheses have been proposed to explain the development of spears and bands [23, 26, 29, 42, 85, 86, 120, 121], most of the freeze-casting literature attributes their formation to a pattern of particle engulfment, rather than particle rejection, at the solidification interface [25, 67, 85, 122, 123]. If the particle fraction within the accumulation region (just above the solid-liquid interface) is below the breakthrough concentration (*i.e.*, where the osmotic pressure of the colloid exceeds the capillary pressure necessary to allow the solidified fluid to invade the pore space [124]), lamellae/dendritic structures form (Fig. 2.4-a, b). Above the breakthrough concentration, lamellae/dendrites are unable to propagate and ice lenses are likely to develop. Within the lensing regime, the main distinction between the banding and spear structures (Fig. 2.4-c and d, respectively) is that the former tends to form discrete bands of solidified fluid and enriched particle layers (*e.g.*, Fig. 1-a of ref. [27] and Fig. 5 of ref. [89]) whereas the latter does not (*e.g.*, Fig. 9-b of ref. [125] and Fig. 2-b of ref. [85]).

2.5. Theoretical model for predicting freeze-casting microstructures

You *et al.* [29] developed a model for predicting the freeze-cast microstructures depicted in Fig. 2.4 based on solidification conditions and suspension characteristics, including: dendritic (Fig. 2.4-b) and lensing regimes, including spears (Fig. 2.4-c) and banding (Fig. 2.4-d). Predictions are based on the relationship between three dimensionless parameters: the Darcy coefficient (D), the film coefficient (F), and a dimensionless parameter Φ , which is given by:

$$\Phi = \frac{\phi_0}{\phi_p - \phi_0} \quad \text{Eq. 2.1}$$

where ϕ_0 is the volume fraction of particles in the bulk suspension and ϕ_p is the volume fraction of particles in the accumulation region, taken as the random close-packed value of 0.64. The dimensionless Darcy coefficient, D , describes fluid flow through the accumulated particle region and is expressed as:

$$D = \frac{\mu V T_m}{k \rho L G} \quad \text{Eq. 2.2}$$

where μ is the dynamic viscosity of the fluid, V is the solidification velocity, T_m is the melting temperature of the fluid, ρ is the density of the fluid, L is the latent heat of fusion of the fluid, G is the imposed temperature gradient, and k is the permeability of the particle accumulation region, given by:

$$k = \frac{r^2 (1 - \phi_p)^3}{45 \phi_p^2} \quad \text{Eq. 2.3}$$

where r is the particle radius.

The dimensionless film coefficient, F , describes flow within the pre-melted liquid film between a particle and the solidification front and it is given by:

$$F = \frac{8\pi^2\sqrt{3}\mu vr^2}{A\lambda^3} \quad \text{Eq. 2.4}$$

where A is the Hamaker constant between the solidified fluid and the particle and λ is an empirical constant, given in Ref. [29]. as 0.225.

Dendritic structures are predicted when $D/(1 + \Phi)$ is greater than one, whereas lensing regimes are predicted when $D/(1 + \Phi)$ is less than one. Summarizing the above equations, transitions from dendritic to lensing regimes are predicted as the solidification velocity (or pulling velocity) decreases, the thermal gradient increases, the particle volume fraction increases, or the particle radius increases [29]. This model does not account for systems with solute effects (*e.g.*, dissolved additives in the suspension, which nearly all freeze-casting studies employ [21]) nor does it account for gravitational effects, such as gravity-driven convective fluid motion or particle sedimentation.

2.6. Gravity-driven convective fluid motion

Convective regimes during directional solidification can generally be categorized by considering: (1) the direction of solidification with respect to the gravity vector and (2) the relative density of rejected solute to solvent. For systems solidified vertically upward (under normal gravity) with rejected solute being heavier than the solvent (as is the case for most freeze-cast/additive systems), solutal convection is generally thought to be stabilized (with exceptions). However, there are two main avenues for which convection can still be introduced: (i) *via* the temperature-dependence of the suspending fluid's liquid density (considering upward

solidification condition where the coldest fluid is located at the base of the sample with warmer fluid above, if the density of the warmer fluid is greater than that of the cooler fluid, as is the case for water, the system is unstable with respect to buoyancy-driven convection) and (ii) *via* thermal conductivity mismatches between the liquid and solid phases [126, 127] and/or between the solid phase and the solidification mold [127, 128]. In the case of thermal conductivity mismatches, a radial temperature gradient across the macroscopic interface (the overall shape of the solidification front generated by the dendritic array, rather than the interface of an individual dendrite) can be induced, causing the macroscopic interface to change shape [129].

General patterns of convective fluid motion corresponding to macroscopic curvature of the interface are shown schematically in Fig. 2.5. Fig. 2.5(a), represents the ideal case where the macroscopic solidification interface is flat. In Fig. 2.5(b), the solidification interface is convex; in this case, convective fluid motion sweeps particles from the center of the interface to the sides, causing a build-up of particles at the mold walls. Conversely, in Fig. 2.5(c), convective fluid motion, reflective of a concave interface, sweeps particles radially inward, causing an accumulation of particles in the center of the solidification interface. While it was stated earlier that solutal convection is generally stabilized in cases where rejected solute is heavier than the solvent and the system is solidified against gravity, that is not necessarily the case in the presence of a macroscopically curved interface because the presence of horizontal concentration gradients may give rise to solutal convection [127].

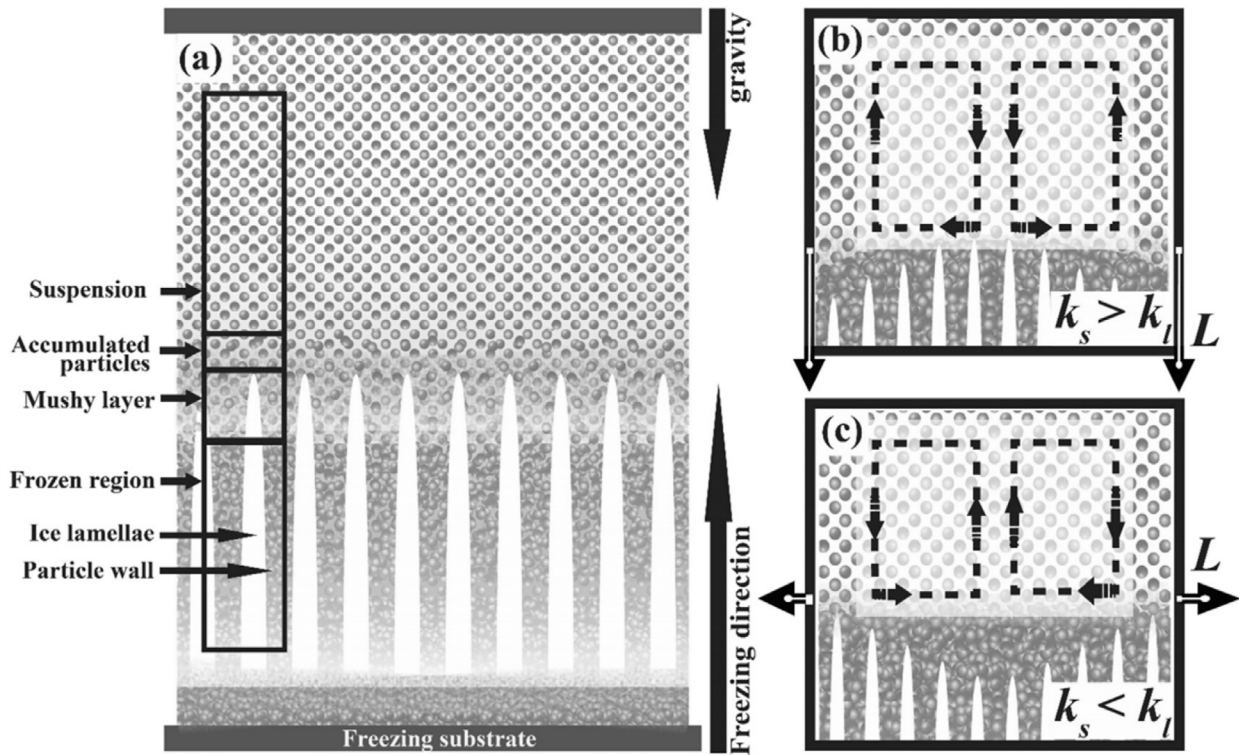


Fig. 2.5. Diagram showing convective fluid motion patterns corresponding to macroscopic interface curvature. The freezing direction is vertically upwards in these diagrams and (a) is representative of a macroscopically planar solidification interface; the particle fraction is relatively homogenous across the interface and the convective fluid motion is limited to that driven by vertical concentration and temperature gradients. The smaller drawings show general convective fluid motion patterns associated with macroscopically (b) convex and (c) concave interface shapes. Here, L is latent heat of fusion and k is thermal conductivity of the solid (s) or liquid (l). Figure extracted without modification from ref. [130].

Gravity-induced convective fluid motion can occur both within the mushy layer and within the bulk liquid. While the fluid motion that corresponds to a macroscopic curvature of the solid/liquid interface is generally considered bulk fluid motion, interdendritic convective flow is observed primarily within the mushy layer (though it can be influenced by bulk fluid motion). This flow can cause what is known as the “upstream effect,” most commonly described in the seawater [131-134] and alloy solidification [135-137] literatures wherein dendrites tilt in the direction of buoyancy-driven convective fluid motion [132]. Interdendritic fluid motion can be driven by shear

flow (across the solid/liquid interface, as depicted in Fig. 2.6-b) that is produced by macroscopic convective fluid motion in the bulk liquid or it can occur independently of any macroscopic convective pattern; in either case, buoyancy remains the driving force [28]. Interdendritic fluid flow is weaker than flow resulting from the macroscopic convection described above (approximately one-thousandth that of the bulk fluid region [138]), but can still present significant microstructural consequences.

In addition to promoting the tilting of dendrites, interdendritic flow offers a potential explanation for the observation of asymmetric, one-sided dendritic arms commonly reported in freeze-casting studies for both particle suspensions [20, 139-146] and polymer solutions [147, 148] where the suspending fluid is water: secondary arm growth is suppressed on the “downstream” side [83, 149, 150]. This is depicted in Fig. 2.6 for upward solidification of water, where (a) shows the “ideal” case, where no appreciable interdendritic flow exists and (b) shows the effect of buoyancy-driven, interdendritic flow for upward solidification (note: the flow pattern depicted is simplified in Fig. 2.6 to show only the overall impact on solidified microstructures; in reality, rotating fluid cells exist in between dendrites [136, 137, 151-155]). Here, shear flow is depicted to be produced due to the presence of macroscopic convective cells located within the bulk suspension region (ahead of the solid/liquid interface) and the direction of the shear flow is consistent with a concave interface curvature. Thus, consequences of interdendritic flow include both: (i) tilting of dendrites and (ii) suppression of secondary dendrite arms on the “downstream” side. The flow direction promotes growth of dendritic arms on the upstream side, where heat is more easily transported away from the dendrites (*via* fluid flow) than on the downstream side. The warmer fluid on the downstream side promotes melting and fragmentation of secondary dendritic arms [137].

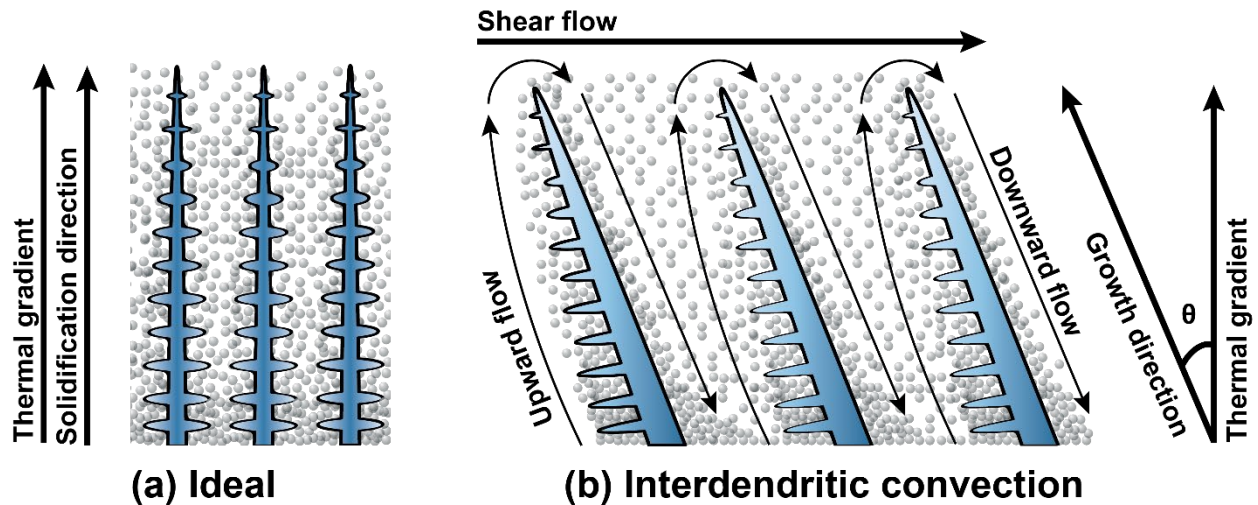


Fig. 2.6. Diagram showing the effect of interdendritic fluid flow on the orientation and side branching of ice dendrites. In the ideal case (a), no appreciable interdendritic fluid motion is present during solidification; the ice dendrites (blue) are oriented parallel to the imposed thermal gradient and secondary dendritic arms are observed on both sides of primary arms. In (b), there is buoyancy-driven convective flow, resulting in: (i) tilting dendrites and (ii) suppression of secondary dendritic arms on the “downstream” side of dendrites. Figure extracted without modification, ref. [89].

Chapter 3. Experimental methods and justification

3.1. Effect of solidification direction in ice-templated microstructures

3.1.1. *Suspension preparation*

Suspensions containing TiO₂ nanoparticles (anatase phase, 99.5% purity, 10-30 nm, specific surface area 50 m²g⁻¹, SkySpring Nanomaterials, Houston, TX) in deionized water were prepared using a mixture of ethylene glycol (Consolidated Chemical & Solvents, Quakertown, PA) and ammonium hydroxide (SEOH, Navasota, TX) as dispersants, and agar (NOW Foods, Bloomingdale, IL) as a binder. First, 5 vol.% ethylene glycol (with respect to fluid volume) was added to degassed, and deionized water and TiO₂ particle fractions (30, 40, or 50 wt.%, corresponding to volume fractions of 10, 15, and 21%) were added. Suspensions were sonicated for five minutes; thereafter, the pH was tested using an Oakton pH 150 meter and adjusted to pH ~9 by adding NH₃ dropwise. Suspensions were ball milled for 20 minutes using a high energy ball mill (yttria stabilized zirconia media), after which, the suspension pH was tested again, and adjustments were made as-needed. Agar (0.2 wt.% with respect to TiO₂ mass) was dissolved in a small amount of reserved DI water; the agar/water solution was added to the ball-milled TiO₂ suspension. A final pH measurement (and adjustment, if needed) was made after the binder addition.

3.1.2. *Directional solidification*

The TiO₂ colloidal suspensions (held at ambient temperature) were injected into solidification molds consisting of PVC tubes (15 mm inner diameter, 1.6 mm wall thickness). A cylindrical aluminum base (1.9 mm thickness) sealed one side of the PVC tubes and a rubber stopper (25 mm thickness) sealed the opposite side. The rubber stoppers contained two holes:

suspensions were injected into one hole until fluid leaked out of the second hole. Both holes were subsequently closed off using epoxy. The suspension fill height was kept to ~ 3 mm to allow for comparison to previous samples solidified on parabolic flights (wherein sample height was constrained due to reduced gravity time durations of ~ 25 s) [[130](#)].

The top surface of a copper box containing dry ice (solid CO_2 sublimating at 195 K) was utilized as a freezing substrate. The substrate temperature, recorded throughout solidification using a J-type thermocouple, was 228 ± 4 K. Samples were solidified under three conditions with respect to the direction of solidification front propagation: (i) upward (liquid on top, solid on bottom, against gravity), (ii) downward (solid on top, liquid on bottom, with gravity), and (iii) horizontally with respect to the gravity vector. These solidification directions are referred to as “Up,” “Down,” and “Horizontal,” respectively. In all cases, a rubber-elastic belt (held at approximately the same tension) was used to hold the solidification mold in contact with the copper box and to ensure consistent thermal contact for all samples, irrespective of solidification direction. Solidification times were estimated by visual inspection (noting the time when the last-to-solidify regions of samples appeared to be frozen through the transparent PVC mold) at ~ 35 - 45 s; samples were left on the copper box for ~ 2 additional minutes to ensure suspensions were fully solidified prior to removal.

3.1.3. *Sublimation and sintering*

Solidified samples were sublimated in a freeze-dryer (Labcono, Freeze Dry System) for at least 24 h at 233 K and low residual pressure (< 3 Pa). After sublimation, samples were placed on an alumina plate and sintered in a box furnace at 1173 K for 1 h in air, using heating and cooling rates of $5 \text{ K} \cdot \text{min}^{-1}$.

3.1.4. Microstructural characterization

Ceramographic examination was conducted using scanning electron and optical microscopy on sintered samples. Specimens were epoxy-mounted, ground and polished. Optical microscopy images were obtained using a Nikon MA200 automated microscope, which was set to obtain 15x15 pixel-grid images across the width and height of each cross-section; a 20% overlap per pixel-grid image was used for image acquisition (pixel grids were subsequently stitched to obtain full cross-section images).

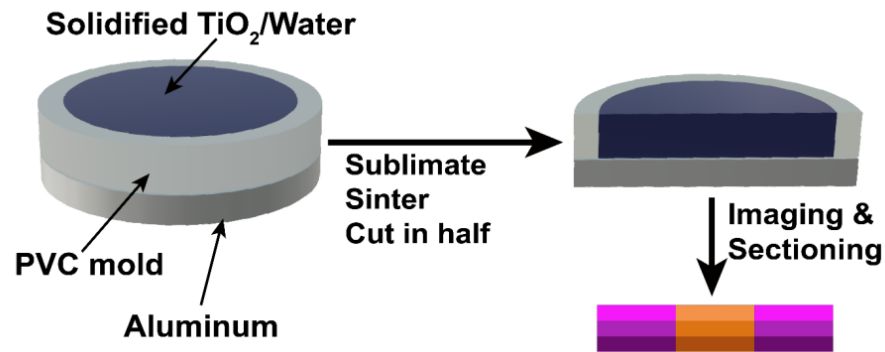


Fig. 3.1. Diagram showing how microstructural data for the study on solidification orientation were categorized. Suspensions were solidified in a PVC mold (15 mm inner diameter, 1.6 mm wall thickness, 3 mm height) with an aluminum base (1.9 mm thickness) as a freezing substrate. After sublimation and sintering, samples were cut in half, mounted in epoxy, and ground and polished; entire cross-sections were imaged. Images were sectioned equally both radially (x3) and vertically (x3) for a total of nine image categories per cross-section. Microstructural data representing the center of the sample were obtained from measurements taken within the orange regions of the diagramed sample; peripheral/outer data correspond to purple regions (where one side is in contact with the mold wall). For all regions, darker colors in the diagram correspond to “first-to-solidify” regions of samples (where that end of the sample is in contact with the aluminum freezing substrate), while lighter colors correspond to the “last-to-solidify” regions. Figure extracted without modification, ref. [89].

Pore and wall measurements were obtained from optical micrographs using longitudinal cross-sections, with the center of each image corresponding roughly to the center of the respective sintered sample; the approximate longitudinal cross-sectional dimensions were 15 x 3 mm. Stitched images were divided equally both radially (x3) and vertically (x3), for a total of nine images per cross-section, for further analysis; Fig. 3.1 shows a diagram of how images were divided. Pore walls were segmented on resulting images using ImageJ/Fiji [156] and applying the Otsu threshold algorithm [157] on contrast-normalized images [158]. A total of 90 samples were analyzed: ten samples from each TiO₂ weight fraction (30, 40, and 50%), for each solidification direction (“up”, “down”, and “horizontal”).

Pore width and wall width were measured over the width and height of each binary image using an in-house program written in C++ and employing the ImageMagick, Magick++ [159] library to decode images into raw pixel color data. For each pixel row in an image, the number of consecutive pixels of each color (white or black) are counted as a segment and the width of each segment (number of pixels) is added to a “black” or “white” vector container. After all segments in each row are counted, a csv file is generated, which provides the number of white or black pixels per segment for each row in the image. For each segment, the number of pixels was converted to a length using the scale (pixels/μm) of the corresponding image. Approximately eight million measurements of each pore and wall width were obtained for the 90 samples analyzed.

Scanning electron microscope (SEM) images were obtained using a Hitachi S-3400N-VP SEM operating at an accelerating voltage of 20 kV; these images were used to make qualitative assessments of pore and wall morphology and for measuring secondary dendritic arms. Due to the low electrical conductivity of TiO₂, backscatter detection under low vacuum was utilized.

3.2. Effect of initial suspension temperature on ice-templated microstructures

3.2.1. *Suspension preparation*

Aqueous TiO₂ suspensions were prepared as described in Section 3.1.1., to obtain 40 wt.% TiO₂ suspensions.

3.2.2. *Directional solidification*

Suspensions were precooled in a refrigerator prior to transfer to solidification molds to one of three temperatures: 0, 4, and 8°C; Teflon molds (20 mm inner diameter, 15 mm height) were used for solidification and were also precooled to the same initial temperature as the suspension. Suspensions were directionally solidified using a thermoelectric cooling device (TEC) as the freezing substrate. An Arduino microcontroller was used to operate the TEC; a cooling rate of 5°C/min with a final setpoint temperature of -20°C was used for solidification experiments, irrespective of initial suspensions temperatures. However, the starting temperature of the TEC was set to the initial suspension.

3.2.3. *Sublimation*

Solidified samples were sublimated in a freeze-dryer (Labcono, Freeze Dry System) for at least 72 h at 233 K and low residual pressure (< 3 Pa).

3.2.4. *Microstructural characterization*

Microstructural examination was conducted using optical microscopy on sublimated (not sintered) samples. Sublimated samples were mounted in Buehler EpoThin 2 epoxy, which was added dropwise (very slowly) to prevent collapse of the structure. Epoxy-mounted specimens were sectioned into thirds vertically, at 5 ± 1.5 , 10 ± 1.5 , and 15 ± 1.5 mm from the base of samples (first-to-solidify region). Sectioned samples were ground and polished and cross-sections perpendicular

to the freezing direction were imaged using a Nikon MA200 automated microscope and a Wild M3Z stereoscope; these images were used for measurements of pore width, wall width, and porosity. Pore and wall width measurements were regionalized; “outer” measurements correspond to values obtained from the periphery of cross-sections; that is, images taken within 1 mm of the outermost edge of the cross-section; “center” measurements correspond to measurements taken within 1 mm of the center of a given cross-section (representing the radial center of the sample); these categorizations are depicted in Fig. 3.2.

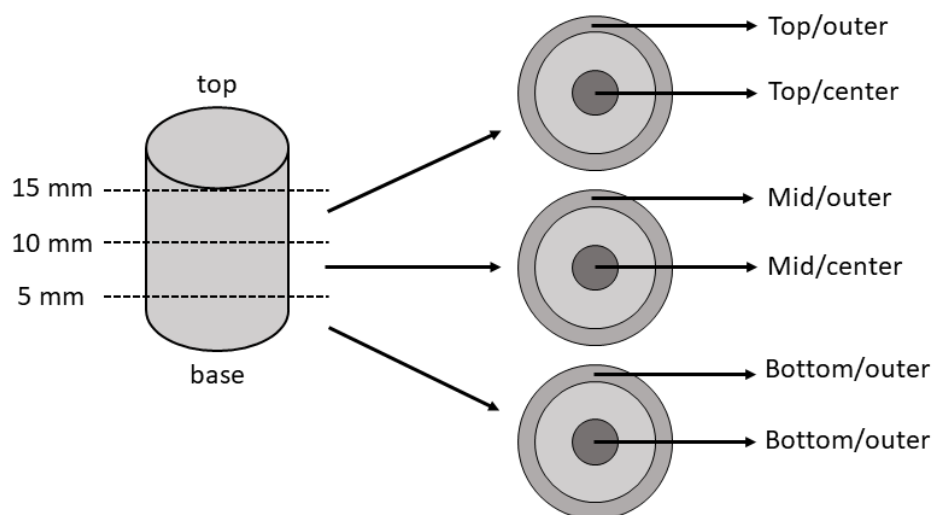


Fig. 3.2. Diagram showing how microstructural data for the study on initial suspensions temperature were categorized. Suspensions were solidified in a Teflon mold (20 mm inner diameter, 15 mm height). After sublimation and mounting, samples sectioned into thirds (at 5 ± 1.5 , 10 ± 1.5 , and 15 ± 1.5 mm from the base of samples, shown in the drawing on the left). The drawings on the right show how microstructural data were regionalized—for each vertical section (bottom, mid, and top), outer data describe measurements obtained within 1 mm of the outermost edge of cross-sections (medium grey, closest to the mold wall) and central data were obtained within 1 mm of the center of cross-sections (dark grey, corresponding to the radial central region of specimens).

3.3. Directional solidification using naphthalene as a suspending fluid

3.3.1. Gas handling

During preliminary testing of directional naphthalene solidification, significant bubble generation was observed, prompting implementation of a gas handling procedure. Indeed, atmospheric gases have relatively high solubility in liquid naphthalene [160-164]. Fig. 3.3 shows nitrogen gas solubility in liquid naphthalene as a function of pressure; these data were reproduced from Gao et al. [163] and correspond to a liquid naphthalene temperature of 104°C. To calculate the solubility of nitrogen gas in naphthalene at atmospheric pressure, linear regression was utilized to fit these data to the line shown in Fig. 3.3 ($\text{mole fraction N}_2 = 0.003 \cdot P + 0.004$, where P is pressure in MPa, $R^2 = 0.999$, $p < 0.001$). Considering initial solidification experiments that employed ~23 g naphthalene, the solubility limit of N₂ is ~18 mL of N₂ gas at 104°C. While solubility data for helium and argon in naphthalene is unavailable, these data are available for benzene [165, 166] (naphthalene consists of two benzene rings); using those data, the solubility limits were calculated as 3.5 and 0.3 mL for argon and helium, respectively, in 23 g liquid benzene.

A solidification test of naphthalene under helium gas was carried out and the resulting, solidified material was investigated for evidence of gas bubble evolution during solidification; no evidence was found (albeit, if helium bubbles did exist in the structure, they would likely have been difficult to see). Nevertheless, evidence of bubble entrapment was observed in naphthalene solidified under normal atmospheric (air) conditions, thus solidification under helium offered an improvement. Accordingly, helium was selected as the cover gas for suspension preparation due to the relatively low solubility of helium in liquid benzene, helium's general high diffusivity, and the results of the naphthalene solidification test under He gas. All subsequent suspension preparation procedures were carried out under helium gas using a Schlenk line.

The Schlenk line built for this work consists of a double bank vacuum/inert gas manifold (Kemtech America, Inc, 22 mm wall tubing) with eight Teflon, high-vacuum valves (allowing for grease-free operation) that operate four ports. Clear Teflon PFA tubing (chemically compatible with naphthalene) is used for connections between Schlenk flasks and the Schlenk line.

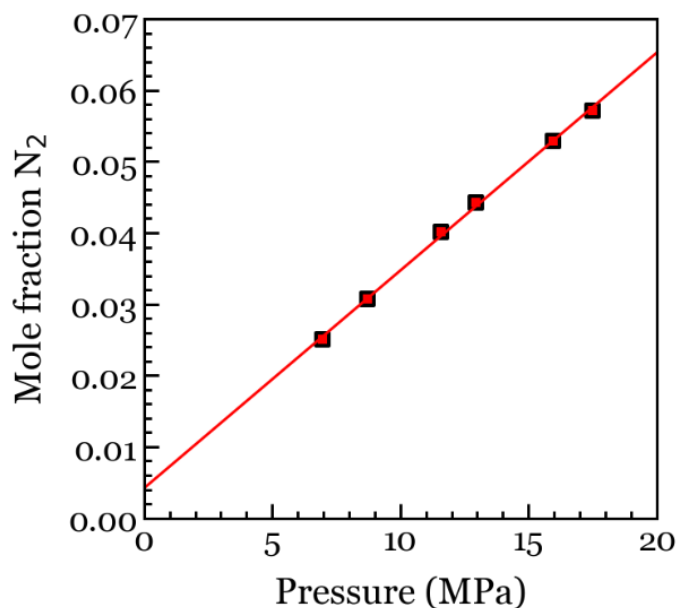


Fig. 3.3. Plot showing nitrogen gas solubility in naphthalene as a function of pressure. These data describe liquid naphthalene held at 104°C; data are reproduced from ref. [163]. The red line in the figure was obtained *via* linear regression (mole fraction N₂ = $0.003 \cdot P + 0.004$, where P is pressure in MPa, $R^2 = 0.999$, $p < 0.001$).

3.3.2. *Naphthalene preparation*

Naphthalene (Sigma Aldrich, St. Louis, MO; 99.6% purity) was vacuum distilled prior to use in suspensions. Distillation methods are generally considered less effective for purifying naphthalene relative to zone-refining due to the formation of azeotropes with common naphthalene impurities [167, 168]. However, some of the most common impurities that pose azeotropic issues also have distribution coefficients that approach one at low concentrations (e.g., benzo[b]thiophene [167, 169, 170] and β -methylnaphthalene [169]); thus, zone-refining alone is also somewhat ineffective for removing those impurities [162, 169]. Given the relatively high initial purity of the as-received naphthalene, the fact that impurities (*i.e.*, surfactant) will be added to “purified” naphthalene to obtain stable particle suspensions, and liquid naphthalene’s high affinity for atmospheric gases [160-164], entrapped gas impurities in the as-received naphthalene are of greater concern relative to solid impurities. Indeed, gas bubbles have been reported to interact with the naphthalene solid/liquid interface under terrestrial gravity conditions [171], and evidence of such was observed in preliminary solidification studies. As these suspensions are being investigated for testing under reduced gravity conditions, this issue is even more potentially detrimental [30, 39, 172, 173].

3.3.3. *Particle drying*

Moisture adsorbed onto particle surfaces has been shown to negatively impact surfactant adsorption when employing apolar suspending fluids [174, 175]; this issue can be mitigated by drying particles prior to incorporation in suspensions [176-178]. Copper particles (spherical, 1 μm , SkySpring Nanomaterials, Inc, Houston, TX) were dried prior to use and otherwise stored in a vacuum desiccator. Batches of Cu particles were dried for 12 h under vacuum in a reaction tube; the reaction tube was partially immersed in a beaker of silicone oil held at $\sim 100^\circ\text{C}$ using a hot

plate. The spherical particle shape and average particle size of the Cu particles before and after drying were verified by particle size analysis using scanning electron microscopy images (diameter = $1.3 \pm 1 \mu\text{m}$, circularity = 0.9 ± 0.1); neither average particle size nor shape was observed to change appreciably after drying (Fig. 3.4 shows an SEM image of Cu particles before and after drying).

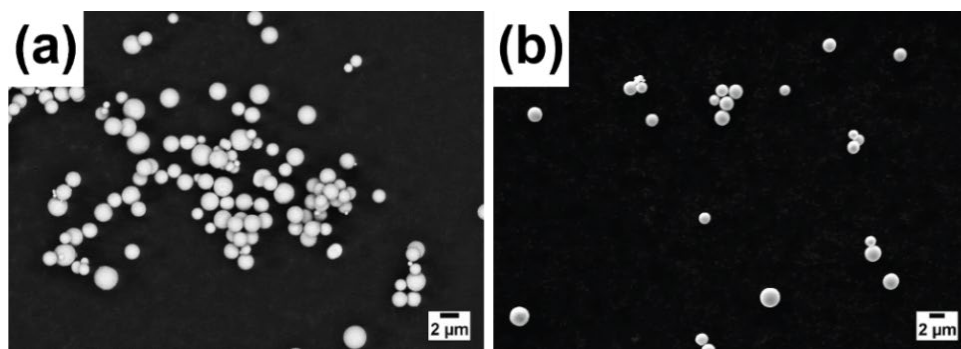


Fig. 3.4. Scanning electron microscopy images of as-received and dried Cu particles used in naphthalene suspensions. The image in (a) shows as-received Cu particles, before vacuum drying; (b) shows particles after vacuum drying for 12 h at $\sim 100^\circ\text{C}$. No obvious signs of particle aggregation are observed from SEM images.

3.3.4. *Surfactant equilibration and suspension preparation*

Surfactant (Aerosol-OT, AOT, Fisher Scientific, Hampton, New Hampshire *or* Hypermer KD-13, Croda Inc., Edison, NJ, USA *or* Pluronic F-68, Fischer Scientific, Hampton, New Hampshire, *or* Triton-X 100, Fischer Scientific, Hampton, New Hampshire) at appropriate weight fractions (0.1, 1, or 2.5 wt.% with respect to intended particle mass, corresponding to 0.05, 0.5, and 1.2 wt.% with respect to naphthalene) was incorporated into vacuum distilled naphthalene *via* stirring for ~ 12 h using a PTFE-coated magnetic stirrer. Schlenk flasks, containing naphthalene/surfactant, were connected to a Schlenk line; gas and vacuum lines were evacuated, and the flask was filled with He gas. The Schlenk flask containing naphthalene/surfactant was

immersed in a beaker of silicone oil that was heated using a hot/stir plate. The temperature of the oil was held at $\sim 90^{\circ}\text{C}$ and aluminum foil was placed over the beaker/flask containing the naphthalene/surfactant to act as a heat reflector. After a 12 h equilibration period, surfactant/naphthalene solutions were taken off of the heat and allowed to solidify.

To create particle suspensions, flasks containing solidified naphthalene/surfactant were removed from the Schlenk line and dried, Cu particles were added at a volume fraction of 5% (corresponding to a Cu particle weight fraction in suspension of 32%). Flasks were reattached to the Schlenk line, the flasks and Schlenk lines (both vacuum and gas lines) were evacuated slowly (to prevent Cu particles from flowing into the lines), and flasks were filled with He gas. Lastly, suspensions were heated to $\sim 90^{\circ}\text{C}$ (*via* flask immersion in silicone oil, as before) and stirred using a PTFE-coated magnetic stirrer for ~ 12 h. Finally, suspensions were sonicated for 2 h in a $\sim 90^{\circ}\text{C}$ water bath. Suspensions were prepared at volumes of either 50 or 100 mL (with equilibration times remaining the same regardless of volume).

3.3.5. Directional solidification

3.3.5.1. Thermal gradient control for naphthalene solidification

Initial naphthalene solidification tests were conducted using a typical freeze-casting set-up (*i.e.*, a mold containing suspension that is temperature controlled at the top and bottom faces providing control over the overall thermal gradient in the sample, but not the thermal gradient within the melt zone, specifically). Numerous suspensions were solidified using this approach, with variations in particle type, size, and volume fraction, as well as surfactant type and weight fraction. In all cases, disordered structures resulted (microstructural directionality with respect to the imposed thermal gradient was not retained over the length of the sample). Fig. 3.5 shows an optical micrograph of a sintered, CuO structure obtained during this initial testing phase where the

solidification direction is from the bottom of the image to the top (the suspension used to fabricate this structure contained 5 vol.% Cu particles; the resulting material was sintered in air, thus the dark, CuO walls show as blue in the image).



Fig. 3.5. Optical micrograph of a naphthalene freeze-cast structure obtained using a gradient temperature freezing set-up. The disordered microstructure shown is of a sintered CuO freeze-cast material where the particle fraction in the suspension was 5 vol.% Cu. The solidification direction is from the bottom of the image to the top.

When the same suspension formulation was solidified using a Bridgman furnace, directional microstructures were obtained (Fig. 3.6 shows a 3D X-ray tomographic reconstruction of the resulting solidified material); thus, it was concluded that the disordered structures obtained using the basic freeze-casting set-up likely resulted from an inadequate control over solidification parameters. This conclusion is consistent with findings from Fabietti *et al.* [[179](#), [180](#)] who reported that instability mechanisms during directional solidification of naphthalene were strongly dependent on the orientation of the interface (which can be influenced by a lack of proper control

over the thermal gradient at the interface [181, 182]). Note: the aforementioned suspension preparation procedures were not used to produce the structures in Fig. 3.5 nor Fig. 3.6, as that procedure was created after these specimens were fabricated (but the same suspension preparation procedure was used to produce both of these structures); these images are shown only to illustrate the importance of a properly controlled thermal gradient during solidification of naphthalene particle suspensions.

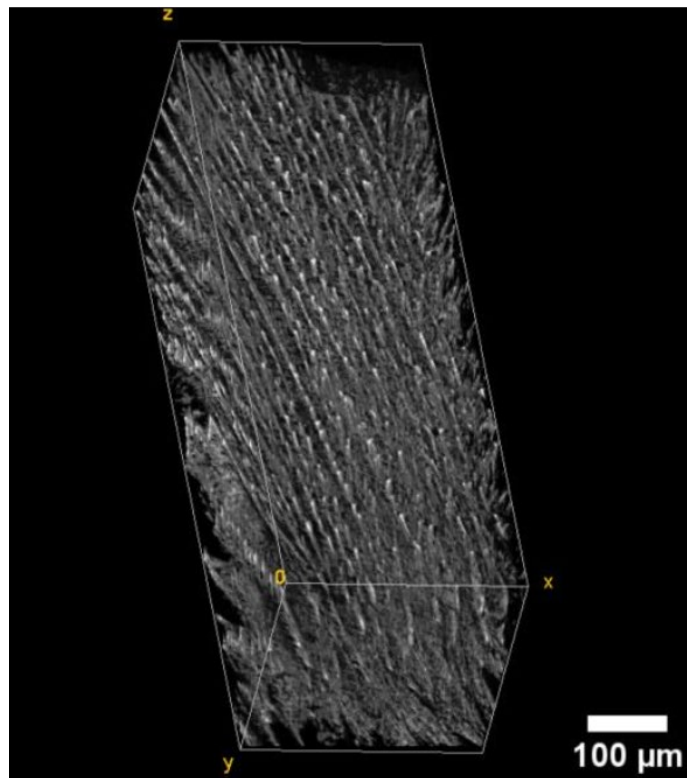


Fig. 3.6. 3D X-ray tomography reconstruction showing the naphthalene freeze-cast structure obtained using a Bridgman furnace. The Cu particle fraction in the naphthalene suspension was 5%; both naphthalene and Cu particles are present in the image, but naphthalene is transparent.

3.3.5.2. *Bridgman solidification*

Experimental results provided in Chapters 6-8 were obtained from directional solidification (of naphthalene suspensions) using a Bridgman furnace. For this furnace, the sample ampoule is held stationary while the furnace is translated vertically upward, promoting upward solidification (a chiller is also located on the upper side of the furnace, thus vertically downward solidification could also be accomplished, but this was not explored here).

The motor driver used for driving the stepper motor that translates the furnace stage was updated for these experiments using a DM542T digital stepper driver with 16 degrees of microstep resolution, corresponding to 200-25,600 pulses per revolution for the system. This provides attainable furnace translation velocities ranging from 0.2 to $>1,000 \mu\text{m} \cdot \text{s}^{-1}$, which is consistent with the growth velocities attainable by the ISS furnace for which the microgravity experiments (which are being defined by this ground testing) are intended (Pore Formation Mobility Investigation, PFMI furnace, attainable solidification velocities, $V = 1\text{-}100 \mu\text{m} \cdot \text{s}^{-1}$ [33, 34, 36, 39]). The controller for the motor driver was also updated to an Arduino microcontroller. The microcontroller code written to operate the furnace is provided in Appendix 3, and calibration tables for software and driver settings relative to furnace translation velocity (obtained *via* physical measurement of this system) are provided in Appendix 4.

The furnace temperature is controlled using an Omega CN370 DIN controller, while the temperature of the cold zone (a copper chiller) is regulated *via* the lab cold water supply (which is actually room temperature). A plot showing the general thermal performance of the furnace is provided in Fig. 3.7, where the temperature setpoint for the furnace was 125°C (dashed line). An

initial temperature overshoot is observed relative to the setpoint but is resolved within the first 20 min of initiating furnace temperature control (this overshoot can more conveniently be avoided by slowly ramping up the furnace, starting at 80°C and increasing the temperature in 20°C increments, waiting for the temperature to stabilize relative to the setpoint prior to increasing the temperature).

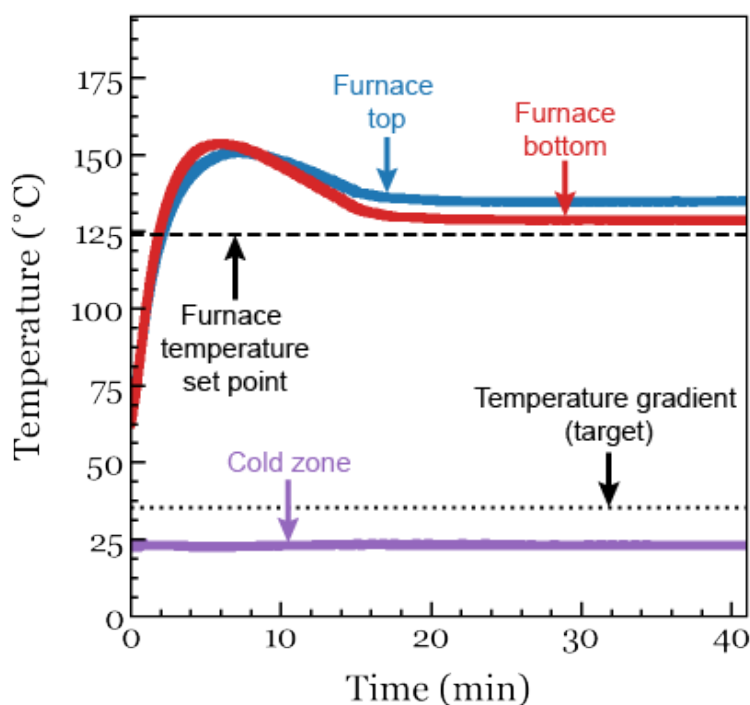


Fig. 3.7. Plot showing the thermal performance of the Bridgman furnace used for directionally solidifying naphthalene particle suspensions. An initial temperature overshoot is observed relative to the temperature set point (dashed line) and is resolved within the first 20 min of initiation of furnace temperature control. Specimens are loaded into the furnace after thermal stabilization. Temperatures within the cold zone (purple line) stay constant throughout experiments.

Quartz ampoules are loaded into the furnace for prewarming (prior to filling with suspension) after thermal stabilization of the furnace. The temperature of the cold zone stays relatively constant at $\sim 25^{\circ}\text{C}$ throughout the experiment (this is true as long as the furnace is not run for more than ~ 3 h straight, at which point the temperature within the cold zone begins to slowly rise without intervention). A temperature gradient between temperature measurement positions at the top and bottom of the furnace is observed; this is likely attributable to convection. This gradient was initially much larger and was minimized (to that shown in Fig. 3.7) with improved furnace insulation (using quartz wool). For suspension solidification, suspensions were poured into prewarmed quartz tubes (10 mm inner diameter, ~ 20 cm fill height) and solidified using furnace translation velocities, $V = 6.5, 38, \text{ and } 80 \mu\text{m} \cdot \text{s}^{-1}$ and a constant thermal gradient of $\sim 35^{\circ}\text{C} \cdot \text{cm}^{-1}$.

3.3.6. *Naphthalene and suspension characterization*

3.3.6.1. Differential scanning calorimetry

A TA Instruments, DSC 250, was used for calorimetry measurements to characterize the melting point for as-received naphthalene, vacuum distilled naphthalene, naphthalene with 1 wt.% AOT, and 5 vol.% Cu suspensions (with 1 wt.% AOT). The temperature accuracy and precision of the instrument is specified at ± 0.05 and $\pm 0.08^{\circ}\text{C}$, respectively. Two cycles of indium calorimetry measurements were conducted to clarify the performance of the specific instrument that was used; for these runs, the melting temperature (T_m , measured using the onset of the melt peak from DSC thermograms) of indium for cycle 1 and 2 were within 0.03°C of each other and within 0.08°C of the indium melting temperature standard (runs using empty pans and an empty instrument were also conducted; those results were unremarkable). Nitrogen is used as the standard purge gas for this instrument. Given the relatively high solubility of nitrogen in liquid naphthalene,

DSC tests were also conducted under helium and compared to results obtained using nitrogen. The difference in T_m with respect to purge gas observed was within normal experimental variation.

During preliminary DSC characterization tests, naphthalene specimens were subjected to two cycles of heating/cooling per test. A systematic increase in T_m was observed for cycle 1 relative to cycle 2; values of T_m for cycle 1 were also often higher than that of pure naphthalene ($T_{m, \text{pure}} = 80.23^\circ\text{C}$ [183]). To better inform experimental design, tests were conducted to examine (i) the effects of heating rate and (ii) the effect of thermal contact between naphthalene and crucibles (Tzero aluminum pans, TA Instruments) on measured values of T_m .

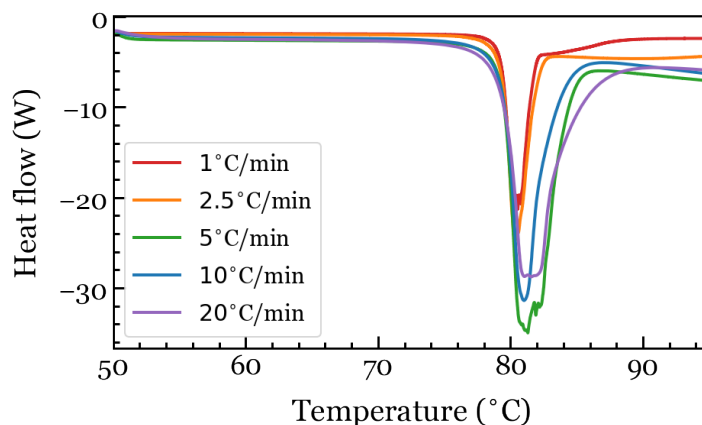


Fig. 3.8. DSC heating cycle curves for naphthalene tested under varying heating rates (1-20 °C/min). The melting temperature of as-received naphthalene, measured using the onset of the melt peak from DSC thermograms, is lowest for the 1 °C/min heating rate condition.

Fig. 3.8 shows DSC heating cycle curves for as-received naphthalene tested with heating rates of 1, 2.5, 5, 10, and 20°C/min; corresponding values of T_m (measured using the onset of peak melt) are provided in Table 3.1. While T_m is physically independent of heating rates, lower heating rates provide better resolution due to thermal gradients that exist in the sample [184]. For this test, higher heating rates corresponded to an increase in measured T_m that was greater than the aforementioned cycle deviation of 0.03°C that was measured for indium (the difference in T_m for the 20°C/min relative to the 1°C/min heating cycle was 0.25°C). Thus, it was determined that a heating rate of 1°C/min was necessary for testing these materials.

Peak heights decrease with decreasing heating rate in Fig. 3.8. The same sample was used for each of the curves shown in Fig. 3.8 and the highest heating rate was tested first; the sample sublimates over time (thus, sample mass decreases) and the y-axis value of heat flow is not normalized by sample mass (to aid in visualization of the melting temperatures). To test the effect of sample mass, the test depicted in Fig. 3.8 was repeated starting at the lowest heating rate; similar results were obtained (*i.e.*, sample mass was not found to be an important parameter for the range of sample masses tested here).

Table 3.1. Melting temperature (T_m) of as-received naphthalene as a function of DSC heating rate. Values of T_m were measured using the onset of the melt peak from DSC thermograms.

Heating rate (°C/min)	Melting temperature (T_m , °C)
1	79.34
2.5	79.42
5	79.52
10	79.56
20	79.59

Table 3.2 shows the results of the thermal contact test. Three specimen/pan interface conditions were tested for as-received naphthalene: (i) one granule of naphthalene with a relatively flat bottom was placed into the DSC pan with a hermetic lid, (ii) the DSC instrument was used to melt naphthalene in the pan (with a hermetic lid affixed) prior to conducting measurements, and (iii) naphthalene was melted and re-solidified in the DSC pan (without a lid) under He (the hermetic lid was then used for DSC testing). In all cases, DSC crucibles were first washed in ethanol. As shown in Table 3.2, T_m for cycle 1 was lowest for the specimen that was melted and re-solidified under helium; the difference between melting temperatures from cycle 1 to 2 (ΔT_m in Table 3.2) was also lowest for this condition ($\Delta T_m = 0.21$ relative to 1.95 and 1.89 for conditions (i) and (ii), respectively). As the effect of melting/solidifying under N_2 relative to He gas was already tested and differences in measured T_m were found to be within normal experimental variance, the differences in measured T_m between specimens melted in the DSC and those melted under He here may be attributable to a crucible lid effect. While evaporate should be removed *via* the purge gas, it is possible that some is condensing on the inside of the lid due during testing, resulting in an inflated measurement of T_m .

Table 3.2. Effect of thermal contact between DSC specimens and crucibles on measured melting temperatures. Melting temperatures (T_m) of as-received naphthalene were measured using DSC under different thermal contact conditions. All tests utilized a heating rate of $1^\circ\text{C}/\text{min}$ and start and end temperatures of 25 and 90°C , respectively. Values of T_m were measured using the onset of the melt peak from DSC thermograms.

Specimen description	Cycle 1 T_m ($^\circ\text{C}$)	Cycle 2 T_m ($^\circ\text{C}$)	ΔT_m
One granule/relatively flat bottom	81.41	79.46	1.95
Melted in DSC before testing	81.33	79.44	1.89
Melted/solidified in pan under He	79.55	79.34	0.21

All DSC results provided in the following were obtained using a heating rate of 1°C/min with specimens melted in Tzero pans under helium gas and closed using hermetic lids. DSC measurements were conducted using start and end temperatures of 25 and 90°C, respectively and two heating/cooling cycles were used for each of 10 specimens measured in each category.

3.3.6.2. Rheometry

Rheological studies were carried out using an Anton Paar MCR 302 rheometer (Anton Paar GmbH, Graz, Austria), equipped with a Peltier temperature controller (P-PTD 200, accuracy ± 0.1 °C). A concentric cylinder (Couette) geometry with a conical bob (CC27, stainless steel with a measuring gap of 1.13 mm), requiring a nominal sample volume of 19.35 mL, was used to determine the viscosity of naphthalene and suspensions. The gap width of 1.13 mm allows for suspensions containing particle/aggregate sizes up to 113 μm to be tested [185] with this system. The concentric cylinder fixture operates under the Searle principle; that is, the inner cylinder (*i.e.*, measuring bob) rotates within the filled sample cup (*i.e.*, the outer cylinder). To homogeneously distribute samples in the shear gap and normalize shear histories of materials studied [186-188], all samples were pre-sheared 60 s at a shear rate, $\dot{\gamma} = 5 \text{ s}^{-1}$ followed by a resting period (no shear) of 180 s prior to beginning measurements.

Fig. 3.9 depicts the measurement limits of this system, including the low torque limit (set by instrument specifications and the Couette geometry employed), which impacts measurements at low shear rate, $\dot{\gamma}$ and the secondary flow limit (based primarily on geometry), which impacts measurements at high $\dot{\gamma}$. The low torque limit boundary was calculated using Eq. 3.1 [189]:

$$\eta > \frac{K \cdot \tau_{min}}{\dot{\gamma}} \quad \text{Eq. 3.1}$$

where η is the minimum measurable viscosity, $\dot{\gamma}$ is the shear rate that corresponds to η in Fig. 3.9, and τ_{min} is the minimum instrument torque (for the MCR 302, $\tau_{min} = 1$ nNm represents the absolute minimum torque for rotational tests). The stress constant, K for the concentric cylinder system was calculated using Eq. 3.2:

$$K = \frac{1}{4\pi l} \left[\frac{1 + \left(\frac{R_o}{R_i}\right)^2}{c_l R_o^2} \right] \quad \text{Eq. 3.2}$$

where l is the bob length (27 mm), R_o and R_i are the radii of the outer and inner cylinders, respectively (14.46 and 13.33 mm), and c_l is the face factor, taken as 1.1.

The highest attainable shear rates (rotation speeds) prior to encountering Taylor secondary flow instabilities [190-193] for the CC27 geometry are represented by the red, “secondary flow limit” boundary in Fig. 3.9 This boundary was calculated using the maximum viscosity threshold for avoiding Taylor vortices [189, 191, 194]:

$$\eta > \frac{(R_o - R_i)^{5/2}}{1,700 \cdot R_i^{1/2}} \rho \dot{\gamma} \quad \text{Eq. 3.3}$$

where ρ is the density of the fluid and the factor 1,700 is valid for Newtonian fluids in the limit of small gaps [189].

Deionized water (a Newtonian fluid with viscosity similar to that of naphthalene) was used to assess limits shown in Fig. 3.9 (black diamond markers). Artifact shear thinning is observed at low shear rate conditions; at $\dot{\gamma} = 5 \text{ s}^{-1}$, $\eta = 1.20 \text{ mPa} \cdot \text{s}$, wherein the measured viscosity is $\sim 0.2 \text{ mPa} \cdot \text{s}$ higher than the expected value of $\eta = 1.00 \text{ mPa} \cdot \text{s}$ for water at 25°C. These shear rates are well outside the low torque limit boundary; thus, this behavior may be attributed to surface tension. Artifact shear thickening is also observed as the shear rate increases; at $\dot{\gamma} = 100 \text{ s}^{-1}$, $\eta =$

1.29 mPa · s, which is ~ 0.29 mPa · s higher than the expected value. Shear rates that corresponded most closely to the expected viscosity were $\dot{\gamma} = 15$ to 30 s^{-1} ; in these cases, the maximum deviation from expected viscosity is 0.03 mPa · s at $\dot{\gamma} = 30 \text{ s}^{-1}$. Similarly, to the low shear rate case, shear rate deviations are not likely attributable to Taylor vortices, specifically, given they fall outside that boundary; other inertia effects may be affecting these measurements, though [189].

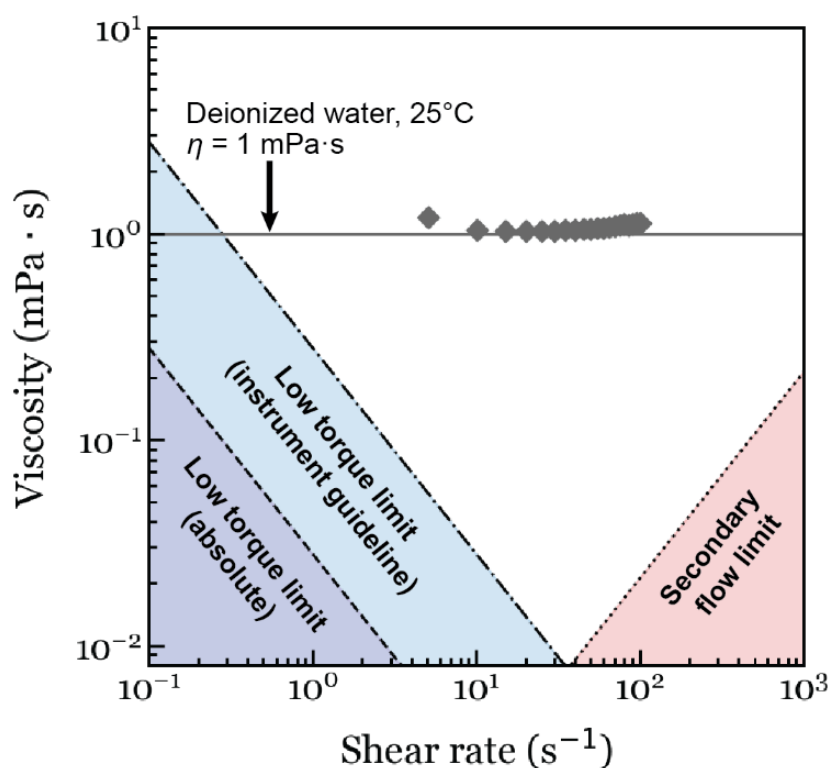


Fig. 3.9. Graph showing the measurement limits of the rheometry system used for characterizing naphthalene suspensions. The data points show viscosity vs. shear rate for deionized water (at 25°C) used to test the instrument capabilities; water is a Newtonian fluid, having a viscosity of $\sim 1 \text{ mPa} \cdot \text{s}$ at 25°C, independent of shear rate. Boundaries for the low torque and secondary flow limit were calculated primarily based on instrument specifications and the employed Couette geometry, respectively (the depicted limits were calculated for naphthalene, specifically, but they do not vary considerably for the water data plotted here).

3.3.7. *Microstructural characterization*

3.3.7.1. *Optical microscopy and measurements of lamellae thickness*

As post-solidification processing steps often result in anisotropic shrinkage [21, 195, 196], microstructure investigations were conducted on as-solidified samples to better correlate solidification/templating processing conditions to microstructural characteristics. For optical microscopy, solidified samples were mounted in epoxy, polished, and imaged using a Wild M3Z stereoscope. Samples were first sectioned into ~2 cm lengths using a glass tube cutter. To prevent reactions between naphthalene and epoxy, the glass was left intact and exposed naphthalene regions (top and bottom of sectioned samples) were wrapped in Teflon tape prior to mounting in epoxy. All samples were stored in a refrigerator (-10°C) prior to analysis to prevent naphthalene sublimation.

Thickness of naphthalene lamellae was measured for directionally solidified suspensions from stitched cross-section images obtained perpendicular to the freezing direction using ImageJ/Fiji [156]. These manual measurements were regionalized using guides drawn on images and only lamellae crossing guides were measured. Fig. 3.10 shows a diagram illustrating how measurements were regionalized; “outer” measurements were taken from a circle drawn at the periphery of cross-section images and “inner” measurements were taken from a ~2.5 mm diameter circle drawn at the center. “Outer-middle” and “middle-inner” measurements were taken from equally spaced circles drawn between the outer and inner circles (thus, the distance between any given circle was ~1.25 mm for the 10 mm sample diameters).

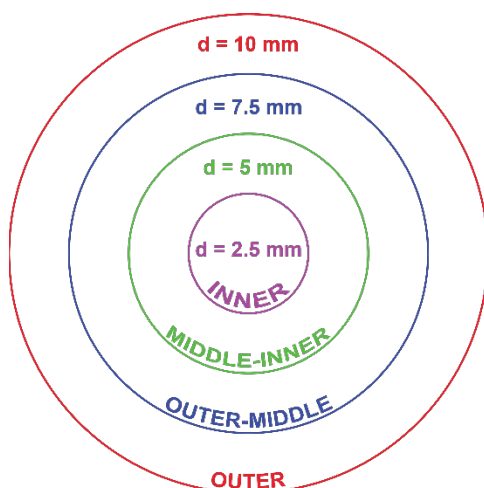


Fig. 3.10. Diagram showing how naphthalene lamellae thickness were obtained with respect to position within samples. “Outer” measurements were taken from a circle drawn at the periphery of cross-section images and “inner” measurements were taken from a ~ 2.5 mm diameter circle drawn at the center. “Outer-middle” and “middle-inner” measurements were taken from equally spaced circles drawn between the outer and inner circles (thus, the distance between any given circle was ~ 1.25 mm for the 10 mm sample diameters).

3.3.7.2. *X-ray computed tomography*

X-ray computed tomography was performed on solidified specimens at the Advanced Photon Source (Argonne National Laboratory, IL), Sector 5-BM-C. Solidified specimens (contained within quartz tubes) were sectioned into ~ 2 cm lengths using a glass tube cutter. To remove the glass, sections were scored along two opposing lengths using a manual glass cutter. After scoring, the cutter was used to lightly tap along the scored lines, and specimens were turned upright and lightly tapped along the circumference of the glass until the glass separated from the samples. (This process was employed after attempting to remove glass with a diamond saw, which resulted in sample damage.) Finally, sectioned samples were further cut down to ~ 0.5 mm cubes

to fit within the parallel X-ray beam and field of view of the camera; sections were re-chilled in a freezer (-10°C) and a chilled razor blade was used to make these cuts. Tomographic experiments were carried out as reported previously [94], wherein radiographic projections of the transmission of monochromatic 45 keV X-rays were captured over a range of 0-180° at 0.18° increments. Greater detail about the experimental set-up, including optics configuration and reconstruction process are described in ref. [94]; a resolution corresponding to a voxel size of 2.4 µm was achieved. Two-dimensional cross-section images were stacked using ImageJ/Fiji [156], and the open-source platform, Slicer 3D [197] was used for 3D volume rendering.

3.4. Statistical analysis

Python was used for all statistical analyses. Data are expressed as mean ± standard deviation. Paired *t*-tests were used to compare means of two groups; one-way ANOVA and post hoc, Tukey-HSD tests were used to compare means between more than two groups. A probability value of $p < 0.01$ was utilized to determine statistical significance.

PART I. AQUEOUS PROCESSING

Chapter 4 and 5 provide experimental results related to directional freeze-casting of an aqueous particle suspension system. Chapter 4 investigates solidification orientation with respect to gravity on microstructural development and Chapter 5 investigates the effect of the initial suspension temperature, where the initial temperatures selected are expected to produce categorically different fluid density profiles in the bulk suspension during the initial solidification phase. Results provided in these chapters provide partial microgravity justification in accordance with RO-1 (Section 1.1).

Chapter 4. Effect of solidification direction on ice-templated microstructures

Substantial material from this chapter is reproduced directly from Scotti *et al.* [89].

4.1. Motivation

Liquid water reaches its maximum density at 4°C ($\sim 1.0000 \text{ g}\cdot\text{cm}^{-3}$) and decreases with both increasing and decreasing temperature: at -2 and 10 °C, the density is $\sim 0.9997 \text{ g}\cdot\text{cm}^{-3}$ [198]. Thus, a monotonic temperature profile imposed during directional solidification creates a non-monotonic density gradient in the water. The direction and magnitude of the density gradient depend on: (i) the direction of solidification and (ii) the temperatures of the liquid at the cold versus hot side of the suspension, respectively. For upward solidification of water (solid ice on bottom; liquid suspension on top; Fig. 4.1-a), the solidification front advances against gravity and the liquid closest to the cold source is less dense than the warmer liquid above and unstable with respect to buoyancy; the cold water (0-4°C) rises.

In alloy solidification, buoyancy-driven convective fluid flow has been shown to result in microstructural inhomogeneities through mechanisms such as dendrite fragmentation, freckling, and the “upstream effect” (dendrites tilt in the direction of flow) [199-210]. For ice-templated, sintered yttria-stabilized zirconia, Bettge *et al.* [211] observed cigar-shaped pores intermixed with typical lamellar channels in cross-sectional images that were taken perpendicular to the solidification direction. The authors posited that the cigar-shaped pore structures resulted from Rayleigh-Bénard convective cells during solidification, which they attributed to the density inversion of water.

Unidirectional ice-templating suspensions are almost always solidified vertically upward, against Earth’s gravity vector [24, 43, 145, 212-215]. The reason for this convention is not

addressed in the literature, but it is likely attributable to ease of set-up. A few cases can be found where horizontal [88, 146, 216] and downward [217-220] solidification techniques were utilized. Of these studies, only Großberger *et al.* [218] acknowledge that the freezing direction may influence microstructures templated during the solidification process. These researchers fabricated ice-templated alumina using a vacuum-induced surface freezing technique. Aqueous suspensions containing 3-13 vol.% Al_2O_3 (500 nm) were held under vacuum and solidification was initiated at the top surface of the suspension; the solidification front proceeded vertically downward, along the gravity vector. The authors reported that lensing defects, which are sometimes observed in ice-templated materials solidified vertically upward [44, 125, 221], were not observed in their materials and posited that their absence could be due to differing gravitational effects during downward (vs. upward) solidification.

As discussed in Section 2.4, lensing defects often arise during solidification as fluid-filled platelets that grow perpendicular to the freezing direction (unlike lamellae, which grow parallel to the freezing direction, Fig. 2.4-a vs. Fig. 2.4-c and -d). After sublimation and sintering, they present as cracks, oriented perpendicular to the freezing direction [85, 125, 221-223]. The formation of lenses during solidification of aqueous particle suspensions has been attributed to a pattern of particle engulfment, rather than rejection, at the solidification interface [25, 29, 67, 85, 122, 123]. During directional solidification, particles are pushed ahead of the solidification front prior to their incorporation within interdendritic space; this creates an enriched particle region (or “particle accumulation layer”) that is located immediately ahead of the solid/liquid interface. During upward solidification, particle sedimentation acts to further increase the particle fraction within the accumulation region. If the particle fraction at the interface exceeds a so-called “breakthrough concentration” [124], ice dendrites are unable to propagate through the particle-enriched region.

The particles within the accumulation region are engulfed by the solid/liquid interface and a particle-free ice layer forms immediately thereafter; this process may repeat provided water and particles are available for incorporation in the ice/particle composite. For downward solidification, particles sediment away from the solidification interface; thus, sedimentation acts to deplete the particle fraction within the accumulation region.

Großberger *et al.* [218] calculated the sedimentation velocity of their suspended, submicron particles (~ 500 nm Al_2O_3) as $0.3 \mu\text{m}\cdot\text{s}^{-1}$ and determined that, for upward solidification, the sedimentation velocity would have been too slow relative to the solidification velocity ($30 \mu\text{m}\cdot\text{s}^{-1}$) to cause an appreciable build-up of particles at the interface. On this basis, the authors argued that gravitational effects were too weak to contribute to ice lens development during solidification of submicron particle suspensions; thus, a different factor must be responsible for their absence in materials fabricated via the downward solidification, vacuum-induced surface freezing technique. However, upward solidification control experiments were not carried out and other gravity-driven effects (*e.g.*, buoyancy-driven convective flow of the liquid) were not considered.

In a previous study using parabolic flights [130], we investigated the effect of gravity during upward solidification of aqueous suspensions (5-20 wt.%) of nanometric TiO_2 by comparing sintered microstructures of materials solidified under normal terrestrial gravity (1 g) to those solidified under reduced gravity (*i.e.*, Martian, lunar and micro-gravity, corresponding to 0.38g, 0.16g and ~ 0 g). Lensing defects were observed in samples solidified from the highest weight fraction suspensions (20 wt.% TiO_2) that were solidified upward under 1g, but not under any of the reduced gravity conditions. The particle size employed (10-30 nm) was smaller than those employed for the 500 nm particles employed by Großberger *et al.* [218] (thus, provided that,

in both cases, the supplier-provided particle sizes are accurate, the sedimentation rates for the TiO_2 particles would be slower). Additional microstructural differences were observed, including improved homogeneity of wall orientation in samples solidified under reduced gravity. In all cases, solidification proceeded vertically upward and the microstructural differences between samples solidified under reduced and terrestrial gravity were attributed to gravity-driven convective fluid flow (*i.e.*, liquid buoyancy) during solidification.

Here, the effect of solidification direction is investigated under constant terrestrial gravity ($1g$), on ice-templated microstructures to better understand the role of buoyancy-driven fluid motion during solidification on the ice-templating process. Aqueous suspensions of TiO_2 nanoparticles (10-30 nm, the same as for our previous study [[130](#)]) are solidified upward (opposite gravity; solid on bottom, liquid on top), downward (with gravity, liquid on bottom, solid on top), and horizontally (perpendicular to gravity), as depicted in Fig. 4.1. Microstructural investigation of sintered samples provides evidence that buoyancy-driven convective fluid flow induces microstructural inhomogeneities in samples solidified upward; no such evidence is observed in samples solidified in the downward nor horizontal orientations. This is consistent with the hypothesis that, during downward (and possibly horizontal) solidification, buoyancy-driven fluid motion occurs far enough away from the interface that the disruption of dendritic growth at the interface is minimized. This is the first study that systematically investigates the effect of solidification direction on microstructures created *via* the ice-templating (and the freeze-casting) technique.

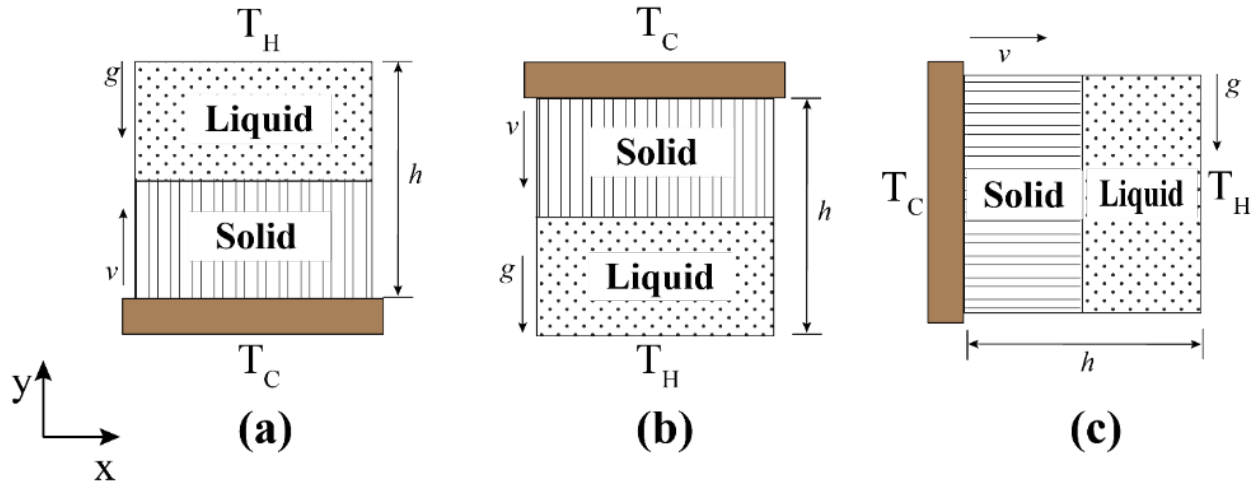


Fig. 4.1. Diagram showing the experimental set-up used for the solidification orientation study. The image in (a) is the “Up” configuration (solid on bottom, liquid on top, solidification front proceeds vertically upward, v , against gravity, g), (b) shows the “Down” configuration (liquid on bottom, solid on top, solidification proceeds downward, along the gravity vector, and (c) shows the “Horizontal,” configuration, where solidification proceeds perpendicular to gravity. T_H and T_C represent the hot and cold side of the mold, respectively, and h is the mold height (the mold is filled completely with the TiO_2 aqueous suspension). Figure extracted without modification, ref. [89].

4.2. Results

4.2.1. Solidification, porosity, and shrinkage

The temperature of the freezing substrate, recorded throughout solidification using a J-type thermocouple, was 228 ± 4 K. Statistically significant differences between freezing substrate temperatures for temperatures acquired when samples were placed on the substrate to those for which they were taken off were not detected. Similarly, the freezing substrate temperature did not vary significantly based on solidification direction. Solidification times were estimated by visual inspection at ~ 35 - 45 s; thus, average solidification velocity for the ~ 3 mm sample height was $75 \pm 10 \mu\text{m} \cdot \text{s}^{-1}$.

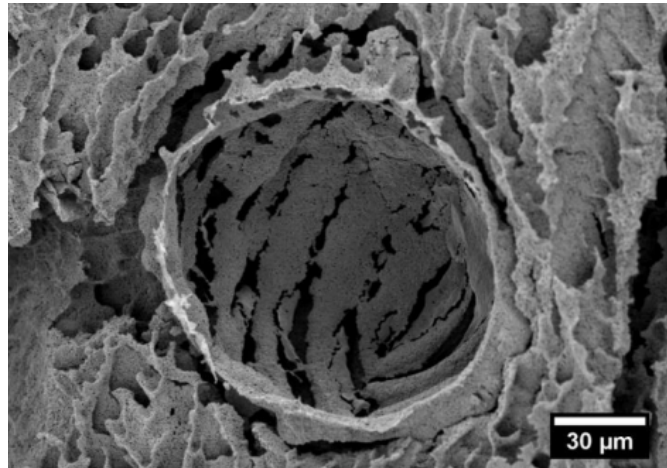


Fig. 4.2. Scanning electron microscopy image of a bubble defect in sintered TiO_2 freeze-cast material solidified vertically downward. The SEM image shows a fractured surface of the freeze-cast material obtained by directionally solidifying an aqueous suspension of 40 wt.% (15 vol.%) TiO_2 particles vertically downward with respect to the gravity vector.

Horizontal and downward solidification requires suspension filling procedures that minimize the transfer of air pockets. Whereas air bubbles rise to the suspension surface during upward solidification, they collect at the solid/liquid interface during downward and horizontal solidification and interact with the solid liquid interface, promoting bubble defects in resulting microstructures [32, 224, 225]. Fig. 4.2 shows an SEM image of a bubble defect in a fractured cross-section of a TiO_2 freeze-cast structure obtained from a 40 wt.% TiO_2 suspension solidified in the downward configuration. No microstructural data were obtained from samples containing bubble-defects and those samples are not included in the sample count shown in Table 4.1.

Macroscopic sintering shrinkage, measured as the change in diameter after solidification relative to that measured after sintering, was $25\pm 5\%$ without statistically significant differences present in terms of TiO₂ weight fraction or solidification direction. Macroscopic porosity, measured by image analysis, was observed to decrease with increasing weight fractions of TiO₂ (51 ± 10 , 48 ± 7 , and $42\pm 9\%$ for 30, 40, and 50 wt.% TiO₂, respectively; Table 4.1 Table 4.1). This is consistent with previous investigations [143, 214] and expected because macroporosity obtained after sublimation and sintering is dependent on the total volume fraction of ice; thus, of fluid in the initial suspension. Significant differences in porosity were not found among the three solidification directions for any given TiO₂ weight fraction.

Table 4.1. Summary of microstructure parameters (pore and wall width, and porosity) of sintered TiO₂ freeze-cast materials directionally solidified against, with, and perpendicular to the gravity vector. A total of 90 samples were analyzed (N , number of samples), including ten samples for each weight fraction (30, 40, and 50 wt.%, corresponding to ~ 10 , 15, and 21 vol.%), solidified under each orientation with respect to gravity, including: against (“Up”), with (“Down”), and perpendicular to (“Horizontal”) the gravity vector.

TiO ₂ (wt.%)	Direction	N	Pore width (μm)			Wall width (μm)			Porosity (%)
			Overall	Center	Radial	Overall	Center	Radial	
30 (10 vol.%)	Up	10	27 $\pm$ 22	39 $\pm$ 27	19 $\pm$ 12	32 $\pm$ 22	56 $\pm$ 37	30 $\pm$ 22	51 $\pm$ 10
	Down	10	7 $\pm$ 5	6 $\pm$ 4	6 $\pm$ 4	8 $\pm$ 6	8 $\pm$ 5	9 $\pm$ 6	
	Horizontal	10	10 $\pm$ 6	11 $\pm$ 6	8 $\pm$ 4	14 $\pm$ 7	14 $\pm$ 7	14 $\pm$ 7	
40 (15 vol.%)	Up	10	27 $\pm$ 18	30 $\pm$ 18	23 $\pm$ 13	30 $\pm$ 16	36 $\pm$ 19	29 $\pm$ 14	48 $\pm$ 7
	Down	10	17 $\pm$ 13	16 $\pm$ 9	17 $\pm$ 10	15 $\pm$ 8	15 $\pm$ 8	15 $\pm$ 8	
	Horizontal	10	8 $\pm$ 5	7 $\pm$ 4	8 $\pm$ 4	8 $\pm$ 4	8 $\pm$ 4	8 $\pm$ 4	
50 (21 vol.%)	Up	10	51 $\pm$ 35	51 $\pm$ 33	41 $\pm$ 26	34 $\pm$ 19	40 $\pm$ 21	33 $\pm$ 16	42 $\pm$ 9
	Down	10	16 $\pm$ 12	16 $\pm$ 10	16 $\pm$ 9	18 $\pm$ 8	18 $\pm$ 9	18 $\pm$ 8	
	Horizontal	10	16 $\pm$ 9	15 $\pm$ 8	14 $\pm$ 8	11 $\pm$ 7	11 $\pm$ 6	12 $\pm$ 7	

4.2.2. Rayleigh-Bénard convective cells

Fig. 4.3 shows polished cross-sections of sintered TiO₂ freeze-cast materials obtained by solidifying suspensions with 40 wt.% TiO₂: (a) upward, (b) downward, and (c) horizontally with respect to the direction of gravity. The center of each image corresponds roughly to the center of each respective sintered sample, *i.e.*, the images extend over the full diameter and height of the sintered samples. Overall dimensions of the samples shown in Fig. 4.3 are: (a) 9 mm length (diameter), 2.5 mm height, (b) 10 mm length; 2.2 mm height, and (c) 9.6 mm length; 2.1 mm height. The reduction in length (diameter) and height from the original solidified dimensions (15 mm diameter, 3 mm height) are attributed to sintering shrinkage and error. Error related to cutting and polishing samples to obtain images that correspond exactly to the center of samples accounts for a reduction of ± 2 mm of the true sample diameter (*i.e.*, the center of images shown are located within ~ 2 mm of the true geometric center of each sample).

The images in Fig. 4.3 (b) and (c) are rotated such that the first- and last-to-solidify regions of each image are shown at the bottom and top, respectively, for all three cross-sections (Fig. 4.3, a-c). Significant misalignment of the wall orientation (*i.e.*, the ice dendrite orientation) with respect to the imposed temperature gradient is observed for the sample solidified upward, Fig. 4.3 (a). Considering a maximum angle of 90° as “full alignment” (wall orientation is parallel to the induced thermal gradient), tilt angles (θ) as low as 50 to 65° with respect to the base of the sample are observed. Misalignment directions correspond to two semicircular regions (red dotted arrows in Fig. 4.3-a) with approximate mirror symmetry about the center line (vertical red dotted line in Fig. 4.3-a). This pattern was consistently observed in nearly all 20 cross-sections of 30 and 40 wt.% TiO₂ suspensions solidified upward (the absence of this pattern for 50 wt.% TiO₂ suspensions solidified upward is attributed to lensing, which is discussed in the following). Minimal

misalignment (~ 70 to 89°) was observed for downward (Fig. 4.3-b) and horizontal (Fig. 4.3-c) solidification. Moreover, no consistent pattern of misalignment was observed across specimens solidified downward nor horizontally (Fig. 4.3-b and c). The location and direction of misalignment, when it existed ($\sim 50\%$ of samples), appeared to be random, and may have resulted from post-solidification processing steps (*i.e.*, anisotropic sintering shrinkage).

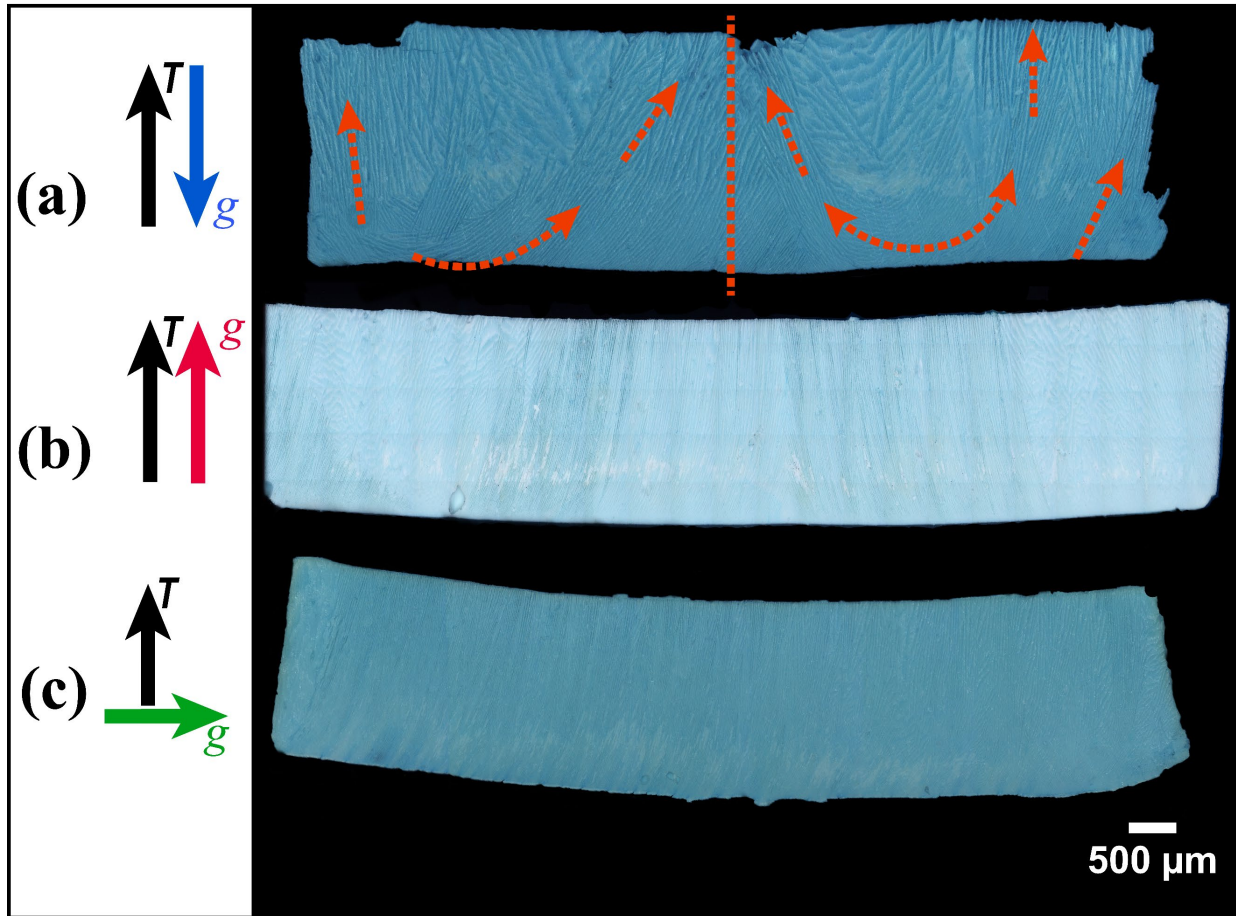


Fig. 4.3. Optical micrographs showing the effect of solidification direction on ice-templated microstructures for 40 wt.% TiO_2 suspensions. Images show longitudinal cross-sections of sintered, freeze-cast TiO_2 obtained by directional solidification of aqueous suspensions containing 40 wt.% TiO_2 nanoparticles (15 vol.% TiO_2), where solidification direction is: (a) upward, (b) downward, and (c) horizontal with respect to the gravity vector. Images in (b) and (c) are rotated such that the first- and last-to-solidify regions of the sample are shown at the bottom and top of all images. Here, T and g are the directions of the imposed temperature gradient and gravity, respectively, during solidification. The full height (~ 3 mm, minus sintering shrinkage of $\sim 25\%$) and full diameter (~ 15 mm, ± 2 mm error, minus sintering shrinkage) of each sample are shown. Error related to cutting and polishing samples to obtain images that correspond exactly to the center of samples accounts for a reduction of ~ 2 mm of the true sample diameter (*i.e.*, the center of images shown are located within ~ 2 mm of the true geometric center of each sample). Figure extracted without modification, ref. [89].

Tankin *et al.* [90] investigated the upward and downward solidification of water using a Mach-Zehnder interferometer. For the upward solidification of water, the cold plate temperature was reduced from 23 to -5°C , while the top of the fluid was held at $\sim 23^{\circ}\text{C}$ (the solidification velocity was not reported). Immediately upon cooling, a parallel row of Rayleigh-Bénard convective cells was observed in the fluid region closest to the cold source; individual cells extended vertically upward from the cold source to the $\sim 6^{\circ}\text{C}$ isotherm (2°C higher than the density maximum of water). With continued cooling and initiation of freezing, the size of individual cells increased while the total number of cells decreased (from three to two cells). An interferogram [90] showing the parallel row of convective cells observed immediately after onset of freezing is shown in Fig. 4.4(a). The red, dashed line in Fig. 4.4(a) indicates the approximate position of the solid/liquid interface (which advanced upward in the direction of the induced temperature gradient, T); the convective cells are located immediately above the solid/liquid interface. As shown in Fig. 4.4 (b), convective cells were also observed for the downward solidification configuration. Here, the solid/liquid interface is located at the top of the image and solidification proceeds downward. For downward solidification, the row of convective cells was confined to the region where the fluid temperature was $\sim 4^{\circ}\text{C}$ or greater; thus, they did not appear to interact directly with the solidification front. A similar observation was made by Brewster *et al.* [226], for the downward solidification of water that contained tracer particles ($40\text{ }\mu\text{m}$ in diameter).

The microstructural pattern present in Fig. 4.3 (a) for upward solidification of aqueous suspensions of 40 wt.% TiO_2 is consistent with the convection pattern observed by Tankin *et al.* [90] for the upward solidification of water (Fig. 4.4-a). Assuming that the microstructural pattern shown in Fig. 4.3 (a) is an imprint of solidification events, it can be concluded that at least two

Rayleigh-Bénard convective cells were present during solidification of these samples. However, since these structures are visualized after solidification, the microstructural imprint is not reflective of the convective cells themselves, but rather a consequence of their interaction with the solid/liquid interface. Further, it is possible that post-solidification processing steps (*i.e.*, sublimation and sintering) may have introduced microstructural changes to the structures templated during solidification. Lastly, additional cells may have been identifiable with three-dimensional imaging techniques. *In-situ* observations of the solidification process, *e.g.*, via synchrotron X-ray tomography, may help clarify these observations.

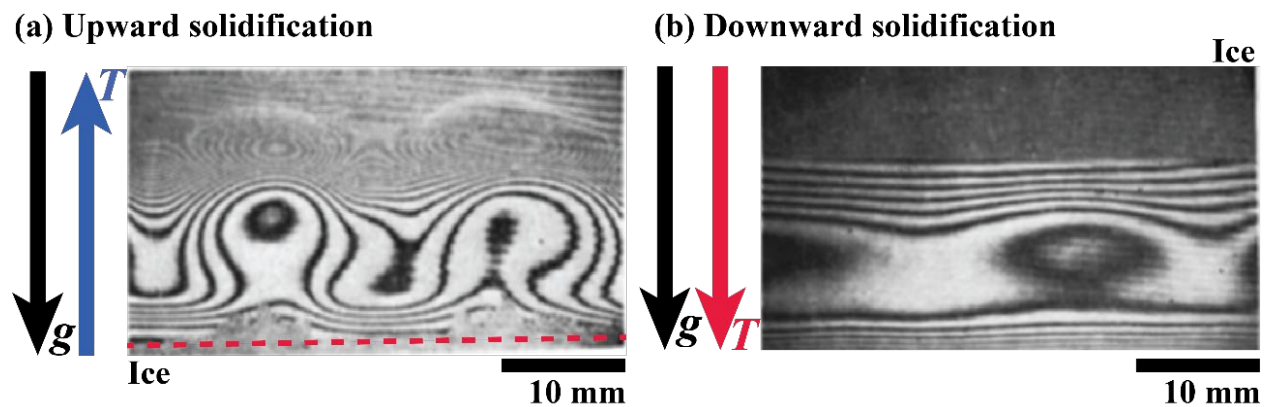


Fig. 4.4. Interferograms show convective currents during (a) upward and (b) downward solidification of water. The direction of freezing is indicated by T (direction of the imposed temperature gradient); the direction of the gravity vector is shown by g , and the red, dashed line in (a) marks the approximate position of the solid/liquid interface. In (b), the solid/liquid interface is located near the top of the image. Figure extracted from Ref. [227] with modification.

4.2.3. Interdendritic fluid flow

As discussed above, significant microstructural misalignment was observed for samples solidified upward, but not for samples solidified downward or horizontally. Deville *et al.* [140, 144, 146] suggest that microstructural misalignment in ice-templated materials results from an imbalance between the anisotropic growth kinetics of hexagonal ice and the induced thermal gradient. Growth along the basal face of ice (typically oriented perpendicular to the direction of heat flow [228-230]) is about 31 and 43% slower than growth along the prism and secondary prism faces, respectively [231]. The authors found that microstructural tilting *decreased* with *increasing* solidification velocity; however, the fastest solidification velocity explored was $\sim 3 \mu\text{m}\cdot\text{s}^{-1}$ [144] (here, solidification velocity is significantly faster, $75\pm 10 \mu\text{m}\cdot\text{s}^{-1}$). Microstructural tilting may also occur due to buoyancy driven convection [153, 181, 232], which can be induced *via* from thermal conductivity mismatches between the solid ice, liquid suspension, and mold material [233, 234] (as an example). These mechanisms should be independent of the direction of solidification. Given that significant tilting was not observed in either downward nor horizontal solidification configurations, an alternative explanation is proposed for the tilting observed here (specifically, for the upward solidification of aqueous TiO_2 suspensions at relatively high solidification velocities, $75\pm 10 \mu\text{m}\cdot\text{s}^{-1}$).

The tilting shown in Fig. 4.3 (a) is consistent with the so-called “upstream effect” described in seawater [131, 134] and alloy solidification [135-137] literature, wherein dendrites tilt in the direction of buoyancy-driven convective fluid motion [235]. The buoyancy-driven convective fluid motion arises from density gradients due to temperature and/or concentration gradients [236]. The upward solidification of aqueous TiO_2 suspensions can be directly compared to the downward solidification of sea ice because, in both cases, the liquid at the solid/liquid interface is buoyant

(due to the salinity of seawater, a density inversion in the liquid is not observed during solidification at typical undercoolings [200, 237]). Thus, the liquid at the solid/liquid interface is denser than the bulk liquid below, promoting buoyancy-driven, interdendritic fluid motion (the warmer, less dense seawater from below flows upward and displaces the colder, denser seawater at the interface). Phase-field modeling and subsequent experimental work on the upward solidification of a succinonitrile-3.5 wt.% H₂O alloy melt with forced, interdendritic flow (induced via shear flow initiated by a rotating magnetic field) revealed a similar effect [83].

The upstream effect results from interdendritic fluid motion, *i.e.*, fluid motion that is largely confined to the mushy region (the region between the fully solidified solid and the fully liquid suspension, where solid ice and liquid suspension coexist [28]). Interdendritic fluid motion can be driven by the shear flow (flow across the solid/liquid interface) produced by macroscopic convective fluid motion in the bulk liquid, ahead of the solid/liquid interface (described here as a row of two Rayleigh-Bénard convective cells). It can also occur independent of the macroscopic convective pattern, with buoyancy remaining the driving force [28]. In either case, interdendritic fluid flow is weaker than flow resulting from the macroscopic convection described above (approximately one-thousandth that of the bulk fluid region [138]).

Interdendritic fluid flow also offers an explanation of the observations of asymmetric, one-sided dendritic arms commonly reported in ice-templating studies for both particle suspensions [20, 139-146] and polymer solutions [147, 148], where secondary arm growth is suppressed on the “downstream” side [83, 149, 150]. This effect was described in terms of Fig. 2.6 (Section 2.6), where shear flow is depicted to be produced as a result of macroscopic convective cells located within the bulk suspension region (ahead of the solid/liquid interface); the direction of the shear flow is consistent with a macroscopic curvature of the interface (specifically, concave).

Consequences of interdendritic flow include: (i) tilting of ice lamellae and (ii) suppression of secondary dendrite arms on the “downstream” side. The flow direction promotes growth of dendritic arms on the upstream side, where heat is more easily transported away from the lamellae (*via* fluid flow) than on the downstream side. The warmer fluid on the downstream side promotes melting and fragmentation of secondary dendritic arms [137, 152].

Fig. 4.5 shows SEM images of polished cross-sections of sintered TiO₂ obtained after upward solidification of a 30 wt.% suspension and Fig. 4.6 (a) shows an optical micrograph of a full polished cross-section of the same sample type. The overall microstructural pattern in Fig. 4.6 (a) is similar to that shown in Fig. 4.3 (a) for 40 wt.% TiO₂ solidified upward, *i.e.*, two semicircular regions with approximate mirror symmetry about the center line are observed. In terms of Fig. 4.6, the image shown in Fig. 4.5 (a) is obtained from the left-hand side of the image, whereas (b) and (c) correspond to the central-right and right-hand side, respectively. Fig. 4.5 (d) and (e) are lower magnification images of (a) and (c), respectively. In all images, epoxy-filled pores are visible as dark regions and sintered, TiO₂ particle walls as light regions.

In Fig. 4.5, evidence of asymmetric, secondary dendritic arms is observed on the right-hand side of particle walls in Fig. 4.5 (a, d) and on the left-hand side of particle walls in Fig. 4.5 (c, e; some are marked with red arrows), which is consistent with the upstream effect described above. In Fig. 4.5 (a, d), secondary dendritic arms are observed on the right-hand side of TiO₂ walls, which corresponds to the left-hand side of ice dendrites (represented by epoxy, shown as dark regions); thus, secondary dendritic arms are suppressed on the right-hand, downstream side of ice dendrites, as shown in the schematic below Fig. 4.5(a). In Fig. 4.5(c, e), the direction of dendrite tilt changes, and the schematic below Fig. 4.5(c) shows the corresponding change in fluid flow direction. Secondary dendritic arms are now absent on the left-hand side of ice dendrites,

which still corresponds to the downstream side; secondary arms are present on the right-hand, upstream side.

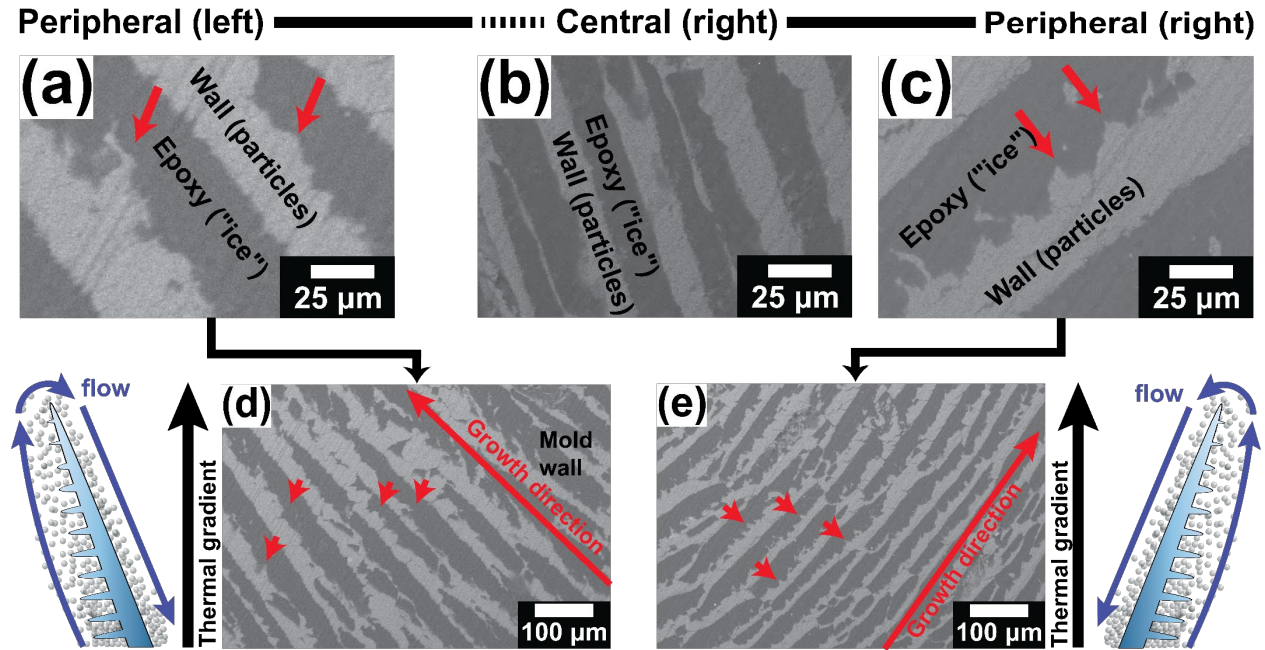


Fig. 4.5. SEM micrographs showing asymmetric secondary dendrite arms in TiO_2 freeze-cast structures that were solidified vertically upwards. Images are of polished longitudinal cross-sections of the sintered, TiO_2 freeze-cast structure; the aqueous suspension contained 30 wt.% TiO_2 nanoparticles (10 vol.% TiO_2), which was solidified against gravity. Images in the top row are obtained from the: (a) left-peripheral (near mold wall), (b) central-right, and (c) right-peripheral (near mold wall) regions of the sample; (d) and (e) are lower magnification images of (a) and (c) respectively. Epoxy-filled pores are the dark regions in the images and sintered TiO_2 particle walls are the light regions. Asymmetric secondary dendritic arms (red arrows) are observed in (a, d) and (c, e) where the ice growth direction diverges significantly from the direction of the imposed thermal gradient; these features are minimized in (b) where the tilt angle (θ ; ice growth direction) is minimized in the central region of the sample relative to the outer regions (near the mold wall). Figure extracted without modification, ref. [89].



Fig. 4.6. Optical micrograph showing the effect of solidification direction on ice-templated microstructures for 30 wt.% TiO_2 suspensions. Images show longitudinal cross-sections of sintered, freeze-cast TiO_2 obtained by directional solidification of aqueous suspensions containing 30 wt.% TiO_2 nanoparticles (10 vol.% TiO_2), where solidification direction is (a) upward and (b) downward. The image in (b) is rotated such that the first- and last-to-solidify regions of the sample are shown at the bottom and top of the image, respectively. Here, T and g are the directions of the imposed temperature gradient and gravity, respectively, during solidification. The full height (3 mm, minus sintering shrinkage of $\sim 25\%$) and full diameter (~ 15 mm, ± 2 mm error, minus sintering shrinkage) of each sample is shown. Error related to cutting and polishing samples to obtain images that correspond exactly to the center of samples accounts for a reduction of ~ 2 mm of the true sample diameter (i.e., the center of images shown are located within ~ 2 mm of the true geometric center of each sample). Figure extracted without modification, ref. [89].

Table 4.2 provides summary statistics for primary and secondary dendritic arm spacing and length for 30 wt.% TiO₂ suspensions solidified upward, downward, and horizontally based on analysis of SEM images for nine sintered samples (three samples per solidification orientation, where secondary spacing is measured from wall imprints). Significant differences in spacing between secondary dendrite arms (λ_2) was not found when comparing measurements between the left and the right regions ($28 \pm 15 \mu\text{m}$ and 28 ± 16 , respectively). Similarly, mean secondary arm length did not vary between left and right regions ($11 \pm 4 \mu\text{m}$ for both). Relative to the images shown in Fig. 4.5 (a) and (c), asymmetric dendritic arms and microstructural tilting are suppressed in Fig. 4.5 (b), which corresponds to the central region of the sample. This is consistent with a reduction of interdendritic flow in the central portion of samples. Here, pores (dendrites) are better aligned with the imposed thermal gradient relative to the outer/peripheral regions (closer to the mold wall), where pores (dendrites) show greater relative tilt with respect to the induced thermal gradient.

Fig. 4.7 shows SEM images of polished cross-sections of sintered TiO₂ obtained by solidifying suspensions with a 30 wt.% initial particle fraction (a, c) vertically downward (with gravity) and (b, d) horizontally (perpendicular to gravity). Evidence of short, secondary dendritic arms are observed on both sides of the sintered-particle walls (yellow arrows). Statistically-significant differences in terms of secondary arm spacing or length were not found when comparing those measured on the right-hand side to those measured on the left-hand side of sintered particle walls for downward nor for horizontal solidification (Table 4.2).

Bridging between particle walls is observed throughout these samples; some bridges are marked by yellow arrows in Fig. 4.7 (c, d). These bridges appear similar to those observed by Cheng *et al.* [238, 239] for the directional freeze-casting of hydroxyapatite particles suspended in

water containing H_2O_2 (where H_2O_2 introduces gas bubbles in the suspension and microporosity in sintered samples); thus, these bridges may have occurred as a result of residual gas within the suspension. As described earlier, whereas air bubbles rise to the suspension surface during upward solidification, they collect at the solid/liquid interface during downward and horizontal solidification.

Here, microstructural evidence of symmetric, secondary dendritic arm growth (present on both sides of lamellae) was shown for downward and horizontal solidification with evidence that primary arms were not significantly tilted with respect to the imposed thermal gradient. By contrast, microstructural evidence of tilted lamellae and asymmetric secondary dendrite arms (secondary arms present on one side of lamellae) were presented for the upward solidification. These results suggest a reduction (or suppression) of fluid flow parallel to the solidification interface for downward and horizontal solidification.

Table 4.2. Effect of solidification direction on primary and secondary dendrite spacing and secondary arm length. Summary statistics are based on SEM investigation of nine sintered samples (N = number of samples) produced from 30% wt.% TiO_2 (10 vol.% TiO_2) aqueous suspensions solidified against (“Up”), parallel to (“Down”), and perpendicular to (“Horizontal”) the gravity vector; secondary arm parameters are measured based on the imprint on TiO_2 walls.

Direction	N	Primary spacing (λ_1 , μm)	Secondary spacing (λ_2 , μm)			Secondary arm length (μm)		
			Overall	Left	Right	Overall	Left	Right
Up	3	25±17	28±15	28±15	28±16	11±4	11±4	10±5
Down	3	14±7	8±4	8±4	8±3	3±1	3±1	3±1
Horizontal	3	8±2	10±4	10±3	10±4	3±1	3±1	3±1

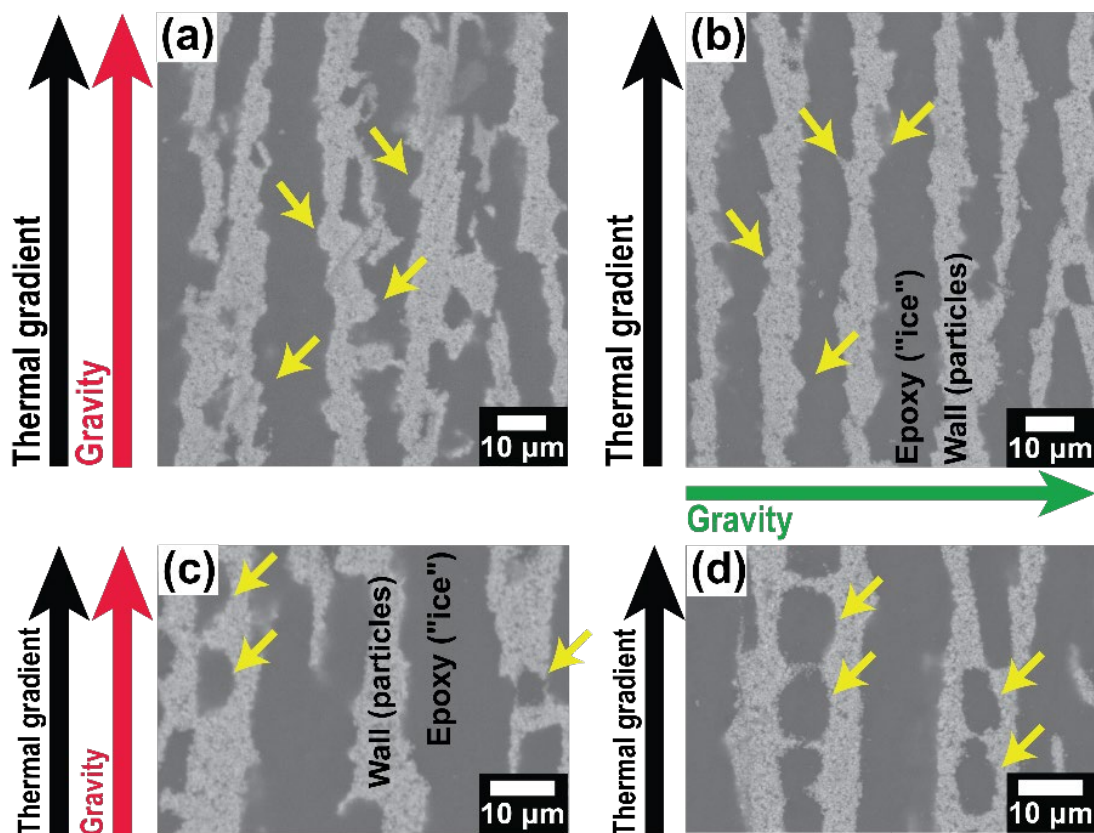


Fig. 4.7. SEM micrographs showing microstructural evidence of symmetric, secondary dendrite arms in TiO₂ freeze-cast structures that were solidified downwards and horizontally. SEM images are of polished longitudinal cross-sections of the sintered, TiO₂ freeze-cast structure; the aqueous suspension contained 30 wt.% TiO₂ nanoparticles (10 vol.% TiO₂), which was solidified (a, c) vertically downward (with gravity) and (b, d) horizontally (perpendicular to the gravity vector). All images are rotated such that the “base” and “tops” of the samples (first- and last-to-solidify, respectively) are shown at the bottom and top of all images. Epoxy-filled pores are the dark regions of the images whereas sintered TiO₂ walls are shown as light regions. Minimal microstructural tilting (divergence between the imposed thermal gradient and the dendrite growth direction) is observed and secondary dendritic arms are relatively symmetric (marked by yellow arrows). Micrographs in (c) and (d) show microstructural bridging (marked by yellow arrows) for both the downward and horizontally solidified samples. Figure extracted without modification, ref. [89].

4.2.4. *Ice lens defects*

Lensing defects were described in Section 2.4 and depicted in Fig. 2.4 as a transition from lamellar/dendritic structures (Fig. 2.4-a, b, unidirectional structures oriented parallel to the direction of the imposed thermal gradient) to spears (Fig. 2.4-c, dendrites that are highly interconnected through excessive secondary arm growth) and banding (Fig. 2.4-d, structures that are aligned perpendicular to the imposed thermal gradient). Both spearing and banding are considered lens defects [29]. As described earlier, lensing defects are the most commonly observed defect in ice-templated materials and their existence significantly compromises mechanical properties [44].

Although various hypotheses have been proposed to explain the development of lensing during solidification [23, 26, 29, 42, 85, 86, 120, 121], most of the ice-templating literature attributes lens formation to particle engulfment, rather than particle rejection, at the solidification interface [25, 67, 85, 122, 123]. During directional solidification, particles are first rejected/pushed by the advancing solid/liquid interface before they are incorporated within interdendritic space. As a result, a particle accumulation region forms directly ahead of the solid/liquid interface. If the particle fraction within the particle accumulation region is below the “breakthrough concentration” (that is, the osmotic pressure of the suspension exceeds the capillary pressure necessary to allow the solidifying fluid to invade the pore space [124]), ice lamellae or dendritic structures form. Above the breakthrough concentration, lamellae/dendrites are unable to propagate and ice lenses may develop.

Ice banding develops when a fraction of particles within the accumulation region is engulfed by the solid/liquid interface (rather than incorporated within interdendritic space), while other particles are pushed ahead of the front [86]. The engulfed particles form a discrete, enriched

particle layer (parallel to the solidification front, perpendicular to the imposed thermal gradient), and a particle-free ice layer (*i.e.*, “ice band”) forms immediately thereafter (*e.g.*, Fig. 1-a of Ref. [27] and Fig. 5 of Ref. [130]). The particle accumulation region is still present after the first ice lens develops and contains particles that were initially pushed during the development of the ice lens as well as additional particles that entered the region through other mechanisms (*e.g.*, sedimentation). This periodic ice banding process may repeat indefinitely, provided water and particles are available for incorporation.

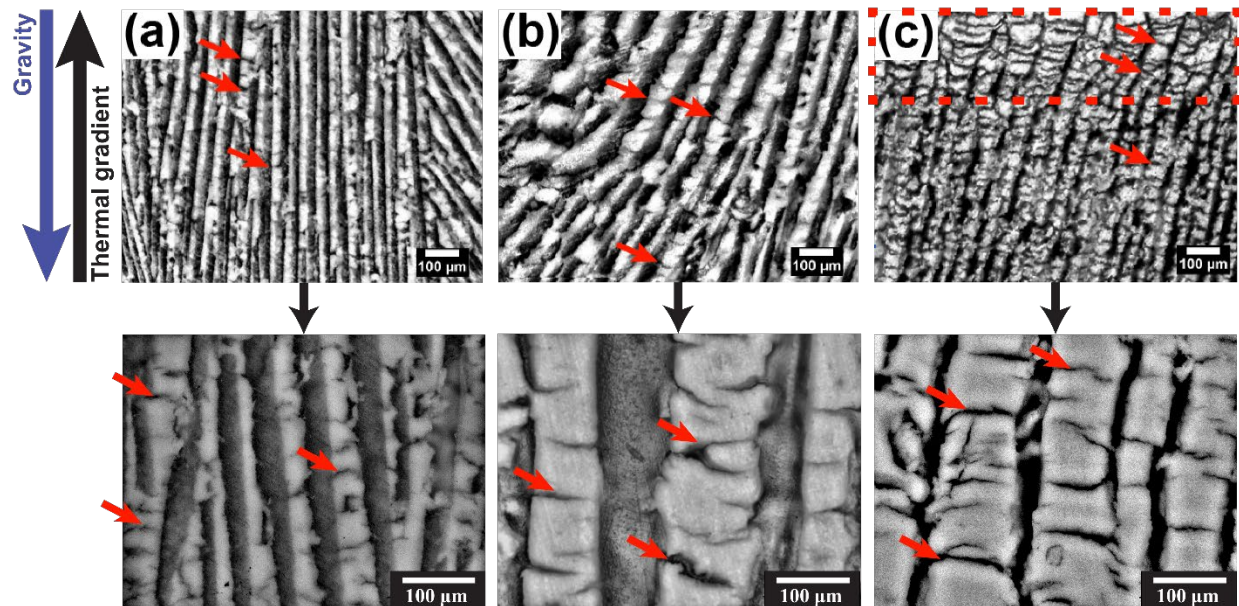


Fig. 4.8. Optical micrographs show microstructural evidence of lensing defects in sintered TiO_2 freeze-cast structures that were solidified upwards, against gravity. Images show polished, longitudinal cross-sections of sintered, freeze-cast TiO_2 obtained by directional solidification of aqueous suspensions containing (a) 30, (b) 40, and (c) 50 wt.% TiO_2 nanoparticles (corresponding to 10, 15, and 21 vol.% TiO_2). Higher magnification micrographs are shown in the second row and correspond to the images above as indicated by black arrows; v and g are the directions of solidification velocity and gravity, respectively, during solidification. Pores and walls are shown in black and white, respectively. Two regimes of ice lens defects are observed. Ice spear defects are visible as thin black microcracks (red arrows, a-c) oriented perpendicular to the freezing direction, stretching across the white TiO_2 walls. The onset of ice band defects is observed toward the top of the image in (c; red box); here, wall merging is observed, and crack length increases in the wider walls. Figure extracted without modification, ref. [89].

The main distinction between the ice banding and ice spear regimes is that the former tends to form discrete bands of ice (and enriched particle layers) whereas the latter does not. For periodic banding, ice dendrites and particle-packed walls that are oriented parallel to the freezing direction are absent. In the ice-spear regime, alternating regions of pores and walls oriented parallel to the freezing direction are observed. However, in sintered samples, the walls contain microcracks that are oriented perpendicular to the freezing direction (*e.g.*, Fig. 9-b of Ref. [125] and Fig. 2-b of ref. [85]). A possible explanation for the ice-spear regime is that, near the breakthrough concentration, water is forced into the already formed particle-packed walls, creating pure-ice-filled layers (oriented perpendicular to the freezing direction) within the vertical wall structures, while the vertical, lamellar ice region remains intact. Lending support to this hypothesis, Peppin *et al.* [67] observed a transition between these regimes where periodic banding ice-lenses were observed for aqueous suspensions containing 74 wt.% (~52 vol.%) kaolinite clay, while a decrease in the initial particle fraction to 50 wt.% (~27 vol.%) produced a structure consistent with the ice-spear regime.

In these samples, ice lens defects were observed in all samples solidified upward, for all particle fractions under study ($N = 30$). Similar defects were not observed in any samples solidified downward ($N = 30$), nor horizontally ($N = 30$). Given that thermal buoyancy flow is stabilized for downward solidification and partially stabilized for horizontal solidification, these observations provide strong evidence that buoyancy-driven fluid flow increases the propensity of ice lens formation during upward solidification (as discussed in the introduction, Stokes' sedimentation velocity of nanometric spheres in water is negligible). These observations are also consistent with results which we reported previously [130], wherein ice lens defects were observed for 20 wt.% TiO_2 suspensions solidified upward under normal terrestrial gravity (1g) but were not observed for

suspensions solidified upward under reduced gravity (where buoyancy-driven fluid motion is reduced).

Fig. 4.8 shows representative images of ice lens defects in sintered TiO_2 for initial particle fractions of: (a) 30, (b) 40, and (c) 50 wt.% (corresponding to 10, 15, and 21 vol.% TiO_2). The defects are visible as black, horizontal lines (cracks, which were previously ice) that stretch across the white, TiO_2 walls. The defects are easier to discern in the higher magnification images provided in the second row of Fig. 4.8. Most defects are observed as horizontal micro-cracks that span nearly the width of individual, sintered TiO_2 walls; these micro-cracks are consistent with the ice-spear regime described above.

Ice lensing crack width (and wall width) is observed to increase with increasing: (i) initial particle fraction in the suspension, (ii) vertical distance from the first-to-solidify region (in contact with the aluminum mold base) to the last-to-solidify region, and (iii) radial distance from the outer wall to the center of the specimen. Fig. 4.9 (a) shows a plot of mean crack length corresponding to the first- and last-to-solidify regions of samples, as measured from images of sintered structures obtained from upward, directional solidification of aqueous suspensions containing 30, 40, and 50 wt.% TiO_2 (corresponding to 10, 15, and 21 vol.% TiO_2). Fig. 4.9 (b) shows the mean vertical distance between the base of samples (in contact with the freezing substrate/aluminum mold base) and the first observations of a crack in sintered structures obtained from the same samples.

Dividing samples in half horizontally, mean crack width for 30 wt.% TiO_2 , is 30 ± 12 and 56 ± 24 μm in the first- and last-to-solidify regions, respectively. At 40 and 50 wt.% TiO_2 , these values increase to 32 ± 14 and 67 ± 23 μm , respectively, within the first-to-solidify regions and to 66 ± 15 and 197 ± 95 μm for the last-to-solidify regions (for 40 and 50 wt.% TiO_2 , respectively). Additionally, (iv) the vertical distance between the base of the sample (in contact with the freezing

substrate/aluminum mold base) and the first observation of an ice lens defect decreases from 267 ± 40 μm for 30 wt.% TiO_2 to 202 ± 24 and 69 ± 14 μm for 40 and 50 wt.% TiO_2 , respectively. That is, ice lens defects develop earlier in the solidification process for suspensions containing a higher initial particle fraction. In the following, it is shown that factors (i) through (iv) lend support to the argument that fluid motion plays a role in initiating a pattern of particle engulfment at the solid/liquid interface that leads to the formation of ice lensing. This is most apparent when considering the 50 wt.% TiO_2 samples where ice lens defects are pervasive.

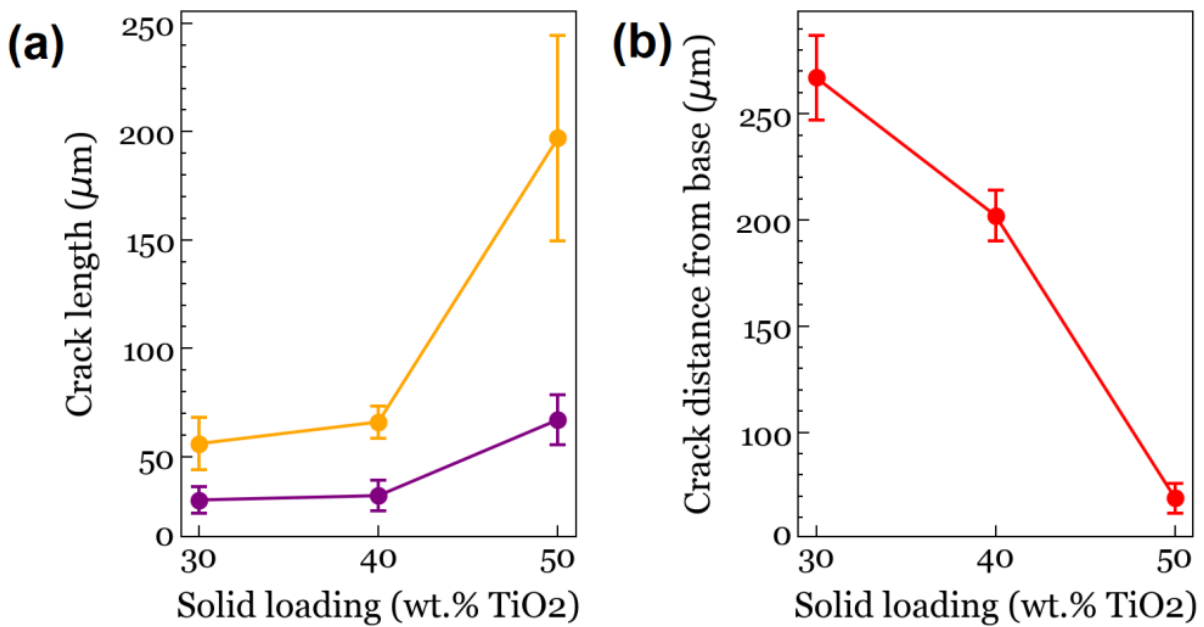


Fig. 4.9. Plots show crack parameters in sintered structures that were solidified upwards, against gravity. The plot in (a) shows mean crack width as measured from the lower (purple) and upper (yellow) half of samples with initial solid loadings of 30, 40, and 50 wt.% TiO_2 (corresponding to 10, 15, and 21 vol.% TiO_2); (b) shows the mean vertical distance between the base of samples (in contact with the freezing substrate/aluminum mold base) and the first observations of a crack. Figure extracted without modification, ref. [89].

Fig. 4.10 shows cross-sectional images of sintered TiO₂ structures that were solidified vertically upward (against gravity) using the highest initial particle fraction of 50 wt.% TiO₂. Fig. 4.10 (a) is taken from the central region of the sample and (b) is obtained from the outermost portion of the sample (the right side of the image corresponds to the peripheral region of the sample in contact with the solidification mold; total length of the image is ~4.5 mm). Ice lens defects are visible as black, horizontal lines (cracks) that stretch across the white, TiO₂ walls. As noted above, crack (and wall) width increases from the base (first-to-solidify region) to the top of the samples; increases of 87% and 194% were noted for 30 and 50 wt.% TiO₂, respectively. The higher magnification images (offset in red boxes) convey that the disparity between 30 (Fig. 4.8-a) and 50 wt.% TiO₂ occurs because of widespread merging of walls (where two or more walls merge into one) in the higher particle fraction samples. This may represent a transition from the ice spear to the periodic banding regime of ice lensing discussed above.

Wall merging occurs at lower sample heights within the central region of 50 wt.% TiO₂ samples (Fig. 4.10-a) than in the outer regions (Fig. 4.10-b). Considering merging of walls that occurs at heights greater than 150 μm from the base of 50 wt.% TiO₂ samples, the mean height at which wall merging is observed is 254 ± 79 and 463 ± 135 μm (from the sample base) for central and peripheral regions, respectively. Within the uppermost region of the 50 wt.% TiO₂ sample depicted in Fig. 4.10, a polygonal pattern develops. A similar pattern was observed by Peppin *et al.* [27, 77] for the upward solidification of 50 wt.% kaolinite powders (~28 vol.%) in water. Green bodies are particularly fragile within this region and portions of samples break off during post-solidification processing. This can be inferred by the jagged top surface of the sample shown in Fig. 4.10. The shorter overall height of the central (a) vs. peripheral (b) images is likely a consequence of this pattern beginning earlier during solidification within the central region of the sample than within

peripheral regions (*i.e.*, sample losses during post-solidification processing are greatest in the central region of samples).

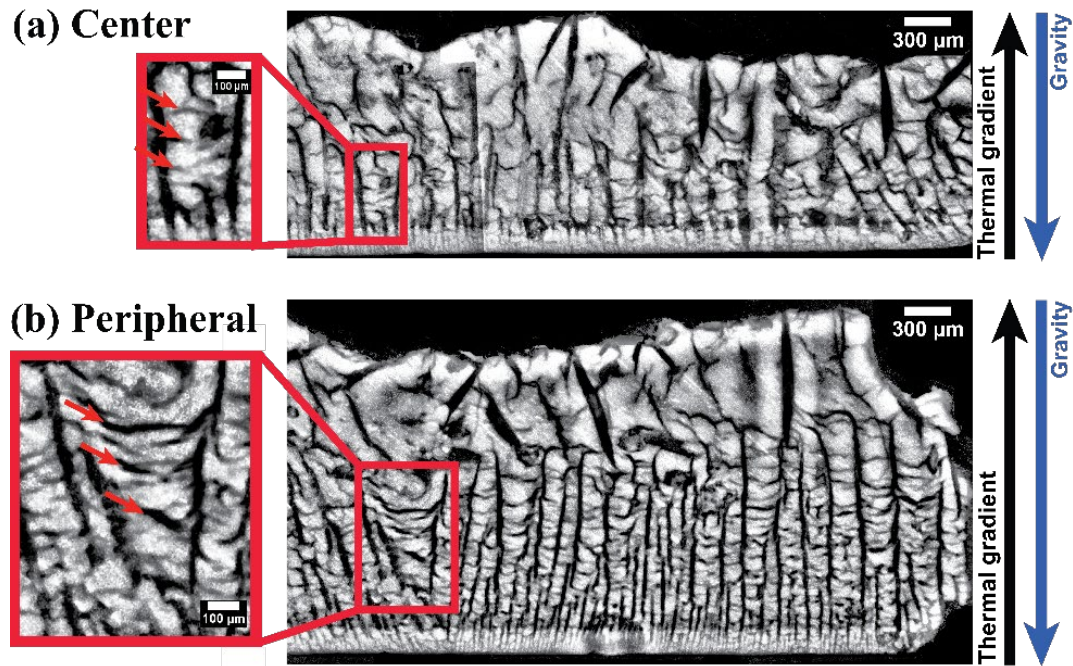


Fig. 4.10. Optical micrographs showing ice lens defects in sintered structures obtained from 50 wt.% TiO_2 suspensions solidified vertically upwards. The images of the polished longitudinal cross-sections show evidence of pervasive ice lens development in a sample solidified upward using the highest initial particle fraction of 50 wt.% TiO_2 particles (21 vol.% TiO_2). The top image (a) is taken from the center of the sample, whereas the bottom image (b) is obtained from the outermost portion of the sample (contact surface with PVC mold is shown on the right in (b)). Arrows indicate directions of (v) solidification and (g) gravity. Pores and walls are shown in black and white, respectively. Ice lens defects are visible as thin black cracks (a few are highlighted with red arrows) oriented perpendicular to the freezing direction, stretching across the white TiO_2 sintered walls. Figure extracted without modification, ref. [89].

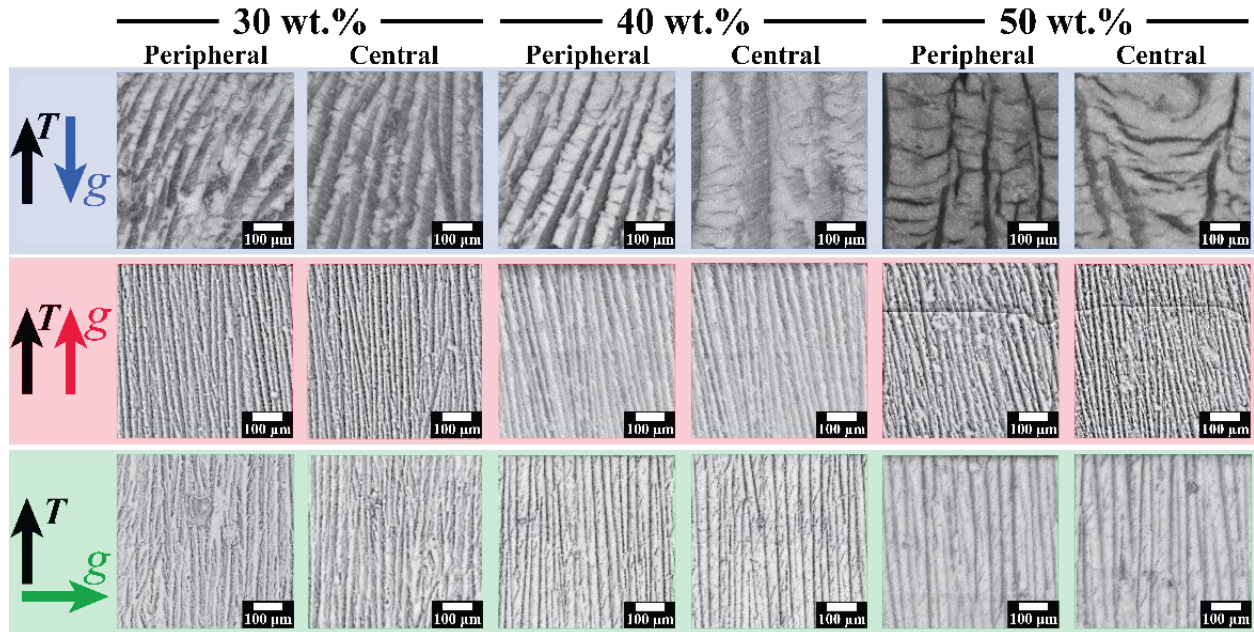


Fig. 4.11. Montage of optical micrographs showing sintered TiO_2 microstructures based on solidification direction, suspension particle fraction, and region within the sintered structure. All images are of polished, longitudinal cross-sections; columns correspond to suspension particle fractions: 30, 40, and 50 wt.% TiO_2 nanoparticles (corresponding to 10, 15, and 21 vol.% TiO_2 , columns 1-2, 3-4, and 5-6, respectively), where the solidification direction is: (blue/top row) upward, (red/middle row) downward, and (green/bottom row) horizontal with respect to the gravity vector (g). Images in the green and red rows are rotated such that the “base” and “tops” of the samples (first- and last-to-solidify, respectively) are shown at the bottom and top of all images. Images shown in the first and second columns of each particle fraction were obtained from the outer “peripheral” and central regions of each sample, respectively. The horizontal line visible in 50 wt.% in images for upward and horizontal solidification is an artifact resulting from image stitching. Figure extracted without modification, ref. [89].

Fig. 4.11 shows optical micrographs of polished cross-sections of sintered materials obtained by directionally solidifying 30, 40, and 50 wt.% TiO₂ suspensions (columns 1-2, 3-4, and 5-6, respectively), where solidification direction (v) is: (blue/top row) upward, (red/middle row) downward, and (green/bottom row) horizontal with respect to the gravity vector (g). Images in (b) and (c) are rotated such that the “base” and “tops” of the samples (first- and last-to-solidify, respectively) are shown at the bottom and top of all images. Images shown in the first and second columns of each particle fraction were obtained from the outer “peripheral” and central region of each sample (the horizontal line observed in 50 wt.% TiO₂ upward and horizontal solidification images is an artifact resulting from image stitching). Fig. 4.11 shows that fine, lamellar microstructures can be obtained for up to 50 wt.% TiO₂ when samples are solidified downward or horizontally (at the solidification velocity explored here, $\sim 75 \mu\text{m}\cdot\text{s}^{-1}$), but not when they are solidified vertically upward.

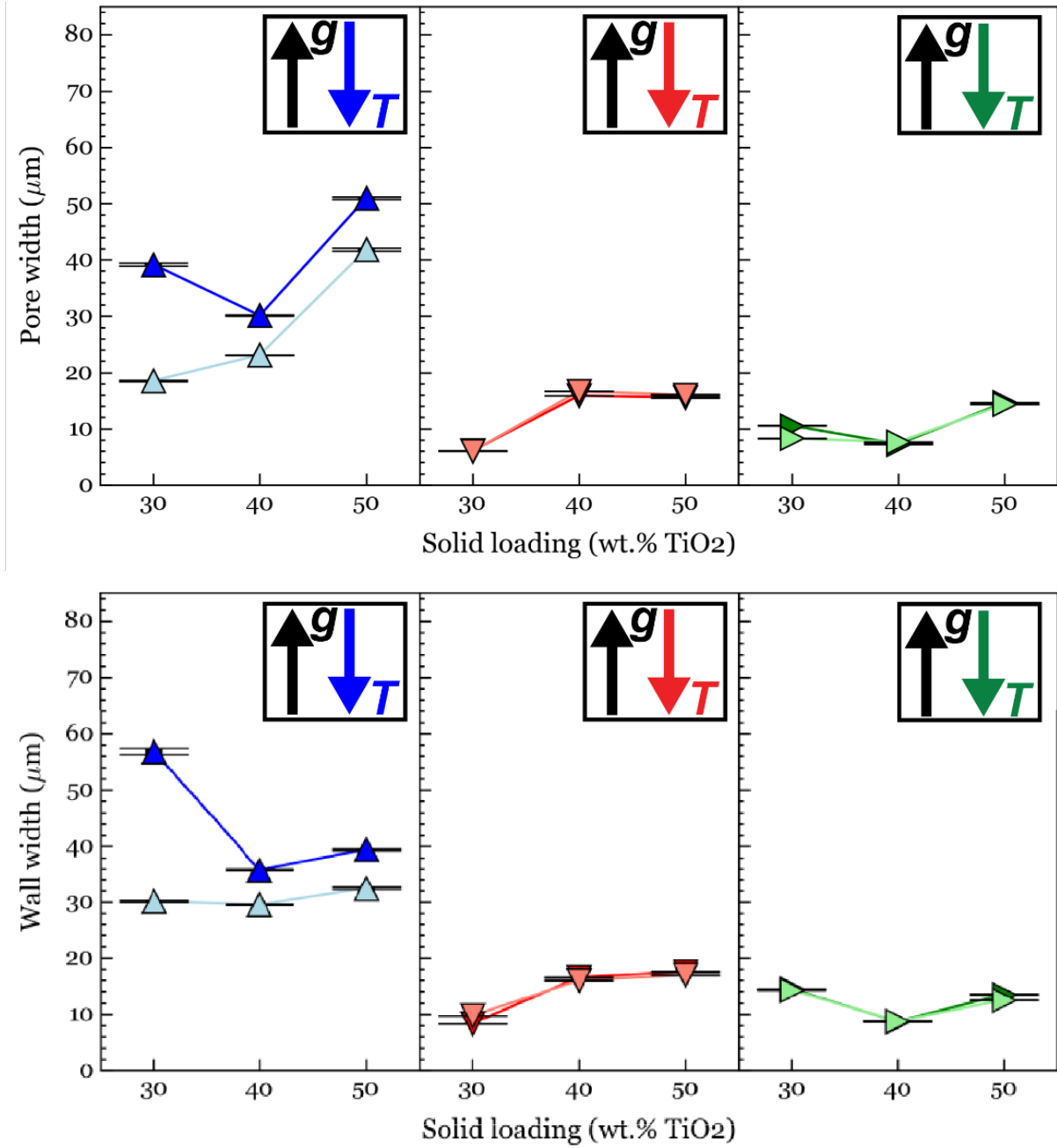


Fig. 4.12. Plots show the effect of solidification direction on pore and wall width. Plots in the top row show pore width; wall width is shown in the bottom row. All measurements were obtained from sintered freeze-cast TiO_2 that were produced from directional solidification of aqueous suspensions containing 30, 40, and 50 wt.% TiO_2 nanoparticles (corresponding to 10, 15, and 21 vol.% TiO_2), where solidification direction was: upward (against gravity, left column/blue), downward (with gravity, middle column/red), and horizontal (perpendicular to gravity, right column/green). The dark and light markers represent data collected in the “center” and “peripheral” regions of samples, respectively. Error bars are derived using a 99.95% confidence interval about the mean. Figure extracted without modification, ref. [89].

4.2.5. *Radial segregation*

Fig. 4.12 shows mean pore width and mean wall width for sintered structures produced from suspensions using TiO₂ weight fractions of 30, 40, and 50% (corresponding to 10, 15, and 21 vol.% TiO₂) for samples solidified (a, d) upward (blue/left), (b, e) downward (red/middle), and (c, f) horizontally (green/right). In comparison to downward and horizontal solidification, an increase in pore width and wall width is observed in samples solidified upward for all TiO₂ weight fractions. This effect is greatest for 30 wt.% TiO₂, where mean pore width is about four times larger when solidified upward compared to downward and about three times as large in comparison to horizontal solidification (27 ± 22 , 7 ± 5 , and 10 ± 6 μm for the up, down, and horizontal solidification directions, respectively; Table 4-1). At an initial particle fraction of 50 wt.% TiO₂, mean pore width is approximately three times as large for upward solidification as compared to horizontal and downward solidification (51 ± 35 , 16 ± 12 , and 16 ± 9 μm for the up, down, and horizontal solidification, respectively; Table 4-1). The same ratios are likewise observed for wall width. Here, these disparities are attributed to the formation of ice lenses (which promotes merging of individual walls into larger walls, as discussed previously).

In a previous study [130], we reported a macroscopically concave solid/liquid interface curvature, with a depression in the center of the sample, during upward solidification of aqueous suspensions of 5-20 wt.% TiO₂; moreover, the depth of the depression was observed to increase as solidification progressed. The freezing set-up utilized here did not allow for observation of the solid/liquid interface during solidification. Nevertheless, the macroscopic microstructural pattern observed for upward solidification (Fig. 4.3-a, two semicircular regions with approximate mirror symmetry about the center line) is consistent with the macroscopic convective fluid flow pattern described previously [130]. Macroscopic interface curvature can result from, among other factors,

a mismatch between thermal conductivities of liquid, solid, and mold. For example, if mold walls are more thermally conductive than solid ice, the interface is expected to be concave because latent heat of solidification is preferentially evacuated through the mold wall [135]. Here (and previously [130]), the thermal conductivity of the PVC mold (~ 0.2 W/m K) is much lower than that of the ice (~ 2.2 W/m K); thus, if a thermal conductivity mismatch was responsible for interface curvature observed previously (and inferred here), the curvature is expected to be convex, rather than concave. Here, it is posited that the concave curvature observed previously (and inferred here) results from the macroscopic convection pattern itself.

A disparity in mean pore width between the outer edge of the sample and its center is expected when a curvature of the solid/liquid interface is present. This so called “radial segregation” occurs because solidification velocity is inversely proportional to the thickness of ice lamellae; faster solidification velocities tend to result in thinner pores [140], and a concave curvature implies solidification velocity is faster at the sides of the mold than the center [240]. In Fig. 4.12, dark markers represent mean values of pore and wall width taken from the center of samples; light markers denote mean peripheral measurements (as discussed above, longitudinal cross-sections are divided in three horizontally; peripheral measurements refer to those obtained from the two outside images and central measurements are taken from the center image). For upward solidification, widths of both pores and walls are larger in the center of samples relative to outer regions, near the mold, for all TiO_2 weight fractions. This effect is highest at 30 wt.% TiO_2 , where mean pore width measured from central and peripheral regions are 39 ± 27 and 19 ± 12 μm , respectively (corresponding to mean wall width from central and peripheral regions of 56 ± 37 and 30 ± 22 μm , respectively). In contrast, for upward and downward solidification, mean values of pore and wall width are nearly the same between central and peripheral locations (statistically

significant differences between these measurements were not found). In other words, evidence of radial segregation in the case of upward solidification is found, but not in downward nor horizontal solidification configurations.

In the alloy solidification literature, axial rotation [240] and/or vibration [201] is sometimes used to counterbalance buoyancy-driven fluid flow which would otherwise lead to radial segregation. For example, for the upward solidification of succinonitrile-0.005 wt.% ethanol alloys, an axial rotation rate of 150 rpm was used to prevent radial segregation [240]. However, for upward solidification of hypereutectic Sn-25Pb where Sn, the species rejected in the melt at the solid/liquid interface, is less dense than the melt and thus buoyant), Grugel *et al.* [241] observed radial segregation regardless of any applied axial rotation; horizontal solidification with axial rotation was needed to offset buoyancy-driven convection and achieve uniformly aligned dendritic microstructures; downward solidification was not tested.

4.3. Model comparison

Fig. 4.13 shows a modified version of the phase diagram provided by You *et al.* [29] for the freeze-casting microstructure model described in Section 2.5; here, data points are included for these experiments (star markers) and our previous work [130] (triangle markers). In terms of Eq. 2.1-Eq. 2.4, the following values are used for this system: the dynamic viscosity of the pure fluid, μ is taken as 1.78 mPa·s for water at 0°C [242]), V is approximated at $75 \mu\text{m} \cdot \text{s}^{-1}$, T_M is taken as the melting temperature of water, ρ is the density of ice, L is the latent heat of fusion of ice, G is the temperature gradient ($21 \text{ K} \cdot \text{mm}^{-1}$), and the particle radius, $r = 15 \text{ nm}$. The Hamaker constant, A between the solidified fluid and the particle is taken as $7 \cdot 10^{-20} \text{ J}$ for TiO_2/ice [243], and λ is an empirical constant, given in Ref. [29] as 0.225

As described in Section 2.5, dendritic structures are predicted when $D/(1 + \Phi)$ is greater than unity, whereas ice lensing regimes are predicted when $D/(1 + \Phi)$ is less than unity. The star markers in Fig. 4.13 represent values calculated based on the present work; specifically, $D/(1 + \Phi) = 1.7, 1.9$, and 2.1 for suspensions containing 10, 15, and 21 vol.% TiO_2 nanoparticles, respectively, *i.e.*, dendritic regimes are predicted for all volume fractions studied here. Dendritic structures were indeed observed for all samples solidified downward and horizontally, but spear and banding regimes were observed in samples solidified vertically upward (for all weight fractions). Triangle markers represent values calculated from our previous work [130] for 5-20 wt.% TiO_2 nanoparticles, where $V = 100 \mu\text{m} \cdot \text{s}^{-1}$. Again, dendritic structures are predicted, yet ice banding was observed for 20 wt.% samples that were solidified under normal terrestrial gravity (but not for samples solidified under reduced gravity). Square symbols from literature values are also shown in Fig. 4.13, including solid red and black markers [87] (Al_2O_3 , $r=160 \text{ nm}$, $G=2.58 \text{ K} \cdot \text{cm}^{-1}$, $\phi_0 = 0.27$, $V=0.5\text{-}10 \mu\text{m} \cdot \text{s}^{-1}$, $A=3.67 \times 10^{-20} \text{ J}$) and red and blue slashed squares [29] (Al_2O_3 , $r = 100 \text{ nm}$, $G = 8.19 \text{ K} \cdot \text{cm}^{-1}$, $\phi_0 = 0.27$, $V = 7.3\text{-}34.6 \mu\text{m} \cdot \text{s}^{-1}$, $A = 3.67 \times 10^{-20} \text{ J}$).

Transitions from dendritic to lensing regimes are predicted as the freezing velocity decreases, the thermal gradient increases, the particle volume fraction increases, or the particle radius increases [29]. This model does not account for systems with solute effects (*e.g.*, dissolved binder in the suspension). However, it is known that the particle fraction within the accumulation region (and by consequence, the propensity for ice lenses to develop) is influenced by suspension characteristics (*e.g.*, suspension stability and particle sedimentation [41, 85]) and solidification conditions (*e.g.*, solidification velocity [87, 88], and as shown here, solidification direction). Here, it is posited that buoyancy-driven fluid motion is also a contributing factor for the development of ice lenses in samples solidified vertically upward, against gravity.

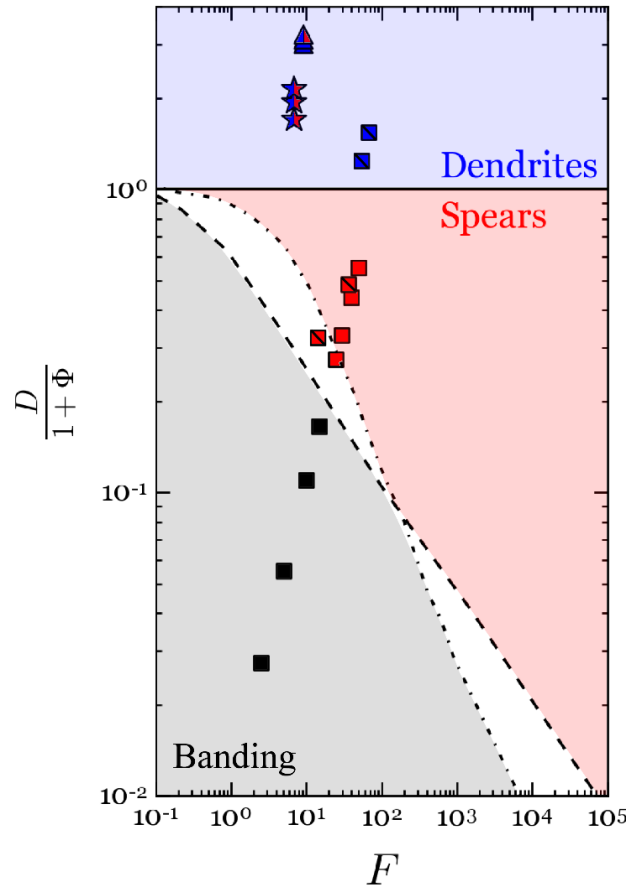


Fig. 4.13. Plot showing predicted microstructures for freeze-cast structures under study with respect to solidification orientation. The depicted microstructural phase diagram is after Ref. [29] and shows predicted ice-templated microstructures, including: dendrites (blue), ice spears (red), and ice banding (grey) based on solidification and suspension parameters. The Darcy coefficient (D), film coefficient (F), and (Φ), are given by Eq. 2.1-Eq. 2.4 (Section 2.4). The star markers represent values calculated based on the present work; dendritic morphologies were observed for all TiO_2 weight fractions (30-50 wt.%; 10-21 vol.% TiO_2) for samples solidified downward and horizontally, whereas lensing regimes (ice lenses and spears) were observed in samples solidified upward (for all weight fractions). Triangle markers represent values measured in our previous work [130] for 5-20 wt.% (2-7 vol.%) TiO_2 , where dendritic structures were observed for all weight fractions under microgravity and ice banding was observed for 20 wt.% TiO_2 solidified upward under normal terrestrial gravity. Square markers represent literature values, including solid red and black solid markers [87] (27 vol. % Al_2O_3 , $r = 160$ nm) and red and blue slashed markers [29] (27 vol.% Al_2O_3 , $r = 100$ nm). Figure extracted without modification, ref. [89].

In the case of a concave solid/liquid interface curvature (described in Section 4.2.5), the depth of the concave depression at the solidification front increases as more particles are collected within the depression. The formation of a concave interface depression for upward solidification is supported by the observation of ice lens defects being formed closer to the base of 50 wt.% TiO₂ samples within central regions, as compared to peripheral regions; in other words, the “breakthrough” particle concentration is reached earlier in the solidification process within the central region of these samples. This breakthrough concentration is typically taken at the close-packing fraction value of 0.64 [27, 124] and represents the point at which the osmotic pressure of the accumulated particle region exceeds the capillary pressure necessary to allow ice to invade pore space [124] where “pore space” refers here to the space between compacted particles within the particle accumulation region (located immediately ahead of the solid/liquid interface).

The initial suspension particle fraction of 50 wt.% corresponds to 21 vol.% TiO₂, which is significantly lower than the breakthrough fraction of 64 vol.%. Nevertheless, ice lens defects were observed, on average, at a height of 69 ± 14 μm from the base for samples containing initial particle fractions of 50 wt.% (21 vol.%). Considering particle rejection by the solidification front as the only mechanism for creating the particle accumulation region, it is practically impossible for the volume fraction of particles at the solid/liquid interface to triple over the short distance that the solidification advances ~ 70 μm ($\sim 2\%$ of the suspension height). Most likely, (i) the particle fraction at the base of the suspension exceeded that of the bulk suspension prior to the onset of solidification (due to sedimentation) and/or (ii) particles were enriched to the solid/liquid interface by other means (in addition to rejection by the solid/liquid interface), as discussed below.

As discussed earlier, the experiments of Tankin *et al.* [90] showed that the onset of buoyancy-driven convective fluid motion occurs when a thermal gradient is imposed. Thus, fluid

motion-induced particle redistribution likely begins before solidification commences. Although the sedimentation rate is negligible for nanometric particles (especially at the high solidification velocities explored here), the sedimentation rate for aggregates of particles may not be. This issue was explored by Lasalle *et al.* [85] with respect to the use of unstable suspensions. In contrast, orthokinetic aggregation (*i.e.*, stirring-induced aggregation) occurs when particles are redistributed by fluid flow. In such a case, the rate of interparticle collisions increases dramatically over that which would be expected via Brownian mechanisms alone. As a result, orthokinetic aggregation produces aggregates rapidly and considerable variation in aggregate size is observed [244]. The production of aggregates of different sizes gives way to an additional mode of aggregation which results from differential sedimentation rates. That is, aggregates of different diameters settle at different rates. Consequently, the particle collision rate is increased further, *i.e.*, particles are provided with an increased number of aggregation opportunities.

A combination of fluid motion-induced particle redistribution and orthokinetic aggregation (and consequent enhanced sedimentation) may have effectively increased the particle fraction at the base of the suspension prior to the commencement of solidification. This may be a contributing factor for why the model developed by You *et al.* [29] accurately predicts the dendritic structures observed here for downward and horizontal solidification, but not the lensing structures observed for upward solidification. If hypotheses posed here are correct, the particle volume fraction at the interface would be higher than that predicted by the model (over the course of solidification); this would lead to increased values of $D/(1+\Phi)$ while F remained unchanged; *i.e.*, in terms of Fig. 4.13, y -axis values would decrease, moving prediction values toward (or within) lensing regime boundaries.

4.4. Conclusion

Ice-templated porous titanium dioxide (TiO_2) structures were fabricated by directional solidification (under thermal gradient) of aqueous suspensions containing 30, 40, and 50 wt.% TiO_2 nanoparticles (corresponding to 10, 15, and 21 vol.% TiO_2) in three different solidification configurations: (a) vertically upward (solid ice on bottom, liquid water on top, against gravity), (b) vertically downward (liquid on bottom, solid on top, with gravity), and (c) horizontal (perpendicular to the gravity vector). Suspended particles were first rejected by the advancing solidification front and later incorporated within interdendritic space. After solidification, ice was removed *via* sublimation and the remaining particle-packed walls were sintered to densify the wall structure. Sintered structures consist of elongated, particle-packed walls separated by pore channels, templated by the ice dendrites. Microstructural investigations were conducted on sintered structures.

Significant tilting of the wall orientation (*i.e.*, the ice dendrite misorientation) with respect to the temperature gradient imposed during solidification was observed in samples solidified upward, but not for downward nor horizontal solidification configurations. These results are consistent with: (i) the presence of a macroscopic convective fluid pattern during upward solidification and (ii) a reduction (or suppression) of interdendritic fluid flow in the cases of downward and horizontal solidification *vs.* upward solidification. For downward and horizontal solidification configurations, ice dendrites show symmetric secondary dendritic arms (both sides of lamellae). By contrast, the misaligned dendrites show asymmetric secondary dendritic features in samples solidified vertically upward (evidence of secondary dendritic arms are present on only one side of lamellae).

Ice lens defects, observed in the sintered TiO_2 walls as cracks oriented perpendicular to the direction of freezing, are observed in all samples solidified vertically upward for all suspension particle fractions. None of the samples solidified vertically downward nor horizontally exhibit these defects. Two ice lensing regimes are observed: (i) ice spear defects (microcracks often spanning the width of particle walls) were observed for samples fabricated using an initial particle fraction of 30, 40, and 50 wt.% TiO_2 , and (ii) ice banding for 50 wt.% TiO_2 samples, which corresponds to a merging of wall structures that increases over the height of the samples. In the last-to-solidify regions of these samples, a polygonal segregation pattern is present, which is consistent with a transition from ice-spear to periodic banding regimes described in the ice lensing literature.

Mean pore width and mean wall width are significantly smaller in samples solidified downward and horizontally in comparison to values measured from sintered samples that were solidified vertically upward. This effect is greatest at 30 wt.% TiO_2 , where mean pore width is more than four times larger when solidified upward compared to the downward solidification configuration and approximately three times as large in comparison to horizontal solidification. Radial macrosegregation is observed for samples solidified upward (at a given height along the solidification direction, pore and wall width at the center of samples are larger than those near the walls of the mold) and is consistent with the development of a concave interface during solidification. Here, radial macrosegregation is attributed to a higher solidification velocity near the mold wall (outer region of the samples) in comparison to that in the center of the samples. Radial segregation is not observed for downward nor horizontal solidification configurations. For upward solidification, the effect is greatest at 30 wt.% TiO_2 , where mean central and outer (closer

to the mold wall) pore widths are 39 ± 27 and 19 ± 12 μm , respectively (corresponding to mean central and outer wall widths of 48 ± 37 and 26 ± 16 μm , respectively).

Chapter 5. Effect of initial suspension temperature on ice-templated microstructures

5.1. Motivation

As discussed in Chapter 4, freeze-cast structures are almost always solidified vertically upward, against gravity. In this configuration, the bottom of the suspension (closest to the cold source), is lower in temperature than the top of the suspension, with a gradient between them. The imposed macroscopic thermal gradient, G_{bulk} , is defined as:

$$G_{\text{bulk}} = \frac{T_H - T_C}{h} \quad \text{Eq. 5.1}$$

where T_H and T_C are the temperatures of the “hot side” (bulk suspension, away from the solid/liquid interface) and “cold side” (freezing substrate), respectively and h is the height of the suspension. As shown in Fig. 5.1, water reaches its maximum density at a temperature of $\sim 4^\circ\text{C}$ and decreases with increasing, and decreasing, temperature. Thus, G_{bulk} , imposed during freezing creates a density gradient in the liquid, which promotes convective fluid motion during solidification [245, 246]. For upward solidification of water, this can result in currents of rotating liquid as the lower density water (closer to the cold source) rises and the higher density water sinks. If the G_{bulk} results in the “hot side” being held at a temperature greater than 4°C , a double liquid density gradient can be introduced (Fig. 5.1, liquid water density is greatest at 4°C and decreases with increasing and decreasing temperature). In such cases, two opposing systems of convective currents may develop [247, 248].

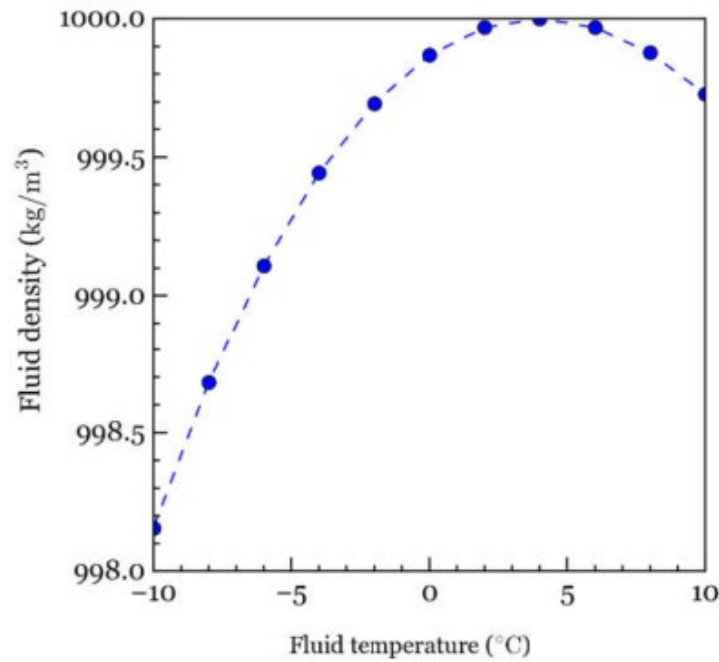


Fig. 5.1. Plot showing the temperature dependence of density for water from -10 to 10°C. Density calculated per ref. [249].

In the previous chapter, it was shown that the solidification direction (or the direction of the imposed thermal gradient with respect to gravity) can impact how buoyancy-driven fluid flow interacts with the solid/liquid interface, thus, the microstructures templated during the freeze-casting solidification process. Microstructures templated *via* upward solidification of aqueous particle suspensions were most impacted by buoyancy-driven flow; these microstructural impacts were minimized in downward and horizontal solidification configurations [89]. Effects related to the magnitude of the imposed thermal gradient were not studied.

Here, aqueous suspensions of 40 wt.% TiO_2 particles are solidified vertically upward using initial suspension temperatures of 0, 4, and 8°C to better understand how the presence of a double liquid density gradients during solidification may (or may not) impact the microstructural

templating process in freeze-cast materials. Microstructure investigations are conducted on sublimated (not sintered) structures to better correlate processing conditions to microstructural characteristics (*i.e.*, to avoid confounding effects of anisotropic sintering shrinkage [196]).

5.2. Results

5.2.1. *Microstructural characteristics*

Fig. 5.2 and Fig. 5.3 show optical micrographs of sublimated TiO₂ freeze-cast structures solidified from aqueous suspensions of 40 wt.% TiO₂ particles where the initial suspension temperatures were 0 and 8°C, respectively. The cross-sections are taken perpendicular to the direction of freezing (freezing direction is out-of-the-page), and images on the left are taken from central regions of samples (within 1 mm of the geometric center), whereas images on the right are taken from outer regions (within 1 mm of the mold wall, see Section 3.2.4 and Fig. 3.2). Fig. 5.2 (a, b) and Fig. 5.3 (a, b) are obtained at ~5 mm from the base of the samples (where “base” is the freezing substrate), whereas Fig. 5.2 (c, d) and Fig. 5.3 (c, d) are obtained from the last-to-solidify region (~15 mm). Blue dye was used in the epoxy during specimen mounting (to aid in visualizing walls *vs.* pores), thus pores show as dark blue regions. Lamellar structures (common with aqueous processing [250, 251]) are observed for all regions, for both initial suspension temperatures.

Increases in both pore and wall thickness are observed between cross-sections taken at heights of ~5 mm relative to those taken at ~15 mm for structures solidified using both 0 and 8°C initial suspension temperatures (Fig. 5.2 and Fig. 5.3, respectively). As described in Section 3.2.2, a linear cooling rate (5°C/min) was used to set the temperature of the freezing substrate over time; specifically, the initial set temperature of the freezing substrate was set equal to initial suspension temperature (either 0, 4, or 8°C) and the set temperature decreased by 5°C/min until reaching a

final temperature of -20°C . Linear cooling rates represent quasi-static approximations to a Stefan problem [252, 253], a two-phase moving boundary problem that assumes one-directional heat flow (*i.e.*, for upward solidification here, heat is assumed to flow through the ice and radial temperature gradients at the solid/liquid interface/heat evacuation at the mold wall are not considered). For freeze-casting applications, linear cooling rates are employed to modify solidification velocity relative to that which would be produced using a constant freezing substrate temperature. For constant freezing substrate temperature approaches, solidification progresses proportionally to the square root of time (generally); thus, as the distance between the solidification front and the freezing substrate increases, lamellar width also increases. While employing linear cooling rates *reduces* microstructural gradients relative to constant cooling approaches, microstructural gradients are still expected, especially over relatively large sample heights or at high cooling rates [21] (exponential cooling functions [254] offer a closer approximation to constant velocity, but are still limited in effective lengths that can be produced due to equipment limitations and assumptions inherent in the Stefan problem formulation [21]). Thus, the general relationship of an increase in pore (lamellae) width with increasing vertical distance from the freezing substrate is expected based on limitations of using linear cooling rates. However, it is also clear that the pore sizes are larger in the samples solidified using an initial suspension temperature of 8°C relative to the 0°C case; this is discussed in the following.

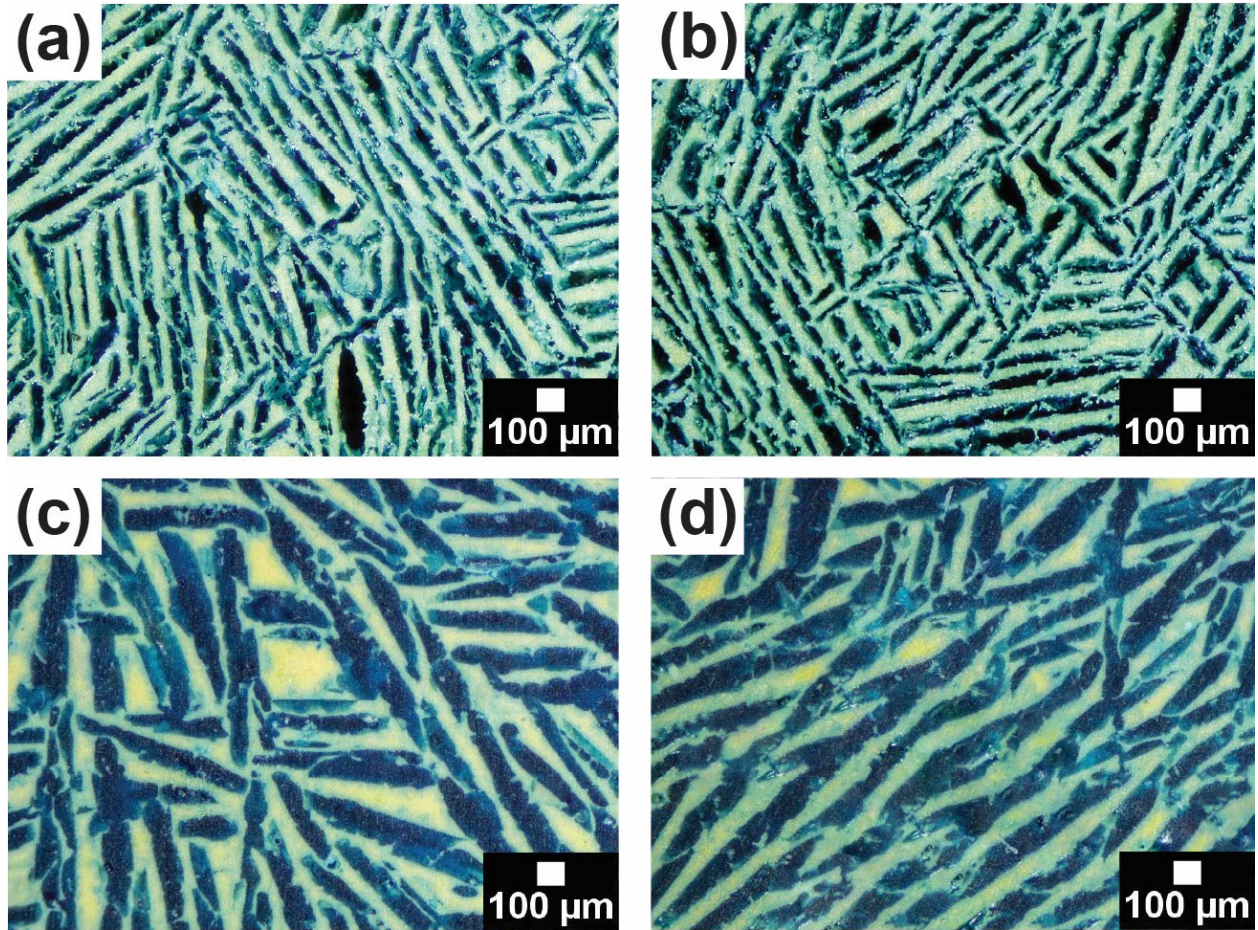


Fig. 5.2. Optical micrographs show perpendicular cross-sections TiO_2 freeze-cast structures fabricated by directionally solidifying aqueous suspensions using an initial suspension temperature of 0°C . The images in (a, b) are obtained from the first-to-solidify region of samples, whereas (c, d) are obtained from last-to-solidify regions; images (a, c) are taken from the radial-central regions and (b, d) are obtained from the outer regions of samples (closer to the mold wall). Here, the freeze-cast material is sublimated but not sintered; blue dye was used in the epoxy during specimen mounting (to aid in visualizing walls vs. pores), thus pores show as dark blue regions.

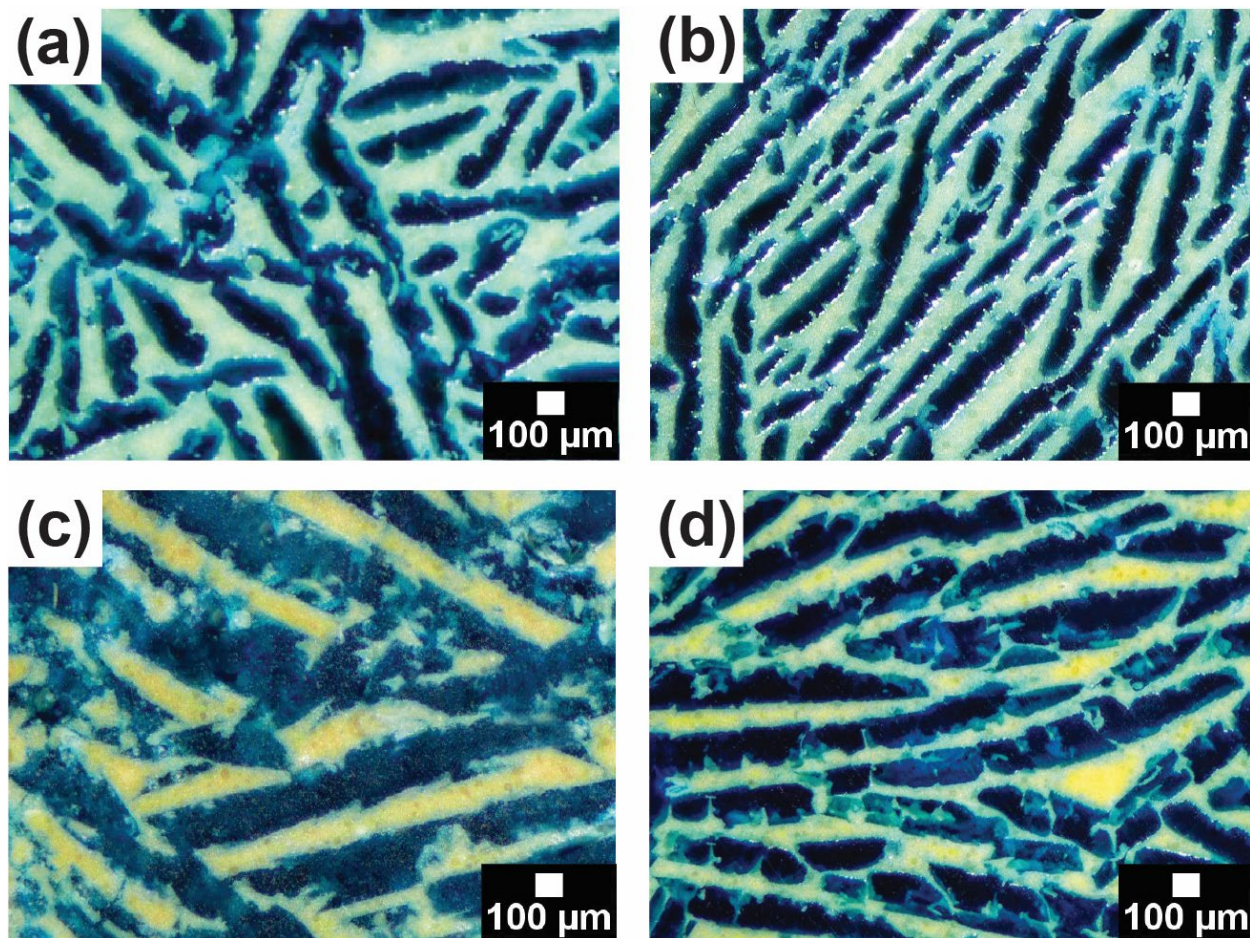


Fig. 5.3. Optical micrographs show perpendicular cross-sections TiO_2 freeze-cast structures fabricated by directionally solidifying aqueous suspensions using an initial suspension temperature of 8°C . The images in (a, b) are obtained from the first-to-solidify region of samples, whereas (c, d) are obtained from last-to-solidify regions; images (a, c) are taken from the radial-central regions and (b, d) are obtained from the outer regions of samples (closer to the mold wall). Here, the freeze-cast material is sublimated but not sintered; blue dye was used in the epoxy during specimen mounting (to aid in visualizing walls vs. pores), thus pores show as dark blue regions.

5.2.2. *Radial segregation*

Fig. 5.4 and Fig. 5.5 show box and whisker plots summarizing pore width and wall width, respectively, as measured in sublimated samples that were directionally solidified using initial suspension temperatures of: 0°C (left plots, blue markers), 4°C (center plots, red markers), and 8°C (right plots, green markers). All measurements were taken from cross-sections perpendicular to the freezing direction; dark markers show “central” measurements (taken from the radially central regions of cross-sections, within 1 mm of the geometric center), whereas light markers represent measurements taken from the outer regions (within 1 mm of the outer edge of the cross-section center; see Section 3.2.4 and Fig. 3.2). The notations, “base,” “mid,” and “top” refer to the vertical positions in the samples the measurements were obtained from. As explained in Section 3.2.4, samples were sectioned at 5 ± 1.5 , 10 ± 1.5 , and 15 ± 1.5 mm from the base of samples, where “base” is defined as the freezing substrate. The minimum and maximum values of boxes in the plot represent the first and third quartiles, respectively; medians are shown as horizontal lines inside the boxes, means are represented by black diamonds, and whiskers represent 1.5 times the interquartile range. Numerical values (mean $\pm$ standard deviation) summarizing these data are provided in Table 5.1.

Radial segregation (a variation in pore size with respect to radial position) is observed for all samples, and the magnitude of the difference between mean pore width measured from central regions vs. outer regions increases with increasing distance from the freezing substrate (base of the sample), irrespective of initial suspension temperature. This effect is greatest for 8°C initial suspension temperature samples where pore width at the base is 74 ± 17 and 45 ± 19 μm for central and outer regions, respectively, and 153 ± 31 and 109 ± 22 μm at the top. Larger pores in the central region of samples relative to outer regions was reported in Chapter 4 and attributed to a

macroscopically concave interface curvature, wherein the solidification velocity at the mold wall is faster relative to central regions. Increasing solid/liquid interface curvature over time has also been reported in the literature [130], which would explain increases in radial segregation as solidification progresses.

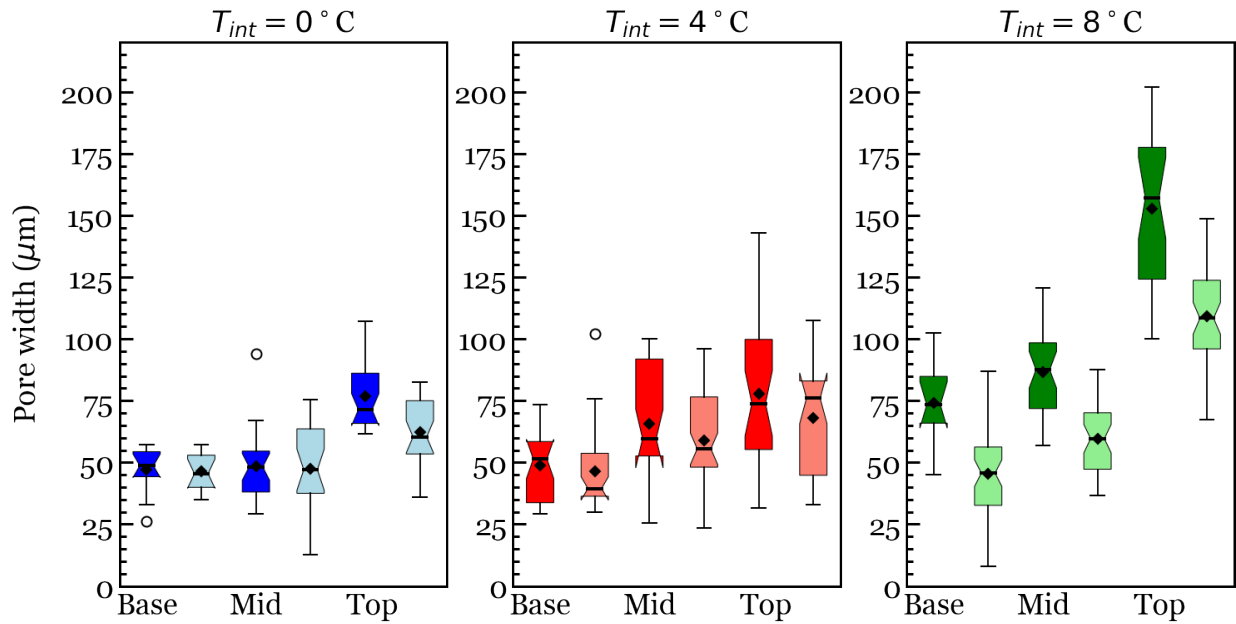


Fig. 5.4. Box and whisker plots summarizing pore width in TiO_2 freeze-cast structures solidified with varying initial suspension temperatures. Data summarized in the plot on the left (blue) was obtained from sublimated specimens that were solidified using an initial suspension temperature of 0°C ; the middle (red) and right (green) plots were obtained using initial suspension temperatures of 4 and 8°C , respectively. All measurements were taken from cross-sections perpendicular to the freezing direction; dark markers show “central” measurements (taken from the radially central regions of cross-sections), whereas light markers represent measurements taken from the outer regions (closer to the mold wall). “Base,” “mid,” and “top” refer to vertical positions (with respect to first- and last-to-freeze regions, respectively); base, mid, and top measurements were taken from samples sectioned at 5 ± 1.5 , 10 ± 1.5 , and 15 ± 1.5 mm from the absolute base of samples. The minimum and maximum values of boxes represent the first and third quartiles, respectively; medians are shown as horizontal lines inside the boxes, means are represented by black diamonds, and whiskers represent 1.5 times the interquartile range.

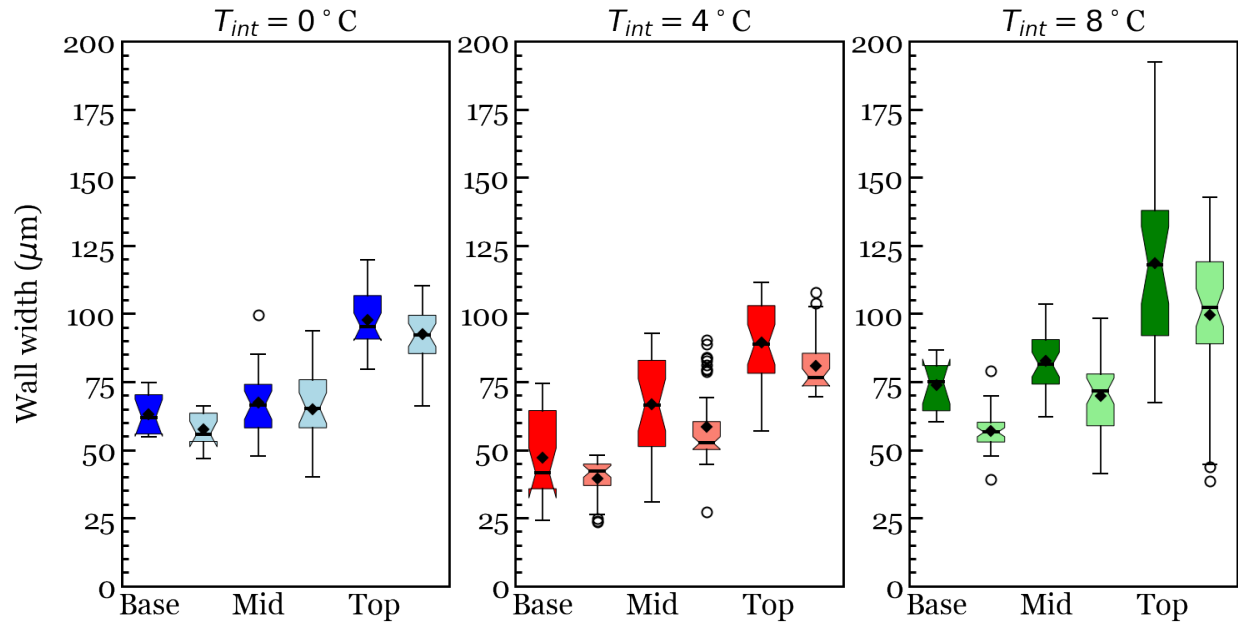


Fig. 5.5. Box and whisker plots summarizing wall width in TiO_2 freeze-cast structures solidified with varying initial suspension temperatures. Data summarized in the plot on the left (blue) was obtained from sublimated specimens that were solidified using an initial suspension temperature of 0°C ; the middle (red) and right (green) plots were obtained using initial suspension temperatures of 4 and 8°C , respectively. All measurements were taken from cross-sections perpendicular to the freezing direction; dark markers show “central” measurements (taken from the radially central regions of cross-sections), whereas light markers represent measurements taken from the outer regions (closer to the mold wall). “Base,” “mid,” and “top” refer to vertical positions (with respect to first- and last-to-freeze regions, respectively); base, mid, and top measurements were taken from samples sectioned at 5 ± 1.5 , 10 ± 1.5 , and 15 ± 1.5 mm from the absolute base of samples. The minimum and maximum values of boxes represent the first and third quartiles, respectively; medians are shown as horizontal lines inside the boxes, means are represented by black diamonds, and whiskers represent 1.5 times the interquartile range.

Table 5.1. Average pore and wall width as measured for TiO₂ freeze-cast materials directionally solidified using initial aqueous suspension temperatures of 0, 4, and 8°C. All measurements were taken from cross-sections perpendicular to the freezing direction; “outer” measurements were taken from the peripheral regions of cross-sections whereas “central” measurements were taken from the center. “Base,” “mid,” and “top” refer to vertical positions (with respect to first- and last-to-freeze regions, respectively); base, mid, and top measurements were taken from samples sectioned at 5±1.5, 10±1.5, and 15±1.5 mm from the absolute base of samples, respectively. Data are expressed as mean ± standard deviation.

	Base		Mid		Top	
	Center	Outer	Center	Outer	Center	Outer
Pore width (μm)						
0°C	47±10	46±7	48±14	47±19	77±14	62±13
4°C	49±13	47±16	66±25	59±21	78±33	68±20
8°C	74±17	45±19	87±16	60±14	153±31	109±22
Wall width (μm)						
0°C	63±8	57±7	67±13	65±14	97±12	92±11
4°C	47±17	39±8	67±18	58±14	89±15	81±10
8°C	74±10	57±7	83±12	70±15	119±35	99±27

While radial segregation is also observed for the 0°C and 4°C initial suspension temperature samples, pore sizes (and differences between values for outer vs. central regions) are relatively comparable in these samples. For example, mean pore width at the base of these samples is 47±10 and 49±13 within the central region for 0 and 4°C samples, respectively, and 46±7 and 47±16 in the outer regions. For measurements representing the top of samples, values increase to 77±14 and 78±33 in the central region and 62±13 and 68±20 in the outer region, for 0 and 4°C samples, respectively. Within the top (last-to-solidify) region, a slightly larger absolute difference between means shows that, on this basis, radial segregation is of a greater magnitude for the 0°C samples relative to 4°C samples. However, the boxplots (Fig. 5.4) show that 4°C samples show

wider distributions (for all regions); thus, these values are likely comparable. Similar relationships are found when comparing average wall width between these samples (Fig. 5.5).

As shown in Fig. 5.1, the density of liquid water reaches a maximum at 4°C; thus, considering T_H from Eq. 5.1 as the initial suspension temperature and T_C as the temperature of the freezing substrate (which starts at the same temperature of the initial suspension temperature and decreases 5°C/min until reaching a final temperature of -20°C), the resulting G_{bulk} should always produces a single density gradient in the liquid for samples produced with initial suspension temperatures of 0 and 4°C. However, this is not the case for samples solidified using an 8°C initial suspension temperature; in this case, a double liquid density gradient is expected. Weng et al. [255] used computational fluid dynamics to model the effect of thermal gradient on water solidified vertically upwards; they found that macroscopic curvature of the solid/liquid interface was greatest for thermal gradients that produced double liquid density gradients *i.e.*, where the hot side was held at $T_H > 4^\circ\text{C}$. Increasing curvature of the solid/liquid interface is expected to lead to an increase in radial segregation [233, 256], as observed here for 8°C initial suspension temperature samples relative to 0 and 4°C samples.

Consistent with the overwhelming majority of freeze-casting studies employing water as the suspending fluid [21], a one-directional cooling technique was used in these experiments and the “hot side” was not temperature controlled beyond controlling the initial suspension temperature (and the temperature of the solidification molds), G_{bulk} changes over the course of solidification due to changes in both T_C and T_H . The temperature of the freezing substrate T_C starts at the temperature of the suspension and is reduced by 5°C/min until reaching a final temperature of -20°C; thus, within two minutes, the temperature of the freezing substrate, T_C is below 0°C for the hottest initial suspension temperature (8°C). As T_H is uncontrolled once the linear cooling rate for

the freezing substrate begins, T_H will decrease over time. Considering heat transfer between ice and liquid water (as this is the cooling case for the suspension once ice forms), neglecting the impact of particle packed beds, assuming a heat transfer coefficient of $100 \text{ W/m}^2 \cdot \text{K}$, and using Newton's Law of Cooling to approximate the time it would take to cool the suspension to 4°C (the density extremum for water), the 8°C suspensions are approximated to reach 4°C about 7 minutes into freezing (~70% of the total freezing time). Thus, the double liquid density gradient is likely present for the majority of solidification. Still, experiments studying microstructural impacts of the double liquid density gradient while controlling the temperature of T_H would be helpful for confirming the relationships observed here.

5.3. Conclusion

Aqueous suspensions of 40 wt.% TiO_2 were prepared and directionally solidified using initial suspension temperatures of 0, 4, and 8°C . As water reaches its maximum density at a temperature of $\sim 4^\circ\text{C}$ and decreases with increasing, and decreasing, temperature, samples solidified using an initial suspension temperature of 8°C were expected to exhibit a double liquid density gradient in suspensions during freezing. Microstructural investigations were conducted on sublimated TiO_2 freeze-cast structures and measurements of pore and wall width were obtained from the bottom (first-to-solidify), middle, and top (last-to-solidify) regions of the sample, which were further regionalized relative to radial position (outer measurements were taken within 1 mm of the mold wall and central measurements were taken within 1 mm of the radial center). Radial segregation (variation in pore and wall width as a function of radial distance) was observed for all samples. The ratio of mean pore width for center vs. radial pores was observed to be greatest when the initial suspension temperature was 8°C relative to the 0 and 4°C cases. That is, the double-fluid density gradient scenario was correlated with greatest degree of inhomogeneity in pore width

distribution across the diameter of these samples, while samples solidified under conditions that promoted the smallest gradient in fluid density exhibited lesser variations in pore width. A similar relationship was observed for particle wall widths.

PART II. NON-AQUEOUS PROCESSING

The following three chapters (Chapter 6 through 8Chapter 8) present experimental results that were used to define the particle suspension system that has been recommended for microgravity solidification experiments intended to take place aboard the International Space Station.

Three potential fluids were initially identified as candidate materials for flight test suspensions, including: succinonitrile (SCN), camphene, and naphthalene. The main considerations in choosing candidate dispersing fluids were: the fluids should have: (i) anisotropic growth kinetics, (ii) thermal properties compatible with the Pore Formation Mobility Investigation (PFMI) furnace (for which ISS-experiments are intended; 0-130°C minimum and maximum temperatures, respectively [36]), be (iii) solid at room temperature (to enable transport of post-experiment samples without the need for refrigeration), and have (iv) compatibility with ISS safety regulations and equipment specifications. Of the fluids selected for consideration, only camphene [257-259] had been previously demonstrated in freeze-casting studies (naphthalene had been used also, but only as part of a fluid system [260-263], which is inherently quite different). Unfortunately, all of the fluids employed in previous freeze-casting studies (except camphene) were deemed unfeasible due to melting temperatures that were incompatible with the PFMI furnace. Given previous experience with camphene and the extensive literature available describing freeze-casting suspensions using camphene as a dispersing fluid, camphene testing was relatively straightforward and good results were obtained (*i.e.*, stable suspensions were produced, and anisotropic structures resulted after directional solidification). However, the fluid was removed from further consideration due to an ISS-equipment compatibility issue that was discovered during a toxicology assessment.

Succinonitrile was used in the previous PFMI investigation [32-34, 39, 172]; thus it was assumed that it would pass the toxicology assessment. SCN has also been used extensively in alloy solidification research [63, 264-270]. Accordingly, this was the first fluid tested with respect to freeze-casting compatibility. While promising initial results were obtained with SCN, the suspension preparation procedures that were being used at the time produced particle suspensions that were inconsistently stable. This lack of reliability motivated freeze-casting compatibility testing of naphthalene. Initial naphthalene tests were also inconsistent, but with changes to both the suspension preparation procedure (*e.g.*, using air-sensitive techniques, discussed in Section 3.3) and solidification procedures (to ensure proper control over the thermal gradient, discussed in Section 3.3.5.1), consistency in both suspension preparation and solidification was achieved.

Five particle types (Cu, Ag, Al₂O₃, Si₃N₄, and SiO₂), ranging in size from 0.08 to 1 μm , were initially chosen for testing in naphthalene. Viable flight test suspensions for the ISS investigation need to show freeze-thaw stability (discussed in Chapter 8); employing larger particle sizes protects against particle aggregation during freeze-thaw [271, 272]. At the same time, the upper bound for particle size is constrained by the model [29] that is intended to be tested as part of the ISS investigation. The particle size range selected represented a trade-off between these considerations. Of the particles initially selected, Cu particles were the most sphere-like (exhibiting the highest circularity values *via* image analysis) and showed the smallest particle size distribution (*via* image analysis); thus, these particles were tested first in suspensions (Al₂O₃ particles were also tested alongside Cu in the event that Cu particles did not pass toxicology assessments for the ISS; these results are not presented here, but similar freeze-cast structures were obtained using Al₂O₃ particles).

Two suspension stabilization mechanisms were chosen for testing to determine which method would produce the most stable naphthalene/Cu suspensions: steric and electrosteric stabilization. For steric stabilization, three surfactants were selected for testing: Triton X-100, Pluronic F-68, and Hypermer KD-13. Triton X-100 was selected due to its previous use in suspensions employing apolar fluids [[273-275](#)], Pluronic F-68 was selected due to literature studies showing promising results in stabilizing suspensions undergoing freeze-thaw cycles [[276-279](#)], and Hypermer KD-13 was selected due to previous experience with Hypermer surfactants. Both Triton X-100 and Pluronic F-68 produced unstable suspensions, which may have resulted from the relatively high temperatures needed for suspension processing [[280](#), [281](#)] (the melting temperature of naphthalene is $\sim 80^{\circ}\text{C}$), thus were eliminated for further consideration. For electrosteric stabilization, only one surfactant was selected for testing: Aerosol-OT (AOT), which has been used extensively to suspend particles in apolar fluids [[174](#), [282](#), [283](#)].

Chapter 6 presents experimental results for naphthalene/Cu particle suspensions sterically stabilized using Hypermer KD-13, Chapter 7 provides results corresponding to suspensions electrosterically stabilized with AOT, and Chapter 8 describes freeze-thaw testing results for both systems. Based on these results, 5 vol.% Cu particles, suspended in naphthalene, and electrosterically stabilized using 1 wt.% AOT (with respect to particle mass) is the suspension system recommended for ISS flight testing.

Chapter 6. Directional solidification of sterically-stabilized Cu/naphthalene suspensions

6.1. Motivation

The microstructures of freeze-cast materials are largely determined during solidification; thus, microstructural parameters can be tuned by modifying suspension characteristics (*e.g.*, fluid type [43], particle size and volume fraction [29, 96], and additives [97, 284]) and solidification conditions (*e.g.*, solidification velocity [29, 252] and thermal gradient [29]). Pore structure is templated by the morphology of the solidified fluid [21, 43]; thus, pore shape of freeze-cast materials is largely controlled by the choice of suspending fluid. Commonly employed fluids, including water [285, 286], camphene [287, 288], and tert-butyl alcohol [289, 290] typically produce lamellar, dendritic, and tubular structures, respectively [19, 21]. A camphor-naphthalene eutectic fluid system has been demonstrated [260-262], wherein the pore structure can be adjusted by changing the composition of the fluid mixture; *e.g.*, from dendrites, to rods, to plates, for hypoeutectic, eutectic, and hypereutectic compositions of camphor-naphthalene, respectively [262]. While these studies demonstrate that adjustments in composition of a fluid system can be used to achieve greater variety in macropore shape, in each of these reports [260-262], microstructural images convey disordered structures (microstructural directionality with respect to the imposed thermal gradient is not retained over the length of samples).

Here, *only* naphthalene is employed as the suspending fluid; naphthalene/Cu particle suspensions are sterically stabilized using a non-ionic, polymeric dispersant, Hypermer KD-13 and directionally solidified to characterize the corresponding microstructure. Naphthalene solidifies with faceted interfaces [291], thus should yield anisotropic pore structures when employed as a freeze-casting suspension fluid. The melting temperature of naphthalene (80°C [292]) and relatively high vapor pressure (130 Pa at 52°C [260]) allows for sublimation at room

temperature/ambient pressure (as reported elsewhere [260-262]). As post-solidification processing steps often result in anisotropic shrinkage (*e.g.*, during sublimation [195] and sintering [196]), microstructure investigations are conducted on solidified structures to better correlate processing conditions to microstructural characteristics.

6.2. Results and Discussion

6.2.1. *Suspension stability*

Naphthalene/Cu particle suspensions (5 vol.% Cu particles, corresponding to 32 wt.% in suspension) were sterically stabilized using 1 wt.% Hypermer KD-13 dispersant with respect to Cu particle mass (0.5 wt.% with respect to naphthalene mass) and suspension stability was assessed by measuring the thickness of particle-depletion regions in solidified samples. As samples are solidified vertically upward, particle sedimentation results in particle-enriched and particle-depleted regions within solidified samples; particle-enriched regions begin at the bottom of solidified samples (first-to-solidify regions) and particle-depletion regions end at the top (last-to-solidify regions). These regions present as a color change in these samples with particle-enriched regions appearing darker due to the dark color of Cu particles relative to naphthalene and particle depletion regions presenting as light orange to nearly clear (practically devoid of particles).

Fig. 6.1 shows the average measured thicknesses of the particle depletion regions as percentages of total solidified sample height (~ 20 cm) for samples solidified using furnace translation velocities of 6.5, 38, and 80 $\mu\text{m/s}$. Samples solidified at the highest furnace translation velocity ($V = 80 \mu\text{m} \cdot \text{s}^{-1}$) show particle depletion region thicknesses that correspond to $30\% \pm 7\%$ of the total sample height. Particle depletion region thickness increases to $58\% \pm 15\%$ for samples solidified using the slowest translation velocity ($V = 6.5 \mu\text{m} \cdot \text{s}^{-1}$), where longer solidification

times promote increased particle sedimentation. The Stokes' sedimentation velocity for $1\text{ }\mu\text{m}$ Cu particles in liquid naphthalene is $\sim 2.7\text{ }\mu\text{m} \cdot \text{s}^{-1}$; this corresponds to a particle depletion region comprising ~ 3 , 7 , and 42% of sample heights for samples solidified at 80 , 38 , and $6.5\text{ }\mu\text{m} \cdot \text{s}^{-1}$, respectively. Thus, particle depletion region thickness observed here is higher than what would be expected from Stokes' sedimentation alone. Suspensions containing 0.1 and $2.5\text{ wt.}\%$ dispersant (with respect to Cu mass) were produced to assess whether the sedimentation rates could be reduced by modifying dispersant concentration; resulting suspensions showed extensive particle sedimentation immediately after preparation, thus were not tested further.

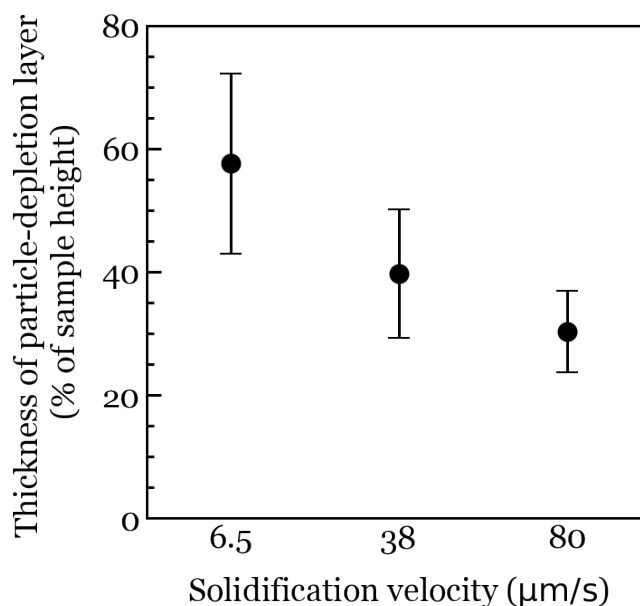


Fig. 6.1. Particle depletion layer thickness observed during solidification of naphthalene/ Cu particle suspensions stabilized with $1\text{ wt.}\%$ Hypermer KD13. Plots show average thickness of particle depletion layers formed (as a percentage of total sample height of $\sim 20\text{ cm}$) during directional solidification of Cu/naphthalene suspensions where the translation velocity of the furnace is $V = 6.5, 38$, and $80\text{ }\mu\text{m/s}$ and Cu particle fraction is $5\text{ vol.}\%$ ($32\text{ wt.}\%$). Error bars represent standard deviation.

6.2.2. Microstructural characteristics

Fig. 6.2 and Fig. 6.3 show optical micrographs of solidified structures obtained by directionally solidifying 5 vol.% (32 wt.%) Cu particle suspensions using furnace translation velocities of $V = 80$ and $38 \mu\text{m} \cdot \text{s}^{-1}$, respectively. Naphthalene, Cu particles, and dispersant are present in these images; naphthalene is transparent and appears black, whereas Cu particles appear golden. Fig. 6.2 (a) and Fig. 6.3 (a) are taken perpendicular to the freezing direction (the freezing direction is out-of-the-page) and images in Fig. 6.2 (b) and Fig. 6.3 (b) are taken parallel to the freezing direction (shown by the white arrow). For both translation velocities, the microstructures observed are lamellar (or plate-like) with dendritic features (*i.e.*, minimal secondary arm growth of naphthalene, resulting in relatively small protrusions on particle walls [140]; secondary arm growth is highlighted using small white arrows in Fig. 6.2-a and Fig. 6.3-a). The observation of highly anisotropic structures is consistent with faceted growth [291] (*i.e.*, relatively high interfacial anisotropy of the solidifying fluid). Microstructural directionality with respect to the imposed thermal gradient (white arrows in Fig. 6.2-b and Fig. 6.3-b) is largely retained over the height of these samples.

Preliminary directional solidification tests of Cu particle/naphthalene suspensions were conducted using a typical directional freeze-casting set-up [21], wherein a mold containing the suspension was temperature controlled at the top and bottom faces, providing control over the macroscopic thermal gradient in the solidifying sample, but not the thermal gradient within the melt zone, specifically. Microstructures similar to those reported in the literature for the camphor-naphthalene fluid system [260-262] were obtained; that is, some local, directional growth of naphthalene was observed, but directionality was not retained over the solidification height for these samples. Fabietti *et al.* [179, 180] reported that instability mechanisms during directional

solidification of naphthalene are strongly dependent on the orientation of the interface (which can be influenced by a lack of control over the thermal gradient at the interface [181, 182]). The improved microstructural directionality shown here was obtained only after using a Bridgman furnace (which inherently provides better control over the thermal gradient at the solid/liquid interface) to directionally solidify these suspensions.

As noted above, the images in Fig. 6.2 and Fig. 6.3 show evidence of secondary arm growth of naphthalene (small white arrows in Fig. 6.2-a and Fig. 6.3-a), but the resulting, particle-wall protrusions are primarily observed on only one side of particle walls. Asymmetric dendritic features, often referred to as “one-sided dendrites” [140], can be promoted due to the presence of interdendritic convective flow during solidification. Similar asymmetric dendritic features were reported in our previous investigation of aqueous TiO_2 suspensions [89]; there, it was proposed that rotating fluid cells between lamellae were promoted due to a shear flow existing at the solid/liquid interface, and the interaction between these fluid flow regimes promoted growth of secondary arms on the upstream side (where heat is more easily transported away from lamellae *via* the fluid flow) and the warmer fluid on the downstream side promoted melting and fragmentation of secondary arms [137]. A similar mechanism can be used to explain the observation of asymmetric dendritic features here.

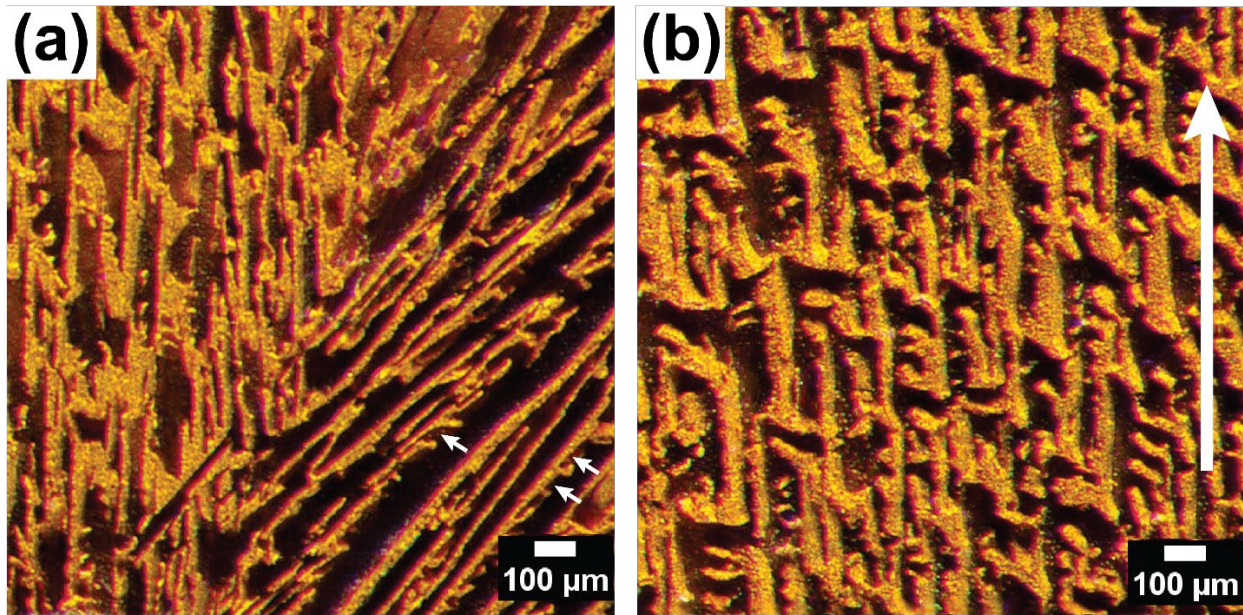


Fig. 6.2. Optical micrographs of Cu/naphthalene suspensions directionally solidified using the fastest translation velocity employed ($V = 80 \mu\text{m} \cdot \text{s}^{-1}$), where cross-sections (a) and (b) are taken perpendicular and parallel to the freezing direction, respectively; the white arrow in (b) shows the freezing direction. Macro-regions of naphthalene show as dark regions in these images; copper particle-packed walls are golden in color. The Cu particle fraction is 5 vol.% (32 wt.%) in suspension and the dispersant concentration is 1 wt.% with respect to Cu mass (0.5 wt.% with respect to naphthalene mass). Asymmetric secondary arm growth of naphthalene is highlighted with small white arrows in (a).

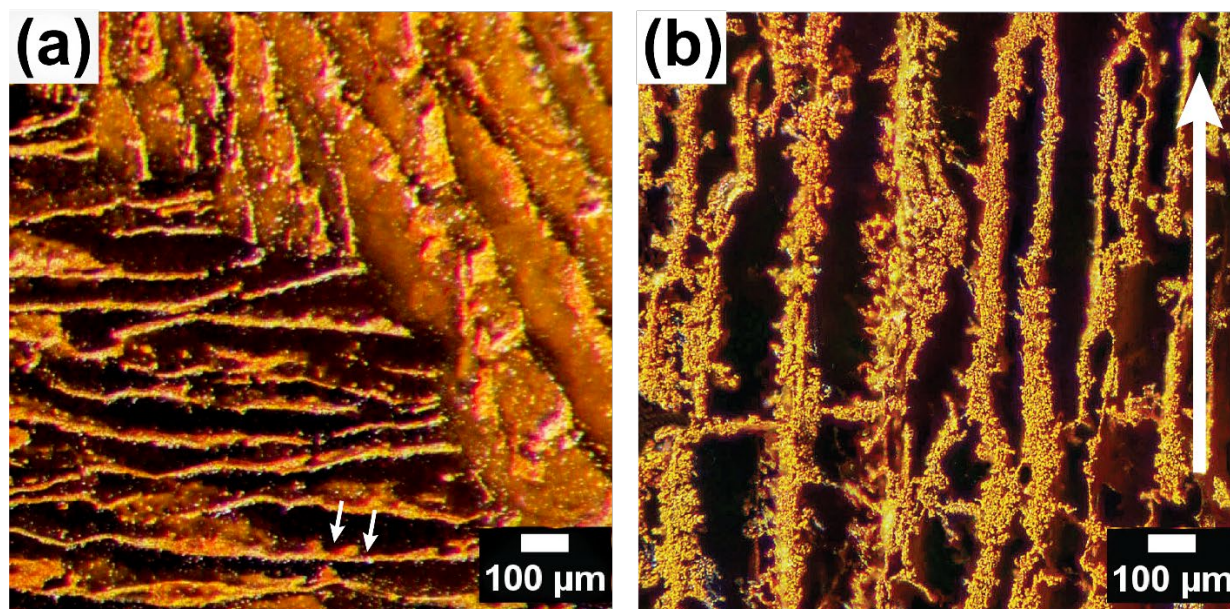


Fig. 6.3. Optical micrographs of Cu/naphthalene suspensions directionally solidified using the intermediate translation velocity employed ($V = 38 \mu\text{m} \cdot \text{s}^{-1}$), where cross-sections (a) and (b) were taken perpendicular and parallel to the freezing direction, respectively; the white arrow in (b) shows the freezing direction. Macro-regions of naphthalene show as dark regions in these images; copper particle-packed walls are golden in color. The Cu particle fraction is 5 vol.% (32 wt.%) in suspension and the dispersant concentration is 1 wt.% with respect to Cu mass (0.5 wt.% with respect to naphthalene mass). Asymmetric secondary arm growth of naphthalene is highlighted with small white arrows in (a).

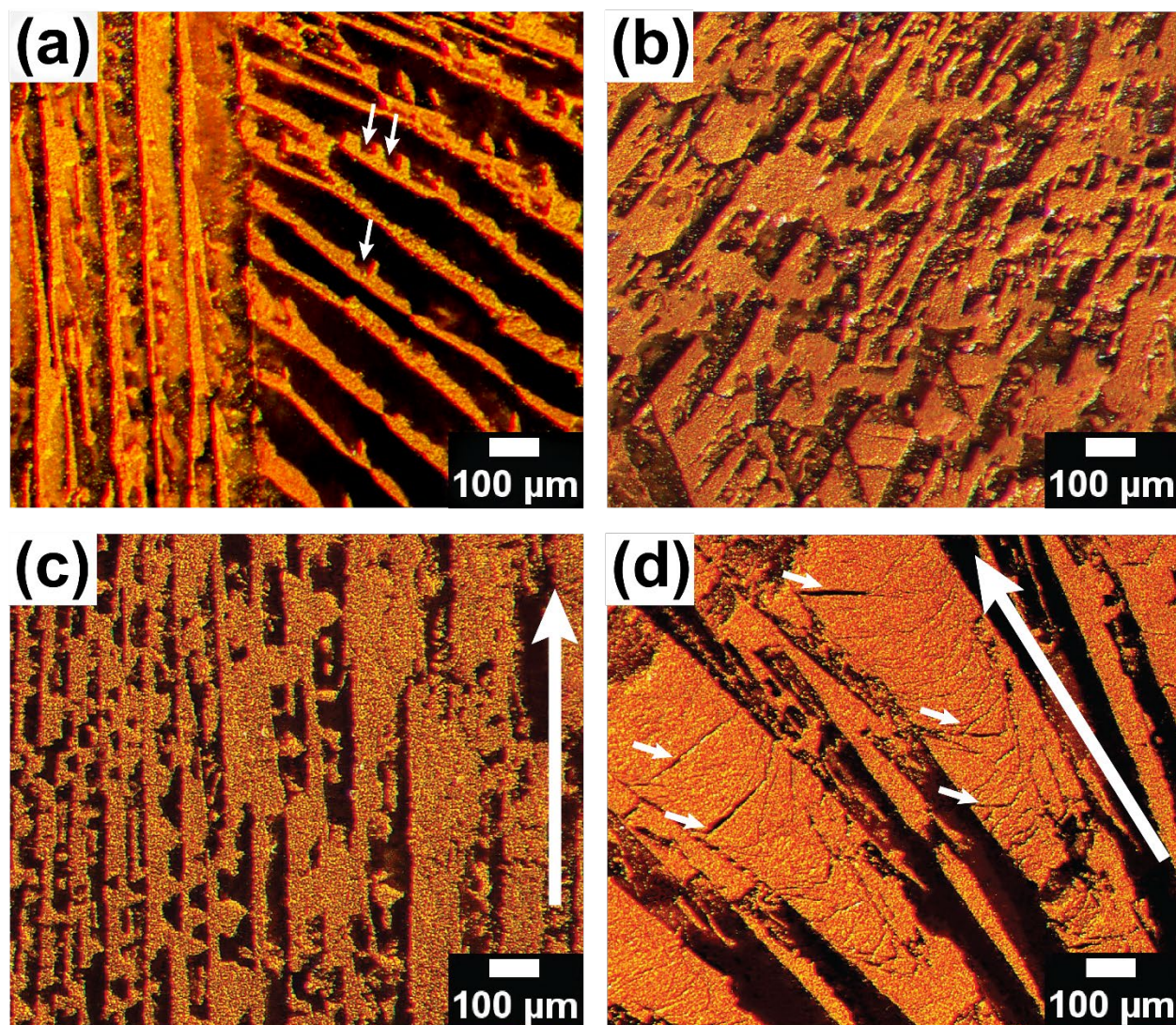


Fig. 6.4. Optical micrographs of Cu/naphthalene suspensions directionally solidified using the slowest translation velocity employed ($V = 6.5 \mu\text{m} \cdot \text{s}^{-1}$), where cross-sections (a, b) were taken perpendicular to the freezing direction and (c, d) were taken parallel to the freezing direction (the large white arrows in (c, d) show the freezing direction). Images (a) and (c) were taken from the outer regions of samples (closest to the ampoule wall) whereas (b) and (d) were taken from central regions. Macro-regions of naphthalene show as dark regions in these images; copper particle-packed walls are golden in color; lensing defects are marked with small white arrows. The Cu particle fraction is 5 vol.% (32 wt.%) in suspension and the dispersant concentration is 1 wt.% with respect to Cu mass (0.5 wt.% with respect to naphthalene mass). Asymmetric secondary arm growth of naphthalene is highlighted with small white arrows in (a).

Fig. 6.4 shows optical micrographs of solidified structures obtained by directionally solidifying 5 vol.% (32 wt.%) Cu particle suspensions at a translation velocity, $V = 6.5 \mu\text{m} \cdot \text{s}^{-1}$; here, (a, b) are taken perpendicular to the freezing direction and (c, d) are taken parallel to the freezing direction (shown by large white arrows). Cross-sections Fig. 6.4 (a) and (c) are taken from the outer region of the sample (closest to the ampoule wall) and Fig. 6.4 (b) and (d) are taken from the central region. Increased wall thickness (or wall merging) is observed in Fig. 6.4 (b) relative to (a), which is suggestive of a microstructural transition from dendrites to banding (bands are fluid-filled platelets, oriented perpendicular to the freezing direction, which are templated into cracks after sublimation [29]; these are easiest to see in parallel cross-sections). The left side of the parallel cross-section in Fig. 6.4 (c) is toward the outer region of the sample; moving towards the right in the image, the width of the particle walls increases (*i.e.*, wall width increases with increasing distance from the ampoule wall). A dramatic increase in wall width is further observed in Fig. 6.4 (d), which represents the central region of the same sample; here, lensing is observed (small white arrows in Fig. 6.4-d).

6.2.3. Radial segregation

Fig. 6.5 shows box and whisker plots describing thickness of lamellae. Measurements obtained from the “outer” (or peripheral, closest to the ampoule wall) regions of cross-sections are summarized in the leftmost plot and the rightmost plot summarizes measurements taken from inner/central regions of samples. The minimum and maximum values of boxes represent the first and third quartiles, respectively; medians are shown as horizontal lines inside the boxes, means are represented by black diamonds, and whiskers represent 1.5 times the interquartile range. Numerical values for the data described in Fig. 6.5 are provided in Table 6.1.

Lamellar thickness is expected to increase with decreasing solidification velocity [140]; taking the furnace translation velocity as roughly equivalent to solidification velocity, this relationship is observed for all regions. For all translation velocities, lamellae are thickest in the outer region of samples and a decrease in thickness is observed with decreasing distance from the center (*e.g.*, for samples solidified at $V = 6.5 \mu\text{m} \cdot \text{s}^{-1}$, lamellae thickness at the outer and inner regions is 74 ± 30 and $36 \pm 15 \mu\text{m}$, respectively; for $V = 80 \mu\text{m} \cdot \text{s}^{-1}$, these values decrease to 45 ± 23 and $19 \pm 10 \mu\text{m}$, respectively). This trend—increasing lamellar thickness at outer/peripheral regions of samples relative to inner/central regions indicates that the local solidification velocity is higher in the central region of the sample relative to the outer region, which is suggestive of macroscopic curvature of the interface during solidification and corresponding convective fluid motion [293]. Similar observations were described in our previous study investigating directional solidification of aqueous TiO_2 suspensions [89], wherein a macroscopic curvature of the solid/liquid interface was proposed to explain radial variation in particle wall width (dependent on distance from the center) and banding present in the central regions of samples. Banding development was attributed to particle build-up within the central region of samples resulting from both the interface curvature itself as well as convective mixing within the bulk liquid, ahead of the solid/liquid interface. Here, suspensions are solidified in the buoyancy-stable configuration for naphthalene (vertically upward, with solid naphthalene below and the liquid suspension above); thus, convective fluid motion is likely promoted due to the presence of radial thermal gradients at the solid/liquid interface.

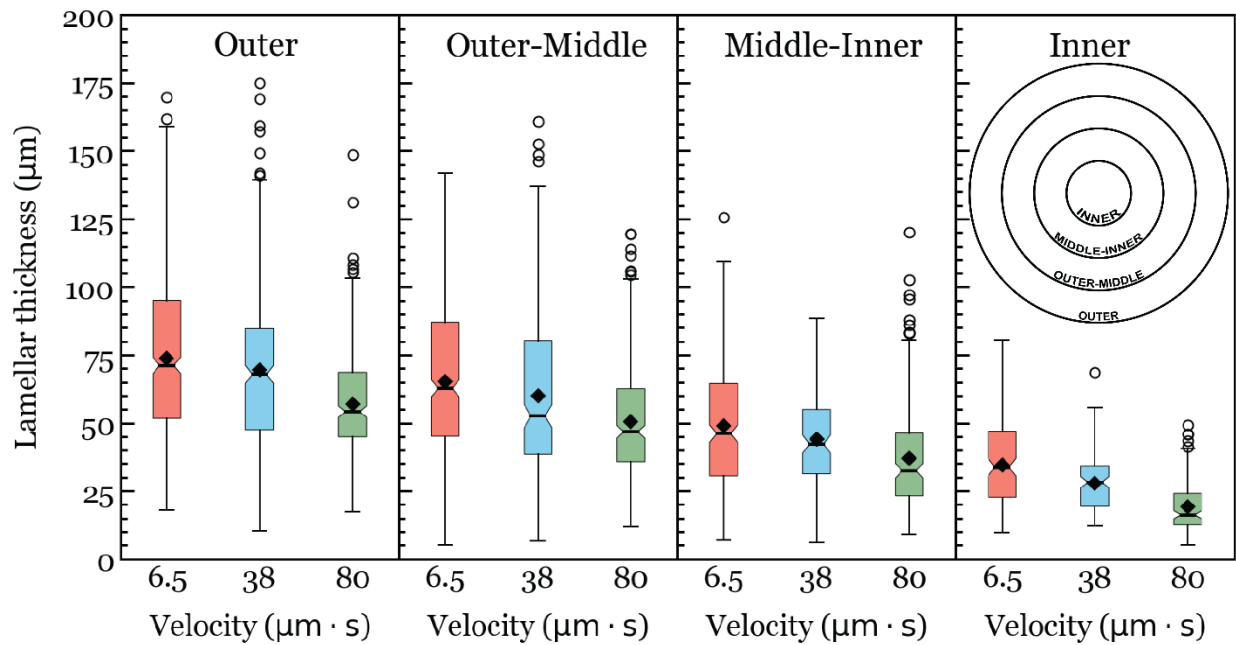


Fig. 6.5. Box and whisker plots summarizing thickness of naphthalene lamellae in 5 vol.% (32 wt.%) Cu particle suspensions stabilized using 1 wt.% Hypermer KD-13 dispersant (with respect to Cu mass; 0.5 wt.% with respect to naphthalene mass) and directionally solidified using furnace translation velocities, $V = 6.5, 38, \text{ and } 80 \mu\text{m} \cdot \text{s}^{-1}$. “Outer” measurements represent values at the outer edge of the cross-sections (closest to the ampoule wall), “inner” values are obtained 2.5 mm from the absolute center of cross-sections; “outer-middle” and “middle-inner” are obtained from equally spaced regions between the outer edge and the inner measurements. The minimum and maximum values of boxes represent the first and third quartiles, respectively; medians are shown as horizontal lines inside the boxes, means are represented by black diamonds, and whiskers represent 1.5 times the interquartile range.

Table 6.1. Thickness of naphthalene lamellae in 5 vol.% (32 wt.%) Cu particle suspensions stabilized using 1 wt.% Hypermer KD-13 dispersant (with respect to Cu mass, corresponding to 0.5 wt.% with respect to naphthalene mass) and directionally solidified using furnace translation velocities of 6.5, 38, and 80 $\mu\text{m} \cdot \text{s}^{-1}$. The thermal gradient, G is constant at $35^\circ\text{K} \cdot \text{cm}^{-1}$ for all tests. All measurements were taken from cross-sections perpendicular to the freezing directions; “outer” measurements represent values at the outer edge of the cross-sections (closest to the ampoule wall), “inner” values are obtained 2.5 mm from the absolute center of cross-sections; “outer-middle” and “middle-inner” are obtained from equally spaced regions between the outer edge and the inner measurements. Data are expressed as mean $\pm$ standard deviation; N is the number of samples.

Velocity ($\mu\text{m} \cdot \text{s}^{-1}$)	N	Naphthalene lamellae thickness (μm)			
		Outer	Outer-middle	Middle-inner	Inner
6.5	3	73 $\pm$ 31	65 $\pm$ 28	49 $\pm$ 23	36 $\pm$ 15
38	3	69 $\pm$ 29	60 $\pm$ 31	44 $\pm$ 17	28 $\pm$ 10
80	3	57 $\pm$ 19	50 $\pm$ 21	37 $\pm$ 20	19 $\pm$ 10

6.3. Model comparison

The You *et al.* [29] model for predicting freeze-cast microstructures based on solidification conditions and suspension characteristics is described in Section 2.5. Using Eq. 2.1-Eq. 2.3, with values describing the system tested here ($T_m = 80.23^\circ\text{C}$ for naphthalene [294], $\rho = 976.7 \text{ kg} \cdot \text{m}^3$ [295], $L = 146 \text{ J/g}$ [296], $G = 35^\circ\text{C} \cdot \text{cm}^{-1}$, $r = 0.5 \mu\text{m}$, $\phi_p = 0.05$, and taking V as equivalent to the furnace translation velocity), the microstructures for all V tested here are within the lensing regime (considering that dendritic structures are predicted when $D/(1 + \Phi) > 1$, whereas lensing regimes are predicted when this value is less than one). Anisotropic, directional structures are observed for $V = 38$ and $80 \mu\text{m} \cdot \text{s}^{-1}$ (inconsistent with model predictions); at $V = 6.5 \mu\text{m} \cdot \text{s}^{-1}$, a transition between dendritic to lensing microstructures is observed from the outer to inner region of the samples. The transition to lensing with decreasing V is consistent with this model, but it is notable that lensing is observed in the central regions of samples *only*; this observation may be

attributable to convective effects [89], which are not accounted for in the model. Discrepancies between model predictions and realized structures for the naphthalene/Cu system are further discussed in Chapter 7.

6.4. Conclusions

Suspensions of 5 vol.% (32 wt.%) Cu particles in naphthalene were sterically stabilized using 1 wt.% Hypermer KD-13 (with respect to Cu particle mass, 0.5 wt.% with respect to naphthalene mass) and directionally solidified to investigate the suitability of naphthalene as a suspending fluid for freeze-casting applications. A Bridgman furnace was used for directional solidification at furnace translation velocities, $V = 6.5, 38, \text{ and } 80 \mu\text{m} \cdot \text{s}^{-1}$, and microstructural investigations were carried out on solidified samples. At $V = 38 \text{ and } 80 \mu\text{m} \cdot \text{s}^{-1}$, lamellar structures exhibiting a preferred growth direction consistent with the direction of the thermal gradient imposed during solidification were observed over the height of solidified samples. At $V = 6.5 \mu\text{m} \cdot \text{s}^{-1}$, a transition between lamellar to lensing microstructures was observed from the outer to inner region of the samples (closest to the ampoule wall relative to central regions). For all V , the thickness of lamellae increased with increasing distance from the outer region of the samples (*i.e.*, lamellae are thinnest in the central regions of samples) and lamellae showed asymmetric growth of secondary arms (secondary arm growth present on only one side of lamellae). Both the presence of asymmetric dendritic features and the radial variation in lamellar thickness are suggestive of buoyancy-driven convective fluid flow during solidification. As suspensions were solidified in a buoyancy-stable configuration for naphthalene (vertically upward, with solid naphthalene below and liquid above), convective fluid motion is likely introduced due to radial temperature gradients that often present during Bridgman solidification.

Chapter 7. Directional solidification of electrosterically-stabilized naphthalene/Cu particle suspensions

7.1. Motivation

In the previous chapter, it was demonstrated that when naphthalene is independently employed as a suspending fluid (and solidified using a Bridgman furnace, see 3.3.5), resulting structures are predominately lamellar and qualitatively show increased directionality relative to previous reports for camphor-naphthalene [260-262]. Porous materials exhibiting lamellar structures are argued to be advantageous when used in applications such as biomedical implants [297], sound absorption [298], and electrodes [299]. To date, lamellar structures have also been reported for freeze-casting systems employing water [140] and dimethyl carbonate [68] as suspending fluids.

In Chapter 6, naphthalene/Cu particle suspensions were sterically stabilized using a non-ionic polymeric dispersant, Hypermer KD-13. While steric stabilization is the most commonly used method for dispersing particles in low-dielectric constant (ϵ) fluids [300-303] (e.g., naphthalene, where $\epsilon \approx 3.2$ at 80°C [304]), enhanced suspension stability has been reported *via* electrosteric stabilization methods [174, 176, 178, 283, 305, 306]. Here, an anionic surfactant, Aerosol-OT (AOT, Fig. 7.1), is used to electrosterically stabilize naphthalene/Cu particle suspensions for directional solidification. When employed at appropriate concentrations in apolar media, AOT forms charge-stabilized, reverse micelles around particles [175, 282] (that is, the polar heads of AOT adsorb to particle surfaces, in some cases, with help from the counterion, Na^+ , which creates a bridge [174]; the polar head groups are drawn inward while the nonpolar tails face outward to the solvent; here, naphthalene). To my knowledge, this is the first directional freeze-

casting study that investigates directional solidification of electrosterically-stabilized suspensions with an apolar fluid.

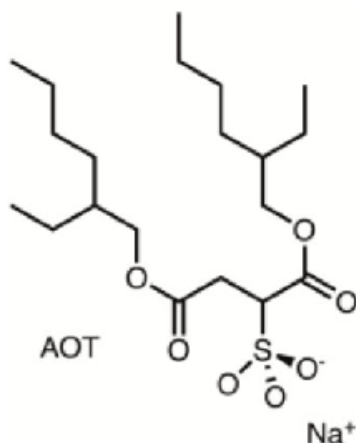


Fig. 7.1. Structure of Aerosol-OT (AOT) surfactant. Figure extracted without modification from ref. [\[307\]](#).

7.2. Results

7.2.1. Differential scanning calorimetry

Table 7.1 provides a summary of DSC results, including melting temperature, T_m and enthalpy of fusion, ΔH_f , obtained for as-received and vacuum-distilled naphthalene, naphthalene and 1 wt.% AOT (with respect to intended Cu mass, corresponding to 0.5 wt.% with respect to naphthalene mass), and naphthalene/Cu particle suspensions containing 1 wt.% AOT (with respect to particle mass, corresponding to 0.5 wt.% with respect to naphthalene mass). The average melting temperature for vacuum distilled naphthalene is 79.64 ± 0.07 °C, representing a melting point depression of ~ 0.6 °C relative to pure naphthalene ($T_m = 80.23$ °C [\[294\]](#)); this melting

temperature is $\sim 0.15^\circ\text{C}$ higher than that measured for as-received naphthalene. Melting points of $>79.6^\circ\text{C}$ for naphthalene are thought to represent a naphthalene content in excess of 98.7% [308]. Freezing point depression resulting from the addition of AOT is $\sim 1.03^\circ\text{C}$ relative to pure naphthalene (0.44°C relative to the vacuum-distilled naphthalene). Additional freezing point depression is not observed with the addition of particles. Peppin *et al.* [27, 119] studied particle-induced undercooling and derived an expression for the thermodynamic freezing temperature for suspensions of hard sphere particles undergoing directional solidification. Particle-induced undercooling of suspensions increases with decreasing particle size and increasing particle volume fraction and is generally negligible for particle sizes greater than ~ 5 nm [21], consistent with these results (where the particle size is ~ 1 μm and the particle volume fraction is relatively low, at 5 vol.%).

Table 7.1. Summary of calorimetry results, including melting temperature (T_m) and enthalpy of fusion (ΔH_f) for naphthalene (as-received and vacuum-distilled), naphthalene with 1 wt.% AOT (with respect to intended particle mass at 5 vol.% Cu, corresponding to 0.5 wt.% with respect to naphthalene mass) and 5 vol.% Cu particles (32 wt.%) suspended in naphthalene with 1 wt.% AOT (with respect to Cu mass; 0.5 wt.% with respect to naphthalene mass). The column, ΔT_m provides the calculated melting point depression relative to pure [294] and distilled naphthalene; N is the number of samples analyzed and $\bar{x}$ and σ are the mean and standard deviation, respectively.

Sample type	N	$T_m(^{\circ}\text{C})$		ΔT_m		$\Delta H_f(\text{J/g})$	
		$\bar{x}$	σ	Pure	Distilled	$\bar{x}$	σ
Naphthalene, pure [294]	-	80.23	-	-	-	146.60	0.60
Naphthalene, as-received	10	79.49	0.07	-0.74	-	143.61	2.16
Naphthalene, vacuum distillation	10	79.64	0.17	-0.59	-	145.07	1.68
1 wt.% AOT	10	79.20	0.09	-1.03	-0.44	141.13	3.56
5 vol.% Cu, 1 wt.% AOT suspension	10	79.33	0.06	-0.90	-0.31	143.23	1.18

7.2.2. Surfactant concentration

Suspensions containing 5 vol.% (32 wt.%) Cu particles in naphthalene and 0.1, 1, and 2.5 wt.% AOT (with respect to Cu mass, corresponding to 0.05, 0.5, and 1.2 wt.% with respect to naphthalene mass) were prepared and directionally solidified to better understand the role of surfactant concentration on suspension stability and resulting microstructures. Fig. 7.2 shows optical micrographs of directionally solidified suspensions containing the lowest concentration of AOT (0.1 wt.% with respect to Cu mass); while naphthalene is present, it is transparent (thus, is shown as black regions in these images; copper particles show as orange; though, the combination of naphthalene's transparency and the use of a stereoscope provides a relatively high depth of field in some of these images). All images in Fig. 7.2 are taken parallel to the freezing direction, and the black arrow shows the direction of furnace translation ($V = 80 \mu\text{m} \cdot \text{s}^{-1}$).

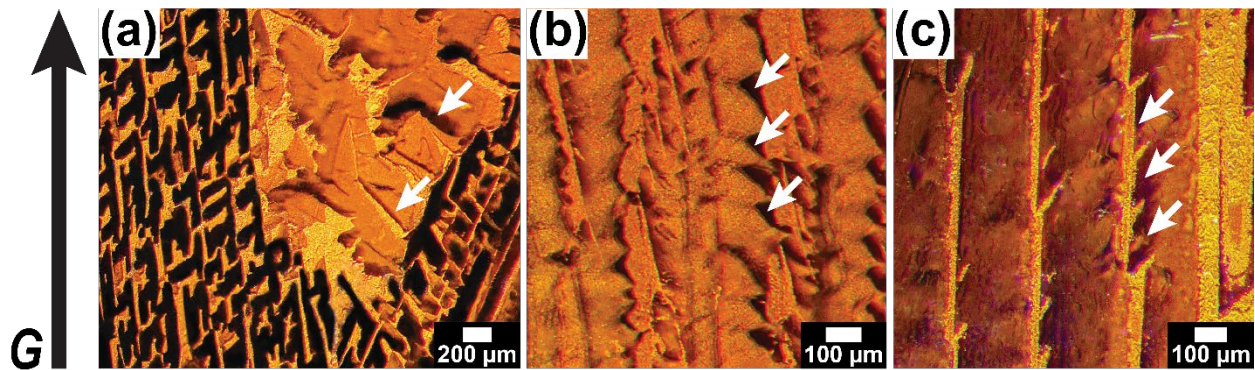


Fig. 7.2. Optical micrographs of directionally solidified naphthalene/Cu particle suspensions containing 0.1 wt.% AOT with respect to Cu mass. The Cu particle fraction is 5 vol.% (32 wt.%) in suspension and the dispersant concentration is 0.05 wt.% with respect to naphthalene mass. The translation velocity of the furnace was $V = 80 \mu\text{m} \cdot \text{s}^{-1}$, and all images were taken parallel to the freezing direction (black arrow). Image (a) shows evidence of banding in the core of the sample (white arrows) which is surrounded by dendrites that are tilted with respect to the induced thermal gradient (G). Images (b) and (c) were taken from the same sample with (b) representing the lower region of the sample (first-to-solidify) and (c) representing the middle region; evidence of asymmetric secondary arm growth is observed, highlighted by white arrows.

Two distinct microstructural patterns are observed over five 0.1 wt.% AOT samples; three of the samples exhibit microstructures represented in Fig. 7.2 (a), where the core of samples show banding (naphthalene and particle wall regions oriented perpendicular to the freezing direction rather than parallel, as they are for dendritic/lamellar growth), with dendritic/cellular growth surrounding the core (here, “cellular” is used to indicate that the connectivity between particle walls is relatively high; after naphthalene sublimation and sintering of the particle walls, the resulting porous structure would be expected to respond mechanically more similarly to a typical cellular solid than a highly anisotropic freeze-cast material, which exhibit anisotropic mechanical properties that depend on the direction of loading [21]). The dendritic/cellular regions are tilted with respect to the induced thermal gradient (which is vertical for these images), and the tilt direction is toward the ampoule wall. Here, samples are solidified vertically upwards; for naphthalene, this is the buoyancy-stable configuration as the density of liquid naphthalene decreases with increasing temperature (for solidification proceeding vertically upward, the liquid at the solid/liquid interface is cooler and denser than the bulk suspension fluid above the solid/liquid interface). However, Bridgman solidification introduces radial temperature gradients, which can lead to macroscopic interface curvature and convective fluid motion [309] (due to radial gradients in fluid density resulting from the radial temperature gradients); microstructural tilting in the direction of convective flow (rather than alignment with the induced thermal gradient) is often observed in these cases [235].

We previously described similar microstructures (tilted dendrites around a central banding region) for aqueous suspensions of TiO_2 directionally solidified using a gradient freezing technique (more typical of freeze-casting work than Bridgman solidification) and solidified in the buoyancy-unstable configuration (which, for water, is vertically upward) [89]. As banding is

typically attributed to a pattern of particle engulfment, rather than rejection, at the solidification interface (and engulfment behavior is expected to increase with increasing local particle volume fractions) [25, 27, 85, 122, 123], banding is attributed to particle redistribution at the solid/liquid interface resulting from macroscopic interface curvature. For a concave macroscopic interface curvature, the local particle fraction is expected to be higher in the center of the sample relative to the periphery [130]; at the particle “breakthrough concentration,” dendrites are unable to propagate through the particle accumulation layer and banding may develop [124].

The remaining two 0.1 wt.% AOT samples exhibit the microstructures shown in the combination of Fig. 7.2(b) and (c), which are taken from the same sample with (b) representing the lower region of the sample (first-to-solidify) and (c) representing the middle region. Here, the particle volume fraction in the first-to-solidify region is higher than in the middle region, where the particle walls are thinner; the top region of the sample is nearly devoid of particles. As the solidification direction is upwards (against gravity), particle enrichment at the base of these samples can be attributed to particle sedimentation. High particle sedimentation rates suggest use of unstable suspensions. Unstable suspensions have also been shown to increase the propensity for lensing [85] as high sedimentation rates increase the local particle fraction at the solid/liquid interface (thus, promote engulfment behavior, as described above). Evidence of asymmetric secondary arm growth is also observed; that is, lamellar structures showing secondary arm growth on one side of lamellae (shown by white arrows in Fig. 7.2-b and c), which is suggestive of interdendritic convective fluid flow [89].

Fig. 7.3 shows optical micrographs of directionally solidified suspensions containing the highest concentration of AOT (2.5 wt.% with respect to Cu mass). Again, all images are taken parallel to the solidification direction (black arrows in Fig. 7.3) and the furnace translation velocity

is $80 \mu\text{m} \cdot \text{s}^{-1}$. Considerable variation in microstructures is observed within these samples, with all samples showing regions of (tilted) lamellae with asymmetric dendritic features. For all five samples, lensing typically occurs in the later-to-solidify regions (vertically, the middle region is shown here). Images in Fig. 7.3 (a-d) are taken from the same sample, where (a) shows a low magnification view of the lower-outer region of the sample and (b) and (c) show higher magnification views. Considerable microstructural tilting with respect to the imposed thermal gradient is observed in Fig. 7.3 (a) and (c), which is suggestive of radial temperature gradients during solidification, as described above. The lower magnification view in Fig. 7.3 (a) shows that tilting is more pronounced closer to the quartz wall (left side of the image) relative to the center, similar to what is observed in the 0.1 wt.% AOT samples where banding is present. The combination of the images shown in Fig. 7.3 (b) and (c) shows that naphthalene is lamellar in structure and exhibits asymmetric dendritic features (white arrows in Fig. 7.3-c). The image in Fig. 7.3(d) is also taken from the lower (first-to-solidify region), but from the central region (away from the ampoule wall); the asymmetric dendritic side arms are pronounced, and the overall structure size (both particle walls and naphthalene thickness) has noticeably increased.

The images in Fig. 7.3(e-g) show banding in the 2.5 wt.% AOT samples which occurs in the later-to-solidify regions of the samples (vertically, the middle region is shown here). Fig. 7.3(e) and (f) are from the same sample, where (e) shows the outer region (closer to the quartz wall, left of the image) and part of the central region (right of the image) and (f) shows the central region only. The outer region of the sample is particle-dense, and the central region shows disordered growth with banding. Some directional (albeit, tilted) growth is observed in some areas, immediately outside the central, disordered-growth region; this is seen in the bottom right corner of Fig. 7.3 (f). Fig. 7.3 (g) shows the central region of a different sample with the beginning of the

outer region at the right side of the image. Again, tilted lamellae (with respect to the imposed thermal gradient) are observed, leading to disordered growth and lensing in the central region of the sample. Here, a dense particle region at the periphery of the sample is not observed.

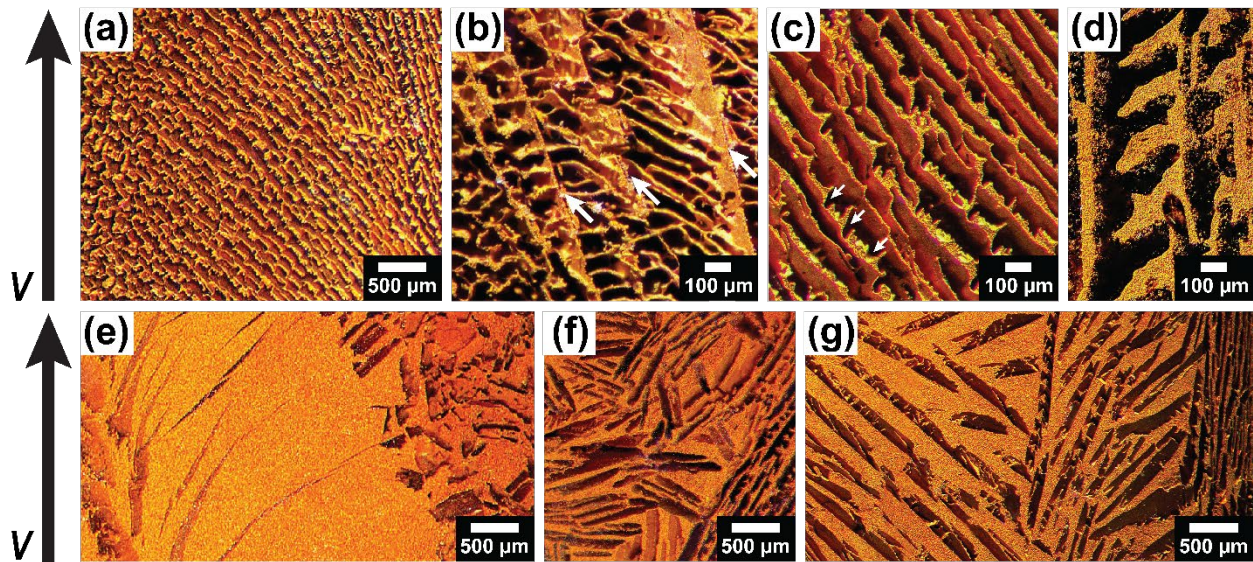


Fig. 7.3. Optical micrographs of directionally solidified naphthalene/Cu particle suspensions containing 2.5 wt.% AOT with respect to Cu mass. The Cu particle fraction is 5 vol.% (32 wt.%) in suspension and the dispersant concentration is 1.2 wt.% with respect to naphthalene mass. The translation velocity of the furnace was $V = 80 \mu\text{m} \cdot \text{s}^{-1}$ and all images were taken parallel to the freezing direction (black arrow). Images (a-d) are taken from the same sample, with (a) showing a relatively low magnification view; (b) shows the lamellar structure of naphthalene, which is arranged in plates (white arrows). Image (c) shows asymmetric secondary arm growth (white arrows); (d) shows the inner-most region of the sample where secondary arm growth is pronounced and lamellae and particle wall width is increased relative to (b, c), which were taken towards the outer region. Images (e-g) show banding in two different samples; in (e), the banding is extreme, presenting as a dense particle region in the outer regions of the sample and disordered structures in the central region; (f) shows a view of the central region only. In (g), directional growth is observed towards the outer region of the sample (right side of the image) and banding is observed in the central region.

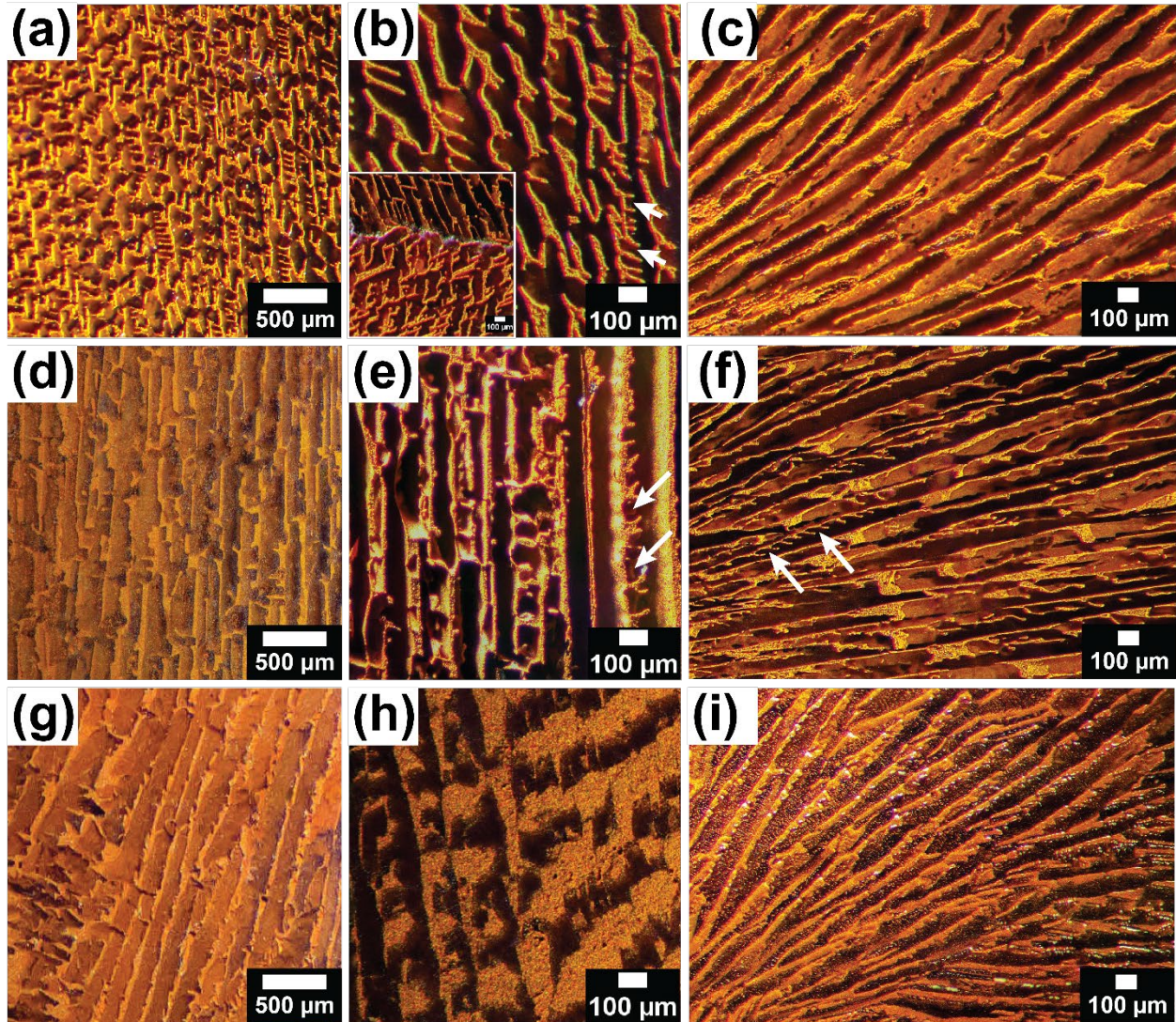


Fig. 7.4. Optical micrographs of directionally solidified naphthalene/Cu particle suspensions containing 1 wt.% AOT with respect to Cu mass. The Cu particle fraction is 5 vol.% (32 wt.%) in suspension and the dispersant concentration is 0.5 wt.% with respect to naphthalene mass. The translation velocity of the furnace was $V = 80 \mu\text{m} \cdot \text{s}^{-1}$ for (a-c), $38 \mu\text{m} \cdot \text{s}^{-1}$ for (d-f), and $6.5 \mu\text{m} \cdot \text{s}^{-1}$ for (g-i). Images (c), (f), and (i) were taken perpendicular to the freezing direction, while other images were taken parallel. Some evidence of secondary dendrite arm growth is marked by small white arrows.

Fig. 7.4 shows optical micrographs of suspensions containing an intermediate concentration of AOT (1 wt.% with respect to Cu mass), where images in Fig. 7.4(a-c) are directionally solidified at the same furnace translation velocity as used for 0.1 and 2.5 wt.% AOT described above ($V = 80 \mu\text{m} \cdot \text{s}^{-1}$). Here, Fig. 7.4(a) and (b) are taken parallel to the freezing direction, whereas (c) is taken perpendicular to the freezing direction. Lamellar structures are observed throughout these samples (while Fig. 7.4-a and b may appear dendritic/cellular, it is clear from the insert in (b) that the overall microstructure is lamellar and (a) and (b) show the dendritic feature pattern arising from secondary arm growth), and banding is not observed; microstructural tilting relative to the imposed thermal gradient is minimal relative to that observed for the other AOT concentrations. Like before, asymmetry in dendritic features is observed, which is highlighted with white arrows in Fig. 7.4(b).

Relative particle sedimentation was assessed for all AOT concentrations by measuring the thickness of the particle-depletion region in solidified samples; as before, this region presents as a color change in solidified specimens, ranging from light orange (relative to dark orange/brown for particle enriched regions) to nearly clear (practically devoid of particles). As shown in Fig. 7.5 (and Table 7.2), the height of the particle depletion region comprises $37\% \pm 10\%$ and $41\% \pm 3\%$ of the total height ($\sim 20 \text{ cm}$) of samples directionally solidified using suspensions stabilized with 0.1 and 2.5 wt.% AOT (with respect to Cu mass), respectively; for 1 wt.% AOT, this region comprised $0.3\% \pm 0.6\%$ of the total solidified height. The Stokes' sedimentation velocity for $1 \mu\text{m}$ Cu particles in liquid naphthalene is $\sim 2.7 \mu\text{m} \cdot \text{s}^{-1}$; for the system employed here, this roughly corresponds to a particle depletion region comprising $\sim 3\%$ of the height of the sample. Thus, the particle depletion layer observed for the 0.1 and 2.5 wt.% AOT samples is considerably higher than what would be expected from Stokes' sedimentation alone, whereas the 1 wt.% AOT samples exhibit lower rates

of sedimentation than expected. For the previous investigation (Chapter 6), where naphthalene/Cu suspensions were sterically stabilized using Hypermer KD-13, particle depletion layers comprised $30\% \pm 7\%$ of the total solidification height, on average, which are lower than those obtained with 0.1 and 2.5 wt.% AOT, but considerably higher than that obtained with 1 wt.% AOT, lending support to the idea that increased suspension stability can be found *via* electrosteric stabilization when employing apolar fluids [174, 176, 178, 283, 305, 306]. Fig. 7.6 shows a comparison of particle depletion layer thickness formed for 1 wt.% AOT suspensions vs. 1 wt.% KD-13 solidified at 6.5, 38, and $80 \mu\text{m} \cdot \text{s}^{-1}$.

While there are better approaches for assessing suspension stability of systems employing apolar fluids (*e.g.*, electrophoretic mobility measurements [174, 283, 310, 311]), these results demonstrate that, for this system, 0.1 and 2.5 wt.% AOT suspensions are unstable and 1 wt.% AOT suspensions are relatively stable. Consistent with these results, Gacek *et al.* [174] studied the dependence of AOT concentration on electrophoretic mobility in SiO_2 , TiO_2 , Al_2O_3 , ZnO , and MgO particle suspensions using Isopar-L as the suspending fluid ($\epsilon = 2.0$) and found that all particle systems showed a similar dependence on AOT concentration with maximum electrophoretic mobility occurring at ~ 1 wt.% AOT (decreased relative mobility, indicating a decrease in suspension stability, was observed above and below this concentration).

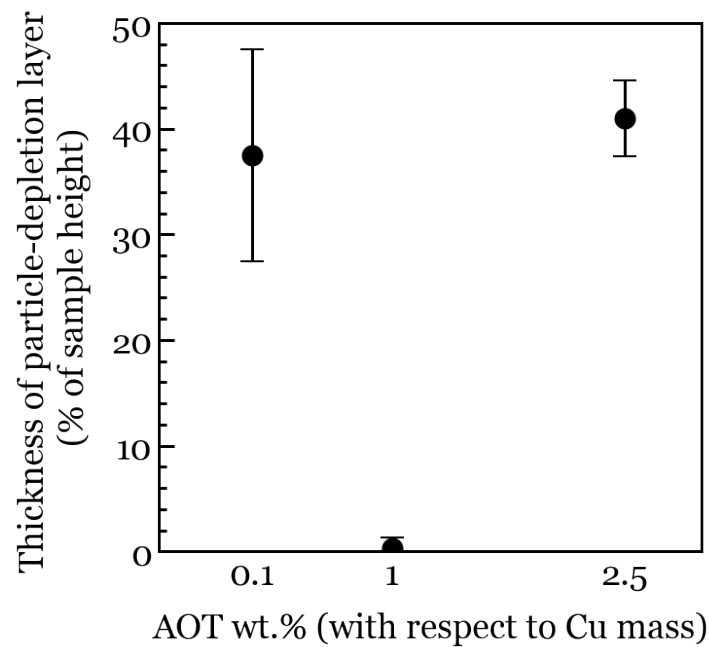


Fig. 7.5. Particle depletion layer thickness observed during solidification of AOT-stabilized naphthalene/Cu suspensions with respect to AOT weight fraction. Plots show average thickness of particle depletion layers formed (as a percentage of total sample height of ~ 20 cm) during directional solidification of 5 vol.% (32 wt.%) Cu/naphthalene suspensions stabilized using 0.1, 1, and 2.5 wt.% AOT (with respect to Cu mass, corresponding to 0.05, 0.5, and 1.2 wt.% with respect to naphthalene mass) where the translation velocity of the furnace is $V = 80 \mu\text{m/s}$ for all. Error bars represent standard deviation.

Table 7.2. Particle depletion layer thickness as observed during solidification of varying weight fractions of AOT-stabilized particle suspensions. Average thickness of particle depletion layers (as a percentage of total sample height of ~ 20 cm) as measured from solidified samples of 5 vol.% (32 wt.% Cu particle/naphthalene suspensions stabilized with AOT (weight fractions are given with respect to particle mass, corresponding to 0.05, 0.5, and 1.2 wt.% with respect to naphthalene mass) and directionally solidified at translation velocities, $V = 6.5, 38$, and $80 \mu\text{m/s}$. The particle depletion layer thickness that would result from Stokes' sedimentation (alone) is also provided.

System	Sedimentation layer thickness (as % of solidified sample height)		
	$V = 80 \mu\text{m/s}$	$V = 38 \mu\text{m/s}$	$V = 6.5 \mu\text{m/s}$
AOT (0.1 wt.%)	$37\% \pm 10\%$	-	-
AOT (1 wt.%)	$0.3\% \pm 0.6\%$	$5\% \pm 5\%$	$20\% \pm 8\%$
AOT (2.5 wt.%)	$41\% \pm 4\%$	-	-
Stokes' sedimentation	4%	7%	42%

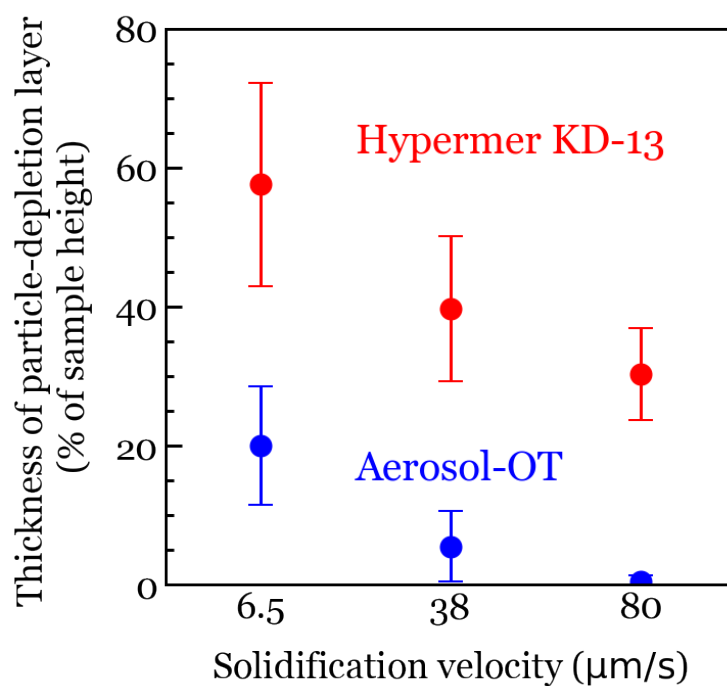


Fig. 7.6. Particle depletion layer thickness observed during solidification of AOT and KD-13 stabilized particle suspensions. Plots show average thickness of particle depletion layers formed (as a percentage of total sample height of ~ 20 cm) during directional solidification of 5 vol.% (32 wt.%) Cu particle/naphthalene suspensions stabilized with (blue) 1 wt.% AOT (with respect to Cu particle mass, corresponding to 0.5 wt.% with respect to naphthalene) and (red) 1 wt.% KD-13 (with respect to Cu particle mass, corresponding to 0.5 wt.% with respect to naphthalene), using translation velocities, $V = 80, 38$, and $6.5 \mu\text{m/s}$. Error bars represent standard deviation.

7.2.3. Furnace translation velocity

Fig. 7.4 shows optical micrographs of 1 wt.% AOT suspensions solidified using three different furnace translation velocities: $V = 80 \mu\text{m} \cdot \text{s}^{-1}$ for (a-c), $80 \mu\text{m} \cdot \text{s}^{-1}$ for (d-f), and $6.5 \mu\text{m} \cdot \text{s}^{-1}$ for (g-i). Images in Fig. 7.4(a, b), (d, e), and (g, h) are taken parallel to the solidification direction, whereas (c), (f), and (i) are taken perpendicular (freezing direction is out-of-the-page). As before, naphthalene and Cu are both present, naphthalene-rich regions typically appear black in these images and the copper particles are orange/brown.

As described above, suspensions solidified at $80 \mu\text{m} \cdot \text{s}^{-1}$ (Fig. 7.4, a-c) show lamellar structures with dendritic features (some are shown by white arrows in Fig. 7.4-b). At $V = 38 \mu\text{m} \cdot \text{s}^{-1}$ (Fig. 7.4, d-f), a plate-like, lamellar structure is observed; again, asymmetric dendritic features are present (shown by white arrows in Fig. 7.4-e, f). Fig. 7.4 (g-i), solidified using a translation velocity of $6.5 \mu\text{m} \cdot \text{s}^{-1}$ also shows a lamellar structure (Fig. 7.4-g), but in this case, banding in the central region of the sample (Fig. 7.4-h) is also observed. Similar to what was shown for the unstable suspensions (0.1 and 2.5 wt.% AOT), a transition to banding is observed with respect to radial distance from the mold wall—directional growth is present closer to the ampoule wall (Fig. 7.4-g); moving towards the central region, thickening of the walls (left side of Fig. 7.4-h, similar to Fig. 7.4-g) is observed, and finally, consistent with banding, naphthalene growth is perpendicular to the imposed thermal gradient (right side of Fig. 7.4-h). The dependence of V on microstructural development is discussed further in Section 7.4.

Fig. 7.7 shows X-ray tomography reconstructions of 1 wt.% AOT suspensions solidified at (a) 80, (b) 38, and (c) $6.5 \mu\text{m} \cdot \text{s}^{-1}$, where all cubes have side lengths of $450 \mu\text{m}$ and freezing proceeds from the bottom to the top for all images. All specimens were taken from outer/peripheral regions of the samples (within $\sim 1 \text{ mm}$ of the ampoule wall). Here, naphthalene plate thickness

(transparent in these reconstructions, but inferred as the spacing between particle-walls) increases with decreasing solidification velocity; this is a well-known relationship observed in freeze-casting and general solidification literature—increasing solidification velocity results in thinner lamellae [140, 312, 313]. Qualitatively, increasing connectivity between particle walls with increasing V is also observed, consistent with observations in aqueous systems where increasing V leads to an increase in secondary arm growth, resulting in increased particle wall connectivity [95, 252].

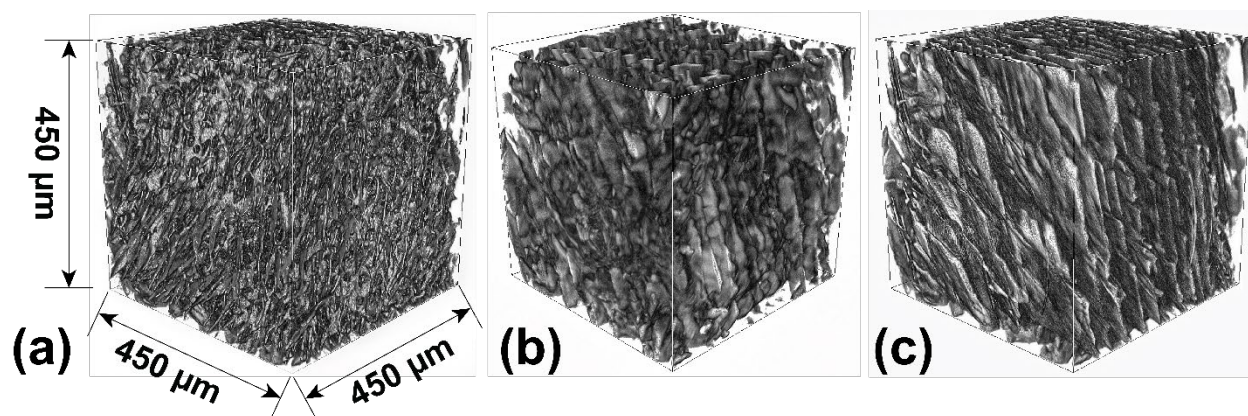


Fig. 7.7. X-ray tomography reconstructions of directionally solidified naphthalene/Cu particle suspensions stabilized using 1 wt.% AOT surfactant. Suspensions of 5 vol.% Cu particles (32 wt.%) in naphthalene were solidified using a furnace translation velocity of: (a) $80 \mu\text{m} \cdot \text{s}^{-1}$, (b) $38 \mu\text{m} \cdot \text{s}^{-1}$, and (c) $6.5 \mu\text{m} \cdot \text{s}^{-1}$; all cubes have side lengths of $450 \mu\text{m}$ and the direction of freezing is from the bottom of cubes to the top. While naphthalene and AOT are present, only the Cu particles are visible here.

7.2.4. Radial segregation

Fig. 7.8 shows box and whisker plots summarizing the widths of naphthalene lamellae for 1 wt.% AOT suspensions solidified at 6.5, 38, and $80 \mu\text{m} \cdot \text{s}^{-1}$. All measurements are taken from cross-sections perpendicular to the freezing direction; “outer” measurements (left-most plot) summarize values obtained from the outer edge of cross-sections, “inner” values (right-most plot) are obtained

2.5 mm from the absolute center of cross-sections; “outer-middle” and “middle-inner” values summarize measurements obtained from lamellae crossing circle guides that were drawn at equal spacing between the outer edge and inner measurements (Fig. 7.8, insert). The minimum and maximum values of boxes represent the first and third quartiles, respectively; medians are shown as horizontal lines inside the boxes, means are represented by black diamonds, and whiskers represent 1.5 times the interquartile range. Table 7.3 provides numerical values of mean $\pm$ standard deviation for these data.

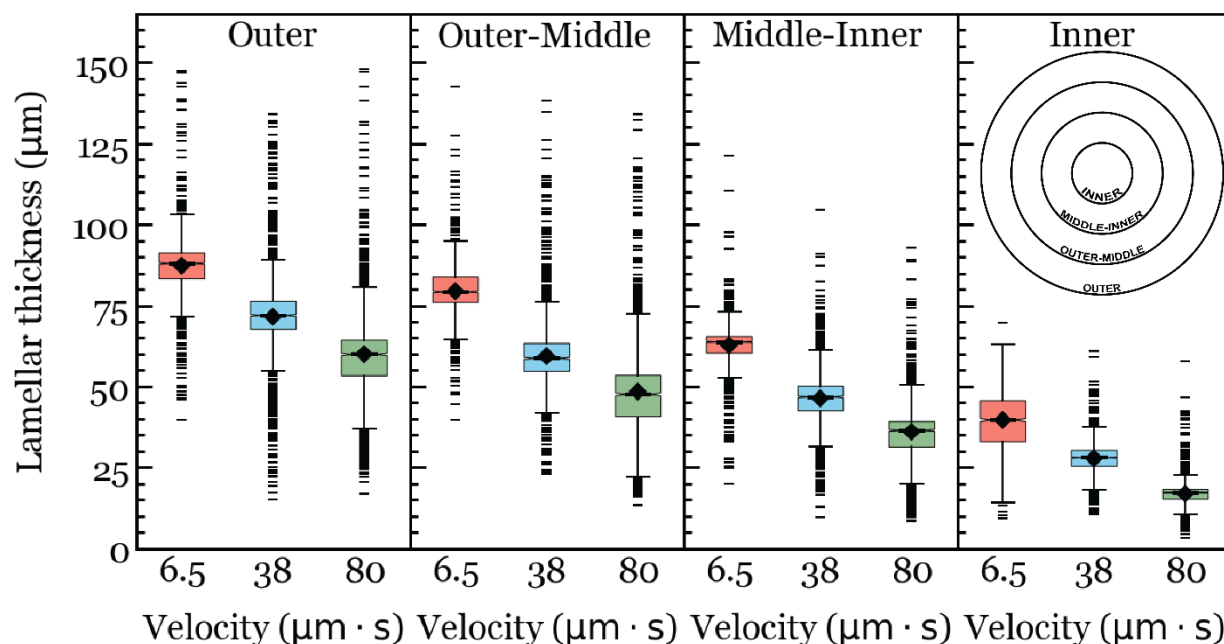


Fig. 7.8. Box and whisker plots summarizing naphthalene lamellae thickness in AOT-stabilized naphthalene/Cu freeze-cast materials. Suspensions of 5 vol.% Cu particles (32 wt.%) in naphthalene were solidified using furnace translation velocities of 6.5, 38, and 80 $\mu\text{m} \cdot \text{s}^{-1}$, while holding the thermal gradient, G constant at $35^\circ\text{C} \cdot \text{cm}^{-1}$; the concentration of AOT is constant at 1 wt.% with respect to Cu particle mass (0.5 wt.% with respect to naphthalene). All measurements were taken from cross-sections perpendicular to the freezing directions; “outer” measurements represent values at the outer edge of the cross-sections, “inner” values were obtained 2.5 mm from the absolute center of cross-sections; “outer-middle” and “middle-inner” were obtained from lamellae crossing circle guides drawn at equal spacing between the outer edge and inner measurements. The minimum and maximum values of boxes represent the first and third quartiles, respectively; medians are shown as horizontal lines inside the boxes, means are represented by black diamonds, and whiskers represent 1.5 times the interquartile range.

Table 7.3. Thickness of naphthalene lamellae in directionally solidified 5 vol.% (32 wt.%) Cu particle/naphthalene suspensions containing 1 wt.% AOT (with respect to Cu mass; 0.5 wt.% with respect to naphthalene mass). Suspensions were solidified using furnace translation velocities of 6.5, 38, and 80 $\mu\text{m} \cdot \text{s}^{-1}$, while holding the thermal gradient, G constant at $35^\circ\text{K} \cdot \text{cm}^{-1}$. All measurements were taken from cross-sections perpendicular to the freezing directions; “outer” measurements represent values at the outer edge of the cross-sections, “inner” values were obtained 2.5 mm from the absolute center of cross-sections; “outer-middle” and “middle-inner” were obtained from equally spaced regions between the outer edge and the inner measurements. Data are expressed as mean $\pm$ standard deviation; N is the number of samples.

Velocity ($\mu\text{m} \cdot \text{s}^{-1}$)	N	Naphthalene lamellae thickness (μm)				
		Overall	Outer	Outer-middle	Middle- inner	Inner
6.5	5	67 $\pm$ 20	87 $\pm$ 11	80 $\pm$ 9	63 $\pm$ 7	40 $\pm$ 9
38	5	51 $\pm$ 19	71 $\pm$ 13	59 $\pm$ 11	46 $\pm$ 9	28 $\pm$ 5
80	5	40 $\pm$ 19	60 $\pm$ 14	49 $\pm$ 14	36 $\pm$ 8	17 $\pm$ 4

As stated earlier, lamellar thickness is expected to increase with decreasing furnace translation velocity [140, 312, 313]; this relationship is observed for all regions (overall values of naphthalene lamellae thickness decrease from $67\pm 20 \mu\text{m}$ to $40\pm 19 \mu\text{m}$ for $V = 6.5$ to $80 \mu\text{m} \cdot \text{s}^{-1}$, respectively). For all velocities, lamellae thickness is largest in the outer region of samples and decreases with decreasing distance from the center (*e.g.*, for samples solidified using $V = 6.5 \mu\text{m} \cdot \text{s}^{-1}$, lamellae thickness at the outer and inner regions are 87 ± 11 and $40\pm 9 \mu\text{m}$, respectively; for $V = 80 \mu\text{m} \cdot \text{s}^{-1}$, these values decrease to 60 ± 14 and $17\pm 4 \mu\text{m}$, respectively). The relationship observed here (increasing lamellae width at outer regions of samples relative to inner regions), indicates that the local solidification velocity is higher in the central region of the sample relative to the outer region [314]. This is suggestive of a macroscopic curvature of the solid/liquid interface [234, 315], characteristic of systems where radial temperature gradients are present [126, 130, 256]. As stated earlier, radial temperature gradients are common for Bridgman solidification, and

these gradients give rise to macroscopic convective patterns which also may promote interdendritic fluid flow [199, 309]. Interdendritic convective fluid flow, which can be produced by a shear flow across the interface [137], is also likely present given the observation of asymmetric dendritic features (dendritic features are suppressed on the “downstream” side due to the downward direction of the fluid flow [89, 309]).

7.3. Model comparison

The You *et al.* [29] model for predicting freeze-cast microstructures based on solidification conditions and suspension characteristics is described in Section 2.5. Using Eq. 2.1-Eq. 2.3, with values describing the system tested here ($T_m = 80.23^\circ\text{C}$ for naphthalene [294], $\rho = 976.7 \text{ kg} \cdot \text{m}^3$ [295], $L = 146 \text{ J/g}$ [296], $G = 35^\circ\text{C} \cdot \text{cm}^{-1}$, $r = 0.5 \text{ } \mu\text{m}$, $\phi_p = 0.05$, and taking V as equivalent to the furnace translation velocity), and considering that dendritic structures are predicted when $D/(1 + \Phi) > 1$, whereas lensing regimes are predicted when this value is less than one, the predicted microstructures for all translation velocities employed here are within the lensing regime. As described earlier, lensing includes both banding (naphthalene platelets oriented perpendicular to the freezing direction) and spears; *i.e.*, the presence of secondary dendritic arm growth that extends into neighboring dendrites, producing a cellular-type structure after sublimation of the solidified fluid.

While dendritic features are present for 1 wt.% AOT solidified at $V = 80 \text{ } \mu\text{m} \cdot \text{s}^{-1}$ (Fig. 7.4-a, b), the insert in Fig. 7.4(b) shows that the overall lamellar structure is retained. At $V = 38 \text{ } \mu\text{m} \cdot \text{s}^{-1}$, the structure is mostly lamellar (*i.e.*, dendritic regime), though some interconnectivity between particle walls, characteristic of spearing, is observed (Fig. 7.8-e). Lamellar, spear, and banding microstructures are observed for samples solidified at $V = 6.5 \text{ } \mu\text{m} \cdot \text{s}^{-1}$ (Fig. 7.2-g, left side of Fig. 7.2-h, and right side of Fig. 7.2-h, respectively), wherein the microstructural

characterization is dependent on radial distance from the quartz wall (likely resulting from macroscopic curvature of the interface due to convection, as explained earlier).

The You *et al.* model [29] does not consider the effect of solute (here, AOT) nor convection during solidification. Thus, in this model, the breakdown of the solidification front is described in terms of particle-induced undercooling and fluid flow; Mullins-Sekerka [72] mechanisms (induced by solute) are not considered. While still an active area of research, factors such as particle size and solidification velocity are thought to influence one destabilization mechanism over the other (with larger particle sizes and increased velocities favoring Mullins-Sekerka instabilities relative to particle-induced instabilities [70]). This may explain why a qualitative agreement with the model (banding is observed for the slowest velocity employed, lamellar structures are observed for the faster velocities) is observed, but not a quantitative agreement. Additionally, as the furnace translation velocity was taken as solidification velocity in the model, local variations in solidification velocity were not accounted for, which are implied with a macroscopic interface curvature (which there is evidence for here, both in that banding is confined to core regions of samples and with respect to radial variation in lamellae thickness).

7.4. Conclusions

Naphthalene/Cu particle suspensions were electrostatically stabilized using an anionic surfactant, Aerosol-OT (AOT), and directionally solidified using a Bridgman furnace. The role of surfactant concentration was studied, wherein 1 wt.% AOT (with respect to Cu particle mass) produced more stable suspensions relative to suspensions containing 0.1 and 2.5 wt.% AOT (with respect to Cu particle mass). Samples solidified from suspensions containing 0.1 and 2.5 wt.% AOT (with respect to Cu mass) showed spear (highly interconnected naphthalene dendrites) and banding (macro-regions of naphthalene solidified perpendicular to the imposed thermal gradient,

rather than parallel) defects and lamellae misalignment (with respect to the imposed thermal gradient). A comparison of the average thickness of particle sedimentation layers formed during solidification for 0.1, 1, and 2.5 wt.% AOT suspensions provides confirmation that 1 wt.% AOT suspensions are more stable than the lower and higher surfactant concentrations studied. At 1 wt.% AOT, the sedimentation layers formed (measured as the length of particle depletion regions in solidified specimens) were smaller than those calculated for Stokes' sedimentation velocity of $1\text{ }\mu\text{m}$ Cu particles in naphthalene; for the 0.1 and 2.5 wt.% AOT suspensions, the sedimentation layers formed were higher than Stokes' calculations.

The effect of furnace translation velocity, V , on microstructural development in solidified structures was studied for naphthalene/Cu particle suspensions stabilized using 1 wt.% AOT (with respect to Cu mass). Lamellar structures were observed for all V (6.5, 38, and $80\text{ }\mu\text{m} \cdot \text{s}^{-1}$), where lamellae thickness increased with decreasing V . At $V = 6.5\text{ }\mu\text{m} \cdot \text{s}^{-1}$, three microstructural patterns were observed with respect to radial position: lamellae structures were observed in peripheral regions, whereas banding were observed in the central regions; spear structures were observed in intermediary regions.

For all furnace translation velocities, lamellae thickness depends on radial distance from the ampoule wall, with the thickest average lamellae located at outer regions. While naphthalene was solidified in the buoyancy-stable solidification configuration (vertically upwards), it is concluded that radial temperature gradients (common in Bridgman solidification) likely induced convective fluid motion, as evidenced by radial segregation in lamellae thickness (characteristic of a macroscopic interface curvature), microstructural variation that depends on radial distance from the ampoule wall (attributed to variation in particle volume fraction with respect to radial

distance from ampoule walls), and the observation of asymmetric secondary dendritic arm growth (characteristic of interdendritic convective fluid motion).

Chapter 8. Freeze-thaw stability of naphthalene/Cu particle suspensions

8.1. Motivation

The investigation of freeze-thaw stability of particle suspensions is relevant for a variety of technical applications [281, 316, 317]. For example, particle suspensions typically have a limited lifetime when stored in a liquid state. This is largely due to physical instabilities of the particles (*e.g.*, resulting in particle aggregation, agglomeration, and/or fusion [301, 318]), and chemical instabilities of suspension constituents (*e.g.*, solubilization of polymers in aqueous suspensions [318] and drug desorption in pharmaceutical applications [319]). Storing suspensions in a solidified state offers a potential solution to these issues, provided that particles can be redispersed after thawing without degradation to suspension stability. In some cases, the freezing process has been shown to prevent and/or reverse particle aggregation [277, 316]. Indeed, freeze-thaw cycles in soils can promote disaggregation of soil particles [320, 321], in some cases, producing colloids that facilitate the transport of environmental contaminants [322]. Other studies have shown that the freezing process increases the propensity of particle aggregation in particle suspensions [302, 323-326]. While this behavior is problematic in applications such as pharmaceuticals, it can be useful in some environmental applications; *e.g.*, repetitive freeze-thaw cycles have been used in soils containing nanoplastics to reduce the mobility of nanoplastic particles through the formation of aggregates [317].

The overwhelming majority of published freeze-thaw suspension studies employ aqueous systems [276, 301, 302, 316, 318, 319, 325-329]; this is likely influenced by the fact that pharmaceutical technologies are a major driver of this research [301, 316, 318, 319, 329]. However, this adds complexity when attempting to apply existing knowledge to non-aqueous systems, especially suspensions employing an apolar suspending fluid (*e.g.*, naphthalene). For

example, within the freeze-thaw literature, there are studies that demonstrate high freezing rates *promote* particle aggregation [277, 328, 330], but there are also studies that show high freezing rates *reduce* particle aggregation tendencies [276, 325]. Aqueous studies commonly employ cryoprotectants (often, carbohydrates) to reduce aggregation during freezing [276, 318, 319, 328]. Factors such as freezing temperature, freezing rate, and particle volume fraction can influence the effectiveness of a given cryoprotectant; specifically, whether a vitreous, protective coating will form around the particles [318]. Another consideration is based on the primary explanation that is offered for particle aggregation during freezing—the freezing process promotes particle aggregation by concentrating particles [325, 330] (decreases in particle-particle distances facilitate particle-particle interactions, which increase the probability that aggregates will form). While the concentration of suspended particles during freezing is commonly observed, irrespective of the suspending fluid, the magnitude of particle aggregation may be higher in aqueous processing given the expansion of ice on freezing (which likely imposes higher mechanical stress on particles relative to liquids that do not expand on freezing, thus further decreasing the average distance between particles).

In this work, naphthalene/Cu particle suspensions are being investigated as a candidate flight test system for directional solidification experiments intended for the International Space Station. Flight ampoules will be filled with suspension materials on the ground and transferred to the ISS in a solidified state (as naphthalene is solid at room temperature). Thus, solidified suspensions will be melted back immediately prior to experiments; suspension stability cannot degrade significantly as a result of that freeze-thaw cycle and, due to ISS safety regulations, employing a mixing or stirring step to help redisperse particles after melt-back and prior to experiments is impractical. From aqueous freeze-thaw studies, it is known that utilizing higher

particle volume fractions suspensions increases the likelihood that particles will aggregate during freeze/thaw [318, 325] (higher particle volume fractions in suspensions inherently decrease particle-particle distance, thus, increase the opportunities for particles to aggregate). As such, the particle volume fraction is kept as low as practically possible, while still being relevant to freeze-casting applications (5 vol.% Cu).

For suspensions employing low dielectric constant fluids (*e.g.*, naphthalene), steric stabilization is the most commonly employed stabilization method [278, 300-303, 331]; polymers adsorbed on particles create a hinderance for particle aggregation. Aggregation that does occur when particles overcome steric repulsion is thought to be reversible [300]. However, bridging flocculation may occur during freeze/thaw testing of these suspensions, especially for suspensions containing a relatively low volume fractions of particles. In this case, two ends of a polymer chain adsorb on separate particles and draw the particles together [316]. Given that, for this application, mixing/stirring during the thawing/particle re-disbursement phase cannot be employed, behavior of this nature would present a barrier to use.

As discussed previously, electrosteric stabilization in low-dielectric constant fluids has been shown to offer increased stabilization relative to steric stabilization alone [174, 176, 283, 305, 306, 332] (and this was observed here when comparing results for AOT and Hypermer KD-13 suspensions, Chapter 7). However, during freeze/thaw particles can coagulate (forming compact particle aggregates that are not broken even by vigorous shaking after thawing [333]) *via* adsorption of counter-ions in the electrical double layer [316]; in these cases, aggregation is thought to be effectively irreversible [271, 300, 334, 335]. Thus, while electrosteric-stabilized suspensions (AOT-stabilized) showed improved stability relative to sterically stabilized

suspensions (Hypermer KD-13) for the naphthalene/Cu system (Chapter 6 and 7), it is unknown how either of these suspension stabilization mechanisms will respond to freeze-thaw testing.

8.2. Approach

To assess freeze-thaw stability for candidate flight systems, suspensions with 5 vol.% Cu and 1 wt.% AOT or 1 wt.% Hypermer KD-13 (with respect to Cu) are prepared as described previously (Section 3.3.4). Prepared suspensions are subjected to an initial freeze in an ultrasonic bath using bath temperature of either ~ 10 or $\sim 50^{\circ}\text{C}$, representing slow (FTS) and fast (FTF) freeze-thaw testing, respectively. Initial freezing is carried out in the ultrasonic bath in an effort to reduce the risk of particle aggregation during freezing; a version of this method has been used in food processing to increase the nucleation rate (through improved heat transfer rates) and promote growth of fine dendrites [336-340]. Dendrite fragmentation and secondary nucleation, which promote disordered microstructures, are also reported *via* this technique [339, 341]. Sonication is also often used in freeze/thaw studies prior to freezing and during or after thawing to break up loose particle aggregates [326, 342]. Here, it is hypothesized that promoting disordered naphthalene growth during the initial freeze cycle will reduce the propensity for particles to be concentrated by growing dendrites. The two bath temperatures (~ 10 or $\sim 50^{\circ}\text{C}$) are used to test the effect of solidification velocity during the initial freeze phase. Suspensions are subsequently thawed and directionally solidified as described previously. Sedimentation and microstructural data are compared between the freeze-thaw groups as well to data obtained from directionally solidified suspensions that were not subjected to an initial freeze-thaw step (no-FT).

8.3. Results

8.3.1. *Particle sedimentation during solidification*

Generally, suspensions that show the greatest resistance to particle aggregation during freeze/thaw cycles are stable in their liquid state [301, 302]. Particle sedimentation is an indicator of suspension instability (especially if sedimentation rates are higher than Stokes' sedimentation rates). As described previously, relative particle sedimentation was assessed during directional solidification of AOT- and Hypermer KD-13-stabilized suspensions by measuring the thickness of the particle-depletion region in solidified samples. Here those values (which represent suspensions that are directionally solidified without first being subjected to a freeze-thaw cycle) are compared to values obtained during directional solidification of suspensions that are subjected to one freeze-thaw cycle. Fig. 8.1 shows the average height of particle depletion/sedimentation layers for (left) 1 wt.% AOT (with respect to Cu mass) naphthalene/Cu suspensions and (right) 1 wt.% Hypermer KD-13 (with respect to Cu mass) suspensions obtained during directional solidification of never-previously-frozen suspensions at furnace translation velocities of $V = 6.5$, 38, and 80 $\mu\text{m/s}$ and freeze-thaw suspensions, including the freeze-thaw-fast (FTF) and freeze-thaw-slow (FTS) cases, which are both directionally solidified at $V = 80 \mu\text{m/s}$ (FTF and FTS suspensions are initially frozen in ultrasonic bath temperatures of 10 and 50°C, respectively). Numerical values for these data are provided in Table 8.1.

As shown in Fig. 8.1, the height of the particle depletion region comprises $0.3\% \pm 0.6\%$ of the total height ($\sim 20 \text{ cm}$) for never-previously-frozen AOT suspensions solidified at a furnace translation velocity of 80 $\mu\text{m/s}$; the particle depletion layer thickness increases to $4\% \pm 2\%$ and $2\% \pm 3\%$ for the FTF and FTS freeze-thaw conditions, respectively (given the measurement approach used, the differences measured between FTF and FTS suspensions are likely within

measurement error; statistically significant differences between means for these groups was not found). Larger differences in particle depletion layer thickness are observed for Hypermer KD-13 suspensions; specifically, for never-previously-frozen, 1 wt.% KD-13 suspensions, the height of the particle depletion layer is $30\% \pm 7\%$; this value increases for the freeze-thaw suspensions to $56\% \pm 6\%$ and $47\% \pm 8\%$ for FTF and FTS, respectively. In all cases, the particle depletion layer observed for Hypermer KD-13 suspensions is higher than the 4% value expected from Stokes' sedimentation velocity calculations for 1 μm Cu particles in liquid naphthalene. For AOT-stabilized suspensions, mean values of particle depletion layer thickness are at or below the Stokes' value for all freezing conditions.

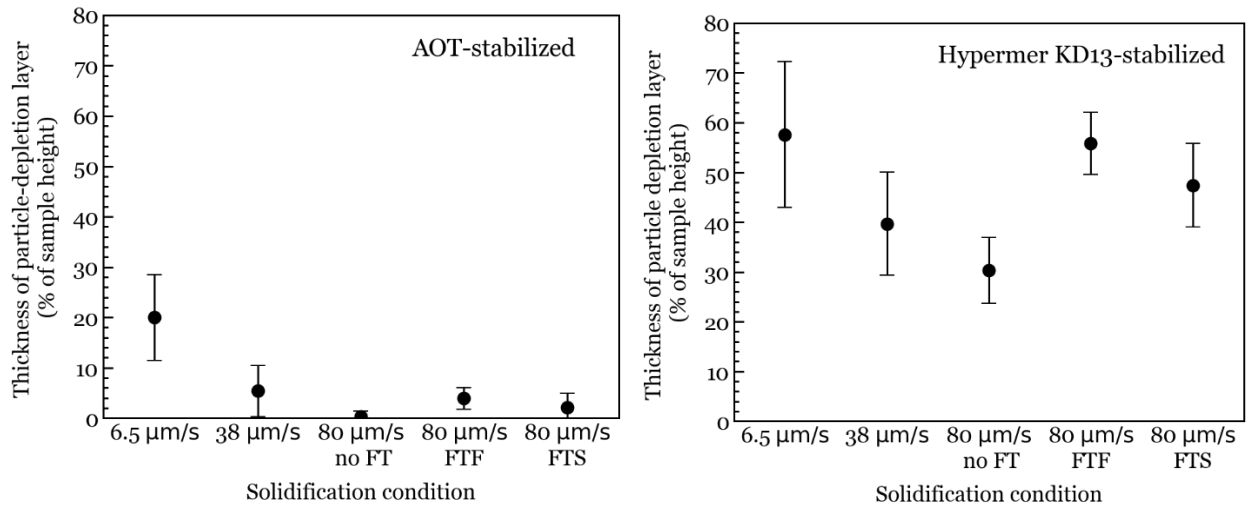


Fig. 8.1. Particle depletion layers observed during solidification of AOT and KD-13 stabilized particle suspensions. Plots show average thickness of particle depletion layers formed (as a percentage of total sample height of ~ 20 cm) during solidification of 5 vol.% (32 wt.%) Cu particles suspended in naphthalene with (left) 1 wt.% AOT and (right) 1 wt.% KD-13 (surfactant weight fractions are given with respect to particle mass, corresponding to 0.5 wt.% with respect to naphthalene mass). The solidification conditions include, standard (no freeze-thaw) solidification at furnace translation velocities, $V = 80, 38$, and $6.5 \mu\text{m/s}$, and freeze-thaw conditions, including “FTF” (freeze/thaw fast) and “FTS” (freeze/thaw slow), where suspensions were subjected to one initial freeze/thaw cycle prior to directional solidification; the initial freezing was conducted in an ultrasonic bath and the “slow” (FTS) or “fast” (FTF) references that bath temperature ($\sim 50^\circ\text{C}$ and $\sim 10^\circ\text{C}$, respectively). All freeze-thaw samples were subsequently directionally solidified at $V = 80 \mu\text{m/s}$. Error bars represent standard deviation.

Table 8.1. Particle depletion layers observed during solidification of AOT and KD-13 stabilized particle suspensions. Average thickness of particle depletion layers formed (as a percentage of total sample height of ~ 20 cm) during solidification of 5 vol.% (32 wt.%) Cu particles/naphthalene suspensions stabilized with 1 wt.% AOT and 1 wt.% KD-13 (surfactant weight fractions are given with respect to particle mass, which corresponds to 0.5 wt.% with respect to naphthalene mass). The solidification conditions include, standard (no freeze-thaw) solidification at furnace translation velocities, $v = 80, 38,$ and $6.5 \mu\text{m/s}$, and freeze-thaw conditions, including “FTF” (freeze/thaw fast) and “FTS” (freeze/thaw slow), where suspensions were subjected to one initial freeze/thaw cycle prior to directional solidification; the initial freezing was conducted in an ultrasonic bath and the “slow” (FTS) or “fast” (FTF) references that bath temperature ($\sim 50^\circ\text{C}$ and $\sim 10^\circ\text{C}$, respectively). All freeze-thaw samples were subsequently directionally solidified at $v = 80 \mu\text{m/s}$. The sedimentation layer thickness that would result from Stokes’ sedimentation (alone) is also provided.

System	Sedimentation layer thickness (as % of solidified sample height)				
	$v = 80 \mu\text{m/s}$	$v = 38 \mu\text{m/s}$	$v = 6.5 \mu\text{m/s}$	FTF	FTS
AOT (1 wt.%)	$0.3\% \pm 0.6\%$	$5\% \pm 5\%$	$20\% \pm 8\%$	$4\% \pm 2\%$	$2\% \pm 3\%$
KD-13 (1 wt.%)	$30\% \pm 7\%$	$40\% \pm 10\%$	$57\% \pm 15\%$	$56\% \pm 6\%$	$47\% \pm 8\%$
Stokes’ sedimentation	4%	7%	42%	4%	4%

8.3.2. *Microstructure investigation*

Microstructures of suspensions directionally solidified using freeze-thaw suspensions were investigated as described previously (Section 3.3.7.1). Fig. 8.2 shows optical micrographs taken perpendicular to the freezing direction for directionally solidified Cu/naphthalene suspensions containing 1 wt.% Hypermer KD-13 surfactant with respect to Cu mass (corresponding to 5 vol.% with respect to naphthalene). The structures in Fig. 8.2 (a) and (b) are obtained from suspensions that were never previously frozen, whereas Fig. 8.2 (c) and (d) are obtained from FTS and FTF suspensions, respectively (where FTS suspensions are initially frozen in an ultrasonic bath temperature of $\sim 50^\circ\text{C}$, and FTF are frozen initially using a bath temperature of $\sim 10^\circ\text{C}$).

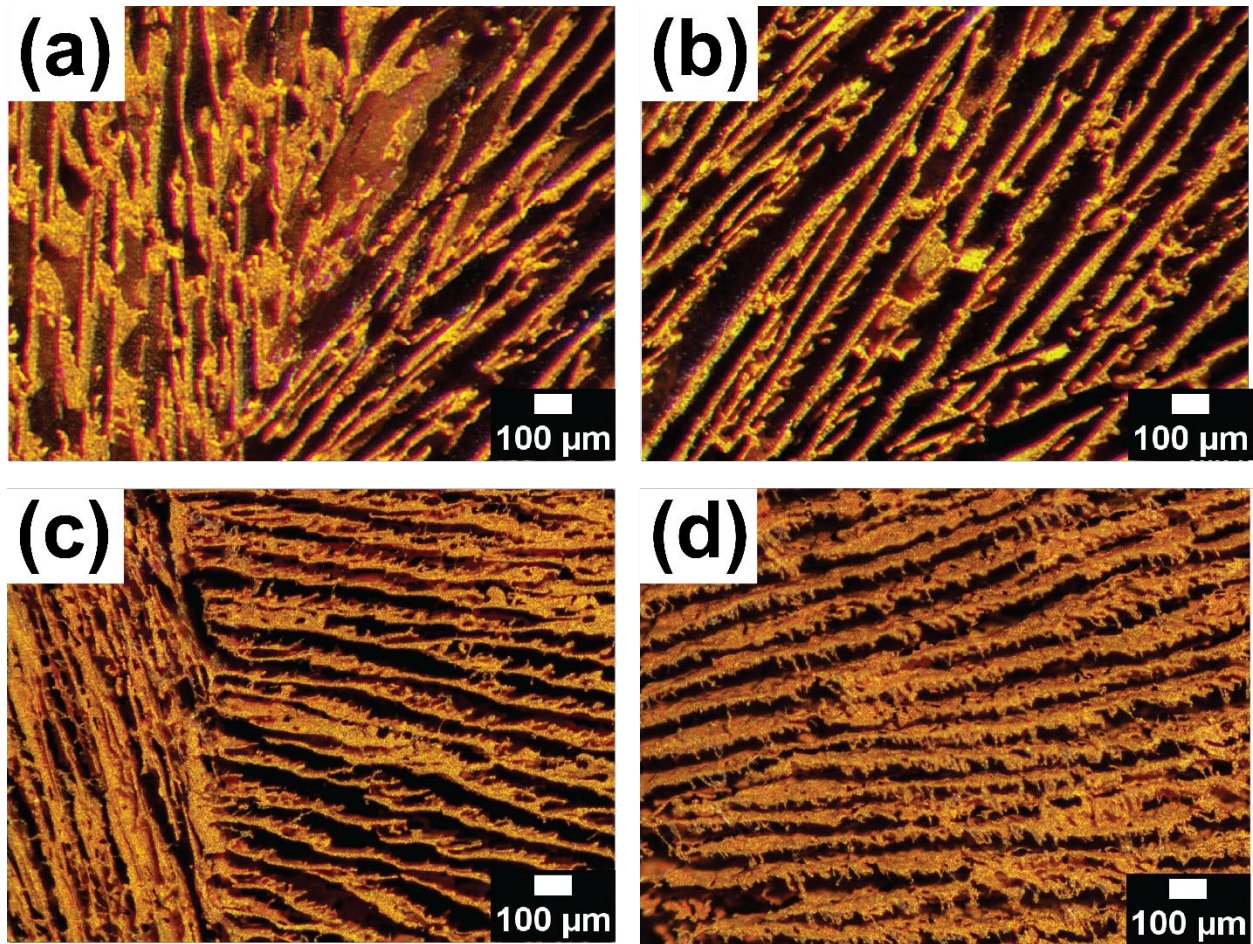


Fig. 8.2. Optical micrographs of copper freeze-cast materials obtained from never previously frozen, sterically stabilized suspensions and freeze-thaw suspensions. The Cu particle fraction is 5 vol.% (32 wt.%) in suspension and the dispersant concentration is 1 wt.% with respect to Cu particle mass. All suspensions were solidified using a furnace translation velocity of $80 \mu\text{m} \cdot \text{s}^{-1}$ and thermal gradient, $G = 35^\circ\text{C} \cdot \text{cm}^{-1}$ where (a, b) were obtained from a suspension that was only solidified once (during directional solidification), the structure in (c) was obtained from a FTS (freeze-thaw-slow) suspension that was subjected to a freeze-thaw cycle prior to directional solidification using an ultrasonic bath temperature of $\sim 50^\circ\text{C}$ and the structures in (d) was obtained from a FTF (freeze-thaw-fast) suspension, where ultrasonic bath temperature was held at $\sim 10^\circ\text{C}$. All images show cross-sections perpendicular to the freezing direction.

For all microstructural images in Fig. 8.2, lamellar naphthalene structures with asymmetric dendritic features are observed (these asymmetries are discussed in Chapter 6 and 7Chapter 7 as likely resulting from convective fluid motion during solidification). Qualitatively, the microstructures of freeze-cast thaw suspensions for this system do not appear to vary considerably; however, Fig. 8.2 (c) and (d) appear somewhat particle-enriched relative to Fig. 8.2 (a) and (b), which may be due to increased particle sedimentation rates for the freeze-thaw suspensions (as described previously).

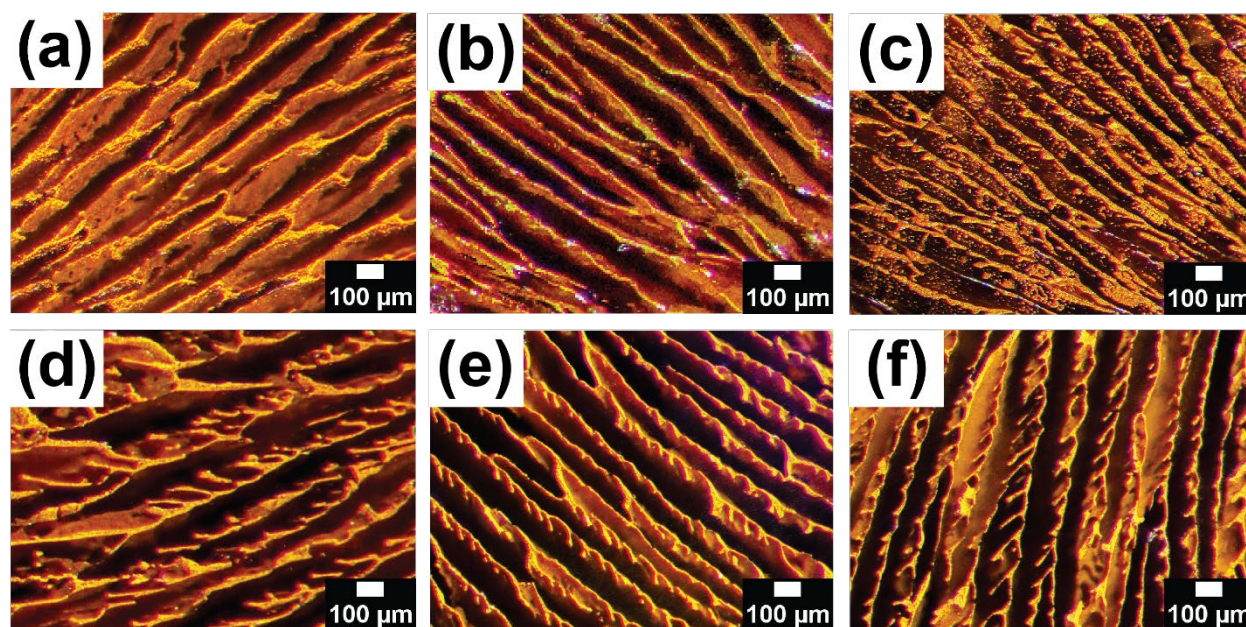


Fig. 8.3. Optical micrographs of copper freeze-cast materials obtained from never previously frozen, electrosterically stabilized suspensions and freeze-thaw suspensions. The Cu particle fraction is 5 vol.% (32 wt.%) in suspension and the dispersant concentration is 1 wt.% with respect to Cu particle mass. All suspensions were solidified using a furnace translation velocity of $80 \mu\text{m} \cdot \text{s}^{-1}$ and thermal gradient, $G = 35^\circ\text{C} \cdot \text{cm}^{-1}$, where images (a, b) were obtained from a suspension that was only solidified once (during directional solidification), the structures in (b, e) were obtained from FTS (freeze-thaw-slow) suspensions that were subjected to a freeze-thaw cycle prior to directional solidification using an ultrasonic bath temperature of $\sim 50^\circ\text{C}$, and the structures in (c, f) were obtained from FTF (freeze-thaw-fast) suspensions, where the ultrasonic bath temperature was held at $\sim 10^\circ\text{C}$. All images show cross-sections perpendicular to the freezing direction.

Fig. 8.3 shows optical micrographs taken perpendicular to the freezing direction for directionally solidified Cu/naphthalene suspensions containing 1 wt.% AOT surfactant. The structures in Fig. 8.2 (a, d) are obtained from suspensions that were never previously frozen, whereas (b, e) and (c, d) are obtained from FTS and FTF suspensions, respectively (where FTS suspensions are initially frozen in an ultrasonic bath temperature of $\sim 50^{\circ}\text{C}$ and FTF are frozen initially using a bath temperature of $\sim 10^{\circ}$). Again, in all cases, lamellar structures with asymmetric dendritic features are observed. Here, the microstructures do not appear to vary appreciably between the never-frozen and freeze-thaw conditions.

8.3.2.1. *Copper particle fraction in solidified samples*

Particle fraction in solidified specimens was measured from cross-sectional microscopy images by binarizing the images and counting the number of pixels corresponding to particle wall regions relative to total pixels; these data are plotted in Fig. 8.4. The particle fraction measured from non-freeze-thaw (no-FT) Hypermer KD-13 suspension solidification images is $41\% \pm 6\%$; slightly higher, but comparable values are found for the freeze-thaw conditions ($44\% \pm 10\%$ and $43\% \pm 10\%$, for fast and slow initial freezing, respectively). However, when the vertical height of the solidified sample from which images were obtained is accounted for, the results are more meaningful: for no-FT samples, the particle fraction within the first 2 cm of solidification is $45\% \pm 5\%$; this value increases to $55\% \pm 3\%$ and $52\% \pm 6\%$ for the FTF and FTS suspensions, respectively. For cross-sections corresponding to vertical solidification distances between 4 and 6 cm, the calculated particle fraction is $39\% \pm 2\%$, $36\% \pm 5\%$, and $35\% \pm 4\%$ for no-FT, FTF, and FTS solidified suspensions, respectively. In Fig. 8.4, black markers are used for overall particle

fractions (comprising both vertical regions), blue markers are used for the 0-2 cm region, and red markers are used for the 4-6 cm region. These results are consistent with sedimentation layer thickness results discussed earlier where the FTF condition was shown to have the highest sedimentation, followed by FTS and no-FT.

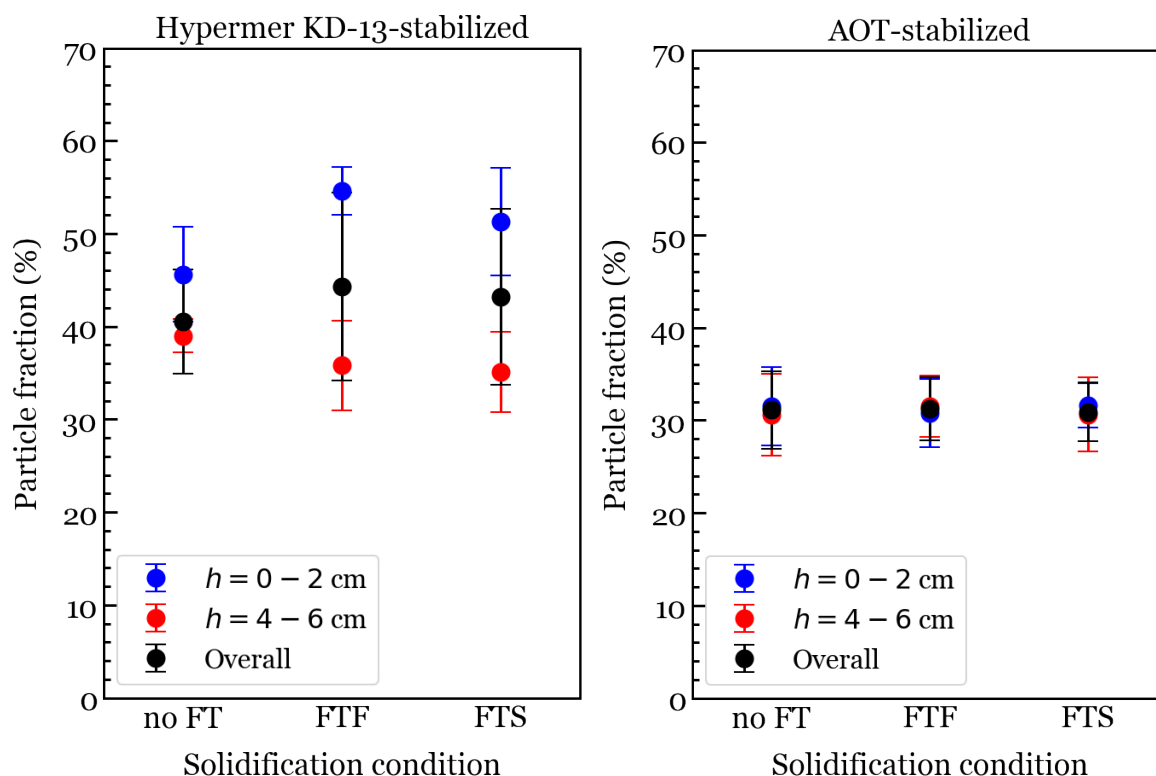


Fig. 8.4. Cu particle fraction measured by image analysis of cross-sections for Hypermer KD-13 and AOT stabilized suspensions directionally solidified with and without an initial freeze-thaw cycle. The Cu particle fraction is 5 vol.% (32 wt.%) in suspension and the dispersant concentration is 1 wt.% with respect to Cu particle mass. All suspensions were solidified using a furnace translation velocity of $80 \mu\text{m} \cdot \text{s}^{-1}$ and thermal gradient, $G = 35^\circ\text{C} \cdot \text{cm}^{-1}$ and contained an initial Cu volume fraction of 5%. For the no FT condition, the Cu/naphthalene suspension that was only solidified once (during directional solidification), for FTF (freeze-thaw-fast) suspensions were subjected to a freeze-thaw cycle prior to directional solidification using an ultrasonic bath temperature of $\sim 10^\circ\text{C}$; the bath temperature was held at $\sim 50^\circ\text{C}$ in the FTS (freeze-thaw-slow) condition. Error bars are derived using standard deviation.

For all Hypermer KD-13 solidification conditions, statistically significant differences between particle fractions within the bottom 2 cm of samples relative to the 4-6 cm region are observed ($p < 0.0001$ in all cases). One-way ANOVA tests were used to compare means for no-FT, FTF, and FTS groups; statistically significant differences were detected for both vertical regions. Post-hoc Tukey-HSD tests showed significant differences between the no-FT condition and both freeze-thaw conditions for both vertical regions; statistically significant differences were not detected between freeze-thaw conditions for either vertical region. These results are consistent with the appearance of the data in Fig. 8.4—within the lower vertical region (0-2 cm, first-to-solidify region, blue in Fig. 8.4), the particle fraction is comparably increased in both of the freeze-thaw conditions relative to the no-FT condition, whereas the particle fraction decreases for both freeze-thaw conditions relative to the no-FT condition for the later-to-solidify region (4-6 cm from the base, red in Fig. 8.4). In all cases, particle fraction is observed to decrease with increasing solidification height (suggestive of particle sedimentation), but these differences are greater for the freeze-thaw conditions (which do not significantly differ from each other, statistically).

The righthand plot in Fig. 8.4 shows calculated Cu particle fractions in suspensions solidified using 1 wt.% AOT; again, overall values for no-FT, FTF, and FTS are shown as black markers, blue markers represent values obtained within 0-2 cm of the solidified height, and red markers were obtained from images representing solidification heights of 4-6 cm. Given the overlap of data points with respect to vertical regions, it is unsurprising that a one-way ANOVA did not detect statistically significant differences between vertical regions for any solidification conditions. Statistically significant differences were also not detected when comparing means of

the no-FT, FTF, and FTS conditions. The overall particle fraction measured from no-FT, FTF, and FTS suspension solidification images is $31\% \pm 4\%$, $31\% \pm 2\%$ and $31\% \pm 3\%$.

Comparing these results for AOT and Hypermer KD-13 supports the following conclusions: (i) the bath temperature for the initial freeze-thaw cycle does not impact suspension stability (as assessed here) and (ii) AOT suspensions show better freeze-thaw stability relative to Hypermer KD-13 suspensions. As such, subsequent analysis is focused on AOT suspensions.

8.3.2.2. *Radial segregation*

Thickness measurements of naphthalene lamellae were obtained from stitched cross-section images taken perpendicular to the freezing direction, as described previously. Fig. 8.5 shows box and whisker plots for measurements obtained from directionally solidified suspensions contained 5 vol.% Cu particles in naphthalene, stabilized using 1 wt.% AOT (with respect to Cu mass); furnace translation velocities were $80 \mu\text{m} \cdot \text{s}^{-1}$ for all conditions. The “STD” (standard) condition is the same as that represented in Fig. 7.8 (for never previously frozen suspensions). Suspensions used in the “FTS” and “FTF” conditions are subjected to one initial freeze/thaw cycle prior to directional solidification; the initial freezing is conducted in an ultrasonic bath and the “slow” (FTS) or “fast” (FTF) references that bath temperature ($\sim 50^\circ\text{C}$ and $\sim 10^\circ\text{C}$, respectively). Measurements obtained from the “outer” (or peripheral regions of cross-sections) are summarized in the leftmost plot and the rightmost plot summarizes measurements taken from the inner region of samples. All measurements are taken from polished cross-sections perpendicular to the freezing directions; “outer” measurements represent values at the outer edge of the cross-sections, “inner” values were obtained 2.5 mm from the absolute center of cross-sections; “outer-middle” and “middle-inner” were obtained from equally spaced regions between the outer edge and the inner measurements. The minimum and maximum values of boxes represent the first and third quartiles,

respectively; medians are shown as horizontal lines inside the boxes, means are represented by black diamonds, and whiskers represent 1.5 times the interquartile range. Table 8.2 provides numerical values for mean $\pm$ standard deviation describing these data.

As observed previously, lamellar thickness increases with increasing radial distance from the center. Within a given region, values of mean lamellar thickness are in relatively good agreement among the freeze-thaw conditions. For the outer region, these values are 60 ± 14 , 54 ± 8 , and 60 ± 11 μm for the no-freeze-thaw (STD), freeze-thaw-fast (FTF), and freeze-thaw-slow (FTS) conditions, respectively. For the inner regions, values for STD, FTF, and FTS are 17 ± 4 , 21 ± 6 , and 20 ± 5 μm , respectively. While some statistically significant differences can be found between groups (*via* one-way ANOVA and post-hoc, Tukey HSD tests), this is likely attributable to the large number of data points collected (2,500 measurements per condition, per region), as relationships between these data hold over all four regions (as would be expected if either of the freeze-thaw conditions impacted lamellae thickness in directionally solidified samples) are not observed.

Table 8.2. Measurements of lamellae thickness for suspension freeze-thaw tests of naphthalene suspensions with 5 vol.% (32 wt.%) Cu particles and 1 wt.% AOT (with respect to Cu mass, corresponding to 0.5 wt.% with respect to naphthalene) solidified using a furnace translation $80 \mu\text{m} \cdot \text{s}^{-1}$. The “no freeze-thaw” condition is the same as that represented in Fig. 8.5; suspensions used in the “freeze-thaw (fast)” and “freeze-thaw (slow)” conditions were subjected to an initial freeze/thaw cycle prior to directional solidification; the initial freezing was conducted in an ultrasonic bath and the “fast” or “slow” denominations reference that bath temperature ($\sim 10^\circ\text{C}$ and $\sim 50^\circ\text{C}$, respectively). All measurements were taken from polished cross-sections perpendicular to the freezing directions; “outer” measurements represent values at the outer edge of the cross-sections, “inner” values were obtained 2.5 mm from the absolute center of cross-sections; “outer-middle” and “middle-inner” were obtained from equally spaced regions between the outer edge and the inner measurements. Data are expressed as mean $\pm$ standard deviation; N is the number of samples.

Condition	N	Primary naphthalene dendrite arm width (μm)			
		Outer	Outer-middle	Middle-inner	Inner
No freeze-thaw	5	60 $\pm$ 14	49 $\pm$ 14	36 $\pm$ 8	17 $\pm$ 4
Freeze-thaw (fast)	5	54 $\pm$ 8	46 $\pm$ 6	32 $\pm$ 5	21 $\pm$ 6
Freeze-thaw (slow)	5	60 $\pm$ 11	47 $\pm$ 9	39 $\pm$ 6	20 $\pm$ 5

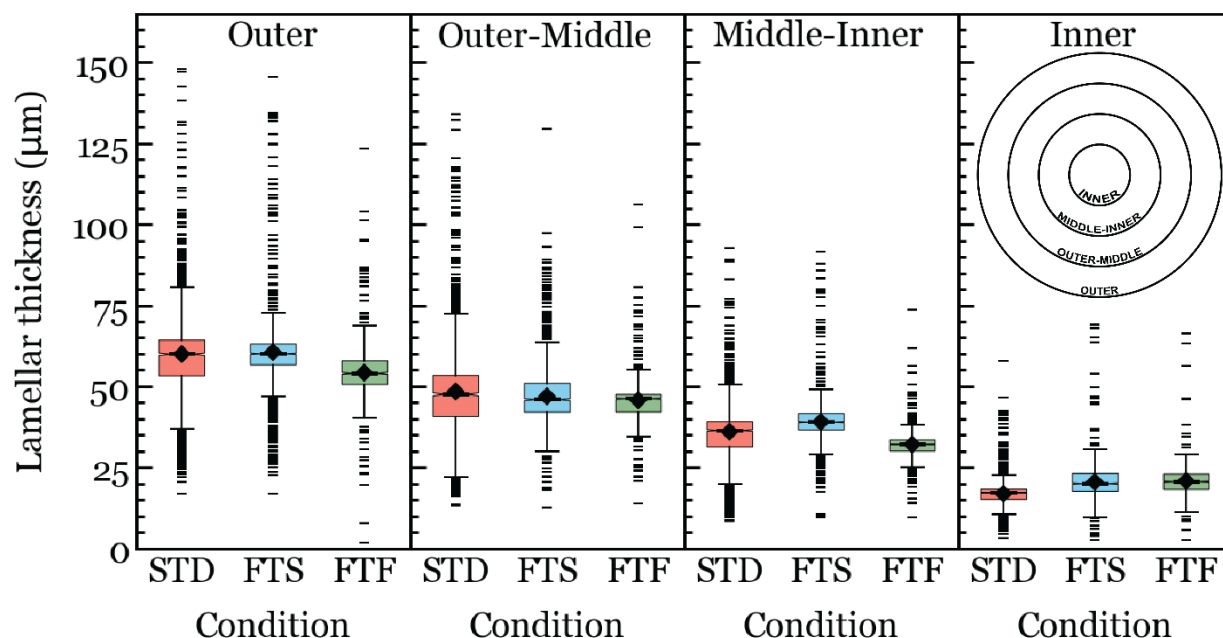


Fig. 8.5. Box and whisker plots summarizing the thickness of naphthalene lamellae for suspension freeze-thaw tests. The Cu particle fraction is 5 vol.% (32 wt.%) in suspension and the dispersant concentration is 0.5 wt.% with respect to naphthalene mass; furnace translation velocities were $80 \mu\text{m} \cdot \text{s}^{-1}$ for all conditions. The “STD” condition is the same as that represented in Fig. 7.8 (for never previously frozen suspensions). Suspensions used in the “FTS” and “FTF” conditions were subjected to one initial freeze/thaw cycle prior to directional solidification; the initial freezing was conducted in an ultrasonic bath and the “slow” (FTS) or “fast” (FTF) references that bath temperature ($\sim 50^\circ\text{C}$ and $\sim 10^\circ\text{C}$, respectively). All measurements were taken from polished cross-sections perpendicular to the freezing directions; “outer” measurements represent values at the outer edge of the cross-sections, “inner” values were obtained 2.5 mm from the absolute center of cross-sections; “outer-middle” and “middle-inner” were obtained from equally spaced regions between the outer edge and the inner measurements. The minimum and maximum values of boxes represent the first and third quartiles, respectively; medians are shown as horizontal lines inside the boxes, means are represented by black diamonds, and whiskers represent 1.5 times the interquartile range.

8.3.3. Rheometry

Rheological studies were carried out to assess the freeze-thaw stability of Cu/naphthalene suspensions containing 1 wt.% AOT (with respect to Cu mass). Fig. 8.6 (a) shows viscosity as a function of shear rate for vacuum distilled naphthalene at 82, 85, and 90°C and Fig. 8.6(b) shows viscosity as a function of shear rate for a suspension of 5 vol.% Cu particles in naphthalene containing 1 wt.% AOT (with respect to particle mass). Data points on both plots represent mean values obtained during steady-state flow using constant shear rate tests; the error bars represent the corresponding standard deviation. In Fig. 8.6(b), red data points represent values obtained for a suspension that was never frozen whereas blue data points were obtained from a thawed suspension that was remelted and tested 24 h after it was solidified. Statistically-significant differences between viscosity values measured for the never-frozen *vs.* the freeze-thaw suspension are not detected. Unchanging rheological behavior for never-frozen *vs.* freeze-thaw suspensions is an indicator of freeze-thaw stability [343].

For particle suspensions, the solid phase (particles) largely determines the rheological behavior [344]. For Newtonian suspending fluids, particle agglomeration (*e.g.*, from freezing and thawing suspensions) in low particle volume fraction suspensions is often identified *via* non-Newtonian behavior of resulting suspensions [188, 345]. This often appears as shear-thinning behavior that results from shear-induced breakage of agglomerates [186, 187, 346] (higher volume fraction suspensions may show shear-thickening as a result of increased frictional forces [186, 346]). The small deviations from Newtonian behavior observed in Fig. 8.6 (b) are similar to the deviations observed in Fig. 8.6 (a) for naphthalene (without surfactant or particles); they are also similar to observations described in Section 3.3.6.2 (and shown in Fig. 3.9) where the measurement limits of the employed rheometry system were explored. Thus, the small deviations from

Newtonian behavior observed in Fig. 8.6 (b) are unlikely a result of particle agglomeration resulting from freeze-thaw for these suspensions. It is notable that the viscosity of the suspension does not increase relative to the viscosity of naphthalene; this may be due to the relatively low fractions of particles and AOT employed (though, it could also be due to particle sedimentation during testing, which did not appear to be relevant here based on physical inspection of suspensions after testing).

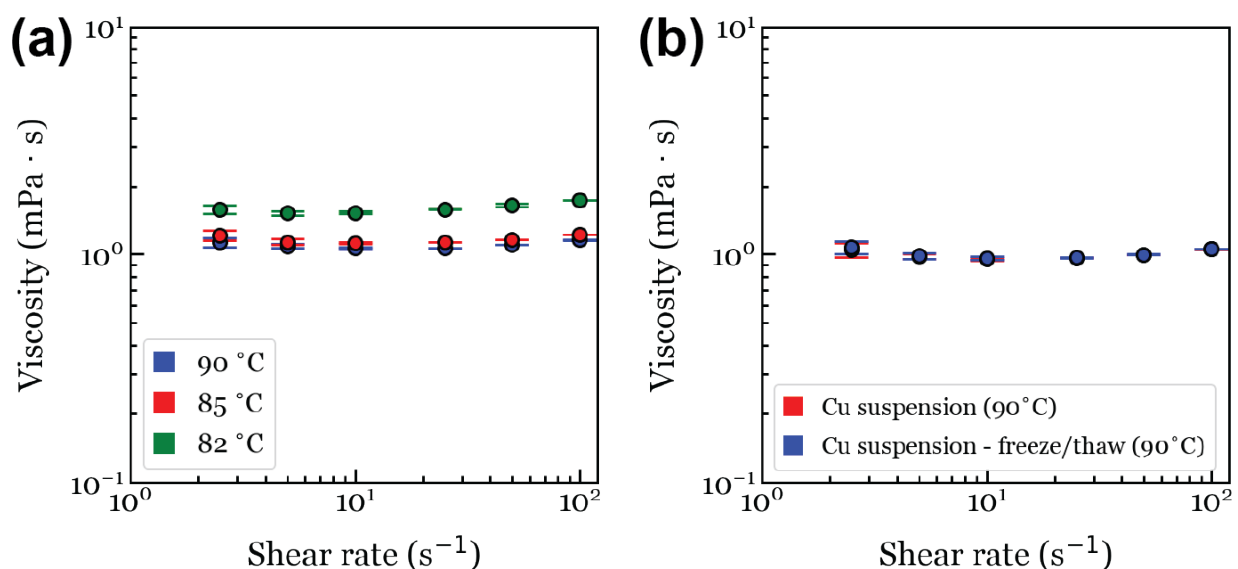


Fig. 8.6. Plots of viscosity vs. shear rate for (a) vacuum distilled naphthalene and (b) AOT-stabilized Cu/naphthalene suspensions. Vacuum distilled naphthalene is tested at 82, 85, and 90°C. The 5 vol.% (32 wt.%) Cu/naphthalene suspensions containing 1 wt.% AOT (with respect to particle mass, corresponding to 0.5 wt.% with respect to naphthalene) are tested at 90°C; in (b), red data points represent values obtained for suspensions that were never frozen whereas blue data points were obtained from thawed suspensions that were tested 24h after the initial solidification. Data points on both plots represent mean values obtained during steady-state flow using constant shear rate tests; error bars represent the standard deviation.

8.4. Conclusion

Two types of naphthalene/Cu particles suspensions are being investigated as candidate systems for intended microgravity solidification experiments on the International Space Station; based on furnace and transport constraints for the intended microgravity investigation, a viable flight suspension system needs to show stability after one freeze-thaw cycle. For the 5 vol.% Cu (1 μm particle size) suspensions under investigation, one system is sterically stabilized using Hypermer KD-14 surfactant, while the other is electrosterically stabilized using Aerosol-OT (AOT) surfactant (in both cases, 1 wt.% surfactant, with respect to Cu mass is used). To assess freeze-thaw stability for these suspensions, both suspension types are subjected to freeze-thaw testing. Initial freezing is carried out in an ultrasonic bath using a bath temperature of either ~ 10 or $\sim 50^\circ\text{C}$ to study the impact of freezing rate on particle aggregation for freeze-thaw suspensions. Freeze-thaw suspensions are subsequently thawed and directionally solidified to characterize particle sedimentation and microstructural characteristics of these suspensions relative to suspensions that were not first subjected to a freeze-thaw step.

Particle sedimentation, as assessed by measuring the height of particle-depletion layers observed during directional solidification, increased for all freeze-thaw systems relative to suspension systems that were not subjected to freeze-thaw, but this effect was greatest for Hypermer KD-13 (steric stabilization) suspensions. For non-freeze-thaw Hypermer KD-13 suspensions, sedimentation layers comprising $30\%\pm 7\%$ of the total solidification height (of ~ 20 cm) were observed; for freeze-thaw suspensions, the sedimentation layer thickness increased to $56\%\pm 6\%$ and $47\%\pm 8\%$ for suspensions that were initially frozen at relatively fast and slow rates, respectively. For AOT suspensions (electrosteric stabilization), the layer thickness for non-freeze-thaw suspensions comprised $0.3\%\pm 0.6\%$ of the total solidification height; layer thickness

increased to $4\% \pm 2\%$ and $2\% \pm 3\%$ for freeze-thaw suspensions using fast and slow initial freezing rates, respectively. In all AOT solidification conditions, mean sedimentation layer thickness was at or below that calculated using Stokes' sedimentation velocity (4% of the total height).

Microstructural investigation of resulting structures showed lamellar structures for all conditions. For the Hypermer KD-13, microstructural images for the freeze-thaw conditions appear particle-enriched relative to the no-freeze-thaw condition (the same is not observed for AOT suspensions). Particle fraction relative to solidification height was measured via image analysis of cross-sections in all sample conditions; these data support the particle sedimentation layer thickness results for all Hypermer KD-13 groups. Statistically significant differences between means were detected for Hypermer KD-13 suspensions solidified without a freeze-thaw cycle relative to both freeze-thaw conditions, but not between freeze-thaw conditions. Statistically significant differences were not detected within the AOT groups. Additional tests of the AOT system, including measuring lamellae thickness and viscosity in the no-freeze-thaw *vs.* freeze-thaw conditions also did not reveal significant differences between these groups.

These results support the following conclusions: (i) the bath temperature for the initial freeze-thaw cycle does not impact suspension stability (as assessed here) for naphthalene/Cu suspensions stabilized with Hypermer KD-13 nor AOT surfactant and (ii) AOT suspensions show better freeze-thaw stability relative to Hypermer KD-13 suspensions.

Chapter 9. Summary, conclusions, and future work

9.1. Summary and recommendations for future work

In Chapter 4, results are presented describing a systematic investigation on the effect of solidification direction (with respect to gravity) on microstructures templated during the freeze-casting solidification process; aqueous suspensions were used. Solidifying in the buoyancy-unstable configuration (vertically upwards) was found to promote defects in resulting materials which could be avoided by solidifying in the buoyancy-stable configuration (vertically downwards); defects observed included: microstructural tilting, asymmetric dendritic features on particle walls, and lensing (cracking, in sintered materials). While the effect of solidification orientation on microstructural development has been studied in alloy solidification (and results from that work are similar to what was presented here), orientation effects had not been considered in freeze-casting systems, despite the fact that the overwhelming majority of published freeze-casting studies employ solidification methods that promote solidification in buoyancy-*unstable* configurations.

In Chapter 5, the same aqueous suspensions are used as in Chapter 4; in this case, the effect of initial suspension temperature on microstructural development was studied. Radial segregation (variation in pore and wall width as a function of radial distance) was observed for all samples, but the magnitude was greatest for samples that were solidified using an initial suspension temperature that is expected to produce a double fluid density gradient in the liquid. That is, the double-fluid density gradient scenario was correlated with greatest degree of inhomogeneity in pore width distribution across the diameter of these samples, while samples solidified under conditions that promoted the smallest gradient in fluid density exhibited lesser variations in pore width. A similar relationship was observed for particle wall width. Similar experiments

investigating the impact of a double density gradient in the liquid during solidification could prove useful; for future experiments, the thermal gradient should be precisely controlled, and *in-situ* thermocouples can be used at various mold heights to obtain thermal traces during solidification. These data can be used to verify the thermal gradient and to better understand the temperature distribution during solidification; comparisons to solidification conditions inducing a single density gradient will likely be scientifically interesting (especially when corresponded to microstructures templated during solidification).

In Chapter 6, it was shown that naphthalene can be used as a suspending fluid for freeze-casting suspensions and the resulting structures are primarily lamellar. While solidified in a buoyancy-stable relative (with respect to fluid density), radial microstructural segregation was still observed and attributed to radial temperature gradients during solidification, a driver for buoyancy driven convective fluid motion. Asymmetric dendritic features on particle walls were also observed and attributed to interdendritic convection. In Chapter 7, naphthalene particle suspensions are electrosterically stabilized, representing the first directional freeze-casting study that investigates directional solidification of electrosterically-stabilized suspensions with an apolar fluid. Suspensions showed increased stability relative to sterically stabilized naphthalene/particle suspensions (Chapter 6); radial segregation and asymmetry in dendritic features were observed in these samples, also.

Fig. 9.1 summarizes microstructural results presented in Chapters 4, 6 and 7 with respect to You *et al.* [29] model predictions, where data point position is based on model predictions and markers are colored based on actual observed microstructures. For the solidification orientation study (directional solidification of aqueous TiO₂ particle suspensions, Chapter 4), observed microstructures ranged from lamellar to lensing (spears and bands), whereas lamellar/dendritic

structures are predicted by the model. Directional solidification of naphthalene/Cu particle suspensions (Chapter 6 and 7) produced lamellar structures for suspensions solidified using furnace translation velocities of $V = 38$ and $80 \mu\text{m/s}$ (where banding and spearing structures are predicted), whereas both lamellar and lensing structures were observed for suspensions solidified at the slowest employed V of $6.5 \mu\text{m/s}$ (where banding structures are predicted). This model does not consider solute-induced morphological instabilities and neglects the effects of gravity-driven convection, which likely contributes to divergencies in observed vs. predicted microstructures observed here.

Chapter 8 presents results of freeze-thaw stability test results for naphthalene/particle suspensions stabilized *via* steric and electrosteric mechanisms. Freeze-thaw suspensions (subjected to an initial freeze in an ultrasonic bath, with temperatures held at either 10 or 50°C) were directionally solidified, particle sedimentation during solidification was quantified, and microstructures of solidified structures were investigated. It was found that electrosterically stabilized suspensions performed better under freeze-thaw testing relative to sterically stabilized suspensions. Sterically-stabilized suspensions subjected to freeze-thaw exhibited significantly increased particle sedimentation relative to no-freeze-thaw suspensions and microstructural images showed that earlier-to-solidify regions were particle enriched relative to later regions for freeze-thaw suspensions. For electrosterically stabilized suspensions, sedimentation was found to be negligible and microstructural parameters (including lamellae thickness and particle fraction) did not change significantly for structures solidified using freeze-thaw suspensions relative to the no-freeze thaw condition. Initial freezing for freeze-thaw suspensions was carried out in an ultrasonic bath for reasons described in Chapter 8, but it is unknown how sonicating during the

initial freeze may have impacted results; studying the impact of conducting the initial freeze under sonication may prove scientifically interesting.

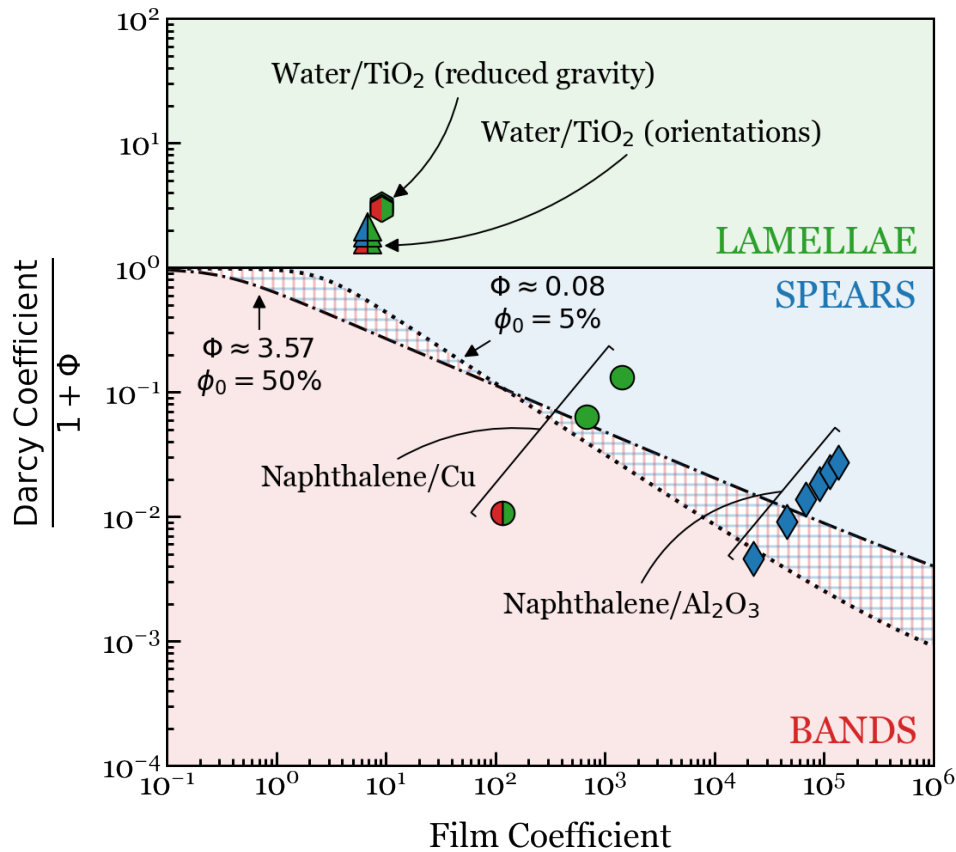


Fig. 9.1. Microstructural phase diagram after ref. [29] showing predicted microstructures, including lamellae (green), spears (blue), and bands (red) based on solidification and suspension parameters. The Darcy coefficient (D), film coefficient (F), and (Φ), are given by Eq. 2.1-Eq. 2.4 (Section 2.4). Data marker position is based on model predictions, whereas markers are colored based on observed microstructures.

Annealing experiments were conducted to establish science requirements with respect to thermal storage of solidified suspensions after flight testing. For these experiments (described in the Science Requirements Document, Appendix 4), microstructural changes were not observed when subjecting solidified samples to temperatures as high as 60°C for one month. A single

laboratory test was conducted at 70°C to get an idea of the upper limit for temperature storage. Within one hour, the microstructure changed drastically, such that directional structures were no longer observed. Thus, annealing experiments conducted between 60 and 70°C would likely prove interesting. Annealing can be used on solidified freeze-cast structures as a post-solidification method for modifying the solidified structure, thus the resulting microstructure (after sublimation and sintering).

9.2. Recommended microgravity experiment plan

Microgravity investigation of the freeze-casting technique will provide a better fundamental understanding of freeze-casting solidification behavior, which will allow for the development of improved processing techniques and better predictive control of materials design. This research is applicable to a wide variety of applications for optimized material fabrication on Earth, on planetary surfaces, and in orbit. The intended microgravity investigation that this thesis work supports entails production of benchmark data necessary to improve predictive control of freeze-cast material design, including producing data applicable for testing the You *et al.* [29] freeze-casting model for predicting templated microstructures based on solidification conditions. Table 9.1 provides the scientific objectives that were developed for the ISS mission, and a brief summary of how these objectives can be met is provided in the following (greater detail is provided in the Science Requirements Document submitted to NASA as part of the Science Requirements Review, Appendix 4).

Table 9.1. Scientific objectives for the ISS investigation, Microstructure Evolution in Freeze-cast Materials.

Objective	Description
SO-1	Test You <i>et al.</i> [29] freeze-casting model under primarily diffusive-growth conditions for each of the microstructures predicted by the model.
SO-2	Characterize the effect of solute relative to particles on the morphological instability/evolution of the solidification front and describe how buoyancy-driven fluid motion changes the magnitude of these relative effects, if it does.
SO-3	Produce and disseminate benchmark data to enable improved Earth-based processing techniques with an emphasis on those data required for model validation and/or improvement.

The suspension system recommended for microgravity testing includes naphthalene as the suspending fluid, 5 vol.% copper microparticles with 1 wt.% Aerosol-OT (AOT) surfactant for achieving stable particle dispersions. Fig. 9.2 shows the You *et al.* [29] model predictions for this suspension system, constrained by the ISS furnace capabilities. To achieve minimum success with respect to SO-1 (Table 9.1), suspensions should be solidified at each of the solidification velocity/thermal gradient combinations marked as orange circles and solid green squares, and microstructures should be investigated and compared to the model. Utilization of a bridge density factor [93, 347] is recommended for distinguishing between dendritic and spearing regimes.

To better understand the interacting roles of particles and solute on the morphological evolution of the solidification front (SO-2, Table 9.1), ampoules containing naphthalene and AOT (solute but no particles) should also be processed, and data collected during solidification for naphthalene with both solute and suspension (solute and particles) samples should be compared. At minimum, the breakdown of the solidification front for both solute and particle suspension/solute samples should be described (using images obtained during solidification). For

particle suspensions, the height of the particle accumulation region should also be measured over the course of solidification (Section 2.3). In addition to helping to clarify destabilization mechanisms, these data, coupled with temperature measurements (*via* the internal, ampoule thermocouples) can be used to test an additional model (ref. [104]; SO-3).

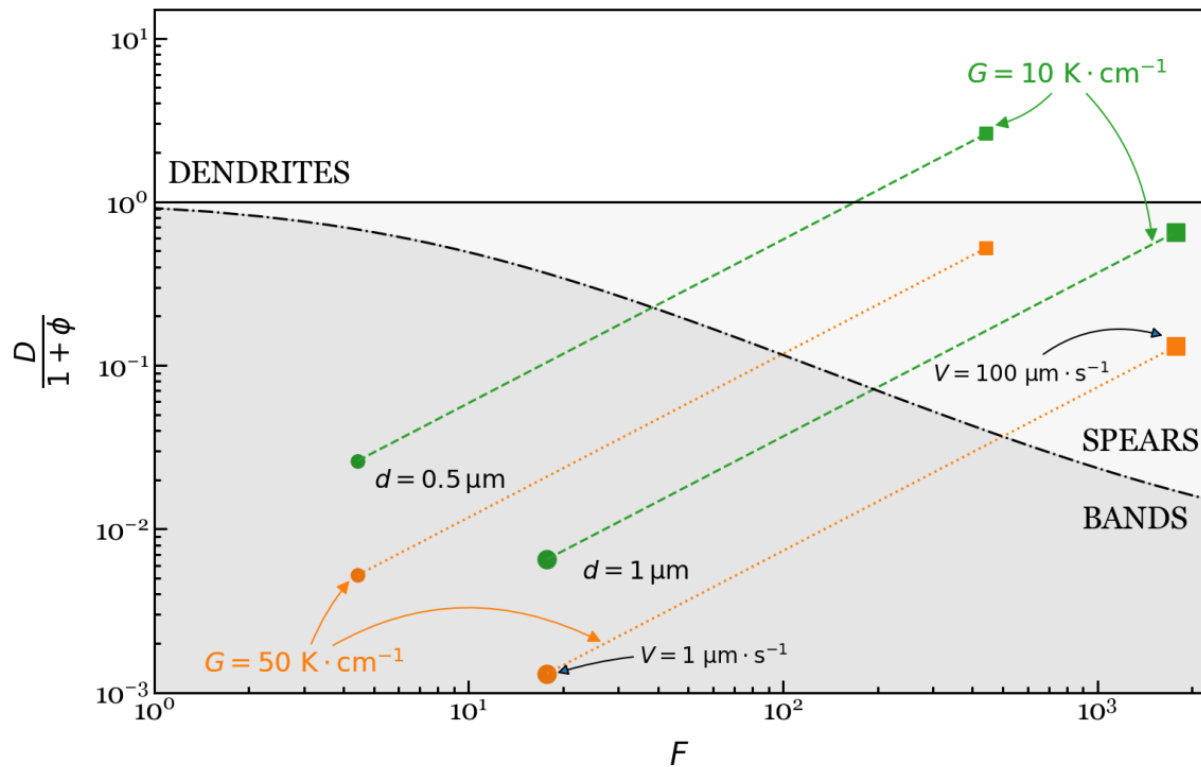


Fig. 9.2. Plot showing You *et al.* [29] model predictions for the intended ISS investigation (film coefficient, F vs. modified Darcy coefficient, $D/(1+\Phi)$) for the particles suspension systems under study, including copper particles of a mean diameter, $d \leq 0.5 \mu\text{m}$ and $d = 1 \mu\text{m}$. Model predictions using primary solidification parameters for achieving minimal success ($V = 1 \mu\text{m} \cdot \text{s}^{-1}$ with $G = 50 \text{ K} \cdot \text{cm}^{-1}$ and $V = 100 \mu\text{m} \cdot \text{s}^{-1}$ with $G = 10 \text{ K} \cdot \text{cm}^{-1}$) are shown as solid orange circles and solid green squares, respectively. The dashed lines show the effect of changing V on model predictions; for the same G , increasing V increases both F and $D/(1+\Phi)$.

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APPENDICES**Appendix 1. Science Requirement Document**

**MaterialsLab Open Science Campaign for
Experiments on the International Space Station**

NASA's Physical Sciences Research Program

Science Requirements Document (SRD)

**Microstructural Evolution in
Freeze-Cast Materials (MEFC)**

Version 1.0

April 17, 2023

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1. Overview and Objectives

1.1. Motivations and Potential Impact

Directional freeze-casting is a solidification technique that produces materials with complex, three-dimensional pore structures [1-3]. The typical directional freeze-casting process is depicted in Fig. 1. First, a suspension of particles is put into a mold (Fig. 1-a). The thermally conductive base of the mold is cooled, promoting nucleation and directional propagation of a solidification front (Fig. 1-b). Initially, the solidification velocity is high and suspended particles are engulfed by the solid/liquid interface (often observed as a dense particle layer at the base of resulting materials [4]). Latent heat release subsequently reduces the velocity of the solid/liquid interface, particles are pushed by the solidification front, and a particle accumulation region forms ahead of the solidification front [4, 5] (Fig. 1-c). As solidification progresses, particles within the accumulation region are incorporated within interdendritic space (Fig. 1-d). After solidification, the solidified fluid is removed via sublimation (Fig. 1-e) and, in the case of ceramic and metal material processing, the resulting scaffold is sintered to densify particle-packed walls (Fig. 1-f). Freeze-casting has broad applicability and has been utilized as a processing method for porous ceramics [6-11], polymers [12-16], and metals [17-19]. A major advantage of the technique is the ability to adjust microstructural properties by manipulating solidification conditions [3, 20]. In turn, this offers the ability to tailor mechanical and physical properties to suit desired applications, further enhancing the cross-cutting nature of the freeze-casting technology.

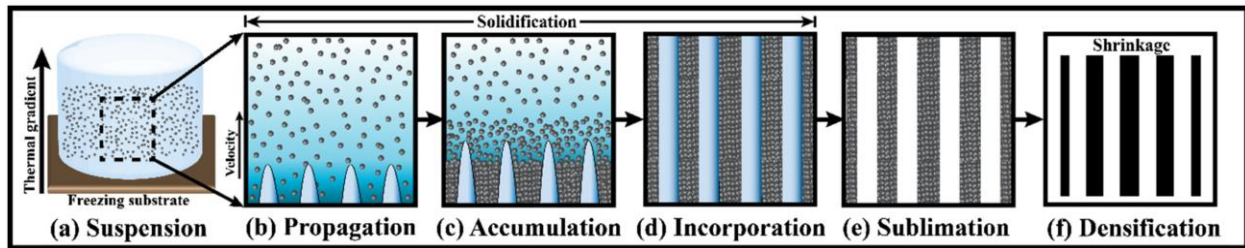


Fig. 1. Directional freeze-casting process: A suspension consisting of particles (grey) dispersed in a fluid (dark blue) is placed onto a freezing substrate (a); after nucleation, dendrites (light blue) propagate in the direction of the thermal gradient while pushing particles away from the moving front (b). An accumulation region of rejected particles develops ahead of the solid/liquid interface (c), inducing particle packing within interdendritic space. After complete solidification (d), the solidified fluid is removed via sublimation leaving elongated pores (white) which template the dendrites (e). In the case of ceramic and metallic materials, the remaining particle scaffold is sintered to densify particle-packed walls (f).

Although freeze-casting has the potential to produce application-specific microstructures, solidification conditions must be properly controlled for precise microstructural control to be achieved. The underlying principles that govern microstructure formation during solidification are not well understood, making *a priori* predictions difficult. Major impediments to the study of these processes are the gravity-driven convection and sedimentation that arise in the liquid due to the combination of temperature and particle and/or additive (e.g., binders, dispersants, surfactants) density/concentration gradients. We posit that buoyancy-driven convection that occurs during solidification as a result of fluid density gradients (induced *via* thermal gradients) acts to increase the particle fraction within the accumulation layer over the course of solidification (*via* fluid flow itself as well as through orthokinetic particle aggregation [21] and subsequent increased sedimentation velocities [22]); these hypothesis are supported by our previous experimental observations [22, 23] of ice lens defects in samples solidified in an orientation such that buoyancy-driven convection was unstable vs. lack of observation for buoyancy-stabilized orientations, microstructural evidence

of Bénard-Rayleigh convective cells during solidification [22, 24] and other defects thought to be gravitationally-driven [22, 23]. Additional support is provided by over forty years of reduced gravity solidification research on metals and alloys [25-34] that has demonstrated detrimental effects of gravity-driven convection on microstructure formation during solidification *via* similar mechanisms as we discuss here. However, current theoretical models describing the freeze-casting solidification process are based on diffusive growth conditions [35-38]; gravity-driven convective effects are ignored.

While the directional solidification of colloidal suspensions is often compared to the solidification of binary alloys [5, 20, 37, 39-43] (with particles taking the role of the solute, the suspending fluid as solvent), freeze-casting systems are often more complex than this because suspensions contain both particles and additives (actual solute), both of which impact (independently and interactively) the morphological evolution of the solidification front [44-47]. Our understanding of how these interactions impact morphological evolution of the solidification front is largely limited to theoretical work that treats these interactions independently (e.g., single particle interactions with a solidification front [48-52] and Mullins-Sekerka, or solute-driven destabilization of the solid/liquid interface [53-57]) and experimental studies carried out under 1g (thus, are complicated by gravity-driven convection and sedimentation) that show these mechanisms are unlikely independent [44-47, 58].

Microgravity investigation of the freeze-casting technique will provide a better fundamental understanding of solidification behavior which will allow for the development of improved processing techniques and predictive control of materials design, applicable to a wide variety of applications for optimized material fabrication on Earth, on planetary surfaces, and in orbit. This investigation entails production of benchmark data necessary to improve predictive control of freeze-cast material design, including producing data applicable for testing a freeze-casting model for predicting templated microstructures based on solidification conditions [37] and broad dissemination of all raw and analyzed data obtained through the PSI and Materials Genome Initiative platforms. Given the cross-cutting nature of the freeze-casting technique, this work is applicable to a wide variety of material types and material applications.

1.2. Overview

The overarching goal of this work is to build a better fundamental understanding of processing/microstructure relationships in freeze-cast materials. The microgravity, directional solidification experiments for this project are intended for processing using the Pore Formation Mobility Investigation (PFMI) furnace on the ISS. The suspension system selected for testing includes naphthalene as the suspending fluid, copper microparticles, and Aerosol-OT (AOT) surfactant for achieving stable particle dispersions. To better understand the interacting roles of particles and solute on the morphological evolution of the solidification front, ampoules containing naphthalene and AOT (solute but no particles) will also be processed, and data collected during solidification for naphthalene with both solute and suspension (solute and particles) samples will be compared. This investigation includes both *in-situ* in-flight investigations of solidification behavior and post-flight microstructural investigation of samples solidified under the microgravity environment.

1.3. Theoretical Background

The tunability of the freeze-casting process is, arguably, the largest advantage the technique has to offer. However, this freedom also adds significant complexity in attempting to understand the complex behavior of the system. As a result of interdependent relationships in the freeze-casting

process, material properties can vary widely even within seemingly similar systems, making predictive control difficult [3, 42, 59, 60]. A sound theoretical understanding is necessary to gain predictive control over freeze-cast microstructural (and, by consequence, functional and mechanical) properties.

1.3.1. Typical morphologies and common defects

The pore morphologies of freeze-cast materials are dictated by the morphology of the solidified fluid. Fig. 2 shows typical morphologies observed in unidirectional freeze-cast materials, including (a) lamellar, (b) dendritic, (c) spears, and (d) bands. In all cases, lamellar and/or dendritic structures are desired (the distinction is dependent primarily on fluid type and suspension additives [3]), whereas spear and banding structures belong to the lensing [37] regimes that are considered defects in freeze-cast materials because their presence significantly compromises mechanical properties in resulting materials [59]. While the morphologies shown in Fig. 2 are most often observed in freeze-cast materials obtained using aqueous suspensions, the transition from unidirectional structures, oriented parallel to the direction of the thermal gradient (*i.e.*, ideal structures, Fig. 2-a, b) to lensing regimes (*i.e.*, defects, Fig. 2-c, d) is not unique to aqueous-based processing [37, 61, 62].

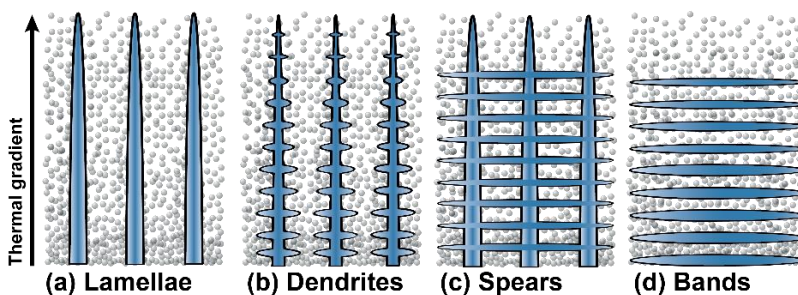


Fig. 2. Schematic showing common morphologies observed in freeze-cast structures, including: (a) lamellar and/or (b) dendritic structures and lensing regimes, including (c) spears and (d) bands.

Lensing defects arise during solidification as fluid-filled platelets, oriented perpendicular to the freezing direction, which are templated into cracks after sublimation. Lensing is studied in a variety of fields, *e.g.*, geology (frost heaves [63]), food engineering [64], and cryobiology [65]. Although various hypotheses have been proposed to explain the development of lenses and bands [5, 37, 38, 60, 66-68], most of the freeze-casting literature attributes their formation to a pattern of particle engulfment, rather than particle rejection, at the solidification interface [40, 69-72]. If the particle fraction within the accumulation region (just above the solid-liquid interface) is below the breakthrough concentration (*i.e.*, where the osmotic pressure of the colloid exceeds the capillary pressure necessary to allow the solidified fluid to invade the pore space [73]), lamellae/dendritic structures form (Fig. 2-a, b). Above the breakthrough concentration, lamellae/dendrites are unable to propagate and ice lenses are likely to develop. Within the lensing regime, the main distinction between the banding and spear structures (Fig. 2-c and d, respectively) is that the former tends to form discrete bands of solidified fluid and enriched particle layers (*e.g.*, Fig. 1-a of Ref. [35] and Fig. 5 of Ref. [22]) whereas the latter does not (*e.g.*, Fig. 9-b of Ref. [74] and Fig. 2-b of ref. [69]).

1.3.2. Morphological instability of the solid/liquid interface

As microstructures of freeze-cast materials are templated during solidification, a sound theoretical understanding of the breakdown and morphological evolution of the solid/liquid interface (from planar to cells, dendrites, *etc.*) is crucial for obtaining predictive control over material parameters. Freeze-casting suspensions typically contain both particles and solute (*e.g.*, dispersants, surfactants, binders), both of which can destabilize a planar interface. The breakdown of a planar

solidification front in the presence of solute can be described in terms of a Mullins-Sekerka [53-57] instability. For particles, this breakdown is described in terms of particle-induced undercooling (which is generally small) [35, 40, 46, 75] and fluid flow: specifically, flow within the liquid separating a particle from an advancing solidification front and flow within the particle accumulation region (the enriched particle region that forms directly ahead of the solid/liquid interface, Fig. 1-c) [37].

While theoretical models considering how the two destabilization mechanisms interact are not presently available, some experimental work has been done [44-47]; these studies have demonstrated that various factors (*e.g.*, particle size [45, 76], solidification velocity [45, 76, 77], volume fraction [78]) promote one destabilization mechanism relative to the other. As Mullins-Sekerka [53] instabilities are largely diffusion-controlled, it has been suggested that the dynamics within the particle accumulation region are particularly important in determining whether a Mullins-Sekerka instability will dominate [45]. For example, during directional solidification of nanometric particle suspensions, diffusion of solute through the particle accumulation region becomes more easily obstructed relative to accumulation regions that form during solidification of larger particle suspensions. Accordingly, nanometric particle suspensions are thought to promote particle-induced instabilities to the solid/liquid interface [45, 76]. The nature of the solute is likely an important factor as well given that typical freeze-casting additives have relatively low diffusion rates and higher propensities for entanglement [45, 79].

Characteristics of the particle accumulation region, including length [45] and particle volume fraction [44], have been used to better understand the transition between the destabilization/morphological evolution mechanisms. As the size of the accumulation region increases, the diffusion path for solute increases, eventually favoring particle-induced destabilization over Mullins-Sekerka-type mechanisms [45]. Lower particle volume fractions within the accumulation region (that is, the effective volume fraction near the solid/liquid interface, not the initial suspension volume fraction) promote destabilization mechanisms that are more representative of Mullins-Sekerka relative to particle-induced destabilization [44]. Importantly, particle volume fraction within accumulation region has been shown to be impacted by suspension stability [4, 69], sedimentation, solidification velocity [66, 67, 80], and solidification orientation with respect to gravity (*i.e.*, buoyancy-driven convection) [22]. As gravity-induced convection induces fluid flow that interacts with the solidification front [81] and causes macroscopic curvature to the solidification front and likely redistributes particles from the bulk suspension into the particle accumulation region [22], solidification studies conducted under $1g$, intended to investigate the relative roles of solute vs. particles on these destabilization mechanisms, are complicated by the presence of gravity.

1.3.3. Theoretical model for predicting dendritic and lensing morphologies

You *et al.* [37] developed a model for predicting freeze-cast morphologies based on solidification conditions and suspension characteristics. Morphologies predicted by the model include dendritic (Fig. 2-b) and lensing regimes, including spears (Fig. 2-c) and banding (Fig. 2-d). Predictions are based on the relationship between three dimensionless parameters: the Darcy coefficient (D), the film coefficient (F), and a dimensionless parameter Φ , which is given by:

$$\Phi = \frac{\phi_0}{\phi_p - \phi_0} \quad \text{Eq. 1}$$

where ϕ_0 is the volume fraction of particles in the bulk suspension and ϕ_p is the volume fraction of particles in the accumulation region, taken as the random close-packed value of 0.64. The dimensionless Darcy coefficient, D , describes fluid flow through the accumulated particle region and is expressed as:

$$D = \frac{\mu v T_m}{k \rho L G} \quad \text{Eq. 2}$$

where μ is the dynamic viscosity of the fluid, v is the solidification velocity, T_m is the melting point of the fluid, ρ is the density of the fluid, L is the latent heat of fusion of the fluid, G is the temperature gradient, and k is the permeability of the accumulated particle region, given by:

$$k = \frac{r^2 (1 - \phi_p)^3}{45 \phi_p^2} \quad \text{Eq. 3}$$

where r is the particle radius.

The dimensionless film coefficient, F , describes flow within the pre-melted liquid film between a particle and the solidification front and it is given by:

$$F = \frac{8\pi^2 \sqrt{3} \mu v r^2}{A \lambda^3} \quad \text{Eq. 4}$$

where A is the Hamaker constant between the solidified fluid and the particle (taken as $1.66 \cdot 10^{-19}$ J for naphthalene/Cu here), and λ is an empirical constant, given in Ref. [37] as 0.225.

Dendritic structures are predicted when $D/(1 + \Phi)$ is greater than unity, whereas lensing regimes are predicted when $D/(1 + \Phi)$ is less than one. Summarizing the above equations, transitions from dendritic to lensing regimes are predicted as the solidification velocity (or pulling velocity) decreases, the thermal gradient increases, the particle volume fraction increases, or the particle radius increases [37]. This model does not account for systems with solute effects (*e.g.*, dissolved additives in the suspension, which nearly all freeze-casting studies employ [3]) nor does it account for gravitational effects, such as gravity-driven convective fluid motion.

1.3.4. Gravity-induced convection during solidification

Convective regimes during directional solidification can generally be categorized by considering: (1) the direction of solidification with respect to the gravity vector and (2) the relative density of rejected solute to solvent. For systems solidified vertically upward (under normal gravity) with rejected solute being heavier than the solvent (as is the case for most freeze-cast/additive systems), solutal convection is generally thought to be stabilized (with exceptions). However, there are two main avenues for which convection can still be introduced: (i) *via* the temperature-dependence of the suspending fluid's density (considering upward solidification condition where the coldest fluid is located at the base of the sample with warmer fluid above, if the density of the warmer fluid is greater than that of the cooler fluid, as is the case for water, the system is unstable with respect to buoyancy-driven convection) and (ii) *via* thermal conductivity mismatches between the liquid and solid phases [82, 83] and/or between the solid phase and the solidification mold [83, 84]. In the case of thermal conductivity mismatches, a radial temperature gradient across the macroscopic interface (the overall shape of the solidification front generated by the dendritic array, rather than

the interface of an individual dendrite) can be induced, causing the macroscopic interface to change shape [85].

General patterns of convective fluid motion corresponding to macroscopic curvature of the interface are shown schematically in Fig. 3. Fig. 3(a), represents the ideal case where the macroscopic solidification interface is flat. In Fig. 3(b), the solidification interface is convex; in this case, convective fluid motion sweeps particles from the center of the interface to the sides, causing a build-up of particles at the mold walls. Conversely, in Fig. 3(c), convective fluid motion, reflective of a concave interface, sweeps particles radially inward, causing an accumulation of particles in the center of the solidification interface. While it was stated earlier that solutal convection is generally stabilized in cases where rejected solute is heavier than the solvent and the system is solidified against gravity, that is not necessarily the case in the presence of a macroscopically curved interface because the presence of horizontal concentration gradients may give rise to solutal convection [83].

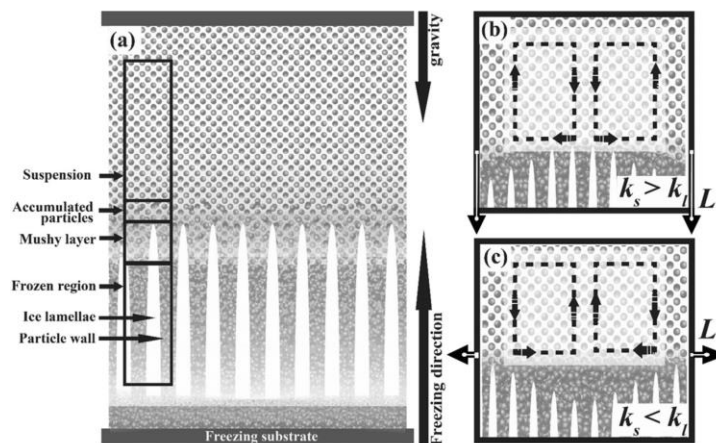


Fig. 3. Schematic showing convective fluid motion patterns corresponding to macroscopic interface curvature; freezing direction is vertically upwards: (a) is representative of a macroscopically planar solidification interface; the particle fraction is relatively homogenous across the interface and the convective fluid motion is limited to that driven by vertical concentration- and temperature gradients; general convective fluid motion patterns associated with a (b) convex and (c) concave interface shape. Here, L is latent heat of fusion and k is thermal conductivity of the solid (s) or liquid (l).

Gravity-induced convective fluid motion can occur both within the mushy layer and within the bulk liquid. While the fluid motion that corresponds to a macroscopic curvature of the solid/liquid interface is generally considered bulk fluid motion, interdendritic convective flow is observed primarily within the mushy layer (though it can be influenced by bulk fluid motion). This flow can cause what is known as the “upstream effect,” (Fig. 4) most commonly described in the seawater [86-89] and alloy solidification [90-92] literatures wherein dendrites tilt in the direction of buoyancy-driven convective fluid motion [88]. Interdendritic fluid motion can be driven by shear flow (across the solid/liquid interface, as depicted in Fig. 4-b) produced by macroscopic convective fluid motion in the bulk liquid or it can occur independently of any macroscopic convective pattern; in either case, buoyancy remains the driving force [36]. Interdendritic fluid flow is weaker than flow resulting from the macroscopic convection described above (approximately one-thousandth that of the bulk fluid region [93]), but can still present significant microstructural consequences.

In addition to promoting the tilting of dendrites, interdendritic flow offers a potential explanation for the observation of asymmetric, one-sided dendritic arms commonly reported in freeze-casting

studies for both particle suspensions [94-102] and polymer solutions [103, 104]: secondary arm growth is suppressed on the “downstream” side [78, 105, 106]. This is depicted in Fig. 4 where (a) shows the “ideal” case, where no appreciable interdendritic flow exists and (b) shows the effect of buoyancy-driven, interdendritic flow for upward solidification. Here, shear flow is depicted to be produced due to the presence of macroscopic convective cells located within the bulk suspension region (ahead of the solid/liquid interface) and the direction of the shear flow is consistent with a concave interface curvature. Thus, consequences of interdendritic flow include both: (i) tilting of dendrites and (ii) suppression of secondary dendrite arms on the “downstream” side. The flow direction promotes growth of dendritic arms on the upstream side, where heat is more easily transported away from the dendrites (*via* fluid flow) than on the downstream side. The warmer fluid on the downstream side promotes melting and fragmentation of secondary dendritic arms [92].

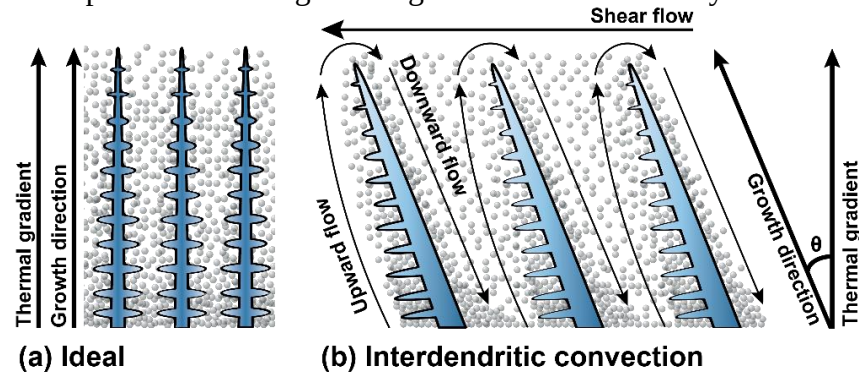


Fig. 4. Schematic showing the effect of interdendritic fluid flow on morphology of ice (blue) dendrites, where (a) no appreciable interdendritic fluid motion is present during solidification, and (b) there is buoyancy-driven convection, resulting in: (i) tilting of ice lamellae and (ii) suppression of secondary dendritic arms on the “downstream” side of ice lamellae.

1.4. Summary of Objectives

The overarching goals of this work are (i) to promote a better understanding of the morphological evolution of the solidification front during freeze-casting to better understand how microstructures, including defects, develop during solidification and (ii) to utilize that information to develop improved processing techniques that enable better predictive control of materials design. The corresponding scientific objectives are delineated in Table 1. The first and third scientific objectives (SO-1 and SO-3) will be accomplished through *in-situ* investigations of solidification and subsequent microstructural investigation of samples solidified under microgravity; SO-2 will be accomplished *via in-situ* investigation only. SO-1 involves collecting and analyzing temperature and image data obtained during solidification, conducting microstructural investigations (of samples solidified under microgravity) and comparing microstructures to those predicted by the You *et al.* [37] model. As this model does not consider suspension additives (*i.e.*, solute) and the relative impact of solute vs. particles on the breakdown and subsequent evolution of the solid/liquid interface is an open research question (Section 1.3.2), we aim to clarify the relative roles of suspension additives and particles on the morphological evolution of the solidification front *via* SO-2. Gravitational effects will be assessed by comparing microgravity data to theoretical models and literature describing experiments carried out under terrestrial gravity conditions. A solidification (morphological evolution and particle redistribution) model will also be developed as part of this work. Raw and analyzed data will be disseminated through the PSI system as well as the Materials Genome Initiative (SO-3).

Table 1. Scientific objectives

Objective	Description
SO-1	Test You <i>et al.</i> [37] freeze-casting model under primarily diffusive-growth conditions for each of the microstructures predicted by the model.
SO-2	Characterize the effect of solute relative to particles on the morphological instability/evolution of the solidification front and describe how buoyancy-driven fluid motion changes the magnitude of these relative effects, if it does.
SO-3	Produce and disseminate benchmark data to enable improved Earth-based processing techniques with an emphasis on those data required for model validation and/or improvement.

2. Experiments in Microgravity and Justification

2.1. Experiment overview

Under microgravity, directional solidification experiments will be conducted using the Pore Formation Mobility Investigation (PFMI) furnace on the ISS. Three sample types will be solidified: (i) suspending fluid with surfactant (suspension additive, AOT), (ii) naphthalene/AOT containing $\sim 1 \mu\text{m}$ Cu particles in suspension, and (iii) naphthalene/AOT containing $\leq 0.5 \mu\text{m}$ Cu particles suspensions. The study of (i) naphthalene/AOT samples (with comparisons to particle suspensions) will allow us to characterize the relative effects of suspension additives (*i.e.*, solute, which for these experiments, includes surfactant) on the morphological evolution of the solidification front (SO-2, Table 1) in the absence of gravity-driven convection. To accomplish SO-1, particle suspensions will be solidified within both the dendritic and lensing regimes (including spears and banding) as predicted by the You *et al.* [37] model for freeze-cast morphologies (Sect. 1.3.3.); to test the model for each of the three predicted microstructures, solidification velocity ($V = 1$ and $100 \mu\text{m} \cdot \text{s}^{-1}$), gradient ($G = 10$ and $50 \text{ K} \cdot \text{cm}^{-1}$), and particle size ($d \approx 1$ and $\leq 0.5 \mu\text{m}$) will be varied.

2.2. Development of flight-test system

In selecting a suspension system (fluid/particles) for flight testing, we considered platform constraints (*e.g.*, safety regulations, equipment specifications, transport requirements) and scientific relevance (*i.e.*, that we could create stable suspensions and achieve anisotropic structures *via* directional solidification). Naphthalene was selected as a suspending fluid after also testing succinonitrile and camphene as candidate materials. Naphthalene has a convenient melting point of $\sim 80^\circ\text{C}$, which is compatible with the PFMI furnace [107] and simplifies the process of returning solidified samples for post-flight test analysis. The use of naphthalene in freeze-cast suspensions has been reported, though only as a fluid system with camphor [108-110]. Five particle types were explored during development tests; Cu particles (SkySpring Nanomaterials, Inc, Houston, TX) were selected due to their spherical shape and availability in our size range of interest (0.5 and $1 \mu\text{m}$).

Naphthalene is solid at room temperature; this was a requirement we set when selecting candidate fluids to avoid a refrigerated transport requirement for sample return (for conducting microstructural analyses). In turn, this complicated our development requirement related to suspension stability as it inherently requires the suspension to survive a freeze-thaw cycle. We conducted freeze-thaw studies with four surfactant systems to assess the risk of suspension destabilization and selected our surfactant, AOT, based on that work; relevant results are presented in the following. Finally, we conducted thermal studies to determine storage temperature requirements of samples after testing/during transport to ensure that no appreciable microstructural changes would occur.

Our suspension preparation procedure is provided in A.1. Calorimetry and rheometry were used to characterize naphthalene, naphthalene and AOT, and our suspensions; some of these results are used as model inputs and are provided in A.2.

2.2.1. Solidification studies

Development of solidification experiments were conducted using a Bridgman furnace. The motor driver on the furnace is a DM542T digital stepper driver with 16 degrees of microstep resolution, corresponding to 200-25,600 pulses per revolution for the system. This provides furnace translation velocities ranging from 0.2 to $>1,000 \mu\text{m} \cdot \text{s}^{-1}$, which is consistent with the growth velocities offered by the PFMI (1 - $100 \mu\text{m} \cdot \text{s}^{-1}$). Results from directional solidification tests carried out using $5 \text{ vol.}\%$ Cu suspensions with $1 \text{ wt.}\%$ AOT (with respect to Cu mass), using a thermal gradient, $G = 35^\circ\text{C} \cdot \text{cm}^{-1}$ and furnace translation velocities, V of 6.5 , 38 , and $80 \mu\text{m} \cdot \text{s}^{-1}$ are presented in the following.

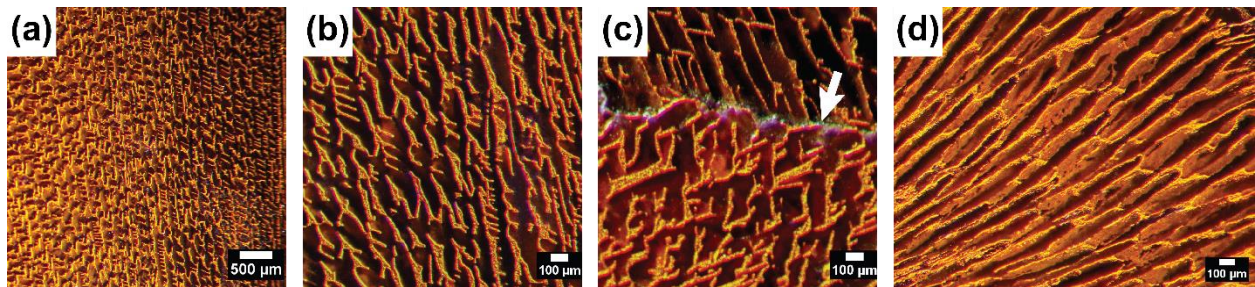


Fig. 5. Optical micrographs of polished cross-sections of Cu freeze-cast materials obtained using a furnace translation velocity, $V = 80 \mu\text{m} \cdot \text{s}^{-1}$ and thermal gradient, $G = 35^\circ\text{C} \cdot \text{cm}^{-1}$; (a-c) are taken parallel to the freezing direction, (b) is a magnified view of (a), (c) shows two orientations of wall structures (arrow), and (d) is taken perpendicular to the freezing direction.

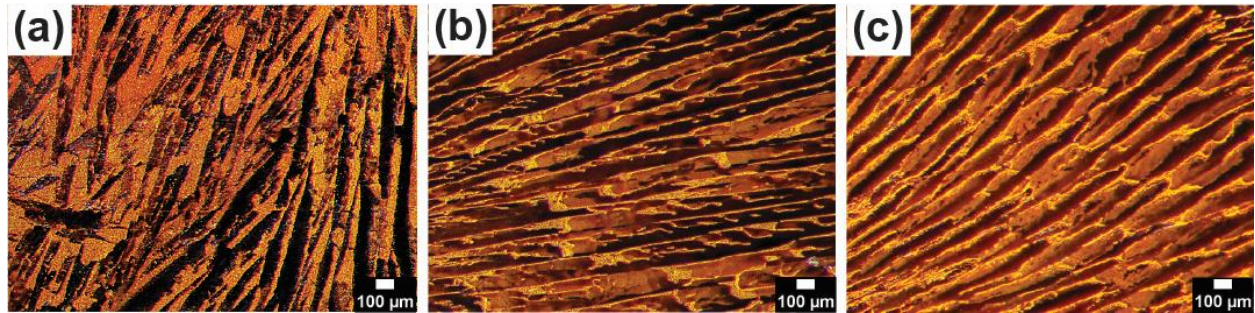


Fig. 6. Optical micrographs of polished cross-sections of Cu freeze-cast materials obtained using furnace translation velocities of (a) 6.5 , (b) 38 , and (c) $80 \mu\text{m} \cdot \text{s}^{-1}$ with constant gradient, $G = 35^\circ\text{C} \cdot \text{cm}^{-1}$. All images are taken perpendicular to the freezing direction.

Optical micrographs of cross-sections showing the microstructure of freeze-cast materials obtained using a furnace translation velocity of $80 \mu\text{m} \cdot \text{s}^{-1}$ are shown in Fig. 5. Images (a) through (c) are taken parallel to the solidification direction and (b) is a magnified view of (a); the image in (d) is taken perpendicular to the direction of freezing. All images were produced *via* polishing of solidified naphthalene/Cu materials (*i.e.*, the naphthalene was not removed *via* sublimation prior to imaging). Plate-like microstructures are observed for both samples, but considerable dendritic features are observed in the sample solidified at $V = 80 \mu\text{m} \cdot \text{s}^{-1}$ (Fig. 5-a, b). The microstructure predicted by You *et al.* [37] is “spears” (*i.e.*, presence of significant dendritic features that extend into neighboring dendrites, producing a cellular-type structure after sublimation of the solidified fluid). The image in (c) shows that, while significant dendritic features are present, a wall-type

structure is retained (white arrow in Fig. 5-c). Asymmetry of dendritic features is observed; this is especially apparent in Fig. 5-b.

Fig. 6 shows optical micrographs of cross-sections perpendicular to the freezing direction for Cu structures solidified using furnace translation velocities of (a) 6.5, (b) 38, and (c) $80 \mu\text{m} \cdot \text{s}^{-1}$. The microstructure predicted by You *et al.* [37] for (a) and (b) is banding, whereas (c) is spears (as above). A banding structure is indeed observed in (a) as for this cross-section orientation, these lens-defects present as a disordered wall structure with wall merging and cracks, all of which are observed in (a). However (b) appears dendritic/spear-like symmetric dendritic features are observed throughout the microstructure. Fig. 6-c is the same as Fig. 5-d.

Primary dendrite arm measurements of naphthalene were obtained from stitched cross-section images taken perpendicular to the freezing direction. To quantify primary arm width variation with respect to radial position, measurements were regionalized: “outer” measurements were taken from circles drawn at the periphery of cross-sections and “inner” measurements were taken from a circle drawn circles drawn at the center of cross-sections having a diameter of ~ 2.5 mm. “Outer-middle” and “middle-inner” measurements were taken from equally spaced circles drawn in between the outer and inner circles (thus, distance between any given circle is ~ 1.25 mm as the sample diameters are ~ 10 mm). A total of 15 samples were analyzed (five samples for each furnace translation velocity); 2,000 primary dendrite arm measurements were taken for each region (at each velocity).

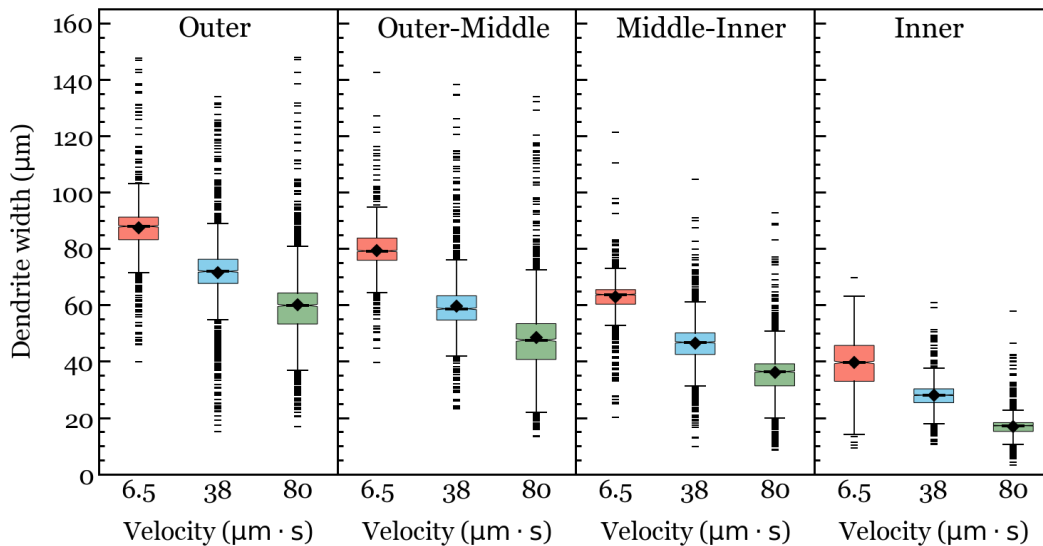


Fig. 7. Box and whisker plots summarizing primary dendrite arm width of naphthalene in 5 vol.% Cu freeze-cast materials solidified using furnace translation velocities of 6.5, 38, and $80 \mu\text{m} \cdot \text{s}^{-1}$, while holding the thermal gradient, G constant at $35^\circ\text{C} \cdot \text{cm}^{-1}$. All measurements were taken from cross-sections perpendicular to the freezing directions; “outer” measurements represent values at the outer edge of the cross-sections, “inner” values were obtained 2.5 mm from the absolute center of cross-sections; “outer-middle” and “middle-inner” were obtained from equally spaced regions between the outer edge and the inner measurements.

Fig. 7 shows box and whisker plots for these data, where measurements obtained from the “outer” (or peripheral regions of cross-sections) are summarized in the leftmost plot and the rightmost plot summarizes measurements taken from the inner region of samples. The minimum and maximum values of boxes represent the first and third quartiles, respectively; medians are shown as horizontal lines inside the boxes, means are represented by black diamonds, and whiskers represent 1.5 times the interquartile range. Table 2 provides numerical values for mean $\pm$ standard deviation for

these data. Dendrite thickness is expected to increase with decreasing furnace translation velocity; this relationship is observed for all regions. For all velocities, dendrites widths are largest in the outer region of samples and decrease with decreasing distance from the center (*e.g.*, for samples solidified at $V = 6.5 \mu\text{m} \cdot \text{s}^{-1}$, dendrite width at the outer and inner regions are 87 ± 11 and $40 \pm 9 \mu\text{m}$, respectively; for $V = 80 \mu\text{m} \cdot \text{s}^{-1}$, these values decrease to 60 ± 14 and $17 \pm 4 \mu\text{m}$, respectively). The relationship we observe here, with increasing dendrite width at outer regions of samples relative to inner regions indicates that the local solidification velocity is higher in the central region of the sample relative to the outer region. The corresponding macroscopic convection pattern is likely characteristic of a convex macroscopic interface (latent heat is evacuated through the solid, Fig. 3-b). Interdendritic convective fluid flow is also likely present given the observation of asymmetric dendritic features.

Table 2. Primary dendrite arm width of naphthalene in 5 vol.% Cu freeze-cast materials solidified using furnace translation velocities of 6.5, 38, and $80 \mu\text{m} \cdot \text{s}^{-1}$, while holding the thermal gradient, G constant at $35^\circ\text{K} \cdot \text{cm}^{-1}$. All measurements were taken from cross-sections perpendicular to the freezing directions; “outer” measurements represent values at the outer edge of the cross-sections, “inner” values were obtained 2.5 mm from the absolute center of cross-sections; “outer-middle” and “middle-inner” were obtained from equally spaced regions between the outer edge and the inner measurements. Data are expressed as mean $\pm$ standard deviation; N is the number of samples.

Velocity ($\mu\text{m} \cdot \text{s}^{-1}$)	N	Primary naphthalene dendrite arm width (μm)				
		Overall	Outer	Outer-middle	Middle-inner	Inner
6.5	5	67 ± 20	87 ± 11	80 ± 9	63 ± 7	40 ± 9
38	5	51 ± 19	71 ± 13	59 ± 11	46 ± 9	28 ± 5
80	5	40 ± 19	60 ± 14	49 ± 14	36 ± 8	17 ± 4

2.2.2. Freeze-thaw studies

As flight ampoules will be filled on the ground and transferred to the ISS in a solidified state, samples will need to be melted back immediately prior to experimental tests and suspension stability cannot degrade appreciably due to that freeze-thaw cycle. While suspensions are sometimes frozen to *prevent* aggregation [111, 112], freezing is also known to *cause* aggregation (freezing pushes particles together, increasing the likelihood of aggregation [113-116]). We conducted freeze-thaw studies using four naphthalene/Cu/surfactant systems to assess suspension destabilization after freeze/thaw. Within the four surfactant types tested, two stabilization mechanisms were studied: steric stabilization and electrosteric stabilization.

For suspensions employing low dielectric constant fluids (*e.g.*, naphthalene), steric stabilization is the most commonly employed stabilization method [115, 117-120]; polymers adsorbed on particles create a hinderance for particle aggregation. Aggregation that does occur when particles overcome steric repulsion is thought to be reversible [117]. Three of the surfactants we tested offered steric stabilization; two of the three (Triton X-100 and Pluronic F-68) produced suspensions that were inconsistently stable even prior to freeze-thaw testing, likely due to thermal degradation of the polymer due to the high melting temperature of naphthalene. The third steric stabilization surfactant, Hypermer KD-13, produced stable suspensions that destabilized after freeze-thaw.

AOT is an ionic surfactant that is used for electrosteric suspension stabilization. Electrosteric stabilization in low-dielectric constant fluids offers increased stabilization relative to steric stabilization alone [121-126]. In this case, we have a non-polar fluid, so the polar head of the surfactant molecule adsorbs to the particle surface (with help from the counterion, which creates a bridge [124]). At the critical micelle concentration, reverse micelles that are charge-stabilized are formed [126-128]. With this system, we have been able to reliably create stable naphthalene/particle suspensions which, as shown previously, produce anisotropic, directional microstructures upon

solidification. Moreover, we did not observe any evidence of suspension destabilization after freeze-thaw. However, tests were conducted after subjecting suspensions to *a single* freeze-thaw cycle; additional cycles may cause degradation not described in the following. Several science requirements (7, 8, 9, and 10) specify that the suspension must remain in the liquid state during various stages of ampoule filling. Also, science requirement 19 specifies a storage transport requirement for suspensions prior to flight testing at $<80^{\circ}\text{C}$ to prevent an uncontrolled freeze-thaw cycle.

2.2.2.1. Solidification studies

To assess their freeze-thaw stability, suspensions with 5 vol.% Cu and 1 wt.% AOT (with respect to Cu) were prepared as described previously. Prepared suspensions were subjected to an initial freeze in an ultrasonic bath using bath temperatures of either ~ 10 or $\sim 50^{\circ}\text{C}$, representing slow (FTS) and fast (FTF) freeze-thaw testing, respectively. Solidified suspensions were melted immediately prior to directional solidification. In an attempt to mitigate the risk of particle aggregation during freezing [113-116], the sonication step was utilized to promote disordered growth during the initial freeze step, which should reduce the propensity for particle aggregation (Science Requirement 10). Fig. 8 shows perpendicular cross-sections obtained from suspensions that were (a) not subjected to freeze-thaw, (b) subjected to freeze-thaw using a sonication bath temperature of $\sim 50^{\circ}\text{C}$ (FTS), and (c) subjected to freeze-thaw using a sonication bath temperature of $\sim 10^{\circ}\text{C}$ (FTF). Particle distribution within these samples appears uniform, irrespective of whether suspensions were subjected to a freeze-thaw step prior to directional solidification.

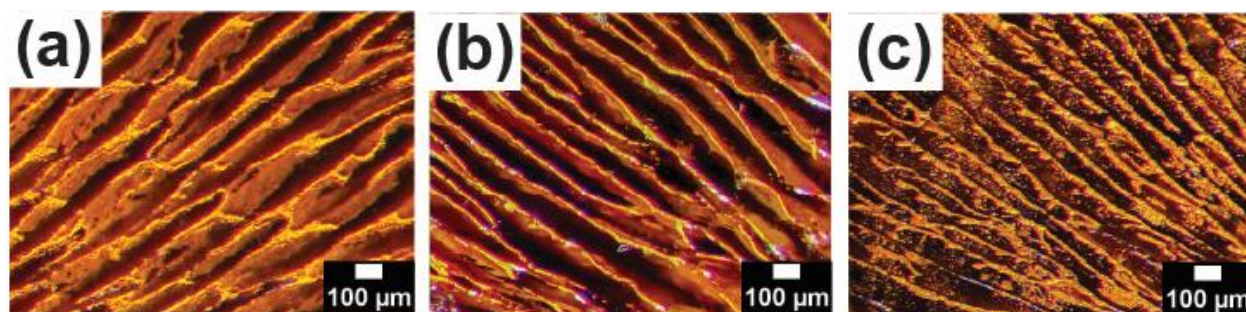


Fig. 8. Optical micrographs of copper freeze-cast materials obtained using furnace translation velocities of $80 \mu\text{m} \cdot \text{s}^{-1}$ and thermal gradient, $G = 35^{\circ}\text{C} \cdot \text{cm}^{-1}$ where (a) was obtained from a 5 vol.% Cu suspension that was only solidified once (during directional solidification) and the structure in (b) was obtained from a suspension that was subjected to freeze-thaw prior to directional solidification. Both images are cross-sections perpendicular to the freezing direction.

Primary dendrite arm measurements of naphthalene were obtained from stitched cross-section images taken perpendicular to the freezing direction, as described previously. Fig. 9 shows box and whisker plots for these data, where measurements obtained from the “outer” (or peripheral regions of cross-sections) are summarized in the leftmost plot and the rightmost plot summarizes measurements taken from the inner region of samples. Table 3 provides numerical values for mean $\pm$ standard deviation for these data. As observed previously, dendrite width increases with increasing radial distance from the center. Within a given region, values of mean dendrite width are in relatively good agreement among the freeze-thaw conditions. For the outer region, these values are 60 ± 14 , 54 ± 8 , and 60 ± 11 for the no-freeze-thaw (STD), freeze-thaw-fast (FTF), and freeze-thaw-slow (FTS) conditions, respectively. For the inner regions, values for STD, FTF, and FTS are 17 ± 4 , 21 ± 6 , and 20 ± 5 , respectively. While some statistically significant differences can be found between groups (*via* one-way ANOVA and post hoc, Tukey HSD tests), this is likely

attributable to the large number of data points collected (2,000 measurements per condition, per region) as we do not observe any relationships between these data that hold over all four regions.

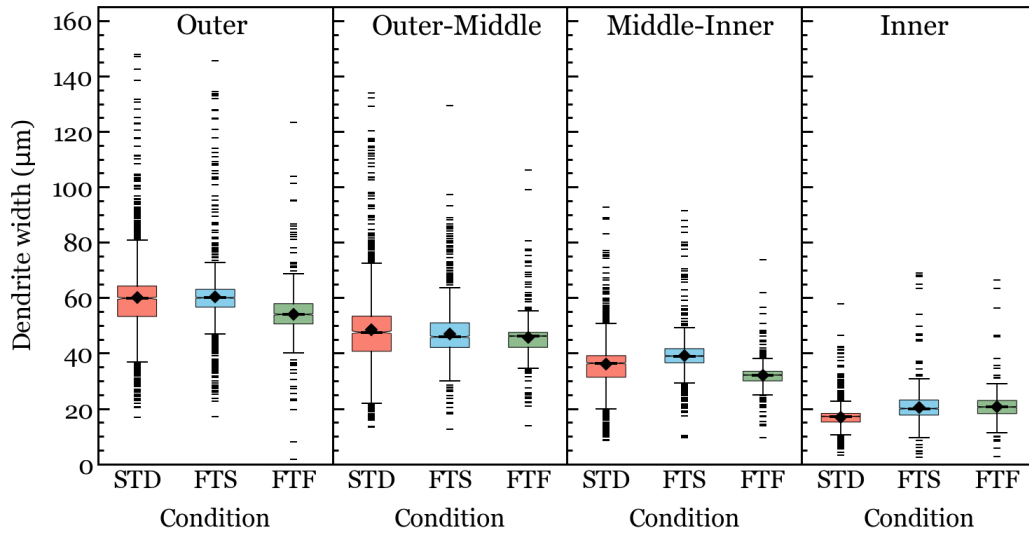


Fig. 9. Box and whisker plots summarizing primary dendrite arm width for suspension freeze-thaw tests of naphthalene with 5 vol.% Cu solidified using a furnace translation $80 \mu\text{m} \cdot \text{s}^{-1}$. The “STD” condition is the same as that represented in Table 2; suspensions used in the “FTS” and “FTF” conditions were subjected to one initial freeze/thaw cycle prior to directional solidification; the initial freezing was conducted in an ultrasonic bath and the “slow” (FTS) or “fast” (FTF) references that bath temperature ($\sim 50^\circ\text{C}$ and $\sim 10^\circ\text{C}$, respectively). All measurements were taken from polished cross-sections perpendicular to the freezing directions; “outer” measurements represent values at the outer edge of the cross-sections, “inner” values were obtained 2.5 mm from the absolute center of cross-sections; “outer-middle” and “middle-inner” were obtained from equally spaced regions between the outer edge and the inner measurements.

Table 3. Widths of primary dendrite arms for suspension freeze-thaw tests of naphthalene with 5 vol.% Cu solidified using a furnace translation $80 \mu\text{m} \cdot \text{s}^{-1}$. The “no freeze-thaw” condition is the same as that represented in Table 2; suspensions used in the “freeze-thaw (fast)” and “freeze-thaw (slow)” conditions were subjected to an initial freeze/thaw cycle prior to directional solidification; the initial freezing was conducted in an ultrasonic bath and the “fast” or “slow” denominations reference that bath temperature ($\sim 10^\circ\text{C}$ and $\sim 50^\circ\text{C}$, respectively). All measurements were taken from polished cross-sections perpendicular to the freezing directions; “outer” measurements represent values at the outer edge of the cross-sections, “inner” values were obtained 2.5 mm from the absolute center of cross-sections; “outer-middle” and “middle-inner” were obtained from equally spaced regions between the outer edge and the inner measurements. Data are expressed as mean $\pm$ standard deviation; N is the number of samples.

Condition	N	Primary naphthalene dendrite arm width (μm)			
		Outer	Outer-middle	Middle-inner	Inner
No freeze-thaw	5	60 ± 14	49 ± 14	36 ± 8	17 ± 4
Freeze-thaw (fast)	5	54 ± 8	46 ± 6	32 ± 5	21 ± 6
Freeze-thaw (slow)	5	60 ± 11	47 ± 9	39 ± 6	20 ± 5

2.2.2.2. Rheometry

Rheological studies were carried out to assess the freeze-thaw stability of Cu/AOT/naphthalene suspensions (procedures are provided in A.2.2). Fig. 10(a) shows viscosity as a function of shear rate for vacuum distilled naphthalene at 82, 85, and 90°C and Fig. 10(b) shows viscosity as a function of shear rate for a suspension of 5 vol.% Cu particles in naphthalene containing 1 wt.% AOT (with respect to particle mass). Data points on both plots represent mean values obtained during steady-state flow using constant shear rate tests; the error bars represent the corresponding standard deviation. In Fig. 10(b), red data points represent values obtained for a suspension that

was never frozen whereas blue data points were obtained from a thawed suspension that was re-melted and tested 24 h after it was solidified. No statistically-significant differences between viscosity values measured for the never-frozen vs. the freeze-thawed were detected.

For particle suspensions, the solid phase (particles) largely determines the rheological behavior [129]. For Newtonian suspending fluids, particle agglomeration (*e.g.*, that which may arise from freezing and thawing suspensions) in low particle volume fraction suspensions is often identified *via* the non-Newtonian behavior of resulting suspensions [130, 131]. This often appears as shear-thinning behavior that results from shear-induced breakage of agglomerates [132-134] (higher volume fraction suspensions may show shear-thickening as a result of increased frictional forces [132, 133]). Thus, significant particle agglomeration resulting from freeze-thaw of our 5 vol.% Cu suspensions is expected to present as shear thinning, which we do not observe here.

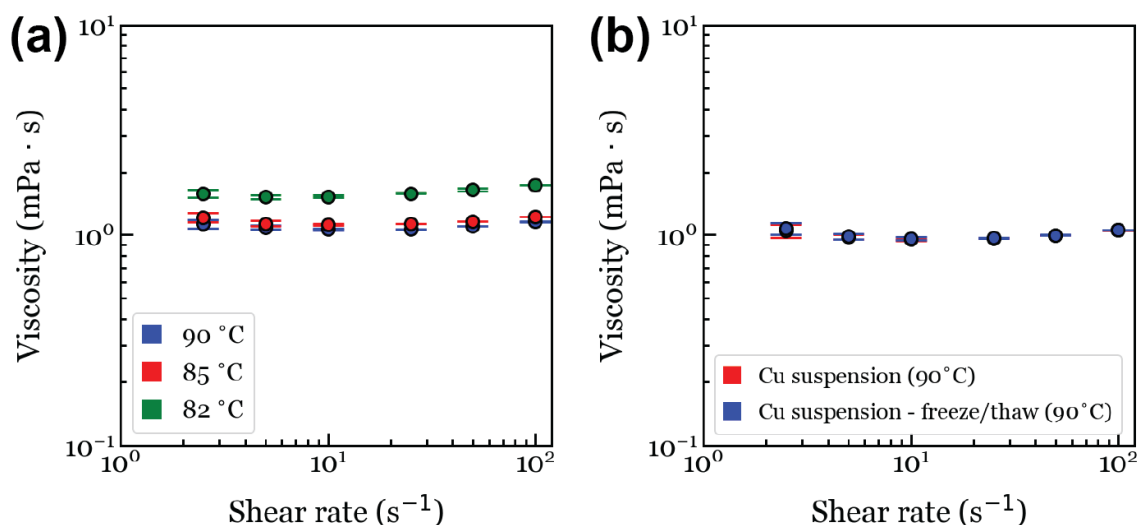


Fig. 10. Plots of shear rate vs. viscosity for (a) vacuum distilled naphthalene tested at 82, 85, and 90°C and (b) a suspension of 5 vol.% Cu particles in naphthalene containing 1 wt.% AOT (with respect to particle mass); in (b), red data points represent values obtained for a suspension that was never frozen whereas blue data points were obtained from a thawed suspension that was tested 24 h after solidification. Data points on both plots represent mean values obtained during steady-state flow using constant shear rate tests; error bars represent the standard deviation.

2.2.3. Thermal requirements study

To determine storage temperature requirements for sample return (that is, the temperature at which no appreciable microstructural changes occur over times well in excess of sample return), we directionally solidified suspensions as described previously, then mounted sectioned cross-sections in epoxy. Samples were ground and polished, and images of cross-sections were obtained to describe the initial state of samples. Subsequently, the exposed naphthalene surface of the mounted sample was sealed by coating it with Torr Seal (applied using a brush) and mounted samples were stored in one of four different storage temperature conditions, at: (i) ~0°C, (ii) room temperature, (iii) ~44°C, and (iv) ~60°C; three samples at each thermal condition were tested. Torr Seal was used to prevent sublimation of naphthalene. Samples were removed from storage, re-polished (thus removing the Torr Seal), and imaged at 1, 7, and 30 days post solidification (each time after imaging, Torr Seal was reapplied and samples were placed back into thermal storage). Regions of each sample were imaged at each time step and dendrite width measurements were taken and compared to the previous time step. Means were compared using *t*-tests and a *p* value of 0.01;

statistically significant differences were not observed for any of the thermal conditions. We ran an additional test at $\sim 75^{\circ}\text{C}$ and images obtained at 1 day showed considerable microstructural changes. Thus, Science Requirement 20 specifies that after flight testing, sample ampoules shall not be stored at temperatures exceeding 60°C .

2.3. Flight hardware and materials

2.3.1. Furnace

Microgravity solidification experiments are intended for the Pore Formation Mobility Investigation (PFMI) [135]. The PFMI furnace allows for a high gradient of $50^{\circ}\text{C}/\text{cm}$, low gradient of $10^{\circ}\text{C}/\text{cm}$, and nominal melt-back and growth velocities of 100 and $1\text{ }\mu\text{m}/\text{s}$, respectively.

2.3.2. Ampoules

The Sample Ampoule Assembly (SSA) as designed for the previous PFMI work [135] is depicted in Fig. 11. Techshot is designing the SSA for this work to be similar in construction to those designed previously, components of which include: the main tube body (composed of Schott 8250 borosilicate glass), Kovar piston assembly, cartridge mount head, and six *in-situ* thermocouples [136]. The inside and outside diameter of the ampoule is ~ 10.9 and 12.75 mm , respectively. To ensure similar thermal behavior with respect to the glass, Science Requirement 3 specifies an internal diameter tolerance of $\pm 0.2\text{ mm}$. Based on toxicology assessments conducted by Techshot, the maximum volume of naphthalene that can be used in an individual ampoule is $\sim 6.8\text{ mL}$. Accordingly, ampoules will be filled with $\sim 5.6\text{ mL}$ of science material, corresponding to an effective science material length of $\sim 6\text{ cm}$ which is shorter than the overall length of the ampoules ($\sim 28\text{ cm}$, not including the piston assembly or insertion of the Kovar head, Fig. 11).

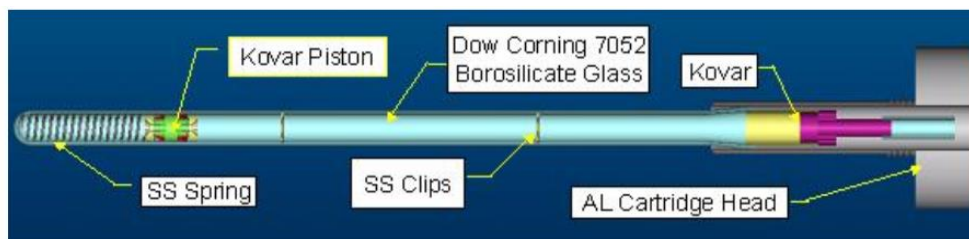


Fig. 11. Schematic showing the ampoule assembly as designed for the previous PFMI experiments (extracted [135]).

2.3.2.1. Volumetric expansion/contraction of naphthalene

The density of naphthalene is temperature-dependent and the molar of the solid and liquid are different; thus, the piston assembly is needed to accommodate volumetric expansion and contraction of the science material during melt-back and solidification (Science Requirement 5). Fig. 12 shows the temperature-dependent density of naphthalene obtained from refs. [137-145]; these data were fitted via linear regression and the resulting equation for the red line shown in Fig. 12 is $\rho_{\text{naphthalene}} = -0.788 \cdot T + 1041.2\text{ kg} \cdot \text{m}^{-3}$, where ρ and T are the densities and temperatures ($^{\circ}\text{C}$), respectively. The minimum volumetric changes that need to be accommodated by the piston system are estimated as $\sim 9\%$. This value was estimated by first considering the maximum densities (minimum volumes) for the fluid systems; we considered the solid phase density at the temperature closest to room temperature for which data were available. For naphthalene, the density at 20°C is reported as $1.025\text{ g}/\text{cm}^3$ [142]. To estimate the minimum densities (maximum volumes), we considered the maximum temperature of the furnace (130°C , [107]) and used the aforementioned linear regression equation to estimate the fluid density at that temperature; at 130°C , the density of naphthalene is estimated at $0.939\text{ g}/\text{cm}^3$.

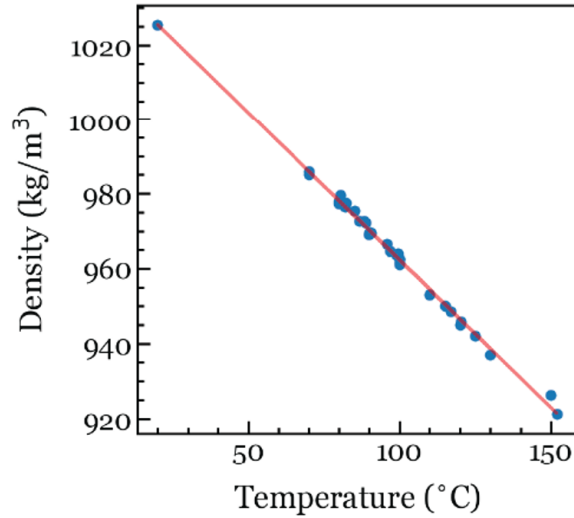


Fig. 12. Plot showing the temperature-dependent density for naphthalene where data were obtained from refs. [137-145]; these data were fitted via linear regression (red line).

2.3.2.2. Thermocouple placement

Fig. 13 shows the desired placement of the six thermocouples within each sample ampoule; the effective science length (60 mm) corresponds to the molten zone; thus, the effective length of the flight samples. Fig. 13(a) shows a longitudinal view where the length of each thermocouple is shown; the solidification proceeds from left to right, as indicated by the arrow, such that the locations for which the thermocouples enter the ampoule is considered the first-to-solidify region of the samples. Thermocouples 1 and 4 have a length of zero with respect to the sample length; that is, they are located at the base of the first-to-solidify region of the ampoules. Thermocouple 3 extends from the first-to-solidify region throughout the length of the sample for a total length of 60 mm; the lengths of thermocouples 3, 5, and 6 are 15, 30, and 45 mm, respectively.

Fig. 13(b) shows the outer and inner diameter of the ampoule (13 and 10 mm, respectively) and the radial placement of the thermocouples (sheathed thermocouple diameter of ~ 0.25 mm, 0.01 in). Thermocouples 2-6 are positioned at equal distances in a semicircle inferior to the imaging direction (indicated with an arrow). Thermocouple 1, which has a length of zero with respect to the sample length, is located directly across from thermocouple 4 (which also has a length of zero with respect to the sample length). The semicircular placement of thermocouples 2-6 is requested in an effort to minimize visual obstruction by the thermocouples during imaging; the placement of thermocouples 1 and 4 will enable determination of any radial temperature gradients at the base of the sample. Fig. 13(c) shows an isometric view of thermocouple placement within the sample ampoule.

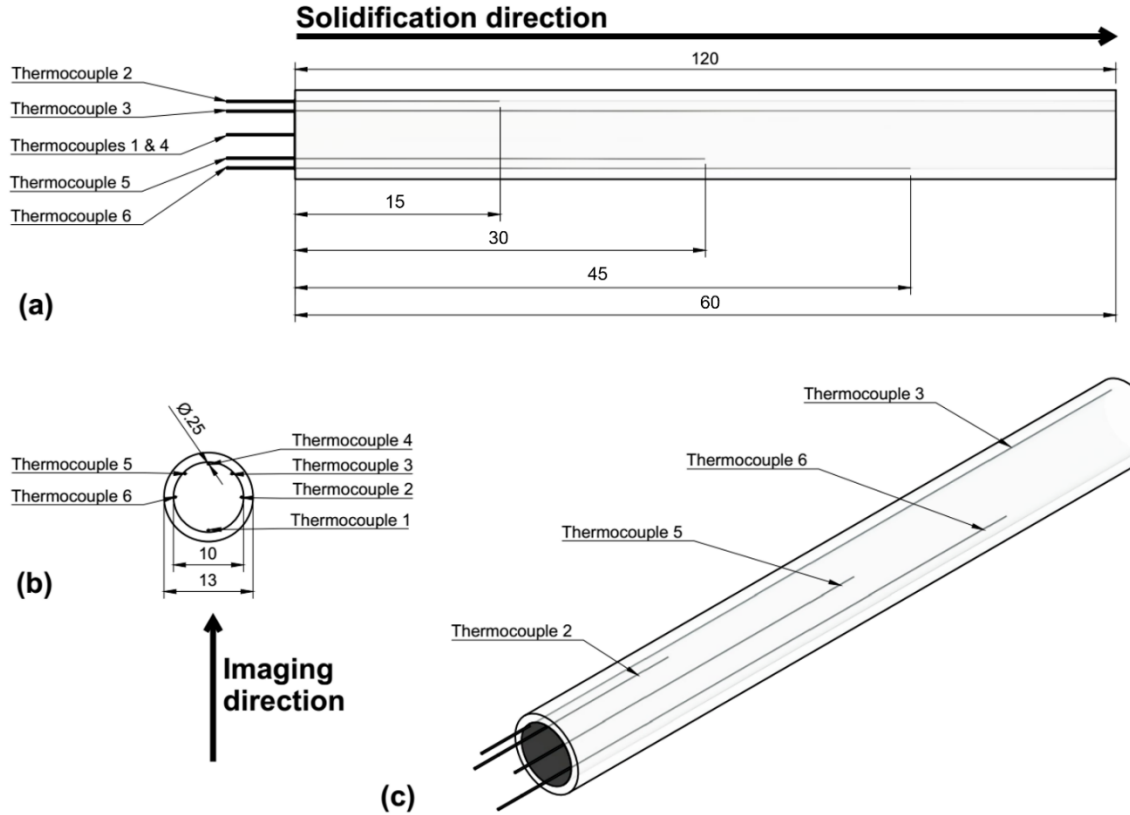


Fig. 13. Schematic showing desired placement of six thermocouples within each sample ampoule; all dimensions in mm.

2.4. Solidification experiments

2.4.1. Melt-back

Samples will be transferred to the ISS in their solidified state. At the beginning of experimentation, the PFMI furnace will melt back the naphthalene/particle suspension in the ampoules approximately 6 cm forming a melt front as planar as possible; that is, the solid/liquid interface will have a deviation in height of less than 0.5 mm as measured from the center of the solid/liquid interface to the edge at the time in which the furnace is at equilibrium and the translation rate is zero (Science Requirement 17). After melt-back is achieved, the sample will be held in the liquid state for 60 minutes to allow for redistribution of particles *via* Brownian diffusion; the 1D diffusion distances for 0.5 and 1 μm particles are calculated as ~ 70 and 50 μm , respectively within this timeframe (Science Requirement 18; see A.3 for calculations). As described in Section 2.2.2, samples directionally solidified during development testing showed relatively uniform particle distributions. Thus, we feel that this particle distribution step will be sufficient for ensuring uniformly distributed particle suspensions for our flight experiments. Lastly, the sample will be re-solidified utilizing the experimental parameters provided in Table 3.

2.4.2. Processing parameters

Fig. 14 shows the You et al. [37] model predictions, in a plot of film coefficient, F , vs. modified Darcy coefficient, $D/(1+\Phi)$, for the particles suspension systems under study in this investigation, including copper particles of a mean diameter, $d \leq 0.5 \mu\text{m}$ and $d = 1 \mu\text{m}$. With other parameter fixed, the film coefficient, F , scales with the product of the solidification velocity V and the square

of the particle size d (see Eq. 4); the Darcy coefficient scales with the velocity, the inverse of the temperature gradient G , and the inverse of the square of the particle size d (see Eqs. 2,3).

Model predictions using our primary solidification parameters for achieving minimal success ($V = 1 \mu\text{m} \cdot \text{s}^{-1}$ with $G = 50 \text{ K} \cdot \text{cm}^{-1}$ and $V = 100 \mu\text{m} \cdot \text{s}^{-1}$ with $G = 10 \text{ K} \cdot \text{cm}^{-1}$) are shown in Fig. 14 as solid orange circles and solid green squares, respectively. The dashed lines show the effect of changing V on model predictions; for the same G , increasing V increases both F and $D/(1 + \Phi)$. As explained in Section 1.3.3, the y-axis value of $D/(1 + \Phi)$ determines whether dendritic or lensing morphologies are predicted; for $D/(1 + \Phi) > 1$, dendrites are expected; lensing regimes are expected when $D/(1 + \Phi)$ is less than unity (solid black horizontal line in Fig. 14). The distinction between spears and bands within the lensing regime (black dashed curve in Fig. 14) is determined by the relationship between $D/(1 + \Phi)$ and F .

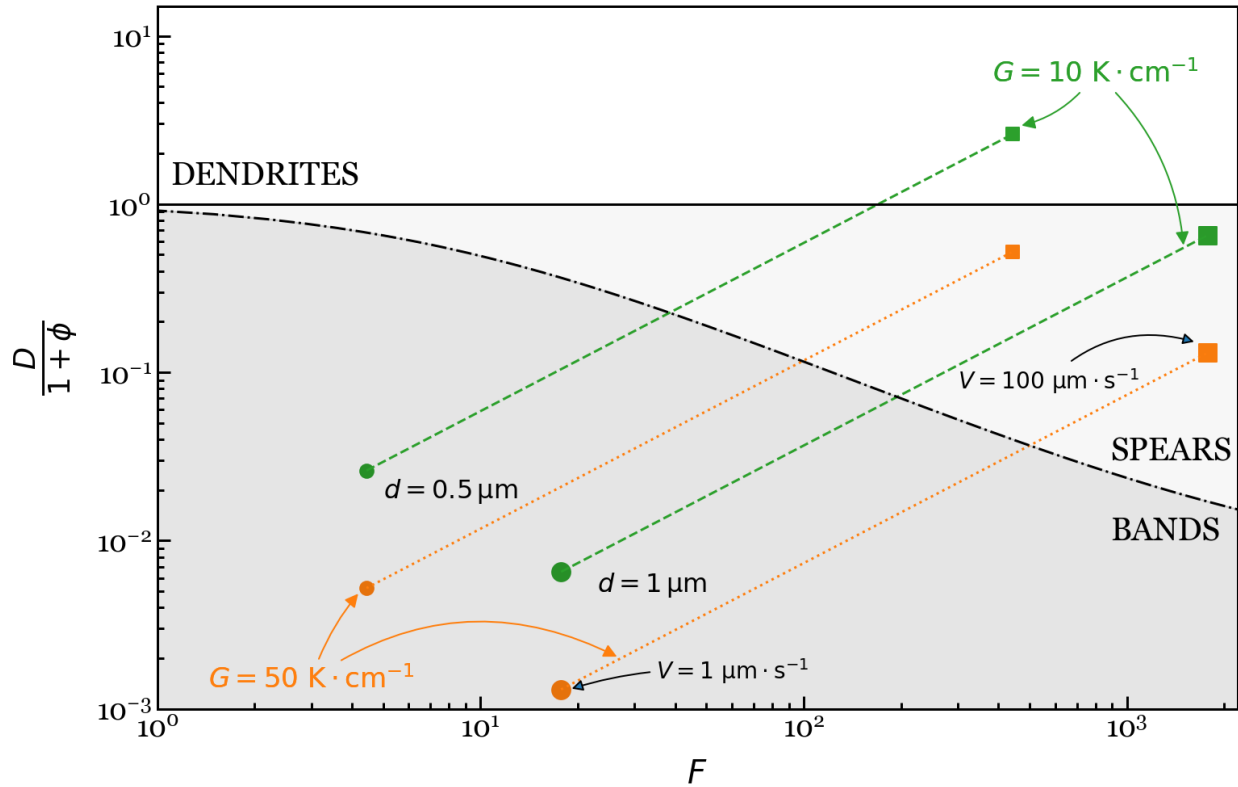


Fig. 14. Plot showing You *et al.* [37] model predictions (film coefficient, F vs. modified Darcy coefficient, $D/(1 + \Phi)$) for the particles suspension systems under study in this investigation, including copper particles of a mean diameter, $d \leq 0.5 \mu\text{m}$ and $d = 1 \mu\text{m}$. Model predictions using our primary solidification parameters for achieving minimal success ($V = 1 \mu\text{m} \cdot \text{s}^{-1}$ with $G = 50 \text{ K} \cdot \text{cm}^{-1}$ and $V = 100 \mu\text{m} \cdot \text{s}^{-1}$ with $G = 10 \text{ K} \cdot \text{cm}^{-1}$) are shown as solid orange circles and solid green squares, respectively. The dashed lines show the effect of changing V on model predictions; for the same G , increasing V increases both F and $D/(1 + \Phi)$.

Table 4 shows a breakdown of our proposed flight-test ampoules and corresponding experiment parameters. Two combinations of furnace translation velocity (V) and thermal gradient (G) will be used: (i) low V , steep G ($V = 1 \mu\text{m} \cdot \text{s}^{-1}$; $G = 50 \text{ K} \cdot \text{cm}^{-1}$) and high V , shallow G ($V = 100 \mu\text{m} \cdot \text{s}^{-1}$; $G = 10 \text{ K} \cdot \text{cm}^{-1}$), targeting the lower left and upper right regions of the plots in Fig. 14, respectively. Two ampoules of naphthalene + surfactant (AOT), without particles, will be prepared at the two selected velocity/gradient combinations. Eight suspension ampoules are required, four for each particle size. Two tests will be conducted at each of the velocity/gradient combinations to

ensure repeatability. Thus, the total number of ampoules required for flight testing is 10, an additional 4 ampoules are requested as spares (Science Requirement 1). Solidification times for these tests are estimated in Table 4 based on the translation velocity and effective “science material” length of 6 cm. The total solidification time required for these runs is 5,050 min (84 h).

To maximize success for this investigation, we are requesting real-time observation and control over furnace parameters during experiment windows (Science Requirement 33). With this capability, we may be able to test additional solidification velocities within the sample ampoule (after verifying a sufficient length of sample has solidified under steady-state conditions).

Table 4. Summary of flight-test ampoules and corresponding experiment parameters.

System	Number of Ampoules	Velocity ($\mu\text{m/s}$)	Gradient (K/cm)	Solidification time (min)
Naphthalene + surfactant	1	1	50	1000
	1	100	10	10
Suspension, $d \leq 0.5 \mu\text{m}$	2	1	50	$2 \times 1000 = 2000$
	2	100	10	$2 \times 10 = 20$
Suspension, $d \sim 1 \mu\text{m}$	2	1	50	$2 \times 1000 = 2000$
	2	100	10	$2 \times 10 = 20$
TOTAL	10			5050

2.5. Development testing

Six ampoules are required for development testing (Science Requirement 2). Techshot will be responsible for preparing flight suspensions (Science requirement 7) and subsequently filling; given the air-sensitivity of the techniques involved (which would impact flight results if done improperly, e.g., *via* introduction of dissolved gas forming bubbles), we are requesting post-SRR development testing to verify these procedures. For these tests, Techshot will prepare suspensions, solidify samples using the PFMI ground furnace, and send NU the solidified specimens for investigation. Through microstructural investigations, NU will determine if significant suspension sedimentation occurred during solidification (*via* disproportionate particle fraction as a function of solidification distance and *via* characteristic microstructures—e.g., lensing when not expected); particle sedimentation during solidification suggests the suspensions were unstable during solidification. NU will also examine specimens for presence of bubbles, which at higher solidification velocities, are visible even in samples solidified under normal gravity. As we have three system types (Table 4), we are requesting verification for each system during this testing phase; we are further requesting two ampoules to be filled for each system type to verify repeatability (for a total of six ampoules).

2.6. Data analysis

2.6.1. Solidification data

The *in-situ* solidification portion of this investigation requires acquisition of images and temperature data during solidification. Imaging during solidification will be used for:

- Tracking the interface position over time—deviations from furnace translation velocity prescribed by the experiment data file will be noted and difference in terrestrial/microgravity velocity perturbations will be elucidated.
- Timestamping thermocouple positions relative to the interface position—data will be correlated to temperature profiles, and later, to microstructural data.
- Measuring the height of the particle accumulation region (Fig. 1-c) to better understand the roles of particle vs. solute on the morphological destabilization of the solid/liquid interface (Section 1.3.2).
- Measuring curvature of the macroscopic interface.
- For surfactant samples, destabilization of the interface (if it occurs) will be characterized (e.g., breakdown into cells, dendrites).

Temperature data will be used to establish the thermal gradient (and verify the thermal gradient remains constant).

2.6.2. Microstructural analysis

Flight samples will be returned for microstructural analysis in their solidified state; microstructural analyses will be conducted on solidified samples using a combination of optical microscopy on cross-sections and X-ray tomography. Quantitative descriptions of microstructures will be made for comparison to the Worster model; a bridge density factor [97, 146, 147] will be utilized to draw a quantitative boundary between dendritic and spear regimes. Microstructures will also be characterized by measuring dendrite width (and regional variation, as was done here in Section 2.2.1), particle wall thickness, and dendrite orientation. Dendritic feature asymmetries will be identified, if they exist.

All microstructural analyses will be correlated to processing conditions through data obtained during *in situ* investigations, including that which describe the morphological evolution of the solidification front, including *in-situ* temperature and image data. Acceleration data will be used to determine the likelihood that any systematic microstructural observations may correlate to g-jitter or any acceleration anomalies.

3. Science Requirements

Item	Component	Requirement	Justification reference(s)
1	Ampoules	10 ampoules required for flight testing and an additional 4 ampoules are requested as spares, for a total of 14 flight ampoules.	2.4. Solidification experiments
2		6 additional flight ampoules are required for development tests that shall be conducted in the ground furnace. These tests shall be carried out before flight testing.	2.5. Development testing
3		Ampoules shall have an internal diameter of 10.9 ± 0.2 mm and a length sufficient for producing samples 6 mm in length.	2.3.2. Ampoules
4		Six internal thermocouples shall be mounted within each ampoule as specified in Fig. 13; mount locations shall not vary between sample ampoules more than 0.5 mm radially or 0.5 mm axially.	2.6.1. Solidification data 2.3.2.2. Thermocouple placement
5		Ampoule assemblies shall accommodate the volumetric expansion/contraction of naphthalene during solidification/melting (Fig. 12) such that there is no solidification shrinkage, and the ampoule glass does not break.	2.3.2.1. Volumetric expansion/contraction of naphthalene
6		Materials used within the sample ampoule assembly (e.g., gas, grease, epoxies, etc.) that may come in contact with the science material (either immediately or over time) shall neither chemically react with, nor dissolve in, the science material (most specifically, naphthalene).	A.1.3. Gas handling
7	Ampoule filling	Techshot shall prepare the science materials as described in Table 4 such that the science materials are transferred into ampoules (by Techshot) in the liquid/never-frozen state.	A.1. Suspension preparation 2.2.2. Freeze-thaw studies
8		Techshot shall transfer liquid science materials into ampoules while ensuring the science materials are not exposed to air at any time for which the science materials are in the liquid state; gases with very low solubility in liquid naphthalene may be utilized during transfer (e.g., helium).	A.1. Suspension preparation 2.2.2. Freeze-thaw studies
9		Techshot shall transfer liquid science materials into ampoules while ensuring the science materials do not solidify during transfer (science materials shall remain molten until controlled solidification is carried out) and the suspension temperature does not rise above 90°C.	A.1. Suspension preparation 2.2.2. Freeze-thaw studies
10		After appropriate volumes of science materials are transferred into ampoules, science materials shall be solidified directionally (along the axial length of ampoules) <i>while</i> sonicating.	A.1. Suspension preparation 2.2.2. Freeze-thaw studies 2.3.2. Ampoules
11		Long time periods of vacuum during transfer of science materials to the ampoules should be avoided to minimize evaporation of naphthalene. Techshot shall measure (and provide to the PI) the mass of the science material before and after transfer to the ampoule to characterize any mass loss due to vacuum.	A.1. Suspension preparation
12		Science material loss (due to transfer to ampoules) exceeding X% is considered excessive; any samples exhibiting mass loss equal/greater to this amount will need to be re-filled with new materials.	A.1. Suspension preparation
13		Development tests shall be conducted to test the ampoule filling procedure developed by Techshot. Solidification tests conducted using a horizontal orientation on the ground furnace shall be utilized to ensure science materials can be transferred without introduction of gas bubbles. No bubbles should be observed on images obtained during solidification at maximum camera magnification.	A.1.3. Gas handling 2.2.2. Freeze-thaw studies
14		Filled ampoules shall be labeled with a sample identification number	Ensure samples can be identified
15	Sample processing	Sample processing parameters, including thermal gradient and furnace translation velocity, shall be set as defined in Section 4.	2.4. Solidification experiments 4. Test matrix

Item	Component	Requirement	Justification reference(s)
16		The thermal gradient shall be defined as the temperature gradient across the solid/liquid interface.	2.4. Solidification experiments
17		At the beginning of experimentation, the PFMI furnace shall melt back samples to a relatively planar interface wherein the height of the solid/liquid interface will have a height of less than 0.5 mm as measured from the center of the solid/liquid interface to its edge, at the time in which the furnace is at equilibrium and the translation rate is zero.	2.4.1. Melt-back
18		After sample remelting (prior to directional solidification), samples shall be held in the liquid state for ~60 minutes to allow redistribution of particles by diffusion.	2.4.1. Melt-back A.3. Justification for thermal hold after melt-back
19	Sample storage	Flight samples shall be stored at temperatures below the melting temperature of naphthalene (60°C) at all times prior to flight tests.	2.2.2. Freeze-thaw studies
20		After flight testing, sample ampoules shall not be stored at temperatures exceeding 60°C	2.2.3. Thermal requirements study
21	Temperature measurement	Temperature readings from in-situ thermocouples shall be conducted at a minimum time increment of 1s (for a total temperature loop time of <8s for six thermocouples)	2.6.1. Solidification data
22	Imaging	Sample illumination shall provide enough light intensity for imaging but shall remain diffuse enough such that glare is avoided.	2.6.1. Solidification data
23		Image acquisition shall begin upon initiation of sample melting and shall end after solidification is complete	2.6.1. Solidification data
24		Acquired solidification images shall show the entire radial cross-section of the sample with the solid/liquid interface in the imaging frame.	2.6.1. Solidification data
25	Flight hardware	The data acquisition system shall measure and record the velocity of the furnace translation at least once every 250 ms	2.6.1. Solidification data
26	Environment	The ambient pressure within the ISS (90-110 kPa) is acceptable during experimentation	
27		Ambient temperature on the ISS is acceptable during experimentation	2.2.3. Thermal requirements study
28		Experiment trials shall be conducted outside of docking periods or during other periods of large accelerations.	
29		Accelerations during testing shall be monitored and recorded.	2.6. Data analysis
30	Data	Data files shall contain a header that contains the following data identifiers: (i) sample ID, (ii) experiment data, (iii) experiment start time, and (iv) experiment end time	2.6. Data analysis
31		Data measurements shall be tagged with a date and time stamp; the time stamp shall include: (i) hour, (ii) minute, (iii) second, and (iv) millisecond	2.6. Data analysis
32		The following critical data parameters shall be downlinked continuously during operations: (i) time, (ii) hot and (iii) cold set temperatures and actual (iv) hot and (v) cold temperatures, (vi) set and (vi) actual translation rates, and (vii) at least two consecutive images (from cameras 1 and 2) every 60 s.	2.6. Data analysis
33		Real-time observation and control over furnace parameters during experiment windows is requested for maximizing success of this investigation.	2.4.2. Processing parameters

4. Test Matrix

Table 5. Test matrix showing sample processing parameters for the ten flight ampoules (SAA) and four back-up ampoules. Acceptable ranges for gradient and translation velocity were determined based on obtaining all microstructures shown in Fig. 14; experiments conducted at $G = 10 \text{ K} \cdot \text{cm}^{-1}$, $V = 100 \mu\text{m} \cdot \text{s}^{-1}$ are most sensitive to these ranges.

SAA	Material	Experimental Parameters		Processing Time (min)				
		Gradient (K/cm)	Velocity ($\mu\text{m/s}$)	PFMI		Total	Crew	Total
1	Naphthalene + surfactant	50 $\pm$ 5	1 $\pm$ 10	+60	1000			
2		10 $\pm$ 5	100 $\pm$ 10	+60	10			
3	Suspension, $d \leq 0.5 \mu\text{m}$	50 $\pm$ 5	1 $\pm$ 10	+60	1000			
4		10 $\pm$ 5	100 $\pm$ 10	+60	10			
5		50 $\pm$ 5	1 $\pm$ 10	+60	1000			
6		10 $\pm$ 5	100 $\pm$ 10	+60	10			
7	Suspension, $d \sim 1 \mu\text{m}$	50 $\pm$ 5	1 $\pm$ 10	+60	1000			
8		10 $\pm$ 5	100 $\pm$ 10	+60	10			
9		50 $\pm$ 5	1 $\pm$ 10	+60	1000			
10		10 $\pm$ 5	100 $\pm$ 10	+60	10			
11	Back-up suspension, $d \leq 0.5 \mu\text{m}$	-	-	-	-	-	-	-
12		-	-	-	-	-	-	-
13	Back-up suspension, $d \sim 1 \mu\text{m}$	-	-	-	-	-	-	-
14		-	-	-	-	-	-	-

5. Success Criteria

5.1. Minimum Criteria of Success

- At least two flight suspensions are solidified within each of the morphological prediction regions of the You et al. [37] model, including bands, spears, and dendrites.
- Surfactant and suspension systems are solidified during flight testing; video and temperature data are used to clarify the relative magnitudes of particles and solute on the destabilization of the solid/liquid interface.
- Flight samples are returned for microstructural analysis; quantitative descriptions of microstructures are made for comparison to the Worster model and microstructural parameters are characterized. Image and temperature obtained during solidification are correlated to microstructural parameters.

5.2. Maximum Criteria of Success

- Using available ampoules, additional solidification velocities are tested over various positions in the samples (after ensuring a sufficient specimen length has solidified under steady-state conditions).
- Back-up suspension samples are tested at additional gradients and/or velocities to further clarify these relationships.

6. Principal Investigator (PI) Deliverables

These deliverables will be disseminated to NASA and the scientific community at large by the following methods:

- Raw and analyzed data will be archived in the Physical Science Informatics (PSI) System,
- Journal publications of the findings, and

- Annual reports for the NASA Task Book

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Appendices

A.1. Suspension preparation

A.1.1. Naphthalene preparation

As-received naphthalene (Sigma Aldrich, 99.6% purity) will be vacuum distilled prior to use in flight suspensions. Distillation methods are generally considered less effective for purifying naphthalene relative to zone-refining due to the formation of azeotropes with common naphthalene impurities [148, 149]. However, some of the most common impurities that pose azeotropic issues also have distribution coefficients that approach unity at low concentrations (e.g., benzo[b]thiophene [148, 150, 151] and β -methylnaphthalene [150]); thus, zone-refining alone is also somewhat ineffective for removing those impurities [150, 152]. Given the relatively high initial purity of our as-received naphthalene, the fact that we will be adding impurities (*i.e.*, surfactant) to “purified” naphthalene to obtain stable particle suspensions, and liquid naphthalene’s high affinity for atmospheric gases [152-156], we are more concerned with removing gas impurities entrapped in the as-received naphthalene relative to solid impurities. Indeed, gas bubbles have been reported to interact with the naphthalene solid/liquid interface even under terrestrial gravity conditions [157], and we have observed evidence of such in our preliminary solidification studies; under reduced gravity conditions, this issue is even more detrimental [136, 158-160].

A.1.2. Particles

Two different Cu particle sizes will be used for flight suspensions. Both size ranges will be obtained from as-purchased, 1 μm copper particles (SkySpring Nanomaterials, Inc, Houston, TX) by separating these particles *via* vacuum filtration. By image analysis, the particle size distribution of these particles will allow separation into two general categories, $d \sim 1 \mu\text{m}$ and $\leq 0.5 \mu\text{m}$; an appropriate filter has been purchased to achieve these distributions.

Moisture adsorbed on particle surfaces has been shown to negatively affect surfactant adsorption when employing apolar suspending fluids [124, 161], such as naphthalene. Carrying out a particle drying step prior to incorporation of particles in suspensions has been shown to be an effective method for reducing moisture content in resulting systems [125, 126, 162-164]. For the Cu suspensions under investigation, particles are dried for 12 h under vacuum in a reaction tube; the reaction tube is partially immersed in a beaker of silicone oil that is held at $\sim 100^\circ\text{C}$ using a hot plate. SEM images of Cu particles taken prior to and after drying are shown in Fig. 15; no obvious signs of particle aggregation resulting from the drying step were observed.

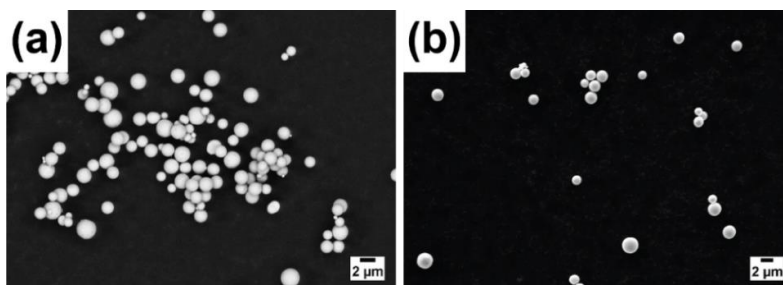


Fig. 15. SEM images of Cu particles (a) before and (b) after vacuum drying for 12 h at $\sim 100^\circ\text{C}$.

A.1.3. Gas handling

The relatively high solubility of atmospheric gases in liquid naphthalene [152-156] requires suspensions to be prepared under controlled atmosphere conditions. Fig. 16 shows nitrogen gas

solubility in liquid naphthalene as a function of pressure; these data were reproduced from Gao et al. [155] and correspond to a temperature of 104°C. To calculate the solubility of nitrogen gas in naphthalene at atmospheric pressure, linear regression was utilized to fit these data to the line shown in Fig. 16 ($R^2 = 0.999$, $p < 0.001$). Our solidification experiments generally employ suspensions containing ~23 g naphthalene; for that quantity, the solubility limit of N₂ amounts to ~18 mL of N₂ gas at 104°C. While we were unable to find solubility data for helium or argon in naphthalene, we were able to find data for solubility in benzene [165, 166] (naphthalene consists of two benzene rings); using those data, we calculated solubility limits of 3.5 and 0.3 mL for argon and helium, respectively, in 23 g liquid benzene.

We carried out a solidification test of naphthalene under helium and investigated the resulting, solidified material. Evidence of gas bubble evolution during solidification was not found in naphthalene solidified under helium; albeit, if helium bubbles did exist in the structure, they would likely have been difficult to see. Nevertheless, we have observed evidence of bubble entrapment in naphthalene solidified under normal atmospheric (air) conditions, thus solidification under helium offered an improvement. Accordingly, helium was selected as a cover gas for suspension preparation due to the relatively low solubility of helium in liquid benzene, helium's general high diffusivity, and the results of our naphthalene solidification test under He.

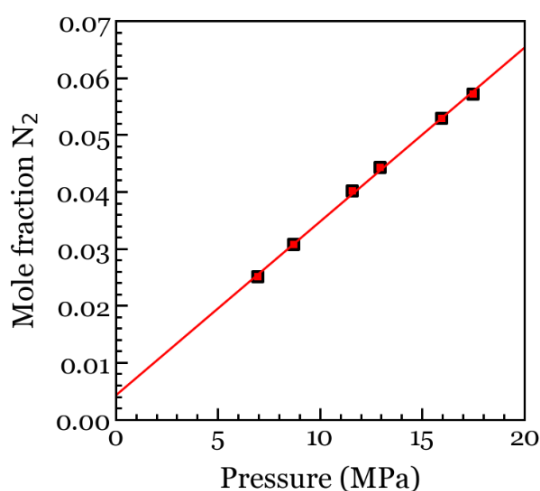


Fig. 16. Plot showing nitrogen gas solubility in naphthalene as a function of pressure at 104°C; reproduced from ref. [155]. The red line in the figure was obtained via linear regression ($R^2 = 0.999$, $p < 0.001$).

A.1.4. Suspension procedure

Flight suspensions will be prepared using the same procedure as we have used for ground testing. First, the AOT surfactant (equivalent to 1 wt.% with respect to the Cu particle mass in the suspension) is incorporated into vacuum-distilled naphthalene via stirring for 12 h under helium. This is accomplished using a Schlenk set-up to minimize exposure to atmospheric gases and partially immersing a Schlenk flask containing the naphthalene/surfactant in a beaker of silicone oil held on a hot/stir plate; the temperature of the oil is controlled to ~90°C throughout the suspension preparation process. Thereafter, dried particles are incorporated (5 vol.% Cu), and the suspension is stirred for an additional 12 h under helium. Next, the suspension is sonicated in a water bath held at ~90°C for 2 h. Finally, suspensions will be transferred into ampoules *in their liquid state, and without intermediate solidification*, using a process developed by Techshot in accordance with Science Requirements 8-13 (in ground studies, we use heated Schlenk lines).

A.2. Suspension characterization

A.2.1. Calorimetry

TA Instruments, DSC 250, was used for calorimetry measurements to characterize the melting point for our specimens. The temperature accuracy and prevision of the instrument is specified at ± 0.05 and $\pm 0.08^\circ\text{C}$, respectively. Table 6 provides a summary of DSC results, including melting temperature, T_m and enthalpy of fusion, ΔH_f , obtained for as-received and vacuum-distilled naphthalene, naphthalene and AOT and Cu particle suspensions using 1 wt.% AOT (with respect to particle mass). The average melting temperature for vacuum distilled naphthalene is $79.64 \pm 0.07^\circ\text{C}$, representing a melting point depression of $\sim 0.6^\circ\text{C}$ relative to pure naphthalene ($T_m = 80.23$ [167]); this melting temperature is $\sim 0.15^\circ\text{C}$ higher than that measured for as-received naphthalene. Melting points of $>79.6^\circ\text{C}$ for naphthalene are thought to represent a naphthalene content in excess of 98.7% [168]. Freezing point depression resulting from the addition of AOT is $\sim 1.03^\circ\text{C}$ relative to pure naphthalene (0.44°C relative to our vacuum-distilled naphthalene). Additional freezing point depression is not observed with the addition of particles in suspension; these results are expected based on particle size and the relatively low volume fraction of particles in the suspensions tested [35, 169].

Table 6. Summary of calorimetry results, including melting temperature (T_m) and enthalpy of fusion (ΔH_f) for naphthalene (as-received and vacuum-distilled), naphthalene with 1wt.% AOT (with respect to intended particle mass at 5 vol.% Cu) and 5 vol.% copper suspended in naphthalene with 1 wt.% AOT (with respect to Cu). The column, ΔT_m provides the calculated melting point depression relative to pure [167] and distilled naphthalene; n is the number of samples analyzed and $\bar{x}$ and σ are the mean and standard deviation, respectively. Surfactant wt.% is given with respect to the actual or intended mass of Cu particles (which corresponds to a particle volume fraction in the suspension of 5 vol.%).

Sample type	n	$T_m(^{\circ}\text{C})$		ΔT_m		$\Delta H_f(\text{J/g})$	
		$\bar{x}$	σ	Pure	Distilled	$\bar{x}$	σ
Naphthalene, pure [167]	-	80.23	-	-	-	146.60	0.60
Naphthalene, as-received	10	79.49	0.07	-0.74	-	143.61	2.16
Naphthalene, vacuum distillation	10	79.64	0.17	-0.59	-	145.07	1.68
1 wt.% AOT	10	79.20	0.09	-1.03	-0.44	141.13	3.56
1 wt.% Pluronic F-68	10	79.22	0.09	-1.01	-0.42	140.28	3.99
5 vol.% Cu, 1 wt.% AOT suspension	5	79.33	0.06	-0.90	-0.31	143.23	1.18

A.2.2. Rheometry

Rheological studies were carried out using an Anton Paar MCR 302 rheometer (Anton Paar GmbH, Graz, Austria), equipped with a Peltier temperature controller (P-PTD 200, accuracy $\pm 0.1^\circ\text{C}$). A concentric cylinder (Couette) geometry with a conical bob (CC27, stainless steel with a measuring gap of 1.13 mm), requiring a nominal sample volume of 19.35 mL, was used to determine the viscosity of naphthalene and suspensions. The gap width of 1.13 mm allows for suspensions containing particle/aggregate sizes up to $113\ \mu\text{m}$ to be tested [170] with this system. The concentric cylinder fixture operates under the Searle principle; that is, the inner cylinder (*i.e.*, measuring bob) rotates within the filled sample cup (*i.e.*, the outer cylinder). To homogeneously distribute samples in the shear gap and normalize shear histories of materials studied [131, 132, 134], all samples are pre-sheared 60 s at a shear rate, $\dot{\gamma} = 5\ \text{s}^{-1}$ followed by a resting period (no shear) of 180 s prior to beginning measurements. Naphthalene viscosity was needed as an input parameter for the You *et al.* model [37]; suspension viscosities were measured to assess the results of freeze-thaw studies (Section 2.2.2).

Fig. 17 shows a plot of viscosity vs. shear rate for vacuum distilled naphthalene tested at 82, 85, and 90°C; these data points represent the mean η measured during steady-state flow using constant shear rate tests at $\dot{\gamma} = 2.5, 5, 10, 25, 50$, and 100 s^{-1} and error bars represent the standard deviation. Naphthalene is a Newtonian fluid; the slight shear thickening and thinning observed at low and high shear rates is representative of the measurement limits of this system.

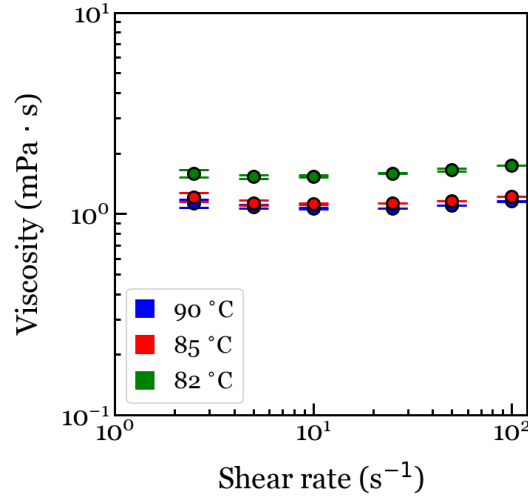


Fig. 17. Plots showing shear rate vs. viscosity for vacuum distilled naphthalene tested at 82, 85, and 90°C. Data points in (b) represent mean values obtained during steady-state flow using constant shear rate tests; error bars represent the standard deviation.

Fig. 18 depicts the measurement limits of this system, including the low torque limit (set by instrument specifications and the Couette geometry employed), which impacts low shear rate $\dot{\gamma}$ measurements and the secondary flow limit (based primarily on geometry), which impacts measurements at high $\dot{\gamma}$.

The low torque limit boundary was calculated using Eq. 1 [171]:

$$\eta > \frac{K \cdot \tau_{min}}{\dot{\gamma}} \quad \text{Eq. 1}$$

where η is the minimum measurable viscosity, $\dot{\gamma}$ is the shear rate that corresponds to η in Fig. 18, and τ_{min} is the minimum instrument torque (for the MCR 302, $\tau_{min} = 1 \text{ nNm}$ represents the absolute minimum torque for rotational tests). The stress constant, K for the concentric cylinder system was calculated using Eq. 2:

$$K = \frac{1}{4\pi l} \frac{1 + \left(\frac{R_o}{R_i}\right)^2}{c_l R_o^2} \quad \text{Eq. 2}$$

where l is the bob length (27 mm), R_o and R_i are the radii of the outer and inner cylinders, respectively (14.46 and 13.33 mm), and c_l is the face factor, taken as 1.1.

The highest attainable shear rates (rotation speeds) prior to encountering Taylor secondary flow instabilities [172-175] for the CC27 geometry is represented by the red, “secondary flow limit”

boundary in Fig. 18. This boundary was calculated using the maximum viscosity threshold for avoiding Taylor vortices [171, 173, 176]:

$$\eta > \frac{(R_o - R_i)^{5/2}}{1,700 \cdot R_i^{1/2}} \rho \dot{\gamma} \quad \text{Eq. 3}$$

where ρ is the density of the fluid and the factor 1,700 is valid for Newtonian fluids in the limit of small gaps [171].

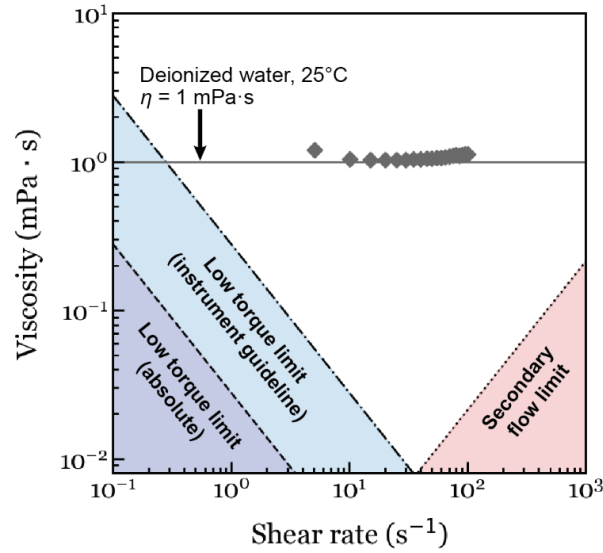


Fig. 18. Plot of shear rate vs. viscosity of deionized water (at 25°C) used to test the instrument capabilities; water is a Newtonian fluid, having a viscosity of ~ 1 mPa $\cdot$ s at 25°C, independent of shear rate. Boundaries for the low torque and secondary flow limit were calculated primarily based on instrument specifications and the employed Couette geometry, respectively (the depicted limits were calculated for naphthalene, specifically, but they do not vary considerably for the water data plotted here).

Deionized water (a Newtonian fluid with viscosity similar to that of naphthalene) was used to assess limits shown in Fig. 18 (black diamond markers). Artifact shear thinning is observed at low shear rate conditions; at $\dot{\gamma} = 5 \text{ s}^{-1}$, $\eta = 1.20 \text{ mPa} \cdot \text{s}$, wherein the measured viscosity is $\sim 0.2 \text{ mPa} \cdot \text{s}$ higher than the expected value of $\eta = 1.00 \text{ mPa} \cdot \text{s}$ for water at 25°C. These shear rates are well outside the low torque limit boundary; thus, this behavior may be attributed to surface tension. Artifact shear thickening is also observed as the shear rate increases; at $\dot{\gamma} = 100 \text{ s}^{-1}$, $\eta = 1.29 \text{ mPa} \cdot \text{s}$, which is $\sim 0.29 \text{ mPa} \cdot \text{s}$ higher than the expected value. Shear rates that corresponded most closely to the expected viscosity were $\dot{\gamma} = 15$ to 30 s^{-1} ; in these cases, the maximum deviation from expected viscosity is $0.03 \text{ mPa} \cdot \text{s}$ at $\dot{\gamma} = 30 \text{ s}^{-1}$. Similarly, to the low shear rate case, shear rate deviations are not likely attributable to Taylor vortices, specifically, given they fall outside that boundary; other inertia effects may be affecting these measurements, though [171].

A.3. Justification for thermal hold after melt-back

Here, we calculate the 1D diffusion distance of particles after melting the solidified suspension. We assume particles are homogenously distributed in the solidified suspension state and particle diffusion distance is calculated along one axis (in reality, particles will diffuse in varying directions to spread out). The diffusion time, t , is:

$$t = \frac{x^2}{2D_0}$$

where x is the mean distance traveled by the diffusing particle along one axis after elapsed time, t and D_0 is the diffusion coefficient.

The diffusion coefficient, D_0 is calculated by considering the particles as hard spheres and using the Einstein-Stokes relation:

$$D_0 = \frac{Tk_B}{3\pi d\mu}$$

where T is the temperature, k_B is Boltzmann's constant, d is the particle diameter, and μ is dynamic viscosity.

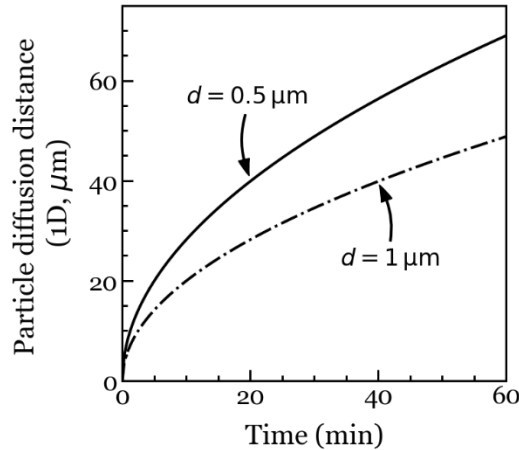


Fig. 19. One dimensional particle diffusion distance after one hour for 0.5 and 1 μm copper particles.

Appendix 2. Pore Formation Mobility Investigation Furnace

The MEFC microgravity solidification experiments, for which this thesis work supports, are intended for processing on the Pore Formation Mobility Investigation (PFMI) furnace [30-39] on the ISS. The PFMI furnace, which is located within the Materials Science Glovebox on the ISS, is a Bridgman-type furnace (Fig. A-1), where the cold zone (comprised of a copper ring which is temperature controlled using thermoelectric cooling devices) is translated across the sample ampoule while the ampoule remains stationary. Exterior surfaces of sample ampoules are coated with a transparent layer of Indium Tin Oxide (ITO), which acts as a resistance heater when current is applied. The temperature gradient within the melt zone is controlled by electrode rings, wherein the forward electrode ring is translated with the cold zone and the aft electrode remains stationary (*i.e.*, translation of the cold zone shortens the hot zone). The PFMI furnace allows for low and high temperature gradients of 10 and 50°C/cm, respectively, and nominal melt-back and growth velocities between 1 and 100 $\mu\text{m/s}$. The minimum and maximum temperatures of the furnace are 0 and 130°C, respectively. Two cameras, mounted to a translation stage on the furnace, are used to visualize the solid/liquid interface during solidification experiments; camera position, zoom, and focus can be modified in real-time *via* ground commanding [39].

The Sample Ampoule Assembly (SSA) as designed for the previous PFMI work is depicted in Fig. A-2; components include: the main body tube (composed of Schott 8250 borosilicate glass), a Kovar piston assembly, cartridge mount head, and six *in-situ* thermocouples. Based on toxicology assessments conducted for this investigation, the maximum volume of naphthalene that can be used in an individual ampoule is ~6.8 mL. Accordingly, ampoules will be filled with ~5.6 mL of science material, corresponding to an effective science material length of ~6 cm which is shorter than the overall length of the ampoules (~28 cm, not including the piston assembly or

insertion of the Kovar head, Fig. A-2). The SSAs are currently being redesigned for this work to accommodate the decreased science material length relative to previous investigations [30-39] conducted on this furnace; most likely, filler material will be used to fill empty space within the main tube body, extending to the cartridge head.

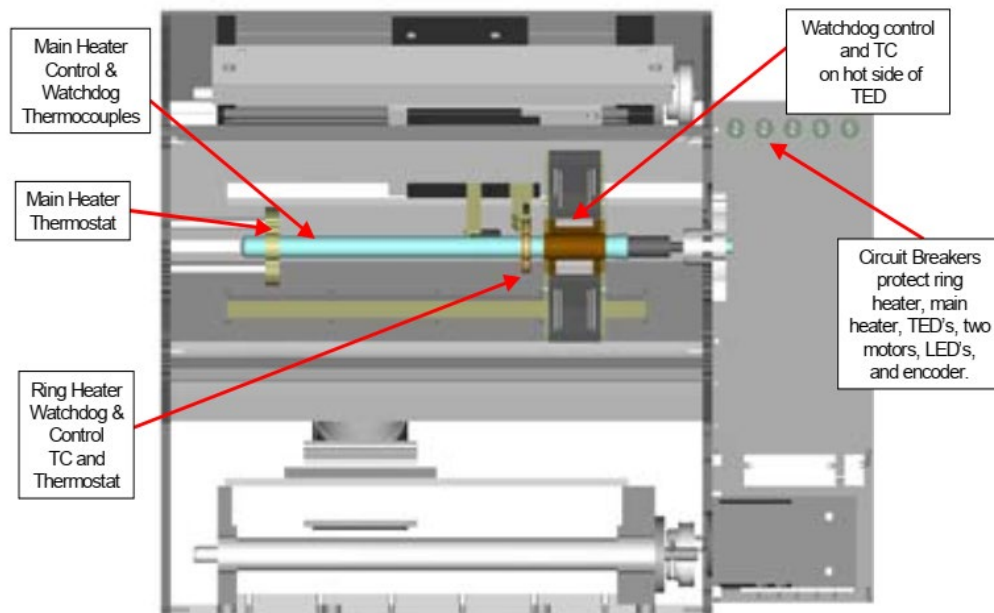


Fig. A-1. Schematic showing the PFMI furnace for which microgravity solidification experiments are intended; extracted without modification, ref. [39].

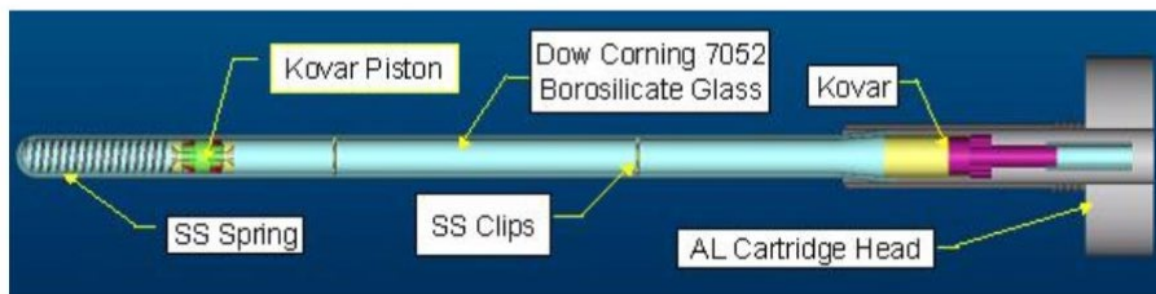


Fig. A-2. Schematic showing the sample ampoule assembly as designed for the previous PFMI experiments; extracted without modification, ref. [39].

The density of naphthalene is temperature-dependent and the molar of the solid and liquid are different; thus, the piston assembly is needed to accommodate volumetric expansion and contraction of the science material during melt-back and solidification. Fig. A-3 shows the temperature-dependent density of naphthalene obtained from refs. [348-356]; these data were fitted *via* linear regression and the resulting equation for the red line shown in Fig. A-3 is $\rho_{naphthalene} = -0.788 \cdot T + 1041.2 \text{ kg} \cdot \text{m}^{-3}$, where ρ and T are the densities and temperatures ($^{\circ}\text{C}$), respectively.

The minimum volumetric changes that need to be accommodated by the piston system are estimated as ~9%. This value was estimated by first considering the maximum densities (minimum volumes) for the fluid systems; we considered the solid phase density at the temperature closest to room temperature for which data were available. For naphthalene, the density at 20°C is reported as 1.025 g/cm^3 [352]. To estimate the minimum densities (maximum volumes), we considered the maximum temperature of the furnace (130°C) and used the aforementioned linear regression equation to estimate the fluid density at that temperature; at 130°C , the density of naphthalene is estimated at 0.939 g/cm^3 .

Fig. A-4 shows the placement of the six thermocouples within each sample ampoule; thermocouples will be used to set the thermal gradient during solidification and for recording temperatures as a function of position with respect to the solid/liquid interface throughout solidification experiments. The effective science length (60 mm) corresponds to the molten zone; thus, the effective length of the flight samples. Fig. A-4 (a) shows a longitudinal view where the length of each thermocouple is shown; the solidification proceeds from left to right, as indicated

by the arrow, such that the locations for which the thermocouples enter the ampoule is considered the first-to-solidify region of the samples. Thermocouples 1 and 4 have a length of zero with respect to the sample length; that is, they are located at the base of the first-to-solidify region of the ampoules. Thermocouple 3 extends from the first-to-solidify region throughout the length of the sample for a total length of 60 mm; the lengths of thermocouples 3, 5, and 6 are 15, 30, and 45 mm, respectively.

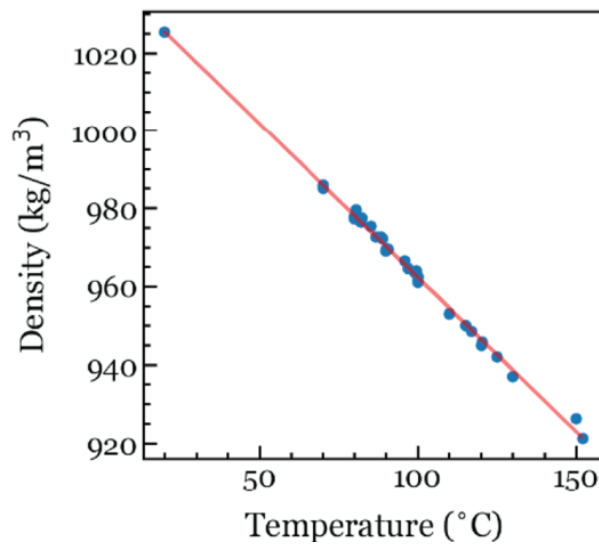


Fig. A-3. Plot showing the temperature-dependent density for naphthalene where data were obtained from refs. [348-356]; these data were fitted *via* linear regression (red line).

Fig. A-4 (b) shows the outer and inner diameter of the ampoule (13 and 10 mm, respectively) and the radial placement of the thermocouples (sheathed thermocouple diameter of ~ 0.25 mm, 0.01 in). Thermocouples 2-6 are positioned at equal distances in a semicircle inferior to the imaging direction (indicated with an arrow). Thermocouple 1, which has a length of zero with respect to the sample length, is located directly across from thermocouple 4 (which also has a length of zero with respect to the sample length). The semicircular placement of thermocouples 2-6 is requested in an effort to minimize visual obstruction by the thermocouples during imaging;

the placement of thermocouples 1 and 4 will enable determination of any radial temperature gradients at the base of the sample. Fig. A-4 (c) shows an isometric view of thermocouple placement within the sample ampoule.

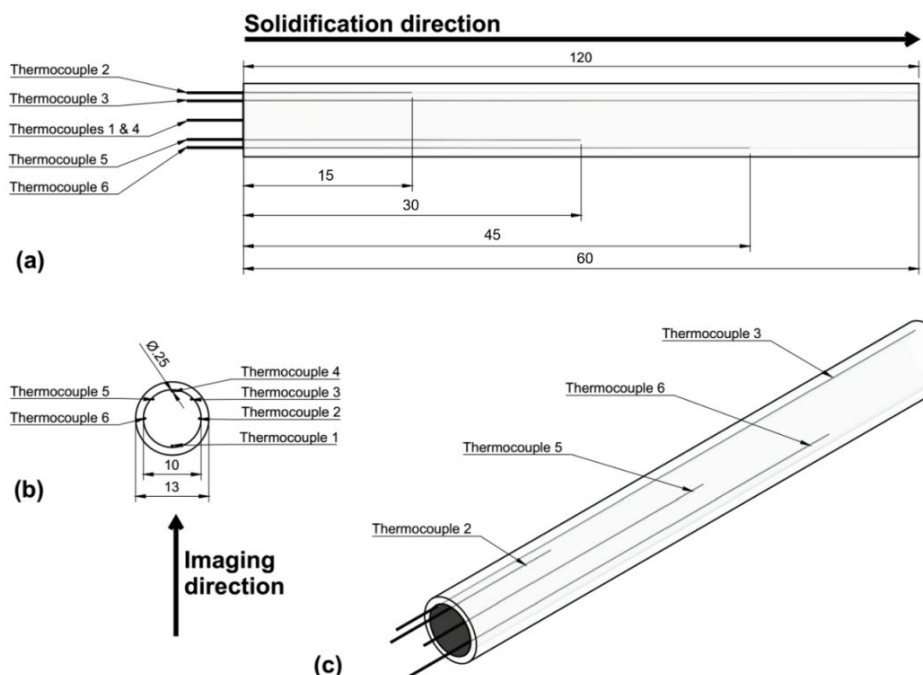


Fig. A-4. Schematic showing desired placement of six thermocouples within each sample ampoule; dimensions are in mm.

Sample ampoules filled with science material will be transferred to the ISS in their solidified state. At the beginning of experimentation, the PFMI furnace will melt back the naphthalene/particle suspension in the ampoules approximately 6 cm forming a melt front as planar as possible; that is, the solid/liquid interface will have a deviation in height of less than 0.5 mm as measured from the center of the solid/liquid interface to the edge at the time in which the furnace is at equilibrium and the translation rate is zero. After melt-back is achieved, the sample will be held in the liquid state for 60 minutes to allow for redistribution of particles via Brownian diffusion; the 1D diffusion distances for 0.5 and 1 μm particles are calculated as ~ 70 and 50 μm ,

respectively within this timeframe. Samples directionally solidified during development testing showed relatively uniform particle distributions. Thus, this particle distribution step should be sufficient for ensuring uniformly distributed particle suspensions for these flight experiments. Lastly, the sample will be re-solidified utilizing provided experimental parameters (*i.e.*, translation velocity and thermal gradient).

Appendix 3. Furnace motor driver controller code

```

#include <AccelStepper.h> // import library (need to install locally)

// ***** USER-DEFINED VARIABLES *****
int stepsMicro    = 4;    // microstepping multiplier
int motorSpeedDOWN = 1000; // [steps/second] POSITIVE == DOWNWARD
int numRevsDOWN   = 2;    // number of revolutions to move DOWN
int motorSpeedUP   = -30;  // [steps/second] NEGATIVE == UPWARD
int numRevsUP     = 15;    // number of revolutions to move UP
int numPasses     = 2;    // number of zone-refining passes
// *****

int stepsRevMotor = 200;    // motor steps/revolution
long stepsRevAct  = stepsRevMotor * stepsMicro; // effective steps/revolution
long numStepsDOWN = stepsRevAct * numRevsDOWN;  // number of steps to take
long numStepsUP   = stepsRevAct * numRevsUP;

bool motorDir      = HIGH;    // default direction for motor, up
int  dirPin        = 6;    // DIR- pin on motor driver
int  stepPin       = 7;    // PUL- pin on motor driver
int  interfaceType = 1;    // driver

// create instance of AccelStepper class
AccelStepper stepper = AccelStepper(interfaceType, stepPin, dirPin);

char receiveCommand;    // command (character) sent from terminal
bool newData = false;

void setup() {
  Serial.begin(115200);    // start serial monitor
  pinMode(dirPin, OUTPUT); // configure pins
  pinMode(stepPin, OUTPUT);
  delay(1000);            // stabilize serial monitor
  Serial.println("enter 'c' to print commands");
  Serial.println(" ");

  digitalWrite(dirPin, motorDir); // set default spinning direction
  stepper.setMaxSpeed(10000);    // [steps/second]; unreliable for > 1000
}

void loop() {
  checkSerial();
}

// check to see if command has been sent

```

```

void checkSerial(){
  if (Serial.available() >0){
    receiveCommand = Serial.read(); // pass value to receiveCommand
    newData = true;

    if (newData == true) {
      switch (receiveCommand) {
        case 'c': // print commands
          printCommands();
          Serial.println(" ");
          break;
        case 's': // stop motor
          Serial.println("Stopping motor");
          stepper.stop();
          Serial.println("done");
          Serial.println(" ");
          break;
        case 'u': // move specified number of revolutions up
          Serial.println("Move revs UP");
          moveRevsUP();
          Serial.println("done");
          Serial.println(" ");
          break;
        case 'd': // move specified number of revolutions down
          Serial.println("Move revs UP");
          moveRevsDOWN();
          Serial.println("done");
          Serial.println(" ");
          break;
        case 'g': // zone-refining for gas; up-direction for x number of passes
          Serial.println("zone-refining GAS");
          zoneGas();
          Serial.println("done");
          Serial.println(" ");
          break;
        case 'i': // zone-refining for impurities; down-direction for x number of passes
          Serial.println("zone-refining IMPURITIES");
          zoneImpurities();
          Serial.println("done");
          Serial.println(" ");
          break;
      }
    }
    newData = false;
  }
}

```

```

void moveRevsDOWN() {
  stepper.setCurrentPosition(0); // set current position to zero

  // serial monitor data print
  Serial.print("motorSpeedDOWN: ");
  Serial.println(motorSpeedDOWN);
  Serial.print("numRevsDOWN: ");
  Serial.println(numRevsDOWN);
  Serial.print("stepsRevMotor: ");
  Serial.println(stepsRevMotor);
  Serial.print("stepsMicro: ");
  Serial.println(stepsMicro);
  Serial.print("stepsRevAct: ");
  Serial.println(stepsRevAct);
  Serial.print("numSteps: ");
  Serial.println(numStepsDOWN);
  Serial.println(" ");
  Serial.println(" ");

  Serial.println("time; runTime; position; revolution");
  Serial.println(millis());

  int  dataTimer = 2000;
  long lastTime = 0;
  long currentTime = millis();
  int  lastRev = 0;
  long runTimer = millis();

  while( abs(stepper.currentPosition()) != numStepsDOWN ) {
    stepper.setSpeed(motorSpeedDOWN);
    stepper.runSpeed();

    long currentPos = stepper.currentPosition();
    int  currentRev = currentPos/stepsRevAct;
    currentTime = millis();
    long timeInterval = currentTime - lastTime;

    if ( (currentPos % stepsRevAct) == 0 ) {
      if ( (timeInterval >= dataTimer) || (lastRev != currentRev) ){
        Serial.print(millis());
        Serial.print("\t");
        Serial.print(currentTime-runTimer);
        Serial.print("\t");
        Serial.print(stepper.currentPosition());
        Serial.print("\t");
      }
    }
  }
}

```

```

    Serial.println(currentRev);

    lastTime = millis();
    lastRev = currentRev;
  }
}
Serial.println(millis());
Serial.println("done");
Serial.println(" ");
Serial.println("-----");
Serial.println(" ");
Serial.println(" ");
}

void moveRevsUP() {
  stepper.setCurrentPosition(0); // set current position to zero

  Serial.print("motorSpeedUP: ");
  Serial.println(motorSpeedUP);
  Serial.print("numRevsUP: ");
  Serial.println(numRevsUP);
  Serial.print("stepsRevMotor: ");
  Serial.println(stepsRevMotor);
  Serial.print("stepsMicro: ");
  Serial.println(stepsMicro);
  Serial.print("stepsRevAct: ");
  Serial.println(stepsRevAct);
  Serial.print("numSteps: ");
  Serial.println(numStepsUP);
  Serial.println(" ");
  Serial.println(" ");

  Serial.println("time; runTime; position; revolution");
  Serial.println(millis());

  int dataTimer = 2000;
  long lastTime = 0;
  long currentTime = millis();
  int lastRev = 0;
  long runTimer = millis();

  while( abs(stepper.currentPosition()) != numStepsUP ) {
    stepper.setSpeed(motorSpeedUP);
    stepper.runSpeed();
  }
}

```

```

long currentPos = stepper.currentPosition();
int currentRev = abs(currentPos)/stepsRevAct;
currentTime = millis();
long timeInterval = currentTime - lastTime;

if ( (currentPos % stepsRevAct) == 0 ) {
  if ( (timeInterval >= dataTimer) || (lastRev != currentRev) ){
    Serial.print(millis());
    Serial.print("\t");
    Serial.print(currentTime-runTimer);
    Serial.print("\t");
    Serial.print(stepper.currentPosition());
    Serial.print("\t");
    Serial.println(currentRev);

    lastTime = millis();
    lastRev = currentRev;
  }
}
}
Serial.println(millis());
Serial.println("done");
Serial.println(" ");
Serial.println("-----");
Serial.println(" ");
Serial.println(" ");
}

void zoneGas(){
  int i;
  for (i = 1; i<=numPasses; i++){
    moveRevsUP();
    moveRevsDOWN();
    Serial.print("END PASS NUMBER: ");
    Serial.println(i);
    Serial.println(" ");
    Serial.println(" ");
    Serial.println("-----");
    Serial.println(" ");
    Serial.println(" ");
  }
}

void zoneImpurities(){
  int i;
  for (i = 1; i<=numPasses; i++){

```

```
moveRevsDOWN();
moveRevsUP();
Serial.print("END PASS NUMBER: ");
Serial.println(i);
Serial.println(" ");
Serial.println(" ");
Serial.println("-----");
Serial.println(" ");
Serial.println(" ");
}
}

void printCommands(){
  Serial.println(" 'c' : print commands");
  Serial.println(" 'd' : move down (revolutions)");
  Serial.println(" 'u' : move up (revolutions)");
  Serial.println(" 'g' : zone-refining GAS");
  Serial.println(" 'i' : zone-refining IMPURITIES");
  Serial.println(" 's' : stop motor");
}
```

Appendix 4. Calibration tables for furnace translation velocity

Table A-1. Furnace translation velocity as measured in terms of microcontroller parameters, “microsteps” and “speed” using a motor driver setting (*via* dip switches on the driver itself) of 12,800 pulses/revolutions.

Microsteps	Speed	Translation velocity ($\mu\text{m/s}$)
4	10000	5,434.15
4	4000	2,173.66
4	1000	543.42
4	500	271.71
4	250	135.85
4	100	54.34
4	50	27.17
4	25	13.59
4	10	5.43
4	5	2.72
4	1	0.54

Table A-2. Furnace translation velocity as measured in terms of microcontroller parameters, “microsteps” and “speed” using a motor driver setting (*via* dip switches on the driver itself) of 400 pulses/revolutions.

Microsteps	Speed	Translation velocity ($\mu\text{m/s}$)
4	1000	6218
4	500	3106
4	100	633
4	10	63

Table A-3. Furnace translation velocity as measured in terms of microcontroller parameters, “microsteps” and “speed” using a motor driver setting (*via* dip switches on the driver itself) of 200 pulses/revolutions.

Microsteps	Speed	Translation velocity ($\mu\text{m/s}$)
4	30	761
4	25	637
4	20	502
4	15	380
4	10	254
4	5	127