Melting kinetics in microgravity

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Abstract. We analyzed the large data archive obtained from microgravity experiments called the Isothermal Dendritic Growth Experiment (IDGE). The final orbital mission of the IDGE allowed streaming of real-time video of crystal growth and melting in low-Earth orbit of high-purity pivalic acid anhydride (PVA). Melting kinetics was observed in detail for the first time under microgravity conditions. Normally, terrestrial gravity precludes observation and analysis of conduction-limited melting by stimulating buoyancy flows and inducing collapse of the solid-liquid structure. The initial dendritic mushy zone melts under steady heating into isolated crystallite clusters that remain stationary within the melt, and eventually shrink toward their complete extinction. Near the end of conduction-limited melting, a few needle-like crystallites remain, exhibiting various axial ratios, $C/A$, of their major ellipsoidal axis, $C$, to their minor axis, $A$. Analysis of their convection-free melting, based on quasi-static thermal conduction, yields rates in agreement with the microgravity video and IDGE thermal data. Theory and experiment compare well, when the melting Stefan numbers, based on thermal data telemetered from the space-borne thermostat are used. Isolated PVA fragments shrink in scale at an accelerating rate toward total extinction. The ‘point effect’ of thermal conduction operates during most of the melting process when $C/A$ remains almost constant. Prior to extinction, when the radius of a typical crystallite’s minor axis approaches circa 100 micrometers, capillary effects become important. Then the crystallite’s $C/A$ ratio abruptly falls toward unity, as the needle-like crystals contract into spheres by accelerated melting near their poles. These experiments, and the accompanying field-theoretic analysis, introduce some new considerations, and raise questions concerning the roles of capillarity, heat conduction, interface shape, and solid-liquid phase change kinetics.

1. Introduction
The recent final launch, and return to Earth, of space shuttle Endeavor to the International Space Station (ISS) leaves just one remaining active member of the Space Transportation System (STS) fleet, Atlantis, now scheduled for its final launch in mid-2011. That will end the 30 year era of orbital space flights by US Space Shuttles. It seems fitting, therefore, to report some additional, but important, details on data obtained through NASA’s microgravity sciences program, derived in that period when NASA was striving to achieve up to 25 Space Transportation System (STS) missions per year.

The author in those halcyon days was Principal Investigator of the Isothermal Dendritic
Growth Experiment (IDGE), which was launched three times aboard shuttle Columbia.\textsuperscript{1} The third orbital mission of the IDGE (on USMP-4) allowed, for the first time, K-band video sequences to be transmitted in real-time at 30 fps of more than 100 sequences of dendritic crystal growth of high purity (4-9s) pivalic anhydride (PVA), each followed by melting. Details concerning the IDGE series of microgravity experiments, and the science derived therefrom, may be found in [3]-[7].

PVA is an organic crystal that melts to form a transparent melt phase of slightly lower density than its FCC crystalline phase. When terrestrial melting experiments were attempted under normal gravity, the melting dendritic crystals detached from the mushy zone and sank through the surrounding melt, quickly settling at the bottom of the sample chamber. The relative motion, or sedimentation, of PVA crystallites sinking through their high-Prandtl number melt precluded quantitative analysis of the heat transfer, as there was significant hydrodynamic interactions between the heat-absorbing crystals and the liquid phase. In microgravity, by contrast, the acceleration of gravity is greatly reduced to circa $g \leq 10^{-7}g_0$, where $g_0 = 9.8 \text{ m-s}^{-2}$ is its terrestrial value, and detached crystal fragments remain motionless within the melt throughout the entire process of melting. Advection melt motions at the solid-liquid interface arising from the small (3%) mass density difference between the solid and melt phases have a negligible affect on heat transfer to or from the solid-liquid interface [8], as does thermal expansion of the PVA melt responding to the release of latent heat [9].

2. Initial freezing and melting
Total melting time (typically 10-30 min.) of the partially solidified dendritic mass depends on the initial melt supercooling, which determines the relative fractions of the solid and liquid phases that comprises the mushy zone structure immediately after its formation. Adiabatic freezing of a supercooling melt constrains the volume fraction of solid to equal the freezing Stefan number, $St^-$, or dimensionless supercooling, namely,

$$St^- = \frac{(T_m - T_0)C_p}{\Delta H_f}, \quad (1)$$

where $T_0$ is the initial (supercooled) melt temperature, $T_m = 35.97 \pm 0.005 \text{ C}$ is the equilibrium melting point of PVA, and $\Delta H_f/C_p = 11.0 \text{ K}$ is the ratio of the latent heat of fusion to the specific heat of the melt. This ratio defines the solid-to-liquid transformation’s ‘characteristic’ temperature.

Figure 1 provides four micrographs from a video sequence of melting imposed on a dendritic mushy zone comprised of about 9% solid. The melt supercooling, $\Delta T = T_m - T_0$, applied prior to initiation of adiabatic dendritic solidification was $\Delta T = 0.97K$, so from Eq. (1) one finds $St^- = 0.088$, i.e. a starting solid fraction of about 9%. The subsequent melting sequence for this cycle then occurred over a duration of 30 min., which was determined by the melt superheating applied to the thermostat to terminate the prior experimental growth cycle by destroying the mushy zone. The value of the superheating for every cycle eventually reached 1.8 K above PVA’s equilibrium melting point, $T_m$, ensuring that every vestige of solid was melted prior to the start of the next freeze-melt cycle. It is also convenient to report the actual superheating, $T_\infty - T_m$.

\textsuperscript{1} \textit{Columbia}, the heaviest member of the STS fleet, was incapable of reaching the near-polar orbit of the ISS. Consequently, \textit{Columbia} was dedicated, in large measure, to launches into low-inclination orbits for the purposes of conducting a wide variety of microgravity experiments in the physical and biological sciences. Before its tragic accident when flying as STS-107, with loss of all crew upon re-entry into the atmosphere on February 1, 2003, \textit{Columbia} provided power, cooling, communications, S- and K-band digital data streams, all in an excellent microgravity environment to support teleoperated scientific experiments on the United States Microgravity Payload (USMP), and astronaut-mediated experiments in SpaceLab and the Shuttle Mid-deck [1] [2].
present during crystallite melting as the dimensionless quantity $S_{t^+}$, which is the melting Stefan number, defined here as,

$$S_{t^+} = \frac{(T_\infty - T_m)C_p}{\Delta H_f},$$

where $T_\infty$ is the temperature impressed by the external thermostat on the melt at the walls of the sample chamber, which are distant from the melting crystals.

![Figure 1. Progressive melting in microgravity of a dense dendritic mushy zone of high-purity PVA. Upper left: Dense mushy zone immediately after adiabatic crystallization contains approximately 9% PVA crystallites by volume. Upper right: Mushy zone coarsens slowly and detaches from the tip of the 1 mm hollow fused quartz injector (centered at the top of each micrograph) through which dendrites emerged into the growth chamber. Lower left: Mushy zone remains stationary and loses crystallites by progressive detachments and melting. Lower right: Remaining crystalline fragments prior to their total extinction by melting.](image)

The melting of a dendritic mushy zone in microgravity involves several distinct stages as suggested by the structures observed in Figure 1:

(i) **Peripheral melting** initiates at the boundary of the mushy zone as shown in the upper left panel of Figure 1. The interior regions do not melt because they are well shielded from
the applied superheating by the dense spatial distribution of interconnected dendrites, as localized peripheral melting converts all the sensible heat reaching it to latent heat. Marsh has discussed the thermal shielding properties of dense mushy zones [10].

(ii) **Coarsening** of the zone interior occurs as neighboring dendritic branches grow and shrink simultaneously. The average thickness of the dendritic elements comprising the mushy zone increases over time in accord with Ostwald ripening kinetics, but the mean volume fractions of solid and melt within the zone remain constant [11]-[15].

(iii) **Detachment** occurs as dendritic side arms pinch off and the mushy zone recedes by melting away from the surrounding hotter melt. The thinning of the density of solid crystallites allows more sensible heat to penetrate the zone, which, in turn, further reduces the volume fraction of solid. This process accelerates until only a small cluster of isolated dendritic fragments remain, as shown in the lower left and right panels of Figure 1. The kinetics of dendritic detachment and melting interactions among neighboring crystallites has been discussed by Lupulescu et al. [16].

(iv) **Capillary-mediated melting** occurs when crystallites melt to a length $C \leq 2$ mm. For a typical ellipsoidal crystallite with $10 \leq C/A \leq 20$, the minor axis length, or equatorial diameter, $A$, would fall in the range 100-200 micrometers. These size scales are in the appropriate range where solid-liquid surface tension effects become noticeable. When a typical dendritic fragment enters this size regime, its $C/A$ ratio falls toward unity, and the crystallite shrinks into a small sphere that rapidly melts to extinction.

Figure 2. **(a)** The Stefan numbers (○) during melting plotted against melting time were obtained from temperature data furnished by telemetry from within the IDGE sample chamber. Data are shown for the first 33 minutes of IDGE cycle 04. Vertical dashed arrow indicates time at which the maximum time rate of change, $dSt^+/dt$, occurs. **(b)** Rate of change of the melting Stefan number (■) versus time, obtained by differentiating the curve $St^+(t)$. The applicable melting Stefan number at the peak of its rate of change corresponds to the value $St^+ = 0.055 \pm 0.004$ for the measured kinetics during this cycle. This value remains nearly constant over the 40 s interval around 740 s. These kinetics are displayed in Figure 4.
2.1. Experimental melting kinetics
The IDGE automated thermostat was designed to provide a constant freezing Stefan number, but not a constant melting Stefan number. An example of the thermal data telemetered from within the sample chamber is shown in Figure 2(a). Here one sees the first 33 min. of mushy zone melting ending IDGE cycle 04. During the first 400 s much of the dense dendritic mushy zone gradually melted, absorbing as latent heat all the heat conducted into the chamber from the surrounding thermostat. Consequently, little temperature rise (or melting Stefan number increase) is experienced initially within the melting solid-liquid mixture. The melting Stefan number increases rapidly after about 500 s as the density of unmelted crystals steadily decreases, lowering the mixture’s ability to absorb the added sensible heat as latent heat. The vertical arrow placed at 740 s indicates the time at which the last few crystallites melted. Beyond this time, and up to about 1900 s, the temperature of the now fully melted chamber rises toward its maximum of 1.8 K above the melting point of PVA. The melt temperature uniformly approaches the thermostat temperature, reducing the thermal gradients between the chamber and the thermostat. This slows, and eventually halts, the rise of the melting Stefan number at its final value of $St^+ = 0.16$. Figure 2(b) shows the corresponding time derivative of the melting Stefan number, $dSt^+/dt$, versus melting time, which peaks around $t = 740$ s. These data confirm the precise time interval over which the last few isolated crystallites underwent isolated melting, and establish quite precisely the applicable melting Stefan number responsible for melting the remaining crystallites.

2.2. Isolated crystallites
Near the end of each melting sequence, a few dendritic fragments remain that undergo melting as isolated crystallites. Figure 3 (a) shows a typical isolated dendritic fragment melting. For those crystallites oriented so its video image appears in true length, software determines a bordering
ellipse defining the solid-liquid interface (dashed curve surrounding the particle) that yields the major and minor axes, and the $C/A$ ratio at that moment during the melting sequence. If a crystallite was well-isolated from all others, and its initial shape lacked strong irregularities or branches, it would continue to shrink by melting at a nearly constant $C/A$ ratio. Figure 3 (b) shows $C/A$ ratio data ($\oplus$) versus time during such an event for an isolated ellipsoidal crystallite melting near the end of melting cycle 60. The remaining crystallites at this stage of melting a mushy zone in microgravity typically exhibited $C/A$ ratios in the range 10-20.

Figure 4. Final 40 s of melting a well-isolated ellipsoidal crystallite starting near $t = 720$ s, cycle 04. Data points (◦) are the crystallite’s major axis length, $C$, versus time, as this crystallite’s $C/A$ ratio slowly increased from 10-15, with a time-averaged value of $\langle C/A \rangle = 12 \pm 1$. The melting Stefan number ($St^+ = 0.057 \pm 0.002$) for the applied superheating of the melt during this interval was obtained from temperature data furnished via telemetry from the IDGE thermostat. See again Figures 2(a) and (b).

Isolated ellipsoidal crystallites that were longer than about 2 mm maintained a nearly constant, or slowly changing, $C/A$ ratio during their initial melting. Such long crystallites exhibited smooth ‘trajectories’ relating how their size, or volume, diminished over time. An example is shown in Figure 4, where the length of a crystallite’s $C$-axis is plotted versus melting time. This ellipsoidal crystallite was almost 0.8 cm in length when it began melting ($t = 0$). It shrank to 0.2 cm at $t = 36$ s, when its axial ratio began a rapid decrease from about 15 toward 1. Note that this melting trajectory also displays a slight ‘kink’ at 36 s. The last video frame and data point (◦) recorded on that trajectory, prior to its rapid extinction as a sphere, occurred at 40 s where $C = A = 0.01$ cm.

3. Theoretical interpretations of melting in microgravity
Two interesting melting phenomena observed by performing IDGE microgravity experiments require modeling and theory for their interpretation. They include: 1) establishing the basis for self-similar melting, i.e., melting at constant $C/A$ of ellipsoidal crystallites with $C \geq 2$ mm, and 2) explaining the sudden onset of spheroidization as the $C/A \to 1$ when the length of ellipsoidal crystallites became smaller than about 2 mm.

The author and former collaborators analyzed basic mesoscopic heat transfer theory pertaining to the melting of isolated ellipsoidal crystallites suspended in a melt undergoing
quasi-static melting [17]. Quasi-static melting of a crystal is based on calculating the thermal current, based on Laplace’s equation, entering or leaving a static solid-liquid interface. Kinematic equations are then formulated to deal with the crystal’s actual loss of volume by melting. The rate of change of the particle’s volume is assumed to occur slowly enough that the surrounding Laplace transport field has sufficient time to adjust to the changing particle shape. Here, quasi-static melting is limited to melting under the condition that \( St^+ \ll 1 \), and that the solid-liquid interface remains isothermal at \( T = T_m \). The maximum value of the melting Stefan number in the experiments was \( St^+ \leq 0.16 \). As discussed in Section 2.1, melting of isolated ellipsoidal crystallites was observed when the melting Stefan number was much smaller, namely, \( St^+ \approx 0.06 \), which adequately satisfies the thermal requirements for quasi-static melting. Only a summary of our detailed potential theoretic analysis [17] will be used here in discussing self-similar melting.

The same authors suggested in a later publication [16] that capillarity was probably responsible for the terminal features of melting in microgravity, where the nearly constant \( C/A \) ratio during self-similar melting suddenly plummets toward unity, resulting in the extinction by melting of a spherical crystal. No direct proof, however, was offered at that time showing that the extremely weak thermal influences of capillarity were, in fact, responsible for altering the shapes of melting crystallites from needle-like ellipsoids to spheres.

### 3.1. Quasi-static theory

The axis-symmetric temperature field, \( T(\vec{r}) \), surrounding an ellipsoidal crystallite, may be non-dimensionalized as a Laplacian potential, \( \vartheta(\vec{r}) \), where the axis threading the crystallite’s north and south poles defines the distance vector \( \vec{r} = 0 \). The heat flow intensity to the crystal is determined by the magnitude of the potential gradient at the solid-liquid interface, which may be determined from the potential’s definition

\[
\vartheta(\vec{r}) \equiv \frac{T(\vec{r}) - T_m}{T_{\infty} - T_m}.
\]

It is useful to express the potential defined in Eq. (3) in orthogonal, curvilinear prolate spheroidal coordinates, \( \vartheta(\xi, \eta, \varphi) \). Consequently, the solid-liquid interface of an ellipsoidal crystallite is considered at present to be the coordinate surface labeled \( \xi = \Xi \), over which the interface potential remains uniform, namely, \( \vartheta(\Xi, \eta, \varphi) = 0 \). This key assumption ignores the effect of interface curvature on the local equilibrium melting point, \( T_m \). The influence of capillarity, which appears towards the end of each melting trajectory, will be considered later in Section 5. The prolate spheroidal coordinate system is discussed in detail by Morse and Feshbach [18], for which we chose to scale the dimensionless coordinates \( \xi \) and \( \eta \) by the interfocal length of the ellipsoidal crystallite, \( a \), defined in [18] as \( a = C/\Xi = A/\sqrt{\Xi^2 - 1} \). Prolate spheroidal coordinates are displayed as the \( \varphi = 0 \) projection shown in Figure 5. The cross-hatched elliptical ‘crystallite’ placed within Figure 5 has a \( C/A \) ratio of almost 10, which is at the lower end of the axial ratios of PVA crystallites studied here; its solid-liquid interface is specified by the coordinate surface \( \Xi = 1.008 \).

In brief, heat flow from the hotter melt to the solid-liquid interface is responsible for melting the ellipsoidal crystal, the centroid of which is located at the origin of these coordinates, \( \eta = 0 \), \( \xi = 1 \). Heat transfer occurs by three-dimensional conduction along the hyperboloidal surfaces \( \eta = \text{const.} \). The isotherms of the resultant quasi-static field in the melt form concentric prolate ellipsoids, \( \xi = \text{const.} \geq \Xi \). The solid-liquid interface, \( \xi = \Xi \), itself remains uniformly at the equilibrium melting point given by the potential surface \( \vartheta(\Xi, \eta, \varphi) = 0 \). The enclosed solid region is consequently isothermal.

The Laplace potential defined in Eq. (3) is based on the total temperature difference through the melt. This potential may be recast using the melting Stefan number, already defined in
Eq. (2), as the measure of melting intensity. Thus, the thermal potential in prolate spheroidal coordinates transforms to

$$\vartheta(\xi, \eta, \varphi) = \frac{1}{\mathcal{S} t^+} \frac{(T(\xi, \eta, \varphi) - T_m)}{\Delta H_f/C_p}, \quad (\xi \geq \Xi)$$  \hspace{1cm} (4)

everywhere throughout the melt, and within the solid to

$$\vartheta(\xi, \eta, \varphi) = 0, \quad (\xi \leq \Xi).$$  \hspace{1cm} (5)

Morse and Feshbach show that the Laplace potential surrounding a prolate spheroid with the fixed interfacial potential $\vartheta(\Xi, \eta, \varphi) = 0$ embedded in a quiescent melt with the far-field potential $\vartheta(\infty, \eta, \varphi) = 1$, is

$$\vartheta(\xi, \eta, \varphi) = 1 - \frac{\log \left(\frac{\xi+1}{\xi-1}\right)}{\log \left(\frac{\Xi+1}{\Xi-1}\right)}.$$  \hspace{1cm} (6)

The gradient field in the melt surrounding the solid-liquid interface associated with this thermal potential is found by taking the partial derivative of Eq. (6) with respect to $\xi$, and then dividing the result by the $\xi$-coordinate’s metric, $h_\xi = (a/2)\sqrt{(\xi^2 - \eta^2)/(\xi^2 - 1)}$. These operations yield a dimensionless, axis symmetric gradient field, $\nabla \vartheta(\xi, \eta, \varphi)$, which when evaluated at the solid-liquid interface, $\xi = \Xi$, gives for its normal component,

$$\nabla \vartheta(\Xi, \eta, \varphi) \cdot \vec{n} = \frac{4}{a} \left(\sqrt{(\Xi^2 - 1)(\Xi^2 - \eta^2)} \log \left(\frac{\Xi+1}{\Xi-1}\right)\right)^{-1},$$  \hspace{1cm} (7)

**Figure 5.** Prolate spheroidal coordinates, $(\xi, \eta, \varphi)$, projected on the plane $\varphi = 0$, as described by Morse and Feshbach [18]. A solid-liquid interface is inserted that projects as the profile $\Xi = 1.008$ surrounding the cross-hatched ‘crystallite’, shown here with an aspect ratio of $C/A ≈ 10$. Isotherms in the melt are denoted as the ellipsoidal surfaces $\xi \geq \Xi = \text{const.}$, which vary in their potential between $\vartheta = 0$ on $\xi = \Xi$, and $\vartheta = 1$ on $\xi = \infty$. The heat responsible for melting the crystal-lite moves along the hyperboloidal sheets $\pm \eta = \text{const.}$.
where $\vec{n}$ is a unit normal vector on the solid-liquid interface. The relationship of the normal component of the interfacial gradient, Eq. (7), to the thermal gradient in the melt surrounding an ellipsoidal crystallite may be found by differentiating Eq. (4) with respect to $\xi$, dividing through by the curvilinear coordinate metric, $h_\xi$, to form the Jacobian transform, and setting $\xi = \Xi$.

$$\nabla \vartheta (\Xi, \eta, \varphi) = \frac{1}{St^+ \Delta H_f} \frac{C_\rho}{\Delta T(\xi, \eta, \varphi)} \frac{\partial T(\xi, \eta, \varphi)}{\partial \xi} \bigg|_{\xi = \Xi}. \quad (8)$$

Rescaling the normal component of the Laplace potential gradient, Eq. (8), through the characteristic temperature of the melting transformation, $\Delta H_f / C_\rho$, multiplied by the system’s melting Stefan number, and substituting the $\xi$-coordinate metric, $h_\xi$, that acts normal to the solid-liquid interface, yields the desired form for the normal component of dimensional interfacial thermal gradient, $\vec{\nabla} T_\Xi \cdot \vec{n}$, namely,

$$\left( St^+ \frac{\Delta H_f}{C_\rho} \right) \nabla \vartheta (\Xi, \eta, \varphi) = \frac{2}{a} \sqrt{\Xi^2 - 1} \left( \frac{\partial T(\xi, \eta, \varphi)}{\partial \xi} \bigg|_{\xi = \Xi} \right) \nabla T_\Xi \cdot \vec{n}. \quad (9)$$

### 3.2. Enthalpy current

The enthalpy flux, $\vec{J}$ entering the solid-liquid interface may be found using Fourier’s law of heat conduction,

$$\vec{J} = -k_\ell \vec{\nabla} T_\Xi, \quad (10)$$

where $k_\ell$ is the thermal conductivity of the melt. The thermal gradient normal to the solid-melt interface, Eq. (9), can be substituted into Fourier’s law to yield the melting flux,

$$\vec{J} = \left[ - \left( k_\ell \frac{4 \Delta H_f}{C_\rho} St^+ \right) \left( \sqrt{(\Xi^2 - 1)(\Xi^2 - \eta^2)} \log \frac{\Xi + 1}{\Xi - 1} \right)^{-1} \right] \cdot \vec{n}. \quad (11)$$

The sensible heat current, $\dot{Q}_{\text{tot}}$, melting the prolate spheroid is the integral of the flux, $\vec{J}$, over its solid-liquid interface, namely,

$$\dot{Q}_{\text{tot}} = \iint_{\text{interface}} \vec{J} \cdot \vec{n} \, dS, \quad (12)$$

where the differential element of interface area on the prolate spheroid, $\xi = \Xi$, is

$$dS = r(\Xi, \eta) d\sigma(\Xi, \eta) d\varphi = r(\Xi, \eta) h_\eta d\eta d\varphi. \quad (13)$$

Here $r(\Xi, \eta) = (a/2) \sqrt{(\Xi^2 - 1)(1 - \eta^2)}$ denotes the radial distance from the major $C$-axis to an arbitrary location, $\eta, \varphi$, on the interface, and $d\sigma = h_\eta d\eta$ is the differential of the curvilinear arc length. The $\eta$-coordinate metric needed to scale arc length, $\sigma$, along an ellipsoidal interface is defined by Morse and Feshbach as $h_\eta \equiv c/2 \sqrt{(\Xi^2 - \eta^2)(1 - \eta^2)}$. Using these transformations with Eq. (13) yields the differential element of interfacial area on a prolate spheroidal crystal as,

$$dS = \frac{a^2}{4} \sqrt{(\Xi^2 - 1)(\Xi^2 - \eta^2)} d\eta d\varphi. \quad (14)$$

Substituting Eq. (11), for the normal flux, and Eq. (14), for the differential interfacial area, into the formula for $\dot{Q}_{\text{tot}}$, Eq. (12), yields the definite integral,

$$\dot{Q}_{\text{tot}} = -\frac{ak_\ell \Delta H_f St^+}{C_\rho} \left( \frac{\Xi + 1}{\Xi - 1} \right)^{-1} \int_{-1}^{1} d\eta \int_{0}^{2\pi} d\varphi. \quad (15)$$
The integration limits on $\eta$ ($-1 \leq \eta \leq 1$) and on $\phi$ ($0 \leq \phi \leq 2\pi$) correspond to integrating the heat fluxes from pole-to-pole over the prolate spheroid. Carrying out the integrations indicated in Eq. (15) introduces the expected spherical image, $4\pi$, and shows that the instantaneous heat current entering a prolate spheroid with an interfocal length $a$ is

$$\dot{Q}_{tot} = -\frac{4\pi a}{\log \left( \frac{\Xi+1}{\Xi-1} \right)} \frac{k_\ell \Delta H_f}{C_p} \dot{St}^+. \quad (16)$$

### 3.3. Kinematic energy balance

The volume of a spheroidal crystal is given by the standard formula [19],

$$V(t) = \frac{\pi}{6} A^2(t) C(t) = \frac{\pi}{6} \left( \frac{C}{A} \right)^2 C^3(t), \quad (17)$$

Sensible heat, $\dot{Q}_{tot}$, provides the latent heat for melting. The time-dependence of the major axis, $C(t)$, is explicitly noted in the RHS of Eq. (17), whereas the spheroid’s aspect ratio, $C/A$, is considered to be constant. The validity of this important approximation, $C/A = \text{const.}$, will be demonstrated later. The time-rate of change of the major-axis length as melting proceeds is related kinematically to the volume derivative at constant $C/A$ as

$$\dot{V}(t) = \frac{\pi}{2} \left( \frac{C}{A} \right)^{-2} C^2(t) \dot{C}(t), \quad (18)$$

where the overdot indicates time differentiation. The rate of enthalpy change associated with the volume change is

$$\dot{H}_{tot} = \frac{\pi}{2} \frac{\Delta H_f}{\Omega} \left( \frac{A}{C} \right)^2 C^2(t) \dot{C}(t). \quad (19)$$

where $\Omega$ is the molar volume of the solid phase. This enthalpy rate expression ignores the imperceptible advection occurring in the melt near the interface caused by the small ($\approx 3\%$) density differences of the phases. Coriell and McFadden have shown that the effect of this advection on the transport of energy to or from a moving solid-liquid interface is negligible for real materials [8]. Work by Karma and Plapp [20] using phase-field computations also confirm the results found by Coriell and McFadden.

The kinematic energy balance under quasi-static conditions is therefore $\dot{H}_{tot} = \dot{Q}_{tot}$. Equating Eq. (19) with Eq. (16) gives

$$\frac{\pi}{2} \frac{\Delta H_f}{\Omega} \left( \frac{A}{C} \right)^2 C^2(t) \dot{C}(t) = -\frac{4\pi a}{\log \left( \frac{\Xi+1}{\Xi-1} \right)} \frac{k_\ell \Delta H_f}{C_p} \dot{St}^+. \quad (20)$$

### 3.4. Melting kinetics in microgravity

Equation (20) provides the differential equation describing quasi-static evolution of a stationary prolate spheroidal crystal of constant axial ratio surrounded by an infinite superheated melt at a Stefan number, $\dot{St}^+$. Equation (20) may now be solved for the kinetic response, $C(t)$, which was measured during the IDGE microgravity melting experiments on PVA by employing the following steps:

\begin{itemize}
  \item [i.] cancel common terms;
  \item [ii.] recognize that $k_\ell \Omega/C_p \equiv \alpha$, where $\alpha$ is the thermal diffusivity of the melt;
  \item [iii.] apply the transformation for the interfocal length, $a = C/\Xi$;
\end{itemize}
iv. separate the dummy variables, $C'$ and $t'$;
v. integrate between the start of melting, $t' = 0$, when $C' = C_0$, and some arbitrary later time, $t' = t$, when $C = C(t)$.

After applying each of the steps enumerated above, one obtains

$$
\int_{C_0}^{C(t)} C' dC' = -\frac{8}{\Xi \log \left(\frac{\Xi + 1}{\Xi - 1}\right)} \left(\frac{C'}{A}\right)^2 \alpha St^+ \int_0^t dt.'
$$

(21)

The integrations in Eq. (21) yield, after several steps of algebra,

$$
C(t) = \sqrt{C_0^2 - \frac{16\alpha St^+}{\Xi \log \left(\frac{\Xi + 1}{\Xi - 1}\right)} \left(\frac{C'}{A}\right)^2 t.}
$$

(22)

Equation (22) may be non-dimensionalized as

$$
\frac{C(t)}{C_0} = \sqrt{1 - K \cdot St^+ \cdot Fo},
$$

(23)

where a melting rate constant, $K$, is defined as

$$
K = \frac{16}{\Xi \log \left(\frac{\Xi + 1}{\Xi - 1}\right)} \left(\frac{C'}{A}\right)^2,
$$

(24)

and the Fourier number (dimensionless melting time) is defined as

$$
Fo = \frac{\alpha}{C_0^2 t}.
$$

(25)

4. Quasi-static melting results

The key theoretical results for predicting the kinetics of quasi-static melting of isolated spheroidal crystallites in microgravity are captured in Eqs. (22)-(25). As an example, Figure 6 shows the crystallite major axis length, $C(t)$, scaled by the starting length, $C_0$, Eq. 23, versus Fourier number, or dimensionless melting time. The value for the rate constant ($K = 360.6$) applied in Eq. (23) is for the same $C/A$ ratio as the PVA crystallite measured in cycle 04, the melting trajectory for which appears in Figure 4, as $C(t)$ versus real time, $t$. The value of the coefficient that converts real time, $t$, to Fourier number ($\alpha/C_0^2 = 1.22$ ms) is based both on the thermal diffusivity for molten PVA at its melting point ($\alpha = 7.0 \times 10^{-4}$ cm$^2$/s) and on the crystallite’s starting length indicated in Figure 4 ($C_0 = 0.758$ cm). The dashed trajectory appearing in Figure 6 is calculated for the experimental Stefan number, $St^+ = 0.057$ measured from the IDGE telemetry data during melting cycle 04. See again Figures 2(a) and 2(b). One notes general agreement between the theoretical prediction and the observed melting trajectory, considering that there are not any adjustable parameters in the theory. More specifically, the initial linear slope of this melting trajectory, when the crystallite was relatively large, is predicted accurately.

The reason that the initial melting kinetics are predicted so well by quasi-static potential theory is that the heat flux to the poles ($\eta = \pm 1$) is exactly $C/A$ times larger than the heat flux to the crystallite’s equator ($\eta = 0$). The influence of the crystallite’s geometry on shaping and concentrating the external potential near the poles is called the ‘point effect’ of diffusion, or, in this case, of heat conduction. Thus the crystal initially melts self-similarly, maintaining a constant axial ratio, because the external heat fluxes to the poles and the equator remain in the fixed ratio $C/A$.
Figure 6. Melting trajectories for various melting intensities, $St^+$, for spheroidal PVA crystallites with $C/A = 12$. Curves are plotted as scaled length, $C(t)/C_0$, versus dimensionless time or Fourier number. $C(t)/C_0$ experimental data are for the crystallite trajectory, $C(t)$, in Figure 4.

The data in Figure 6 also show that the initial close fit gradually deteriorates as the crystallite shrinks further, with the observed melting rate gradually occurring faster than that given by quasi-static theory. The slight ‘kink’ occurring over the last 30% of the observed melting trajectory, as the crystallite’s length decreased below about 2 mm, causes additional departure from the theoretical predictions.

5. Capillarity
5.1. Background
Capillarity—the influence of solid-liquid interfacial energy—occurs during melting in sufficiently small crystallites. Observations from IDGE experiments in microgravity indicate that when the equatorial radius of an ellipsoidal PVA crystallite falls below about 100 micrometers, so that the crystallite is approximately 2 mm in length, capillarity phenomena become significant and begin to influence the melting kinetics. See again Section 2.2. Quasi-static melting theory, outlined in Section 3.1, ignores capillarity through its approximation that the solid-liquid interface remains at a constant potential. The temperature shift, or capillary correction to the equilibrium melting temperature, $\delta T$, is given by the Gibbs-Thomson-Herring equation [24]-[26],

$$
\delta T(\Xi, \eta) = T_e(\mathcal{H}) - T_m = -\frac{\gamma_{s\ell}(\theta) + \gamma_{\theta,\theta}}{\Delta S_f/\Omega} \mathcal{H}(\Xi, \eta),
$$

where $\mathcal{H}$ is the mean curvature $^2$ at an arbitrary point $(\Xi, \eta)$ on the solid-liquid interface. $\gamma_{s\ell}(\theta)$ denotes the interfacial free energy per unit area at some location $(\Xi, \eta)$, where the energy at that point varies anisotropically with the local normal angle $\theta$. The term $\gamma_{\theta,\theta}$ is the second angular

$^2$ We adopt the convention that the mean curvature, $\mathcal{H}$, of a convex solid-liquid interface, e.g., where melt surrounds a spheroidal crystal, is positive.
derivative of the energy, also known as the torque or ‘interfacial stiffness’. The solid-liquid free energy of pure PVA was measured by several investigators [21]-[23]. The mean interfacial energy of PVA is \( \langle \gamma_{s\ell} \rangle = 2.8 \pm 0.3 \) mJ/m\(^2\) [21, 23], with a four-fold anisotropy of 3-5\% about the \((100)\) zone axis [21, 22]. Equation (26) is easily converted to the capillary-dependent interface potential

\[
\vartheta(\Xi, \eta) = \frac{\Omega T_m C_p}{\Delta H_f} \left( \frac{\gamma_{s\ell}(\theta) + \gamma_{\theta\theta}}{St^+} \right) \mathcal{H}(\Xi, \eta). \tag{27}
\]

5.2. Capillary influence on heat flux

The Stefan numbers applied by the IDGE thermostat during each melting cycle as the last, isolated crystallites melted, typically were in the range of 0.03 \( \leq St^+ \leq 0.06 \). Although the equilibrium temperature shift along the curved interface does directly affect the point-to-point value of the local Stefan melting number, this direct influence is extremely small. Even near the poles, where the curvature is greatest, the effect of capillarity on the value of \( St^+ \) is only about 1 part in \( 10^4 \) [16]. Thus, the external sensible heat flux arriving from the melt is only trivially influenced by capillarity.

There is, however, an indirect effect of capillarity on the total heat flux reaching the poles. This indirect effect occurs because the non-isothermal temperature distribution along the curved solid-liquid interface causes thermal gradients to develop between the equatorial region, where the curvature and temperature shift are smaller than near the poles, where the curvature and temperature shift are much greater. In fact the curvature at the poles is \((C/A)^2\) times greater than the curvature at the equator. These temperature differences develop rapidly close to the poles, so even small temperature differences acting over small distances can stimulate significant heat fluxes within the crystallite. When the internal heat flux is added to the external heat flux near the poles it accentuates the melting rate at the poles.

S. Salon performed finite difference computations to evaluate the nature of the internal heat fluxes due to capillarity. (Private communication, S. Salon, Rensselaer Polytechnic Institute, Troy, NY, USA, 2005) Salon computed the internal and external fluxes reaching the poles in prolate spheroids of varying axial ratios and major axis lengths for a range of melting Stefan numbers. He numerically computed the Laplace field to high precision within the solid and melt phases, i.e., both inside and outside the solid-liquid interface. The interfacial energy parameters and the thermal diffusivity for PVA were used to check the influence of capillarity.

Figure 7(a) shows computational results for the influence of capillarity on the increase in the total flux reaching the poles of a prolate spheroid versus \( C/A \), due to heat flow internal to the crystal. Results are displayed for two axial lengths, \( C = 2 \) cm and \( C = 0.5 \) cm. One notes that the internal heat flux increases rapidly with increasing \( C/A \) and decreasing crystallite size. Figure 7(b) exhibits a useful regularity in judging the strength of the capillary-induced internal flux responses. If the percent flux increase at the poles is multiplied by the crystallite’s major axis length, \( C \), the data sets for different size crystals collapse to a unique value for each \( C/A \). Thus, using the curve in Figure 7(b) for the crystallite tracked in Figure 4, where \( C/A = 12 \), one finds that the percent increase in polar flux when \( C = 0.2 \) cm is appreciable, viz., about 15\%.

The capillary-mediated fluxes at the poles of this crystal would continue to increase rapidly with the inverse of the size of the shrinking crystallite. The increase in internal heat flux is then mitigated, and ultimately reduced, by the decrease in the \( C/A \) ratio as spheroidization from melting progresses.

6. Conclusions

(i) The IDGE experiments, launched aboard Columbia in the mid-to-late 1990s, collectively delivered a rich archive of solidification and melting data in microgravity. Those data
Figure 7. (a) Internal heat flux, resulting from capillarity, versus axial ratio, for prolate spheroids with major axes $C = 2.0$ cm (●), and $C = 0.5$ cm (●). (b) Percent flux increase at the poles times the major axis length, $C$, versus axial ratio. Both data sets from (a) combine here to yield identical values accumulated during the final IDGE mission allows detailed analysis of melting kinetics for pivalic anhydride (PVA) crystallites.

(ii) The dendritic mass, or PVA mushy zone, melted initially from its periphery, and as progressive melting caused detachments and fragmentation, gradually reduced the dense mushy zone to a few isolated, needle-shaped crystallites, about 1-2 cm in length. These crystallites melted maintaining a nearly constant $C/A$ ratio, as their length was reduced to about 2 mm.

(iii) Upon reaching a pole-to-pole length of circa 2 mm, the $C/A$ ratio drops from values in the range 10-20, toward unity. Finite difference computations that include capillarity show that when prolate spheroids with $C/A$ ratios in the range of 10-20 shrink to about 2 mm, the internal heat flux conducted to the poles increases. Thus, the poles receive an increase in total heat flux that accelerates their melting rate, causing rapid spheroidization. This process is substantially completed just before extinction occurs.

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