DATA AND MODELING OF DENDRITES SUBJECT TO A STEP CHANGE IN PRESSURE (TDSE)

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There is considerable interest in dendritic solidification because of the influence dendrites have in the determination of microstructure, and thereby in the physical properties of cast metals and alloys. Current theories and models of dendritic growth generally couple diffusion effects in the melt with the physics of the interface. Data and subsequent analysis prior of the tip growth speed and radii of thermal succinonitrile dendrites in the near-convection free, on-orbit, free-fall environment demonstrate that these theories yield predictions that are reasonably in agreement with the results of experiment. However, data and analysis for assessing the interfacial physics component of theory are not sufficiently detailed or definitive. To study fundamental aspects of dendritic interface stability, we are measuring and modeling the kinetics and morphology of dendrites as they evolve from one well-defined steady state at a pre-set supercooling, through a transient stage, to a different well-defined steady state.

More specifically, we subject succinonitrile dendrites, growing under steady-state conditions, to a rapid change in pressure. This leads to a rapid change in thermal driving force from the corresponding change in both the equilibrium melting temperature due to the Clapeyron effect, and a change in the far-field temperature due to adiabatic temperature changes in the bulk liquid and solid. Subsequently, we observe transformations from a well-characterized initial state into a new steady-state. Initial data reveal that the dendrite tip velocity changes almost as fast as the pressure charges, while the tip radius changes occur more slowly, taking from 10 – 60 seconds depending on the size of the step change and the final supercooling. Computer modeling of this process shows both agreements and disagreements with the experimental data. In making these observations and measurements, we are gaining new understandings of interfacial dynamics and state-selection physics.

Introduction

Dendritic solidification is one of the simplest examples of pattern formation where a structureless melt evolves into a complex crystalline microstructure. Dendrites are known to occur in the solidification of water, salts, organic materials, and most commonly and importantly, in metals and alloys. There is considerable engineering interest in dendrites because of the role dendrites play in the determination of the physical properties of cast materials. In addition, dendritic solidification has become a well-studied model in the fields of non-equilibrium physics, and computational condensed matter material physics [1].

Keywords: dendrite, solidification, microstructure, interfacial, Clapeyron, flight
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Current theories of dendrite formation contain two independent components. The first concerns the transport of heat and solute from the solid-liquid interface into the melt. The second involves the interfacial physics that selects the unique growth velocity and tip radius of curvature from a spectrum of possibilities that are all consistent with the heat transport and conservation of energy at the crystal-melt interface. Until recently, neither aspect of the theory could be tested critically because of the effects of gravity-induced convection, which modifies the transport processes, and alters the growth kinetics [2].

To circumvent this difficulty, benchmark data were obtained in microgravity during two flights of the Isothermal Dendritic Growth Experiment (IDGE), using succinonitrile (SCN) as the test material [3, 4]. SCN is an organic material that acts as a BCC metal analog. The data and subsequent analysis of the dendritic tip growth speed and radii of curvature for these SCN dendrites demonstrated that although the theory yields predictions that are in reasonable agreement with the experiment, several significant discrepancies occur. However, some of the discrepancies can be understood by a consideration of the diffusion of heat from three-dimensional dendritic structures [5, 6]. The data and analysis for assessing the pattern selection physics are less definitive.

Current investigations by other researchers are studying, isolated single dendrites, dendritic side-branching, aligned dendritic arrays, and equiaxed dendritic growth. Some of these investigations recognize that in addition to the study of steady-state growth features, where the tip region of the dendrite grows at a constant speed, dendrites also exhibit time-dependent, non-steady features. For example, time-dependent side-branches emerge, amplify, and eventually coarsen.

The work presented here represents preliminary results from our activities to study fundamental aspects of time-dependent dendritic growth, while retaining the advantages of working with a single, isolated dendrite.

We are investigating transient and time-dependent dendritic growth by employing the relatively large Clapeyron effect in SCN with pressure changes. A rapid change in a solidifying system's hydrostatic pressure quickly changes the liquidus temperature, and induces a change in the temperature gradients at the interface. With this approach, we have observed and measured the kinetics of isolated dendrites as they evolves from one well-defined steady-state velocity, at a pre-set supercooling, through a transient stage, to a new well-defined steady-state velocity at the altered pressure-supercooling state.

Background

A major challenge in measuring and analyzing the transient behavior of isothermal dendrites growing from an initial nucleus is defining precisely the initial conditions from which the dendrite evolves. The experiment described in this paper obviates this difficulty, because the transient instead occurs between two well-characterized steady states—controlled by pressure, rather than between an ill-defined initial state and the final steady state.

The definition of the melting temperature, T_m, is the temperature at which the liquid and solid phases co-exist in equilibrium. The melting temperature of a pure material has a well-established value, which varies as a function of pressure. In materials that expand on melting (well known exceptions being water and silicon), pressure favors the solid phase as atoms or molecules are squeezed (on average), slightly closer together. The increase in pressure does work on the solid, decreasing bond lengths, and raising the melting temperature. This effect is classical, and can be derived from general thermodynamic principles yielding

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the Clapeyron equation,

$$\frac{\Delta T}{\Delta P} = \frac{T_m(v_l - v_s)}{h_f} \qquad (1)$$

where ΔT is the change in melting temperature resulting from a change in pressure, DP, and vl and vs are the specific volumes of the liquid and solid phases, and hf is the latent heat [7]. We measured directly the Clapeyron effect in high-purity SCN by two independent techniques and determined that $\Delta T/\Delta P$ = 24.5±0.5 mK/atm [8].

The Clapeyron effect is well known in solidification theory and has been hypothesized as the explanation for cavitation induced nucleation. However, it is usually assumed that the Clapeyron effect is too small to be of interest in the solidification of metals and alloys. This is a reasonable assumption for most materials, but not valid in the unusual case of SCN, which has a Clapeyron effect that is many times larger than most metals and a unit supercooling that is many times smaller. Thus, the ratio of the Clapeyron Effect to the Unit Supercooling is 25 to 200 times larger for SCN than for typical metals. This indicates that pressure effects can be important in the solidification of SCN (at least for the purpose of conducting basic research).

The Clapeyron coefficient of 24.5 mK/atm can be used in a straightforward manner to quickly change a crystal-melt interface's equilibrium melting temperature, and, thereby, its supercooling. If this is done for an isolated isothermal dendrite growing at steady state, the supercooling, and the associated free energy for dendritic growth, becomes instantaneously and globally altered. This approach, allows acquisition of a series of unique measurements of non-steady-state dendritic kinetics, and permits observations of the transient evolution of the morphology.

If a pressure-mediated melting temperature change is carried out for an isolated dendrite growing at steady state under some initial supercooling, the dendrite needs to respond by eventually adopting a new steady-state that is appropriate to the new supercooling. If we designate in advance a particular target supercooling, we can achieve that supercooling by starting at a supercooling either above or below that supercooling, and then apply upward or downward pressure quenching as needed. To properly calculate what that final supercooling is, one must account for the influence of the adiabatic pressure-volume work done on the melt. From the thermodynamics of the combined first and second laws, one can show that the change in the melt temperature (or similarly, crystal temperature) with pressure is,

$$\frac{\Delta T}{\Delta P} = \frac{\beta v T}{c_p} \qquad (2)$$

where β is the isothermal compressibility, v is the specific volume, T is the temperature of the melt prior to the pressurization, and c_p is the constant pressure specific heat. For SCN, this is approximately 13 mK/atm, confirmed by both calculation and direct measurement.

Experiment Description

The experiments described here were conducted using ground-based hardware originally produced and used by the Isothermal Dendritic Growth Experiment (IDGE) to study dendritic growth of succinonitrile and pivalic acid under both ground and microgravity conditions. Additional detailed information describing the IDGE can be found elsewhere [9, 10].

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Apparatus

The experimental apparatus is centered about the sample material, contained by a stainless steel growth chamber located within a temperature-controlled bath. The growth chamber interior volume communicates with the bath via a stainless steel bellows, permitting the pressure in the bath to be transmitted into the chamber interior. Nucleation of dendritic crystals was achieved through the use of a hollow stinger tube that penetrated the wall of the growth chamber. The exterior end of the stinger tube was capped and surrounded by a thermoelectric cooler. The interior end was open, allowing the sample material in the chamber to also fill the stinger.

During the operation of the experiment, each dendritic growth cycle began by completely melting the SCN, followed by lowering the melt's temperature to the desired supercooling. After the supercooled melt's temperature reached steady state, the thermoelectric cooler was activated. This nucleated a small crystal in the end of the stinger, which then propagated down the stinger tube to emerge into the chamber as a freely growing dendrite. Upon reaching steady state growth, the hydrostatic pressure of the surrounding thermal bath was changed via a pneumatically operated piston. This pressure was transmitted to the sample via the bellows, causing a change in the operating state of the dendrite. From here, the dendrite was observed as it attempted to acquire a new set of steady state operating conditions. Once one of these "growth cycles" was completed, a new growth cycle was initiated by re-melting the sample and proceeding as described above. This arrangement produced dendritic crystals grown with the bath steady state temperature controlled to within 0.002 K (spatially and temporally).

During the growth cycles, once a crystal emerged from the stinger, images of the dendrites were obtained from two perpendicular views using electronic cameras which provided the spatial and temporal resolution that is necessary to study the transient aspects of the growth process. Specifically, an imaging chip array was used of 640 x 480 pixels (256 gray-scale levels) and an imaging rate of approximately 30 frames per second (~30 Hz).

Analysis Techniques

The data presented here from the 30fps video cameras has an optical resolution that related to the base size of an individual pixel in the video camera's imaging array. Each pixel, after correcting for the magnification of the optics system, images a region of the growth chamber that is approximately 22 mm high and 22 mm wide. This value constitutes the raw measurement precision for the tip position data. It is necessary to improve upon this precision by applying a sub-pixel resolution image analysis method to each image in the growth cycle.

The method used for the data presented here begins by examining the first and last image frames of a growth cycle. The dendrite tips are found in these images using a row-by-row search to locate the lowest pixel in the field of view that is darker than a specified threshold value. If there are more than one pixel in a row satisfying this criteria, an average is calculated to obtain the horizontal coordinate. With these crude estimates of the tip positions at the beginning and end of the growth, it is possible to construct a vector that can be used to predict where the tip will be in all frames during the growth, provided the frame number and frame rate are incorporated. This tip-location prediction scheme improves processing efficiency, though is only capable of resolving information on the order of 22 microns (one pixel).

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Using this predicted tip location, a second stage of refinement is added to the sub-pixel interpolation processing of each image. This is achieved by overlaying a "sampling line" along the predicted vector and determining the point along this vector where the image intensity crosses a selected threshold value. However, the sampling line is treated as "thick" in that it also comprises of several pixels on either side of the mathematical line, creating an averaging effect. Additionally, interpolation is applied to determine the threshold location more precisely. By incorporating a statistically larger number of pixels in this second stage of refinement, resolution is improved to approximately 7 microns (~1/3 pixel). However, the horizontal coordinate is constrained to fall along the predicted vector line. In practice, this is not usually a significant issue, since these dendrites tended to grow within about 10 degrees of vertical, and, once started, do not deviate in direction under nominal growth conditions.

The final stage of resolution enhancement is achieved by a somewhat unorthodox approach, which has the advantage of incorporating still more (statistically speaking) information concerning the tip location. Figure 3 shows a typical image of a dendrite tip (video image in 3b). Using the refined tip location (stage 2, described above) as a reference location, a box is created around the tip. Next, the centroid of the pixel intensity within this box is calculated. In practice, the coordinates of this centroid exhibit a resolution of approximately 2 microns (~1/10 pixel). This approach doesn't actually locate the tip's interface. Instead, it uses more data to obtain a more consistent reference point, which serves to track the tip's movement over time. The size of the sampling box used in the centroid calculation is somewhat arbitrary. The concerns in its selection are primarily over obtaining a balance between the desire to have a large number of data points contributing to the measurement, and avoiding the inclusion of side branches. When information that is obtained from regions further removed from the tip is used, nascent side branches can contribute to the centroid calculation in a periodic manner.

Once extracted from the images, the tip positions are then converted into a displacement vs. time data set that is used for subsequent analysis. The displacement is calculated relative to the tip position in the first available frame of video [9]. The radii measurements are based on 35 mm film following the procedures described in reference [4]. However, at this point the details of the optic system have not be tailored to produce the best quality images, and thus the uncertainties in these measurments are larger then those quoted in reference [4].

Results

The experiments described above were conducted for a variety of pressure change magnitudes and directions, and with a variety of supercooling levels. What follows is a qualitative survey of typical observations.

An increase in hydrostatic pressure is expected to result in an increase in the interface's equilibrium temperature, and thus an increase in the temperature gradient and supercooling which drives the solidification process. Figure 1 plots the dendrite tip displacement vs. time of such an experiment. The velocity of this growth (i.e. the slope) is indeed observed to increase after the pressure change, confirming the general feasibility of the experimental procedure. Earlier we reported in the transition from an initial low velocity to a final higher velocity, that the dendrite had a short transient where it initially slowed [11]. That report however was in error as the observed short initial transient was due to an instrument error.

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When the melt's hydrostatic pressure was instead decreased during the growth, as expected, the growth rate also decreased.

The tip position data (as a function of time) is the primary measured data in these experiments. It is desirable to convert this information into the dendrite tip growth velocity. Due to the point-by-point variability of these measurements, instantaneous measures of the velocity are best interpreted when they incorporate some form of moving average or data smoothing. However, for the data reported here, the correction to account for the instrumental error added so much noise that a velocity plot is not useful, even using a moving average. Nevertheless, we compare the experimental data to the modeling data modeling with respect to the velocity versus time rendering of the data.

For the range of supercoolings and pressure change magnitudes, the characteristic time necessary to reacquire the new steady-state velocity was too similar to the pressure transition time to been seen as independent of the pressure transition. The best that we can say is that it must be on the order of 0.2 s or less.

When we began these measurements, we had no estimate of the time scale involved for the dendrite to respond to a change it its conditions. In the case of velocity measurements, low spatial resolution data at 30 fps was more than adequate to see, recognize, and perform preliminary analysis on the velocity changes that occurred. These observations were reported above.

Assessing the response of the tip radii of curvature (i.e., the tip size) is a more difficult task, as the number of photographs, the time between photographs, and the optical quality of the images were not well tailored for quantifying the radius changes that occurred. This was particularly the case for dendrites grown at larger supercoolings and with smaller supercooling steps.

Despite these challenges, we did obtain sufficient data to verify the basic concept and approach, and to know how to set the parameters for future improvements in data acquisition. Based on a first sampling, we believe that the initial and final radii are different enough (under these conditions) to be measurable.

When measurable, the transient phase of R transpires in an exponential manner (at least for the larger tips with larger ΔT_{step}). Lastly, the duration of the transient appears to be a function of supercooling where the transition time ΔR is longer at lower ΔT_{mean}.

Additional higher quality data would enable us to measure how the interface shape evolves during the transient phase. We have no reason to expect that it will retain the same shape during the transition. In addition, the transient period as a function of ΔT_{step} and ΔT_{mean} should be measurable. For some growths, though not all, the transient is clearly identifiable and appears to be completed within the period of data acquisition, even when crudely measured using the initial data.

Simulations

The data presented here demonstrate the effectiveness of using pressure changes to influence the process of dendritic crystal growth. Here, we describe the results obtained from numerical simulations of the governing equations for heat transport during solidification of SCN. Our simulations start from an initially small spherical nucleus of supercritical size (i.e., unstable with respect to perturbations), onto which we

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add small random perturbations. The equation is the heat conduction equation, which is solved in both the liquid and solid phases.

The simulation is performed in a finite domain, where the external boundary is at any desired location and with a prescribed temperature that could arbitrarily be set to any value at any time during the simulation. The time-dependent calculations were performed using finite difference techniques and using the Triad Field Formalism (Pines et. al [12]). In this technique, the governing equations are mapped using three fields onto a fixed computational domain. The location of the dynamically evolving interface is solved as a part of the solution. The code uses highly efficient operator splitting techniques with arbitrary precision. The code was previously used and extensively tested against analytical results (where available) and experimental data from the IDGE experiment. The code incorporates adiabatic temperature changes and the Clapeyron effect for application to the TDSE research program.

We have explored several key features of the solution obtained from the numerical simulations of the experiment. We begin by imposing a pressurization/de-pressurization cycle of ca. 265 psi, with a time constant for the exponential pressure changes of 2 seconds. The supercooling was set to approximately 0.1 K. For this simulation, the tip position vs. time behaves similarly to the experimental data discussed previously.

It is evident that pressurization produces a faster tip velocity. An interesting feature is that the tip velocity changes to a higher value quickly at first, then decreases slightly, after which is slowly evolves to a final steady state. Additionally, there is a decrease in tip velocity upon de-pressurization. The down-pressurization does exhibit the slight over-response as did the up-pressurization, but then rapidly achieves its final steady state. The radius of curvature at the tip transitions is in accord with the supercooling conditions, but as seen experimentally, the change occurs even more slowly than the tip velocity. It is important to note that both the V and R values are in reasonable agreement with the experimental values from IDGE for the same level of supercooling. Additionally it should be noted that simulations performed starting with different random small perturbations always result in the same final steady values of R and V.

Discussion

Of interest are the hysteresis measured in the simulated values of V and R following the pressurization and de-pressurization cycle, and the lack of hysteresis in the Péclet number. Comparable experiments have not yet been performed, and thus we are not yet able to evaluate this simulation result, and may not until we can perform the appropriate experiments in a convection-free environment. In addition, the simulation although in agreement with some of the experimental data, is in disagreement with other experimental observations. Further analysis of these comparisons provides an opportunity to identify either aspects of the experimental configuration that are not being modeled, or aspects of solidification that are not being modeled.

We see additional agreements and disagrements when we compare both the traid field formulation simulation and the experimental data to phase field models of dendritic grorth of liquid crystals subject to pressure changes [13].

Future Efforts

The preliminary observations and comparisons that have been presented here demonstrate that there is much more to be learned by studying pressure-mediated dendritic growth. In reaching this end,

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experiments are being planned which will incorporate larger changes in supercooling (pressure), a wider range of average supercoolings, measurements of the characteristic length scales (tip radius of curvature), side branching characteristics, the influence of convection, and the process of single dendrite coarsening.

Acknowledgements
This work is supported by NASA's Microgravity Science and Application Division under contract number NAG8-1488, formally with liaison through A. Jackman, and D. Smith at NASA's Marshall Space Flight Center and now through B. Guynes and S. Paley, also at NASA's Marshall Space Flight Center.

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