Pressure-mediated effects on thermal dendrites

M.B. Koss¹, J.C. LaCombe²,⁎, A. Chait³, V. Pines³, M. Zlatkowsk³, M.E. Glicksman⁴, P. Kar⁵

¹Department of Physics, College of the Holy Cross, Worcester, MA 01610, USA
²Metallurgical and Materials Engineering, University of Nevada, Reno, Mail Stop 388, Reno, NV 89557, USA
³NASA Glenn Research Center, Cleveland, OH 44135, USA
⁴Materials Science and Engineering Department, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

Received 20 December 2004; accepted 4 February 2005
Available online 29 March 2005
Communicated by A.A. Chernov

Abstract

We subjected succinonitrile dendrites growing under steady-state conditions to a rapid change in thermal driving force through a step-change in pressure. This change in pressure caused a corresponding change in the equilibrium melting temperature due to the Clapeyron effect, and a shift in the temperature field due to an adiabatic temperature change in both the solid and its melt. The new thermal conditions caused the dendrites to transition from well-characterized initial steady states to states appropriate for the new operating conditions. The initial and final states are clearly discernable, but the onset of the change in tip radius lags behind the change in tip velocity even though the total transition times appear to be similar. During the transition, a fast growing, small dendrite emerges out of the tip of a slow growing, large dendrite. Lastely, the pressure changes appear to destabilize the interface, which leads to the initiation of a dominant side branch. This work constitutes evidence that pressure changes quantifiably change growth behavior and can be used as a perturbation to influence interfacial morphology in a well-characterized free dendritic growth system. This hints at how such a mechanism may be used to control growth microstructures.

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PACS: 68.70.+w; 81.30.Fb; 64.70.Dv

Keywords: A1. Crystal morphology; A1. Dendrites; A1. Interfaces; A1. Morphological stability

1. Introduction

A crystalline solid in contact with its melt will solidify by advancing the crystal–melt interface. The interface may remain relatively smooth and
featureless (stable) if the energy transfer occurs in
the direction that is through the solid. Additionally, the interface may develop (unstable) fingers,
cells, or dendrites that are all typical of instabilities
that can form during growth if the energy transfer
is through a supercooled liquid. The motion of the
interfacial front in the unstable-dendritic case is
governed by the interplay between two simple and
familiar processes: the irreversible diffusion of
thermal energy and the reversible work done in the
formation of new surface area via phase transfor-
mation.

Solidification environments encountered in ty-
pical metallurgical processes, such as casting and
welding, frequently provide conditions that result
in this (unstable) dendritic growth. The tree-like
structures that result (dendrites) are important
because their shape, size, and speed of growth lead
to an as-cast microstructure that profoundly
influences the materials eventual mechanical,
electrical, and chemical properties. Consequently,
it is necessary to understand the basic process of
dendritic growth in order to improve processing
conditions for optimization of solidification mi-
crostructures.

Over the past decade substantial progress has
been made in understanding many of the details of
single isothermal dendritic growth, especially in
regards to thermal diffusion. Nevertheless, there
remain some challenging scientific problems to be
solved with regards to interfacial stability, time-
dependent, and non-isothermal, multi-dendritic
growth, i.e., the complicated physics of dendrites
in the mushy zone.

The “mushy zone” formed during dendritic
solidification processes is the region where solidi-
fication is actively occurring, and the material is
part liquid, and part solid (hence the term “mushy
zone”). The activity in this zone is transient in
nature, and is critical to many industrial processes.
It consists of many dendrites, each growing in a
complicated non-isothermal manner, interacting
with its neighbors. Ultimately, it is desired to
understand this process in its entirety, but to reach
this goal, it is necessary to first understand fully
how individual dendrites form in isolated environ-
ments as well as those that more closely represent
the full complexities of a mushy zone (i.e., subject
to influence from surrounding dendrites). That is,
we need to bridge the gap between our under-
standing of an isolated isothermal dendrite and the
final, as-cast microstructure of metal and alloys.

To better understand the basic physics of
interfacial tip selection, stability, and time-depen-
dent non-isothermal dendritic growth we are
employing the relatively large Clapeyron pressure
effect in succinonitrile (SCN) [1]. A change in a
solidifying system’s hydrostatic pressure changes
the liquidus temperature, and thereby induces a
modification of the temperature gradients at the
interface. With this approach, we can measure the
kinetic behavior of isolated dendrites as they
evolve from one well-defined steady-state velocity
at an initial supercooling, through a transient
stage, to a different velocity at the altered pressure-
supercooling conditions. By using relatively fast
pressure changes (on the order of 2–4 s), the time-
scale for pressure-related changes in growth
behavior becomes well separated from the much
slower thermal time-scale for long-range energy
transfer. This then gives us the benefits of working
with isolated, well-characterized single dendrites,
but under non-isothermal and complicated, but
well-controlled dynamic conditions.

2. Background

2.1. Overview of issues in dendritic growth

The scientific discussion and description of
dendritic growth is commonly divided into two
related components: steady-state aspects and non-
steady-state aspects. This is due to the nature of
the various characteristic features of these complex
objects. For example, the tip region of a dendrite is
considered to be (largely) acting in steady state,
i.e., it can be defined by two measurable para-
eters that remain fairly constant during the
growth process: the radius of curvature at the
tip, \( R \), and the growth rate, \( V \). Other aspects that
are considered to be non-steady-state include the
side branch structure, which varies in time (in a
reference frame moving with the tip). All of these
parameters have been shown to scale with the
driving force of the process, the supercooling (or supersaturation) of the melt.

Unique predictions of the two measurable steady-state parameters (\(V\) and \(R\)) by both current theories of dendrite growth and large-scale numerical simulations of dendritic growth are usually composed of two independent components. The first concerns the transport of energy 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 combinations that are consistent with the energy transfer and conservation of energy at the solid–melt interface.

A full discussion of heat transfer and interfacial physics leading to unique \(V\) and \(R\) predictions is essentially a textbook topic, and is well described by Kurz and Fisher [2] in their graduate level text. We will recap briefly that textbook level discussion here as it provides a good starting model for launching a discussion of current issues.

The modern theory of dendritic growth began with Ivantsov, who treated the dendritic crystal as a paraboloid of revolution with a fixed radius of curvature, \(R\), growing at a constant velocity, \(V\). Ivantsov assumed that all the energy released by solidification diffuses away from the isothermal paraboloidal crystal–melt interface via the melt phase, and solved the related diffusion equation in co-moving paraboloidal coordinates, scaled by the only obvious length in the problem, the (unknown) tip radius of curvature. This yielded an equation for the growth Péclet number, \(Pe\) (\(Pe = VR/2\alpha\), where \(\alpha\) is the thermal diffusivity of the melt phase) as a function of dimensionless supercooling, \(\Delta\), where \(\Delta = c_p(T_m - T_\infty)/h_f\), \(T_m\) is the melting temperature, \(T_\infty\) is the temperature of the melt far from the interface, \(h_f\) is the molar latent heat of fusion, and \(c_p\) is the constant pressure, molar specific heat. As is well known, this transport solution provides an incomplete description of steady-state dendritic growth insofar as it specifies only \(Pe\) as a function of the \(\Delta\). That is, the individual observable experimental variables, \(V\) and \(R\), are not predicted uniquely.

As Langer pointed out in his seminal 1980 review article [3], much of the (then) recent history of the dendrite problem consisted of attempts to re-introduce a second independent length scale via surface energy capillarity. This led to the description of Langer and Muller-Krumbhaar's Marginal Stability Theory, which, via capillarity and the Mullins-Sekerka instability, provided the necessary second equation, \(2\pi d_0/(VR^2) = \sigma^*\), where \(\sigma^*\) is defined as a universal scaling or "selection" constant and \(d_0 = \Omega/c_p T_m h_f^2\) is the capillary length, where \(\Omega\) is the molar volume, and \(\gamma\) is the solid–liquid interfacial free energy. Thus, with \(Pe\) and \(\sigma^*\), one can solve simultaneously for a \(V\) and \(R\) that are the unique predictions of a steady-state dendritic growth theory, depending, in principle, only on \(\Delta T = T_m - T_\infty\), and a few material constants.

Important theoretical and experimental developments and commentary beyond the textbook level are presented by Langer in his review article [3], by Pelcé in his 1988 book [4], by Pomeau and Ben Amar in their chapter, in Godresche's book [5], and by most recently by Davis in his monograph [6]. The two most important storylines in dendritic growth theory contained in these references are the development of what is now called microscopic solvability theory (MST) as a solution to the Nash–Glicksman equation [7], and in the computation techniques of phase field modeling. This has lead to the crucial understanding that the anisotropy in surface energy acts as a singular perturbation that uniquely selects the tip radius of curvature and growth velocity. Phase field modeling recasts MST in a field theoretic language appropriate for a computational solution.

In practice, however, none of these theories or computation techniques at this time actually provide a zero-parameter basis for dendritic pattern selection. This is known because the predicted value of the scaling constant, \(\sigma^*\) is not the value of \(\sigma^*\) observed in experiments. Nevertheless, values for the scaling constant are generally calculated from measured growth data as a convenient way of classifying results from specific experiments.

Despite these theoretical advances, until as recently as 10 years ago, neither the energy transfer nor the interfacial selection aspects of theory were tested critically because of the effects of gravity-
induced convection (on the Earth), which modifies the transport processes, and alters the growth kinetics [8]. Several of the authors of this manuscript obtained benchmark data using SCN as a model material in an orbital, apparent microgravity environment where convective effects were essentially eliminated [9,10]. The data and subsequent analysis of $V$ and $R$ demonstrated that although the basic theories yield predictions that are in reasonable agreement with experiments, there were still several significant discrepancies. Some of the discrepancies can be understood by a careful consideration of the diffusion of energy from complex three-dimensional dendritic structure [11]. The data and analysis for assessing the interfacial physics are considerably less definitive.

The data and analysis from convection-free experiments on dendritic growth of pivalic acid (PVA) essentially confirm the SCN findings. PVA was selected for use as a second model material because it has many of the advantages of SCN in that it is transparent, well characterized, and melts at moderate temperatures—all of which make experimentation easier. In addition, PVA, despite having a smaller surface energy than SCN, has a surface energy anisotropy that is 10 times larger than in SCN. As surface energy anisotropy is a key parameter in current theories, PVA is a logical choice for experimental scrutiny. In addition, because of improvements in instrumentation, we were able to obtain 30 frame/s video data (though at low spatial resolution). Our subsequent analysis of these video data revealed several non-steady-state features—not only do convection-free PVA dendrites grow at a non-constant-average velocity, but the velocity varies continuously in a complex manner that is at least partially related to the dendrites side-branch generation [11,12].

These recent observations of the time-dependent aspects of dendritic growth add to the accepted importance of other observed time-dependent features (such as side branching). However, it is interesting to note that until recently, the majority of dendritic growth theories dealt mainly with the steady-state aspects of the growth process, despite the acknowledged importance of the side branching (owing to the perceived complexity of representing this analytically). The historical development of dendritic growth theory was built around the experimental observations that the tip region (without the constantly evolving side branches) is shape preserving in time, which lends itself for use as a simplifying assumption in models such as the Ivantsov theory. The Ivantsov theory has been generally validated by on-orbit convection-free experiments, and is considered a valid explanation of the energy transfer aspects of the process. This success has indirectly led to many subsequent expansions of the theory to also describe the process under the same underlying assumption of steady growth—despite the clear presence of significant time-dependent components of the process.

However, it appears that the paraboloidal dendrite tip is an anomaly in solidification phenomena. Other common solidification geometries (e.g., sphere, cylinder, plane, etc.) solidify into their pure melts a time-dependent manner. Even important regions of the dendrite itself (such as the side branches) grow in a transient manner. Later stages of dendritic solidification, such as coarsening, are also transient in nature, although for fundamentally different reasons. A natural question that arises in a comprehensive study of the dendritic solidification process is concerned with the appropriateness of the a priori assumption of steady-state conditions in selection theories. The observation (within experimental limits) of a steadily growing dendrite does not imply that the process is inherently steady. This is especially true for non-linear phenomena (to which the dendrite belongs), as well as to dynamic stability related processes that underlie the selection dynamics of a particular dendritic growth state.

This then calls for experimental data and methods to characterize important time-dependent and dynamic dendritic growth phenomena. The Clapeyron effect enables these types of investigations.

2.1.1. Background on the Clapeyron effect

The melting temperature of a material, $T_m$ is the temperature at which the liquid and solid phases co-exist in equilibrium. The melting temperature of a pure (bulk) material has a well-established value, which varies as a function of pressure—a
relationship that is commonly referred to as the Clapeyron effect. This effect is classical, and can be derived from general thermodynamic principles yielding the Clapeyron equation,

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

Here $\Delta T$ is the change in melting temperature resulting from a change in pressure, $\Delta P$, and $v_l$ and $v_s$ are the molar volumes of the liquid and solid phases, and $h_f$ is the molar latent heat of freezing [13]. As reflected in Eq. (1), the Clapeyron effect, $\Delta T/\Delta P$, can be calculated from a knowledge of $T_m$, $v_l$, $v_s$ and $h_f$. However, in practice, the experimental uncertainties in the determination of the specific molar volumes of the individual phases can lead to a significant uncertainty in the calculated dependence of the melting temperature on pressure, $\Delta T/\Delta P$. Therefore, we directly measured the Clapeyron effect in high-purity SCN by two independent techniques and determined that $\Delta T/\Delta P = 1.667 \pm 0.027 \text{mK/psi}$ [1].

While not entirely unknown in solidification science, the Clapeyron effect is usually assumed to be 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 case of SCN which has a Clapeyron effect that is many times larger than most metals and a unit supercooling ($h_f/c_p$) that is much smaller. Thus, the ratio of the Clapeyron effect to the unit supercooling forms a figure of merit that is 25–200 times larger for SCN than for typical metals. This sensitivity to pressure changes makes SCN very useful in the study of dendritic crystal growth, and thus makes its use central to the experiments proposed here (Fig. 1).

To calculate what that final supercooling is after a pressure change, one must also account for the influence of the adiabatic pressure–volume work done on the molten and solid SCN. From the combined first and second laws of thermodynamics, one can show [14] that the change in the melt temperature (or similarly, crystal temperature) with an adiabatic change in pressure is

$$\frac{\Delta T}{\Delta P} = \frac{\beta v T}{c_p},$$  \hspace{1cm} (2)

where $\beta$ is the isothermal compressibility, $v$ is the isothermal expansivity, $T$ is the temperature, and $c_p$ is the specific heat at constant pressure.

Fig. 1. Figure of merit for the importance of the Clapeyron effect on solidification formed by the ratio of the Clapeyron coefficient to the unit supercooling. The number in parenthesis is the figure of merit normalized to the figure of merit for SCN.
where $\beta$ is the coefficient of volume expansion (expansivity), $v$ is the specific volume, and $T$ is the temperature of the melt prior to the pressurization. If we assume that $\beta$ is independent of pressure and that $c_p$ is independent of temperature, then Eq. (2) yields $0.911 \pm 0.034 \text{mK/psi}$ for molten SCN. This compares well with an average experimentally derived value of $0.871 \pm 0.007 \text{mK/psi}$. Thus, when the pressure is raised, the melting temperature also rises in accordance with the Clapeyron effect, but the temperature of system is also raised uniformly due to the adiabatic response. The net change in supercooling is therefore the Clapeyron effect minus the adiabatic response, which yields approximately $0.796 \text{mK/psi}$. If the pressure is lowered, the reverse changes take place, also yielding a net supercooling response of $-0.796 \text{mK/psi}$. Both of these modes of operation can readily be applied in experimental practice.

2.1.2. The Clapeyron effect and dendritic growth

This paper demonstrates how to employ the Clapeyron effect to intervene during a dendritic solidification process and rapidly change the total supercooling (free energy). Use of the Clapeyron effect to rapidly and accurately change the growth environment of a dendrite in a repeatable and observable manner has great promise to advance our understanding of microstructure evolution, liquid–solid phase transitions, and interfacial effects, all key components of dendrites in the mushy zone.

This is a novel approach to modifying solidification processes, which are conventionally governed through thermal boundary conditions, and have characteristically slow thermal response times. With the Clapeyron effect, we can initiate a rapid change in the driving “force” and then observe and measure the kinetics and morphology of the resulting isolated dendrite, as it evolves from a well-defined initial steady-state, through a transient stage, to a different, well-defined, final steady-state. While this type of experiment can serve as a baseline model for many of the conditions that dendrites are subject to in more complex casting processes, for scientific purposes, it is very useful to study single dendrites (i.e., the process is simpler).

When applied to the well-defined conditions of an isolated dendrite growing under nominally “steady-state” conditions, a rapid change to the supercooling allows acquisition of data describing the non-steady-state dendritic growth kinetics as a function of the initial and final states. That is, when faced with a step-change in the driving force, a dendrite needs to respond by eventually adopting a new steady state that is appropriate to the new supercooling ($\Delta T_f$). A broad variety of experimental permutations can be investigated to explore the growth kinetics, including studies of the end-point supercoolings (initial, final), the pressure change magnitude and sign, superheating of the melt, coarsening (i.e., $\Delta T_f = 0$), and hysteresis behaviors.

Broadly construed, in the long run we advocate and plan on capturing unique data on two lines of inquiry. We will investigate both fundamental issues in dendritic solidification and how dendrites respond to external stimuli. More specifically, the dynamic data on transient and non-steady-state behavior will confirm and extend the science of the now well-understood thermal effects, and provide critical insight into interfacial dynamics and tip selection where important open questions remain. The analysis on interfacial dynamics addresses directly the physics of selection. As compared to the physics of energy transfer in dendritic growth, much less is known of this process. In addition, by focusing on transient effects during the growth of isolated dendrites, we examine in a repeatable and controlled way, the physics of the mushy zone, where dendrites are constantly being subjected to changing conditions. In the mushy zone, a full understanding of dendritic growth and energy transfer is important, but not sufficient, as the dendrite must constantly re-adjust to the ever-changing environment, and thus is constantly changing its tip growth velocity, radius of curvature, and other growth characteristics with respect to the thermal conditions.

In the short term, the results of this paper form an experimental confirmation and proof of concept that the Clapeyron effect can be employed as hypothesized, and includes preliminary results from the technique as well.
Experimental work by others that have employed a type of rapid temperature change and observed the response of a dendrite include the use of heating the tip region of a dendrite with a modulated laser beam, or providing fluid flow changes near the solid–liquid interface [15–17]. The major experimental challenge in measuring and analyzing transient and non-steady-state dendritic behavior is that it is difficult to repeat or characterize the initial and final conditions from which, and/or to which, a dendrite evolves.

The proposed experiments in SCN described here attempt to obviate this difficulty by causing the transient or non-steady-state transition to occur between two well-characterized and repeatable sets of conditions. Sawada et al. [18,19] have previously shown that pressure can be used to control solubility, while Börzsönyi et al. [20,21] have both grown 2-D dendrites in a liquid crystal, and simulated this growth with a phase field model, with oscillating pressure conditions.

Somboonsuk and Trivedi [22] have performed directional solidification experiments where a steady-state $V$ and $R$ were established, then the velocity was increased to a new steady-state value, and then returned to the original steady-state value. In doing this they established the uniqueness of the tip radius as the final steady-state radius was the same as the initial. Unlike the SCN experiments described here, the control parameter is the velocity and not the supercooling. The results reported here thus advance and add to these earlier studies with the detailed experimental observations of free (3-D) dendritic growth in pure SCN—a frequently and well-studied dendritic crystal forming system, subject to a step change in pressure.

3. Experimental apparatus and procedures

The experiments described here were conducted with the experimental apparatus, with pressure control added, used to study dendritic growth of SCN and pivalic acid (PVA) previously described [10]. Detailed information describing the apparatus can be found there. The apparatus is centered about the sample material contained within a windowed stainless steel growth chamber placed within a temperature-controlled bath. The growth chamber interior volume (approx 2” to a side) mechanically 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 is achieved through the use of a hollow stinger tube that penetrates the wall of the growth chamber. The exterior end of the stinger tube is capped and surrounded by a thermoelectric cooler. The interior end is open, allowing the sample material in the chamber to also fill the stinger.

During the operation of the experiment, each dendritic growth cycle begins by completely melting the SCN, followed by lowering the melt’s temperature to the desired supercooling at the chosen initial pressure. After the melt temperature reaches the target supercooling, the thermoelectric cooler is activated. This nucleates a small crystal in the end of the stinger, which then propagates down the stinger tube and emerges into the chamber as a freely growing dendrite. After the dendrite achieves steady-state growth, the hydrostatic pressure of the surrounding thermal bath is changed via a pneumatically operated piston. The typical monotonic, exponential, smooth pressure increase or decrease usually takes approximately 3–4 s, but sometimes much longer, and in the present apparatus is not a well-controlled parameter.

The dendrite is observed as it evolves away from its initial state and, if time and conditions permit, acquires a new set of steady-state characteristics consistent with the new operating conditions. Once one of these growth cycles is completed, a new growth cycle is initiated by raising the temperature of the bath, melting the sample, and proceeding as described above by setting a target supercooling. During the preliminary tests described here, this arrangement produced dendritic crystals grown with the bath’s steady-state temperature measured to within 0.002 K both spatially and temporally.

During these growth cycles, once a crystal emerged from the stinger, images of the dendrites were obtained from two perpendicular views using electronic cameras, which provide the minimum
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 × 480 pixels (256 gray-scale levels) and an imaging rate of approximately 30 frames/s (30 Hz).

The data presented here from the 30 fps video cameras has an optical resolution that is related to the base size of an individual pixel in the video cameras imaging array. Each pixel, after correcting for the magnification of the optical system, images a region of the growth chamber that is approximately 22.1 µm high and 21.5 µm wide. These values also constitute the raw measurement precision for the tip position data. It is necessary to improve upon this precision by applying a statistically based sub-pixel resolution image analysis method to each image in the growth cycle.

Using this system, dendrite tip locations were obtained as a function of time (which leads to the growth rate, $V$). Uncertainty in the measured tip positions, at present, is approximately 2 µm, which is considerably less than the pixel size of 22 µm. [23]. The analysis of 35 mm film data (higher resolution than the video data) was handled in close accordance to the techniques and procedures developed for previous experiments [10].

The initial, proof-of-concept experiments described above were conducted for a variety of initial supercoolings with supercooling changes, $\Delta T_{\text{step}}$, limited to ±90 mK, as a greater supercooling change would have required a pressure change that would have damaged the temperature control tank. What follows is typical of what we observed.
An increase in hydrostatic pressure raises the interface’s equilibrium temperature, and thus increases the supercooling that drives the solidification process. The dendrite tip position as a function of time is the primary measured data in these experiments (Fig. 2). In the case where $\Delta T_i = 0.79\,\text{K}$ and $\Delta T_f = 0.87\,\text{K}$, the velocity of this growth (i.e. the slope) is indeed observed to increase after the pressure change from 134 to 161 $\mu\text{m/s}$. This confirms the general feasibility of the experimental procedure. Both the initial and final velocities are consistent with what would be expected given the initial and final supercoolings (based on earlier measurements [10]).

A careful examination of the transition region seems to indicate that before the transition from an initial low velocity to a final higher velocity, the dendrite had a short transient during which it initially slowed. This conclusion is incorrect as the observed short initial transient is caused by the flexure of an as-yet unidentified component of the apparatus where the stinger tip (which should be in a fixed position) moves approximately 0.4 $\mu\text{m}$ per psi of pressure change. We are currently designing a growth chamber where this is addressed, but for the data under discussion here, we need to simply eliminate the few seconds of tip position/velocity data corrupted by the hardware flexure during the pressure change.

Although the tip position as a function of time is the primary measured data, it is useful to convert this information directly into dendrite tip growth velocity. However, 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.

Because of the limited number of images from the photographic data set, some of the examination of the transition region is better accomplished by an examination of the video data. Clearly, limitations due to the spatial resolving capability of the current experimental setup prevent accurate, scaled measurements of the tip radius of curvature directly from video images. To be sure, this method suffers from the lower spatial resolution of the video as compared to the 35mm film, but still permits a more complete time characterization of the key experimental parameters, $V$ and $R$, as they evolve and transition from the initial steady-state, and subsequently the evolution of key dendritic growth parameters such as the Péclet number, $Pe$, and the scaling constant, $\sigma^*$. However, in the end, the apparatus described and modified for larger pressure steps, combined with the developed data reduction techniques, allows us to observe the instantaneous and moving average velocity of the tip, and an approximate tip radius of curvature, at 30fps.

4. Results and discussion

4.1. Experimental results and discussion

We report now on a preliminary set of measurements from a data run with relatively large pressure changes (290 psi), obtained using a modified pressure-hardened thermal control tank. This produced a supercooling change of approximately 0.250 mK.

These techniques applied to the growth cycles described above yield the tip radius of curvature, the tip velocity, and the pressure, all as a function of time (Fig. 3). The units of tip radius are “arbitrary” since the methodology is still being validated (and do not precisely agree with the radii results from photographic data), but the time variation of $R$ is valid. In addition, the temperature of the growth chamber itself, and the temperature of the surrounding bath do not change equally to that of SCN (due to different expansivity), which sets up a temperature difference between the sample and its surroundings that the temperature control cannot address quickly. Currently, this lack of control of the far-field temperature may limit these experiments to more of how the dendrite “departs from the initial state”, rather than a rigorous observation on how it “approaches the new steady state”. Never-
theless, this potential limitation has not precluded several novel observations from these experiments.

In these data the initial and final states are clearly identifiable. Most importantly, the tip velocity is observed to respond much more quickly to pressure change than the tip radius data. In fact, the transition in velocity appears to be almost complete before the radius even begins to change. Furthermore, visual examination of $V(t)$ in this case is somewhat ambiguous, but suggests that the time to approach the new steady state is anywhere from as fast as the pressure changes to approximately 10 s. Similar visual examination of $R(t)$ indicates time constants for approaching the new steady state of approximately 10–15 s, at best approximately the same as the velocity transition time or longer, in addition to the clear and unmistakable delay in the radius’ transition.

Prior to the initial testing of the system, we had no established estimate of the time scale involved for the dendrite to respond to a change in its environment. Therefore we sampled the transition using the standard video at 30 fps. This turned out to be more than sufficient. Given the current apparatus and pressure change method, flexure of the pressurized thermal tank, and for the range of

![Dendrite tip radius of curvature (in arbitrary units) and tip velocity as a function of time.](image)

Fig. 3. Dendrite tip radius of curvature (in arbitrary units) and tip velocity as a function of time. The velocity data during the 6s of pressure change is not available, as the entire frame of reference moves as the pressure changes. The velocity appears to immediately begin to change on pressurization whereas the radius does not even begin to change until several seconds after the pressure change is complete.
supercoolings and pressure change magnitudes sampled so far, we conclude that the characteristic time necessary to re-acquire a new steady-state velocity cannot be fully determined because in many cases it was seen to keep pace with the pressure change itself. The fastest pressure change we were able to induce was approximately 0.4 s, which serves as a lower bound to the velocity transition time. The radius changes however are readily apparent—even with the low spatial resolution. In the long term, the transient period for both $V$ and $R$ as a function of $\Delta T_{\text{step}}$ and $\Delta T_{\text{mean}}$ or $\Delta T_i$ and $\Delta T_f$ should be measurable, and we have begun to examine these transition times [24].

Although the change in tip radius with pressure change is evident even in the low spatial resolution video images (Fig. 4), additional higher quality data is necessary to enable us to determine how the interface shape evolves during the transient phase. However, precise quantitative measurements are especially difficult in this regime because during transition, there is insufficient morphological change to fully quantify the qualitative changes that are readily observed by eye over the short time period when the radius changes most rapidly. Furthermore, there is no reason to expect that the dendrite will retain the same shape during the transition (e.g. paraboloidal, etc.). Thus, the difficulty in improving this quantitative measurement as the dendrite in transition goes well beyond the spatial resolution of the image as the dendrite forms a sort of dendritic chimera (a mythological beast with the head of a lion and the

![Fig. 4. Time sequence of video images (time sequence increasing from a to d). Even at this resolution, the change in tip size is readily apparent. In addition, a dominant side-branch eventually emerges from the spot on the dendrite pointed out by the arrow.](image)
body of a goat or an imaginary monster made of incongruent parts) where we see the head of a small-tipped fast-growing dendrite attached to the body of a large-tipped slow-growing dendrite (Fig. 5).

This is best seen in the series of four dendrite edges extracted from photographs exposed every 14.5 s (Fig. 6). The first two profiles at $t = 0$ and 14.5 s, are of tip radii of 46.8 and 46.5 $\mu$m, respectively, both recorded at a supercooling of $\approx 0.25$ K, and prior to any change in pressure, growing with a tip interface velocity of $\approx 18$ $\mu$m/s. At $t \approx 22–24$ s, the pressure changes to $\approx 294$ psi, which changes the supercooling to $\approx 0.5$ K. At $t = 29$ s, about 5 s after the completion of the pressure change, the interface is slightly more advanced than it would have been without the change, and the tip radius of curvature is about 31.9 $\mu$m. At $t = 43.5$ s, the tip radius has become 28.7 $\mu$m, and the tip velocity is 50 to $60 \mu$m/s as the far-field temperature of the thermal bath drifts so that the supercooling is between 0.5 and 0.6 K. Although by the time the first high spatial resolution photograph after the pressure change has been recorded (Fig. 5), much of the transition has occurred unobserved. The first post-pressure photograph makes clear that even 5 s after the conclusion of the pressure change, the dendrite is still in transition, and forms the chimera. Despite this limitation, the time lapse series of dendritic interfaces successfully shows both the velocity transition and the tip radius of curvature transition, while explicitly showing the evolving shape of the dendrite during the transition. Most notable is the emergence of a dominant side-branch correlated to the location of the tip when the pressure was changed.

Lastly we note that the appearance of a dominant side branch (Fig. 6), which apparently was instigated by the pressure change that created the transition. The initial appearance of this dominant side-branch (Figs. 4b–d and 6 show that it emerges eventually from just above the
location of the dendrite tip position when the pressure was changed. As side branching is a highly non-linear phenomena, it suggests the potential for using pressure changes not only as a means to better understand the phenomena of interfacial stability, sidebranch formation, and the so-called “selection” process in dendritic growth theory, but perhaps also as a way to actually engineer microstructure in practical engineering alloys.
4.2. Modeling results and discussion

In this section we compare our experimental results to time-dependent simulation calculations performed using finite difference techniques via the Triad Field Formalism of three of the authors of this paper [25]. In this technique, the governing equations, including a time-dependent Clapeyron effect and the adiabatic temperature change, are mapped using three fields onto a fixed computational domain. The location of the dynamically evolving interface is 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 previous dendritic growth experiments.

Sample results of this numerical model are presented here depicting the tip velocity as a function of time during pressurization and depressurization events (Fig. 7). An interesting feature is that the tip velocity changes quickly at first, then decreases slightly, after which it slowly evolves to a final steady state. Additionally, there is a decrease in tip velocity upon down-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 of the tip (Fig. 8) transition is in accord with the supercooling conditions, but as seen experimentally, the change occurs even more slowly than the tip velocity. The steady state $V$ and $R$ values from this model are in reasonable agreement with the experimental values from previous diffusion limited dendritic growth experiments for the same level of supercooling. The product of $R$ and $V$ as expressed by the Péclet number can be calculated from this, or other simulation conditions (Fig. 9). It is evident that the Péclet number too reaches a constant value, which incidentally, compares well enough with the value calculated from the Ivantsov theory (corrected for wall effects) or directly from the diffusion limited dendritic growth data. Whereas the simulation predicted hysteresis for the simulated values of $V$ and $R$ in the pressurization and de-pressurization cycle, the simulation predicted a lack of hysteresis in the Péclet number. Comparable experiments have not yet been performed, and are not yet possible with the current apparatus.

\[ \Delta T_{\text{init}} = 0.142 \text{ K}, \Delta T_{\text{fin}} = 0.32 \text{ K}, t_p = 2 \text{ sec} \]

Fig. 9. Péclet number as a function of time predicted by Triad field numerical model. Pressurization at ~295 s, and depressurization at ~380 s. Note the predicted lack of hysteresis in the Péclet number despite that both the tip velocity and tip radius had significant hysteresis.
Despite the good agreement with some of the experimental data, the model is still in disagreement with other experimental observations. Further analysis of these comparisons provides an opportunity to identify whether aspects of the experimental configuration are not being modeled, or aspects of solidification process itself are not being modeled. The Ivantsov theory for heat transfer is still obeyed as evidenced by the constancy of the Pe’clet number when the supercooling level return to its previous value.

We also note that Börzsönyi et al. [20,21], have performed phase field calculations of dendritic solidification of liquid crystals subject to step-wise pressure changes. However, both the phase field model and the Triad field formulation predict the over-response in velocity that we do not see experimentally, though the two models differ after that over-response. We are therefore forced to conclude that neither the Triad field formulation nor the phase field model contain all the proper physics influencing the interface, and that there are important differences between the two simulation models. That admission aside, the key question remains as to what interfacial physics need to be included in a model to understand the experimental data, or to simulate nature properly with respect to predicting how thermal dendrites depart from and approach steady-state growth.

5. Conclusions

We have conducted experiments and performed analysis that demonstrates that moderate pressure changes create measurable differences in both the growth rate, $V$, and the tip radius of curvature, $R$. Furthermore, the time it takes for the radii to begin to move away from one steady state or to re-acquire a new steady state was observed to lag behind the transition in velocity, which appears to keep pace with the pressure change itself.

Based on the above-described combination of film, and video analyses, we have demonstrated the basic feasibility of using pressure via the Clapeyron effect to study transient and non-steady-state effects in dendritic growth, particularly in the physics of tip selection. Modeling efforts that have been conducted to support these experiments are able to describe some aspects of the growth process, but not all. Additional experiments are needed to elucidate the shortcomings of the model, and changes in the physics included in the model are needed so that the model can better match the data.

Lastly, the observations presented here suggest the potential for using pressure change not only to better understand the phenomena of interfacial stability, side-branch formation, and the so-called “selection” process in dendritic growth theory, but also as a way to use pressure steps or oscillations to control or engineer dendritic microstructures as shown by the emergence of a dominant side-branch from the location of the tip when the pressure change is applied. At present, we are undertaking such applied efforts.

Acknowledgements

This work was supported by NASA’s Physical Sciences Research Division (Code UG) under contract number NAG8-1756, with liaison through the Microgravity Research Program at NASA’s Marshall Space Flight Center with supplemental support from The Nevada Space Grant Consortium and NASA under award number NNM04AA22G. For assistance with this work, we thank T.K. Pendergrass, and A. Jackman, at NASA’s Marshall Space Flight Center, D. Malarik, D. Schrage, J. Ogrin and J. McDade, at NASA’s Glenn Research Center, and Peter Staffier, Bill Bukala, Stefanie Carrabba, and Dave Reis, at the College of the Holy Cross.

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