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THE TRANSIENT DENDRITIC SOLIDIFICATION EXPERIMENT (TDSE)

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Dendritic solidification is a common mode of solidification. It is also an important model problem in non-equilibrium physics and pattern formation physics. Current theories couple the transfer of latent heat with selection mechanisms at the interface. Measurements of succinonitrile (SCN) dendrites in microgravity show reasonable agreement between heat transfer predictions and experiment. However, data and analysis for assessing interfacial physics theories are less definitive. We are studying, and will present data on, transient effects in dendritic growth of SCN. We employ the Clapeyron pressure/melting temperature effect to make a rapid change in a sample's hydrostatic pressure, and thereby rapidly change the specimen's melting temperature, forcing the dendrite to select a new steady-state. These initial measurements show some surprising and non-intuitive effects.

I. Introduction

Dendritic solidification is a well-studied model problem in the fields of pattern formation, non-equilibrium physics, and computational condensed matter and material physics. There is also considerable engineering interest in dendrites because of the role they play in the determination of microstructures in cast materials, which in turn influence a material's physical properties [1].

Most theories of dendrite crystal formation consist of two components [2, 3], 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 such possibilities that are consistent with transport and conservation of energy at the crystal-melt interface. Until recently, neither of these two aspects 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 [4].

II. Background

Benchmark data consisting of dendritic tip growth speed and radii of curvature were obtained for succinonitrile (SCN) dendrites grown in a convection-free microgravity environment. Analysis shows that although the theory yields predictions that are in reasonable agreement with the experiment, there were significant discrepancies observed, particularly in assessing interfacial pattern selection [4].

As a follow-up to the microgravity experiments, we are investigating transient and time-dependent dendritic growth by employing the relatively large Clapeyron pressure effect in SCN [5]. A change in a solidifying system's hydrostatic pressure changes the liquidus temperature, and induces a change in the

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temperature gradients at the interface. With this approach, the kinetics of isolated dendrites were measured as they evolved from one well-defined steady-state velocity, at the initial supercooling, through a transient stage, to a final well-defined steady-state velocity at the altered pressure-supercooling state. By using fast pressure changes, the time-scale for pressure-related changes in growth behavior becomes well separated from the much slower thermal time-scale for long-range heat transfer.

The equilibrium melting temperature T_m is the temperature at which the liquid and solid phases co-exist in equilibrium for some specified pressure. For most materials that contract on melting (the well-known exceptions being water and silicon), increased pressure favors the crystalline phase, as atoms or molecules are squeezed (on average), slightly closer together. This effect is classical, and can be derived from general thermodynamic principles and is known as the Clapeyron equation [6].

As such, the Clapeyron effect is well known in solidification science and for example 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 may be a reasonable assumption for many materials, but in the unusual case of SCN, that has a Clapeyron effect of 24.5±0.5 mK/atm [5], it is not. The Clapeyron effect in SCN is many times larger than in most metals, moreover the characteristic supercooling of ~23 K 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. The large Clapeyron effect and the small characteristic supercooling may be exploited in a straightforward manner to effect fast changes in SCN's crystal-melt equilibrium temperature. Changing the interfacial temperature relative to the surrounding melt temperature changes the supercooling. This allows acquisition of non-steady-state dendritic growth kinetics, and permits observations during the transient evolution of the morphology between steady states.

When the pressure-mediated melting temperature change is carried out for an isolated dendrite growing at steady state under the initial supercooling, the dendrite responds by eventually adopting a new steady-state that is appropriate to the new supercooling. To calculate the final supercooling properly, one must also account for the influence of any pressure-volume work done throughout the adiabatic crystal/melt system. From the combined first and second laws of thermodynamics, the effect can be calculated. For SCN, the adiabatic temperature change has been measured to be 12.81±0.03 mK/atm, which is in reasonable agreement with calculation [7].

III. Experiment Description

The experiments reported here used the ground-based hardware built and used originally in the above-mentioned, convection-free microgravity study of dendritic growth [4]. The experimental apparatus surrounded the sample material, contained by a glass and stainless steel growth chamber, located within a precision (± 2mK) temperature-controlled bath. The growth chamber interior volume communicated with the bath via a stainless steel bellows, permitting the pressure field 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 well-isolated 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, measured to within

0.001 K spatially and temporally. 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 which was recorded using video equipment. Upon achieving steady state growth, the hydrostatic pressure of the surrounding thermal bath was changed suddenly via a pneumatically operated piston. The typical monotonic, exponential, smooth pressure took *ca.* 0.2s, whereas a comparable decrease took *ca.* 0.4s. The pressure was immediately transmitted to the sample via the bellows, causing a change in the final operating state of the dendrite.

Once a crystal emerged from the stinger, images of the dendrites were obtained from two perpendicular views using electronic cameras with an imaging chip array of 640 x 480 pixels, 256 gray-scale levels, at a magnification of 0.46 and a storage rate of approximately 30 frames per second. Each pixel images a region of the growth chamber that is 22.15 µm high and 21.52 µm wide, however image processing and analysis techniques allowed us to locate the position of the dendrite tip to a resolution of approximately 2 microns (~1/10 pixel). This approach does not attempt locating the crystal-melt interface at the tip. Instead, it uses additional image data to obtain a consistent reference with respect to the dendrite that serves to track the dendrite's advance over time.

IV. Experiment Results

The experiments described above were conducted for two pressure change magnitudes, with both increases and decreases, for a variety of initial supercooling levels between 0.9 and 0.3 K. An increase in hydrostatic pressure is expected to result in an increase in the interface's equilibrium temperature, an increase in the far field temperature, and a net increase in supercooling — resulting in an increase in the temperature gradient which enhances the solidification process. Using a pressure increase of 6.6 atm (applied within the initial steady state), the growth rate does indeed increase as expected from 15.3 µm/s to 26.0 µm/s. However, if the period of time immediately after the pressure change is examined more closely, it becomes apparent that prior to the overall increase in growth rate, the dendrite actually first slows down, and in this case, momentarily melts back.

Although the melt-back of the interface was observed in several growths with pressure increases, it was not universal. In a growth with $\Delta T_{init} = 0.58$ K and a larger initial velocity of 67.7 µm/s, there was a change to $\Delta T_{fin}=0.63$ K, and a final velocity of 84.0 µm/s after a pressure increase of 4.2 atm. But, in the transient period immediately after the pressure increase, the dendrite only slows down, never quite melting back prior to accelerating to its eventual higher final speed. The initial decrease in velocity before the final increase is however, consistent for all cycles with pressure increases regardless of the initial velocity.

The comparison and examination of the transition region is best accomplished by an examination of the instantaneous and moving average velocity. For an increase in pressure of 6.6 atm, the velocity drops momentarily, prior to approaching the final, higher value (Figure 1). For a pressure drop of 6.8 atm, (Figure 2), we see precisely the reverse situation. In this case, the intermediate transient is evident through a brief, unexpected rise in velocity.

For the investigated range of supercoolings and pressure changes, the characteristic time necessary to re-acquire the new steady-state velocity was quantified by the time needed for the residuals from a linear fit of the displacement data to decrease to 37% of their initial magnitude (at the onset of the

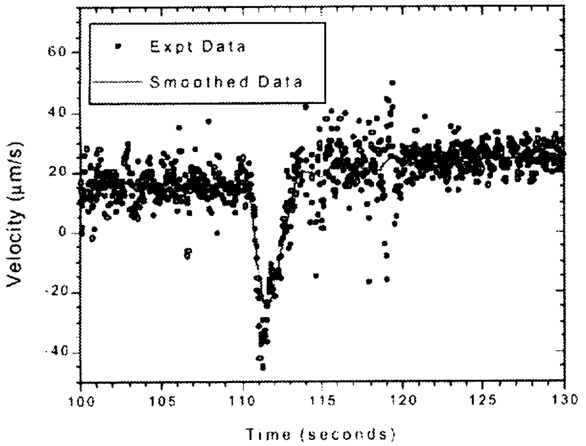

Figure 1. Velocity vs. time plot for pressure increase that causes a supercooling increase from $\Delta T_{init} = 0.25$ K to $\Delta T_{init} = 0.33$ K.

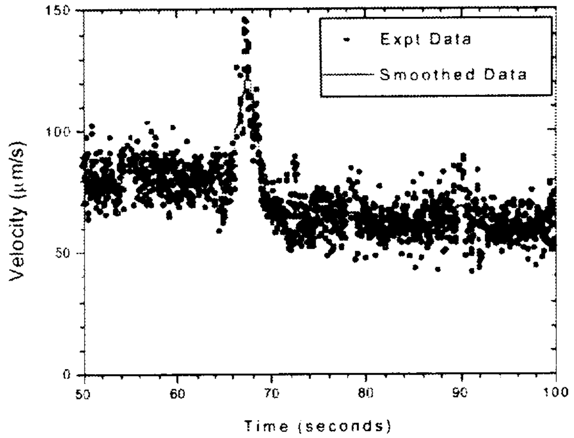

Figure 2. Velocity vs. time plot for pressure decrease that caused a supercooling decrease from $\Delta T_{init} = 0.60$ K to $\Delta T_{init} = 0.52$ K.

transient). In these experiments, this time was observed to be on the order of two seconds and was independent of both the mean supercooling and the change in supercooling linked to the change in pressure.

V. Simulation Results

We have explored several key features of the solution obtained from the numerical simulations of the experiment. The time-dependent calculations were performed using finite difference techniques and using the Triad Field Formalism (Pines *et. al* [8]). 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 verses time (Figure 3) behaves similarly to the experimental data discussed previously. It is evident that pressurization produces a faster tip velocity (the slope of the line). An interesting feature is that the tip velocity changes to a higher value 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 de-pressurization. The down-pressurization does exhibit the slight over-response as did the up-pressurization, but then rapidly achieves its final steady state.

VI. Discussion

While the simulations are in agreement with some of the experimental data, it is in disagreement with the key experimental observation of the meltback. The initial reversal effect we report above after fast pressure changes has to our knowledge not been observed previously, not observed in our initial simulations, nor was this effect noted by Börzsönyi *et al.* [9], who performed phase-field calculations of dendritic solidification of liquid crystals subject to step-wise pressure oscillations.

In the experiments, for the case of down pressurization, the general form of the local temperature gradients appears to change so that the net heat flux is into the interface. The pressurization change was monotonic and therefore, is not the cause of the net flux into the interface. Additionally, the characteristic time of the velocity transient is seen to be largely insensitive to the supercooling regime.

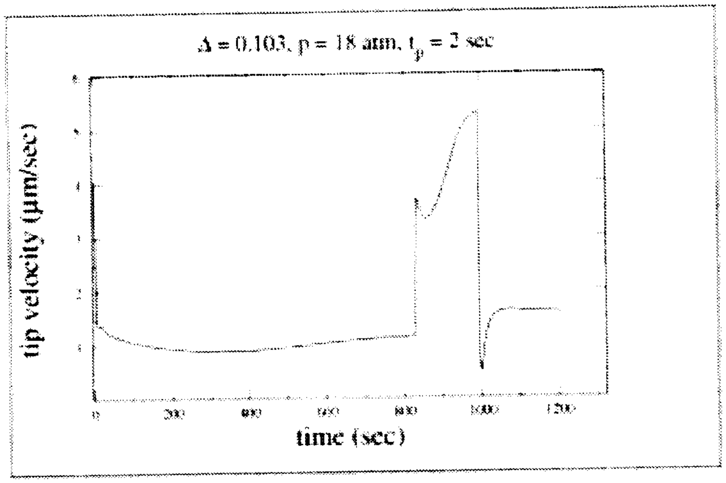

Figure 3. Velocity vs. time plot for a pressure increase of 264 psi from an initial supercooling of $\Delta T_{init} = 0.103$ K over 2 seconds, followed by a pressure drop of 264 psi.

In trying to explain this newly observed phenomena, we note that in principle, dendritic solidification is always a non-equilibrium process. In practice, dendritic growth and many other solidification processes are successfully treated as "quasi-equilibrium" processes, where the "local equilibrium" melting temperature has proven to be a useful physical construct. We suggest that the local equilibrium of the interface may in fact be violated. Thus the Clapeyron and adiabatic effects take place essentially instantly, while the interface temperature follows that of the adjacent solid and liquid. Here, the interface is not at the equilibrium temperature, but is being driven to it during the subsequent growth process, and this yields the melt back or slowing down. Thus, our observations suggest that this conventional approach does not suit the careful experiments described herein during the early transition from an initial steady-state.

This proposed scenario is phenomenological. We offer here a specific mechanism to understand how this occurs based on a non-equilibrium Clapeyron effect where the ability of a phase to accommodate molecules from the other phase can be very different. To illustrate this non-equilibrium process, we used the previously discussed transient solidification simulation code, with the added physical description of a non-equilibrium Clapeyron coefficient. In these simulations, the relaxation time constant, τ, was fixed at 1.6 seconds for two different pressurization-depressurization cycles using characteristic times for the pressure application of t_p,= 0.2 and 2 seconds. For these simulations, the tip displacement with time varies with different pressurization rates. The important observation is that, in this model, the short-term behavior (slowing down or growth reversal) is clearly present. This reversal, depending on the simulation pressurization rate, occurs even though the final steady state velocity is independent of the pressurization rate (Figure 4). This behavior is consistent with experimental observations to date in that it both eliminated the rapid increase and over response with the proper reverse in velocity, and the total time for the achievement of the new steady-state is decreased to reasonable agreement with the experiment.

VII. Conclusions

The observed transient phenomena described above were not part of the TDSE's original scientific objectives. Instead, they constitute important early findings of both the experimental and modeling components of this effort. Additionally, preliminary investigation indicates that although this intermediate-transient behavior reveals a new, fundamental kinetic effect in dendritic growth processes. Further-

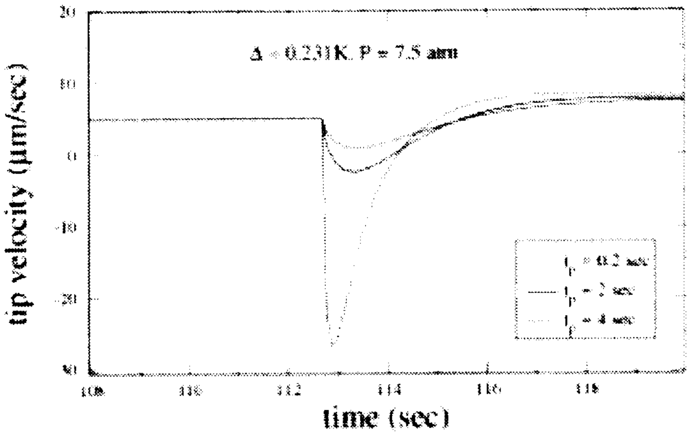

Figure 4. Velocity verses time plot for a pressure increase of 110 psi from an initial supercooling of $\Delta T_{init} = 0.231$ K over 4.0, 2.0, and 0.2 seconds, respectively.

more, this interfacial effect has much broader concerns to solidification in that it may also apply to non dendritic solidification phenomena.

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