THE TRANSIENT DENDRITIC SOLIDIFICATION EXPERIMENT (TDSE)

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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. As most researchers on dendritic growth invariably note, there is considerable engineering interest in dendrites because of the role dendrites play in the determination of physical properties of cast materials. In addition, dendritic solidification has become a well-studied model in non-equilibrium physics, and computational condensed matter material physics [1].

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 combinations that are consistent with the heat transfer and conservation of energy at the solid-melt interface. Until recently, neither aspect of the theory could be tested critically on the earth because of the effects of gravity-induced convection, which modifies the transport processes, and alters the growth kinetics [2,3].

Benchmark data were obtained in microgravity from two flights of the Isothermal Dendritic Growth Experiment (IDGE), using succinonitrile (SCN) [4-9]. SCN is an organic material which acts as a BCC metal analog. The data and subsequent analysis on the dendritic tip growth speed and radii of SCN dendrites demonstrated that although the theory yields predictions that are reasonably in agreement with the results of 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. 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 Transient Dendritic Solidification Experiment (TDSE) attempts to study fundamental aspects of time-dependent growth, while retaining the advantages of working with a single, isolated dendrite. The TDSE will also attempt to acquire benchmark microgravity data, and provide analyses on transient and time-dependent dendritic growth by employing the effect of the relatively large Clapeyron pressure-mediated melting temperature effect in SCN. A fast change in a sample's hydrostatic pressure quickly changes its liquidus temperature, and thereby provides either more or less free energy or supercooling. With this approach, we plan to observe and measure the kinetics and morphology of isolated dendrites as they evolves from one well-defined steady-state, at a pre-set supercooling, through a transient stage, to a new well-defined steady-state at the altered pressure/supercooling state.

The Clapeyron Effect

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. Therefore, an increase in pressure does work on the solid, and raises its stability and melting temperature. This effect is classical, and can be derived from general thermodynamic principles yielding the Clapeyron equation,

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

where ΔT is the change in melting temperature resulting from a change in pressure, ΔP, and v_l and v_s are the specific volumes of the liquid and solid phases, and h_f is the latent heat [10].

In principle, 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 volumes of the individual phases often leads to a large percentage uncertainty in the calculated differences in their specific volumes, which is the numerator of Eq.(1) and, hence, to large uncertainties in the pressure-induced change in the melting

temperature. In the course of developing the IDGE, where small pressure changes occurred, an accurate value for $\Delta T/\Delta P$ was needed to validate procedures. 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. Figure 1 shows the equilibrium melting point of SCN as a function of the applied pressure. These data, pressure changes up to 2 atm, directly confirm our earlier measurements of the Clapeyron coefficient using other techniques [11].
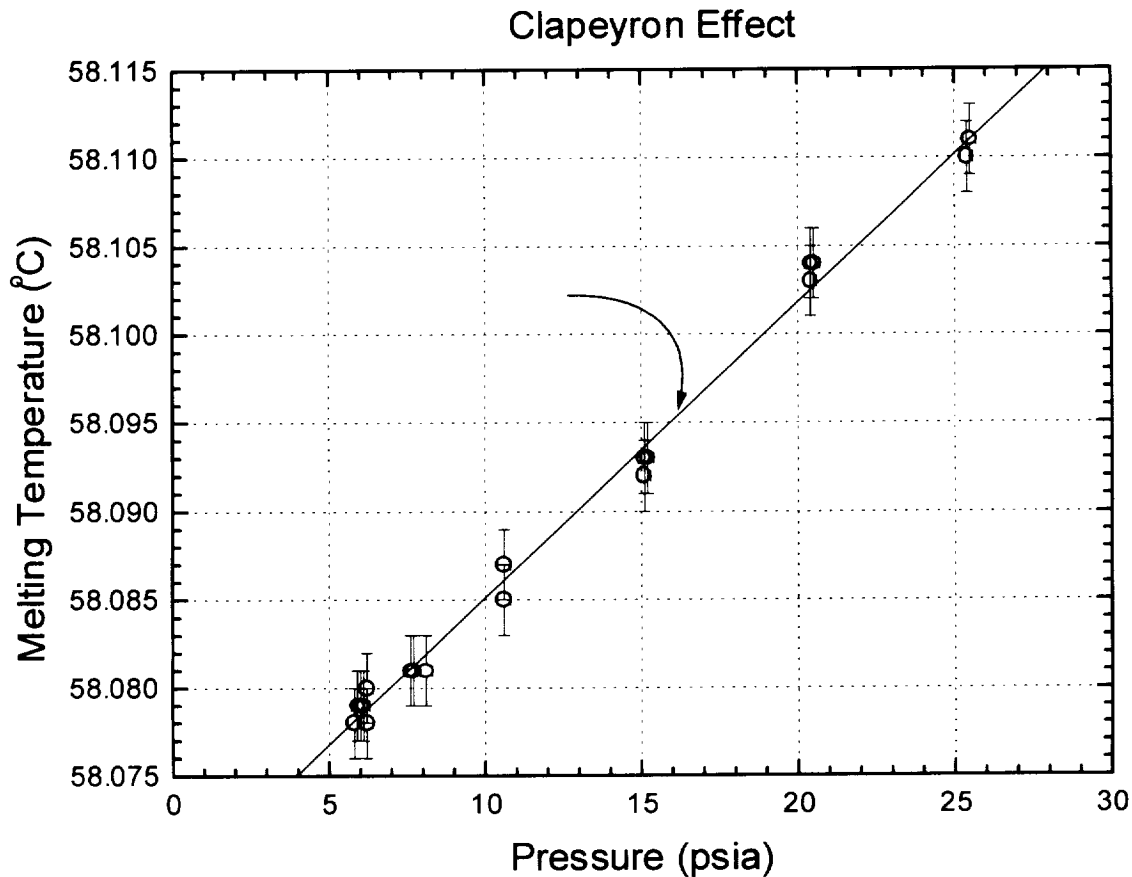

Figure 1. The Clapeyron effect in SCN.

According to Pippard [10],

> The comparison by James and William Thomson in 1849-50, of the actual pressure variation of the melting-point of ice with that predicted by Clapeyron's equation is of historical interest as being perhaps the first successful application of thermodynamics to a physical problem, and the success of this simple test undoubtedly contributed largely to the spirit of confidence which underlay and encouraged the rapid development of this subject.

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As such, 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 good assumption for most materials, but not valid in the unusual case of SCN which has a Clapeyron effect that is many times larger then in 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 then for typical metals, and indicates that pressure effects can be important in the solidification of SCN (at least for the purpose of conducting basic research).

The Transient Dendritic Growth Experiment (TDSE)

A Clapeyron coefficient as large as 24.5 mK/atm can be used in a straightforward manner to change quickly a solid-liquid interfaces equilibrium melting temperature, and, thereby, its supercooling. If this were done for an isothermal, isolated, dendrite growing at steady-state, the supercooling, and the associated free energy for dendritic growth, would be instantaneously and globally altered. This approach, would allow acquisition of a series of unique measurements on non-steady-state dendritic kinetics, and permit observations of the transient evolution of the morphology.

If a pressure-mediated melting temperature change were carried out for an isolated dendrite growing in at steady-state at some initial supercooling, the dendrite needs to respond by eventually adopting a new steady-state, appropriate to the new supercooling. If we designate in advance a particular target supercooling, we can achieve that supercooling starting at a supercoolings 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 effect of the adiabatic pressure-volume work done on the melt. From the basic thermodynamics of the combined first and second laws, one can show that the temperature change in the melt temperature with pressure is,

$$\frac{\Delta T}{\Delta P} = \frac{\beta v T}{c_p},$$

(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.

Thus, for the experiment, one could produce a sequence of dendritic growth runs that all terminate in a final steady-state chosen at a fixed target supercooling, but starting at a range of supercooling, at 0.025, 0.050, 0.10, 0.20, and 0.40 K above and below the common final supercooling. A particular sequence of supercooling adjustments as large as 0.4 K could be accomplished by a pressure variation in SCN of about 40 atm. This includes both the pressure mediated change in melting temperature at the interface and the adiabatic pressure-volume work temperature change of the melt. One could either

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start from an elevated pressure and release it (down-quench), or start from a low pressure and raise it (up-quench). For each dendritic growth run we would record the dendritic growth kinetics and morphology of the initial and final steady-states, and the transient evolution of the transition connecting the two well-defined, dynamic states. Figure 2 shows a picture that represents schematically what is described in the text.
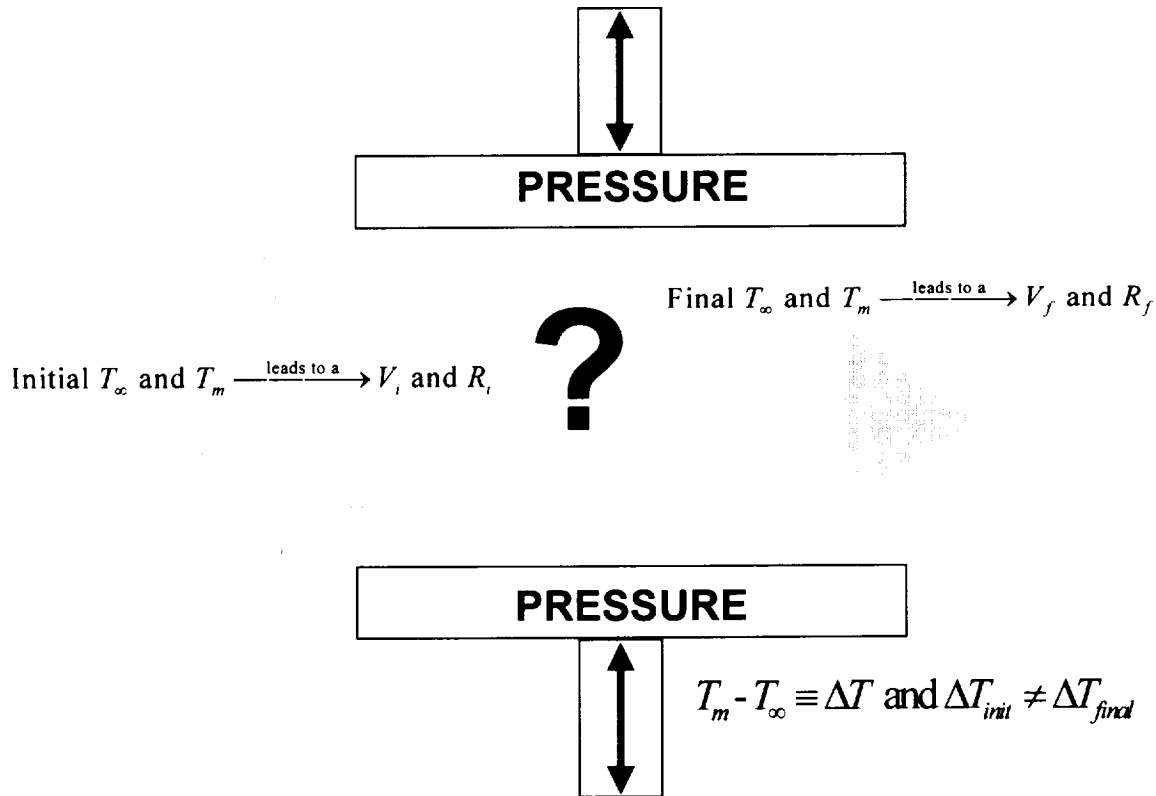

Figure 2. Schematic of Transient Dendritic Solidification Experiment (TDSE).

Preliminary Modeling Results

In addition to the experiments described above, the project has a modeling component (by the co-investigators at LeRC). The scope of this effort is to develop and conduct large scale numerical simulations of the fully transient, non-linear solidification pressurization process. These simulation use a finite-difference, operator splitting, dynamic grid generation technique to track the radius of curvature and the velocity from an initial solidification of a small spherical nucleus with arbitrary initial conditions.

For an developmental test case of an initial supercooling of 0.1 K, we simulate the growth due to an exponential pressurization over 2 seconds to 35 atm, and a final supercooling of 0.36 K, followed by an exponential de-pressurization over 2 seconds back to 1 atm.

The preliminary findings indicate that the tip velocity responds very rapidly to

pressurization/de-pressurization, which reflects a rapid change in the local net heat flux corresponding to the new supercooling. Tip melting is evident following de-pressurization to accommodate a larger tip radius. The tip radius responds much more slowly for the parameter values used. The tip velocity oscillates following pressurization, but responds smoothly following de-pressurization. There is active side-branching following pressurization to accommodate reduced tip radius, and a much smoother transition to a large tip radius. This preliminary data is insufficient to determine possible hysteresis, in accordance to a two parameter selection model [12], following pressurization/depressurization cycling.

Summary and Conclusions

The study of steady-state dendritic growth has both validated many element of transport phenomena in dendritic growth, and yielded many new insights. Further development in simulation and modeling are needed, as is further understanding of the role of selection or scaling in dendritic growth. The TDSE is contributes to the further study of dendritic phenomena my carefully measuring and modeling transient effects on dendritic growth.

The major challenge encountered in measuring and analyzing the transient behavior of isothermal dendrites is defining precisely the initial conditions from which or to which the dendrite evolves. Our proposed pressure-mediated TDSE microgravity experiment, obviates this difficulty, because the transient occurs between two well-characterized steady-states, rather than between an ill-defined initial state and the final steady state. The major results expected are unique data on transient behavior that will extend the scientific bounds from the now well-understood thermal effects, and provide insight into interfacial dynamics where open questions remain.

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