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# Dynamic stability of detached solidification

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ABSTRACT

A dynamic stability analysis model is developed for meniscus-defined crystal growth processes. The Young–Laplace equation is used to analyze the response of a growing crystal to perturbations to its radius and a thermal transport model is used to analyze the effect of perturbations on the evolution of the crystal-melt interface. A linearized differential equation is used to analyze radius perturbations but a linear integro-differential equation is required for the height perturbations. The stability model is applied to detached solidification under zero-gravity and terrestrial conditions. A numerical analysis is supplemented with an approximate analytical analysis, valid in the limit of small Bond numbers. For terrestrial conditions, a singularity is found to exist in the capillary stability coefficients where, at a critical value of the pressure differential across the meniscus, there is a transition from stability to instability. For the zero-gravity condition, exact formulas for the capillary stability coefficients are derived.

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## 1. Introduction

In detached Bridgman solidification, a gap exists between the growing crystal and the crucible wall. The distance of this gap can be on the order of 10–100 µm. The liquid remains in contact with the crucible wall and a meniscus bridges the gap between the crucible and crystal at the liquid–crystal–gas triple phase line (TPL). Observations of detached solidification date back to the NASA Skylab mission [1,2] and reviews of detached solidification seen in microgravity experiments have been given by Duffar et al. [3] and Regel and Wilcox [4]. Observations of detachment in microgravity experiments were prevalent because the pressure head in the melt is reduced by six orders of magnitude. Since the initial microgravity experiments, there have also been numerous reports of detached solidification under terrestrial conditions. These reports for Ge and Ge-rich alloys, antimonides, CdTe, and nonsemiconductor materials are reviewed by Duffar and Sylla [5]. Crystals grown by detached solidification (also referred to as dewetted solidification) exhibit significant improvements over crystals grown by the standard methods. Factors leading to such improvements include a reduction in both thermal and mechanical stresses that normally result from the interaction between the crystal and crucible and reduced nucleation of grains and twins at the crucible wall. These improvements have led to considerable efforts to both understand and control the detached solidification process. Reviews of these efforts can be found in Cröll and Volz [6] and Duffar and Sylla [5].

Detached solidification in a crucible, whether by the Bridgman or vertical gradient freeze (VGF) techniques, requires the existence of a meniscus between the crystal and crucible. The existence of this meniscus puts detached solidification into the class of crystal growth techniques in which capillarity plays a major role. This class of meniscus-defined techniques includes Czochralski, float-zone, edge-defined film growth (EFG), and the micro-pulling down technique. The shape of the crystal in these techniques depends on capillary forces that are influenced by system parameters that can vary during growth. A goal in each of these methods is to keep the shape or diameter of the crystal relatively constant, or at least keep it to within a defined range. To accomplish that goal, it is necessary to understand the dynamic stability process.

The exact treatment of the shape stability of growing crystals involves the three-dimensional numerical modeling of the evolution of thermal, convective, and solutal fields, coupled with capillary forces and incorporating the appropriate time-dependent boundary conditions. Of course, simplifications to a fully three-dimensional model are often justified and approximate numerical models can provide insight into the physical mechanisms involved in shape stability. Numerical models have been developed for dynamic stability in detached solidification in the limit of zero gravity [7, 8]. Using a numerical thermocapillary model that included mass transport, Yeckel and Derby [7] found only a weak

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sensitivity of capillary dynamics to heat transfer. They also confirmed a possible mechanism in which undercooling in the melt ahead of the TPL can lead to reattachment [9]. Balint and Epure [8] determined that if the residual gas pressure across the meniscus was kept within a certain range, than the process would remain stable.

An alternative to full numerical modeling is an approach we designate as dynamic growth stability (DGS), which is based on the stability of motion equations developed by Lyapunov [10]. This approach involves the formulation of a system of linearized dynamic equations that govern the most significant variables of the growth process. For many crystal growth processes, including detached solidification, the most relevant dynamic variables are the instantaneous radius and interface position of the growing crystal. Other potential variables are pressures in the system and additional spatial variables. According to Lyapunov [10], for the chosen set of variables $X_i$, there is a coupled set of autonomous differential equations

$$\frac{dX_i}{dt} = f_i\left(X_1, X_2, ..., X_n, \frac{dX_1}{dt}, \frac{dX_2}{dt}, ..., \frac{dX_n}{dt}, C\right), \quad i = 1,\ 2 \ldots, n, \tag{1}$$

where $t$ is time and $C$ represents the set of controlled growth parameters. We are interested in the stationary values of the variables $X_i$ which satisfy

$$f_i(X_1, X_2, ..., X_n, C) = 0, \quad i = 1,\ 2, \ldots, n. \tag{2}$$

Lyapunov [10] proved that solutions to Eq. (1) are stable if the following set of linearized equations are stable:

$$\frac{d\delta X_i}{dt} = \sum_{j=1}^{n} \frac{\partial f_i}{\partial X_j}\delta X_j, \tag{3}$$

where $\delta X_i = X_i - X_i^0$. Stability is achieved when all the roots $s$ of the following characteristic equation have negative real components:

$$\det\left(\frac{\partial f_i}{\partial X_j} - s\delta_{ij}\right). \tag{4}$$

The DGS approach is valid when heat and mass transport dominate the crystallization process and when kinetic effects can be neglected. This is normally the case in real systems with typical translation rates. In the DGS approach, only perturbations of the averaged interface position are considered. This is in contrast with the Mullins and Sekerka [11,2] linear stability model, where a general perturbation is Fourier decomposed, and all perturbation wavelengths of the interface shape are studied. Both the DGS and Mullins and Sekerka stability analyses ignore the initial transient stage after the growth process is subjected to an instantaneous perturbation. Rather, the governing stability equations capture the evolution of the perturbed state at a later stage. However, the perturbation transients are usually many orders of magnitude faster than the characteristic times for the global processes and a quasi-steady state approximation is usually well justified to simplify the analysis. DGS analysis has been applied to the Czochralski [13–15], Verneil, float-zone, and several other shaped crystal growth techniques [15]. The interface position is related to the thermal transport in the system and is affected by perturbations to thermal gradients in both the solid and liquid states. Thus, the analysis can be sensitive to the details of the thermal model. As an example, there is a factor of 4 difference in the thermal gradient at the solid-liquid interface between the DGS Czochralski analyses conducted by Hurle et al. [13] and Satunkin [14].

DGS analysis has been applied to detached solidification in the limit of zero gravity, considering only the effects of capillarity [16,17] and under the combined effects of capillarity and heat transfer [18–20]. It has also been conducted for detached solidification under terrestrial conditions, considering only capillary effects [21–23]. As discussed by Yeckel and Derby [7], under microgravity conditions heat transfer and capillary effects become largely decoupled and so dynamic stability depends solely on capillary effects. This is because in zero gravity, with the absence of a pressure head, heat transfer cannot change the pressure at the meniscus and thus has no effect on the meniscus shape or the gap width. If thermal effects are ignored, then the criterion for dynamic stability reduces to satisfying a single mathematical inequality. Namely, that the derivative of the slope of the meniscus at the TPL with respect to the crystal radius be greater than zero [15]. In microgravity, satisfaction of this inequality is equivalent to the criterion that if the meniscus is concave at the TPL then the growth will be stable [16]. Note that these previous stability analyses of detached solidification did not consider a thermocapillary model under terrestrial conditions.

In this work, we develop a linear dynamic stability analysis which can be applied to meniscus-defined crystal growth techniques. The model considers both capillarity and thermal effects under terrestrial conditions. Since the problem is linear, the capillarity and thermal aspects of the problem are developed independently. The capillarity problem follows closely the DGS framework but the thermal effects are treated differently. Indeed, the governing equations of the model do not form a system of coupled differential equations. The model is developed in Section 2 and then applied to the specific technique of detached solidification in the later sections.

## 2. Dynamic stability analysis model

The analysis is restricted to just two transient variables of interest: the radius $R(t)$ and the interface position $H(t)$. According to the DGS analysis (see Eq. (3)), the set of linearized stability equations for these variables becomes

$$\delta\dot{R} = A_{RR}\delta R + A_{RH}\delta H, \tag{5a}$$

$$\delta\dot{H} = A_{HR}\delta R + A_{HH}\delta H, \tag{5b}$$

where $\delta R$ is the perturbation of the crystal radius and $\delta H$ is the perturbation of the interface from its steady-state position. A general solution to Eq. (5) will result in a linear combination of two exponential functions with complex exponents. The perturbations may grow or decay depending on whether the real component of these exponents is positive or negative. As described by Tatarchenko [15], Eq. (4) leads to the following conditions, both of which must be met for stable growth:

$$A_{RR} + A_{HH} < 0, \tag{6a}$$

$$A_{RR}A_{HH} - A_{RH}A_{HR} > 0. \tag{6b}$$

Analysis of the crystal growth process provides the four coefficients $A_{ij}$. Of course, the accuracy of the stability analysis depends on how well the equations leading to these coefficients capture the actual physical phenomena that occur during the growth process. A meniscus shape analysis provides the coefficients in Eq. (5a) and consists of solving the Young–Laplace equation. A thermal analysis provides the coefficients that occur in Eq. (5b). In the DGS approach, the thermal analysis consists of approximating the heat equation by a one-dimensional differential equation and obtaining the coefficients by analyzing the perturbed steady-state equations. In our view, this treatment is physically correct for the $A_{HH}$ coefficient, but a difficulty arises with the coefficient $A_{HR}$. The problem is that the perturbation to the thermal field by a change in radius of the crystal at the interface does not involve a uniform instantaneous change in crystal dimension for the entire crystal length. Rather, we have to consider the previous evolution of the crystal