Weak Stefan Formulation for Bulk Crystal Growth with Non-smooth Interfaces

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Abstract

Most heat transfer models for bulk crystal growth rely on the classical Stefan formulation to evaluate interface motion during phase change. However, when the interface is non-smooth the use of the classical Stefan formulation may lead to singularities. To address this problem, we propose a simulation model based on the weak formulation of the Stefan problem. Numerical solutions of the weak Stefan formulation are obtained using the finite volume method. This approach provides an energy conserving discretization scheme that accurately evaluates heat transfer around non-smooth interfaces. We apply the weak formulation to numerically simulate the solidification of silicon in the horizontal ribbon growth process. Results exhibit a limitation on the ribbon’s pull speed, which previous classical Stefan models have failed to demonstrate. A comparison of heat transfer between radiation and gas cooling shows that gas cooling increases the pull speed limit for the same amount of heat removed.

1 Introduction

Simulation and modeling play an important role in the safe and reliable operation of crystal growth furnaces [1]. At their core, crystal growth models describe a process of phase transition taking place across a moving interface. The physics of phase transition can be complicated, and will depend on the scale of the process and the properties of the materials involved. Still, a first order model for phase transition can be developed, based on the basic principles of mass and energy conservation. These models belong to a well known class of mathematical formulations known as the Stefan problem [2].

Solving a Stefan problem in 2 or 3 dimensions can be challenging since the shape of the interface is not known beforehand. Therefore, crystal growth models often rely on numerical techniques to obtain accurate solutions [3]. Methods based on Galerkin finite element combined with arbitrary Lagrangian-Eulerian (ALE) approach have been used in a variety of crystal growth models due to their high spatial accuracy [4][5]. Helenbrook and Hrdina [6] developed an adaptive mesh algorithm to track the interface using triangular, ALE moving mesh to tackle large unsteady interfacial deformations. Finite volume methods using interface tracking algorithms are used in [7][8] to build 3D models for the Czochralski process. Weinstein et al. [9] applied a Lattice Boltzmann model to track interface evolution while accounting for anisotropic interface attachment kinetics. Other approaches that track the interface evolution implicitly, like phase field models, are also used to model crystal growth [10]. However, they are better suited to model phase transition at the microscopic level based on thermodynamic considerations, like dendrite growth and phase boundaries [11][12].

Despite the ubiquity of Stefan problem in modeling crystal growth processes, certain problems exist in its application. One major problem is the use of the strong formulation, also known as
Figure 1: Examples of ill-defined interface velocity at non-smooth corners in bulk crystal growth

the classical formulation, of the Stefan problem to model non-smooth interfaces. An interface is termed non-smooth if the unit normal at any point on the interface is not uniquely defined. On a smooth interface the strong form of the Stefan condition based on energy conservation is given by

$$\left[ k_l \nabla T_l - k_s \nabla T_s \right] \cdot \hat{n} = -\rho L \vec{v} \cdot \hat{n}, \quad (1)$$

where $\hat{n}$ is a unit vector normal to the interface; $k_s$, $k_l$ are the thermal conductivities and $\nabla T_s$, $\nabla T_l$ are the temperature gradients for the solid and liquid phase. $\rho$ denotes the density of the solid phase, $L$ is the latent heat of fusion and $\vec{v} \cdot \hat{n}$ denotes the velocity of the interface from solid to liquid. Equation (1) holds point-wise everywhere on the interface.

The assumption on the smoothness of the interface puts a restriction on the applicability of the classical Stefan formulation. This is especially relevant for crystal growth systems since the occurrence of non-smooth interfaces is routine [10, 13, 14]. Figure 1 provides two example of frequently encountered situations in crystal growth where the classical Stefan formulation is not applicable. Figure 1a is a close-up of a crystal growth configuration around a triple point. The solidification interface makes an angle $\theta$ with the free surface. In the case of a faceted growth, $\theta$ can be a fixed angle [15, 16, 17]. The unit normal is uniquely defined everywhere on the interface except at the triple point. At the triple point, the tip grows with a velocity of either $v$, if measured from the direction of $\hat{n}_1$; or $v \sin \theta$, if measured from $\hat{n}_2$. This presents an ambiguity in the choice of the normal velocity in the Stefan condition (1). A similar problem exists in systems with facet growth [18, 19, 20], as shown in figure 1b, where the normal component of the interfacial velocity cannot be uniquely defined.

Using the classical Stefan formulation to model interfaces that are non-smooth can lead to incorrect results [21, 22, 23]. This is because the limit of the energy balance equation on an arbitrarily small neighbourhood of a non-smooth interface does not exist and only the integral form of the energy balance makes sense. In the context of bulk crystal growth systems, the use of the classical formulation has created singularities around triple points and facet corners, which has made the analysis of heat transfer difficult.

In the Bridgman process, theoretical and numerical solutions have shown singularities at the intersection of crucible walls with the interface [24, 25]. This has lead to the phenomenon of
“Interface effect”, which makes it difficult to control the interface shape \([26, 27]\). Singularities have also been observed near the triple point in the Czochralski process \([28, 29]\). Asymptotic analysis have found the order of these singularities to be dependant on the angle prescribed by the triple point or the facet corners \([30, 31]\). As a result, the use of numerical techniques that rely on piecewise polynomials may not represent heat transfer at such points \([32]\).

One particular crystal growth method where singularities have made it difficult to provide robust predictions is the horizontal ribbon growth (HRG) process \([33, 34, 35]\). In this process, thin sheets of single crystal silicon are produced directly from the melt. Figure 2 provides a schematic of the growth zone in the horizontal ribbon growth furnace. Cooling is applied at the top surface of a molten bath and a seed crystal is inserted horizontally to nucleate the growth process \([36]\). The thickness of the growing crystal is controlled by manipulating the cooling rate and the pull speed \((v)\). A higher pull speed provides less exposure to cooling and thus produces thinner ribbons. However, experiments have shown that the HRG process exhibits a limitation on its pull speed, which also constraints the size of the ribbon’s thickness \([37]\). Theoretical modeling and simulations have not provided any conclusive explanation for the pull speed limit \([38, 39, 40, 41, 42, 43]\). This has hindered the scale up of the process, since it has not been possible to increase production speed to meet industrial standards \([44]\).

The aim of this paper is to develop a theoretical framework for simulating crystal growth based on the weak formulation of the Stefan problem. We apply this theory to the numerical simulation of the horizontal ribbon growth process. At the same time, we keep the formulation general enough to be applicable to other areas of crystal growth as well. Although fluid flow, meniscus stability and impurities play an important role in the stable operation of the horizontal ribbon growth process \([45, 46, 47, 48]\), here we decouple these phenomena and focus only on the conductive heat transfer aspect of the process. In doing so, we are able to provide an explanation for the occurrence of some phenomenon, like the limitation on pull speed, observed in experiments.

![Figure 2: Schematic of the horizontal ribbon growth process around the growth zone](image-url)
2 Mathematical Formulation

Consider the process of solidification to take place inside a bounded domain $\Omega$, belonging to a subset of the Euclidean space $\mathbb{R}^n$ ($n=2,3$). We shall assume that the process occurs at a constant volume, i.e., no volume change associated with phase change. The domain is occupied by a pure material capable of attaining two phases, liquid and solid, at a sharp melting point $T_m$. To simplify fluid motion, the material is assumed to move at a uniform speed, $v$, throughout the domain. The analysis is carried out in a Lagrangian frame of reference, so the material appears stationary in this reference frame.

The time interval for analysis is set to $]0,\tau[\,$, where $\tau$ is a constant and define $Q := \Omega \times ]0,\tau[$. An energy balance carried out over any volume $V$ with surface area $A$ gives

$$
\int_{\Gamma} \left[ \frac{\partial}{\partial t} \int_V U \, dV + \oint_A \vec{f} \cdot \hat{n} \, dA \right] \, dt = 0 \quad \forall \quad V \times \Gamma \subseteq Q
$$

(2)

where $U$ is the density of internal energy within volume $V$ and $\vec{f} \cdot \hat{n}$ is the flux of the energy transferred through the boundary $A$. The energy balance holds over any time interval $\Gamma \subseteq ]0,\tau[$. The use of the integral form is advantageous as it reduces the requirements on the regularity of the solution, for in general $U$ and $\vec{f}$ will be discontinuous at the phase interfaces. Since we carry out our analysis in a Lagrangian reference frame, conduction is the only main source of energy transport within the material. Therefore, the energy flux at any point inside the domain is given by the Fourier law:

$$
\vec{f} = -k \nabla T.
$$

(3)

Additional information on the nature of $U$ will be needed for (2) to be suitable in practise. This will be given by an energy-phase rule, which is a modification of the temperature-phase rule in [2], to account for metastable states.

2.1 The Energy-Phase Rule

![Energy-Phase rule](image)

Figure 3: Energy-Phase rule
We define a solid fraction field, \( \chi \in [0,1] \), to denote the phase of the material at any point in \( Q \). \( \chi = 1 \) corresponds to the material in the solid phase and \( \chi = 0 \) to the material in the liquid phase. An intermediate value of \( \chi \) may denote a fine solid-liquid mixture at the macroscopic length scales. For our formulation, we require that the phase change only occurs at the melting point \( T_m \), during which the temperature remains constant until \( \chi \) changes phase to either 0 or 1. The formulation should also allow for the existence of supercooling in absence of nucleation during extreme cooling. These features are captured through an energy-phase rule of the form given below:

\[
U = \begin{cases} 
\rho c_s(T - T_m) & \chi = 1 \\
\rho L \chi & \chi \in (0, 1), T = T_m \\
\rho L + \rho c_l(T - T_m) & \chi = 0.
\end{cases}
\]

(4)

Figure 3 illustrates the essential features of the energy-phase rule. The internal energy is considered to be a multi-valued function of the temperature that branches at two points. The choice of the branch depends on whether a phase change is initiated as the temperature approaches the melting point. The criteria for initiating a phase change is determined by a set of rules discussed in section 4.1. Since metastable states, like a supercooled melt, are often observed in practise, this energy-phase rule allows us to model the physics of crystal growth in a manner that is representative of experimental systems.

Substituting (4) in (2), the energy balance equation can be re-written as:

\[
\int_{\Gamma} \left[ \frac{\partial}{\partial t} \int_V (\rho c_\chi (T - T_m) + \rho L \chi) dV + \oint_A \vec{f} \cdot \vec{n} dA \right] dt = 0 \quad \forall \ V \times \Gamma \subseteq Q,
\]

where \( c_\chi \) is equal to \( c_s \) in the solid phase and equals to \( c_l \) in the liquid phase.

3 Simulation Modeling

Figure 4: Simulation domain and initial seed configuration of the HRG process

To test the utility of our weak formulation, we carry out finite volume simulations to model the growth of a silicon ribbon in a horizontal ribbon growth process. The simulation is carried out in a rectangular domain of size 1mm \( \times \) 10mm around the growth tip of the ribbon. The shape and size of control volumes are usually chosen based on the geometry of the domain and the accuracy needed for the required engineering application. For our simulations, we divide the domain into rectangular control volumes \( (V_i) \) of size \( \Delta x = 5 \mu m \). The time interval for simulation will be divided into equal open intervals \( \Gamma_n \) of size \( \Delta t \).

Each cell element \( V_i \times \Gamma_n \) of \( Q \) will be categorized to either of the three domains: solid \( Q_s \), liquid \( Q_l \) or interface \( Q_I \). Phase change will be restricted to take place only in the interface domain.
In the solid $Q_s$ or liquid $Q_l$ domain, no phase change occurs so the energy balance equation (5) reads
\[
\int_{\Gamma_n} \left[ \rho c_j \frac{\partial T_j}{\partial t} \Delta x - D f_i \right] dt = 0 \quad \forall \ V_i \times \Gamma_n \subseteq Q_j, \ j = \{s,l\},
\] (6)

where $T_j$ is the temperature field averaged over the control volume $V_i$. $D$ is the difference operator and $D f_i = f_R - f_L + f_T - f_B$ denotes the intensity of the heat flux removed from the control volume $V_i$. $f_R, f_L, f_T$ and $f_B$ represent the heat fluxes from the right, left, top and bottom walls of $V_i$ respectively.

The interface is characterized as a region of phase change with constant melting point $T_m$. Therefore, the energy balance equation (5) in the interface domain ($Q_I$) is written as
\[
\int_{\Gamma_n} \left[ \rho L \frac{\partial \chi_i}{\partial t} \Delta x - D f_i \right] dt = 0 \quad \forall \ V_i \times \Gamma_n \subseteq Q_I
\] (7)

where $\chi_i$ is the solid fraction averaged over the control volume $V_i$. Equation (7) equates the intensity of latent heat released due to phase change to the intensity of heat removed from a control volume of size $\Delta x$.

Equation (6) and (7) are conservative discretizations of the balance equation (5), i.e., the flux on the boundary of one cell equals the flux on the boundary of the adjacent cell. Since the conservation holds at the discrete level; if the numerical method converges, they can be proven to converge to a weak solution of the conservation law (5) using the Lax-Wendroff theorem [49].

In a Stefan problem, the solid-liquid interface behaves like a moving boundary that evolves continuously over time. Due to this, the proposed simulation scheme proposed relies on the categorization of each cell element at the beginning of every time step. Therefore, a capture rule is required to determine the propagation of the interface for numerical simulations.

### 3.1 Interface Propagation

In the classical Stefan formulation, phase transition occurs only at the interface, between the boundaries of the solid and liquid phases. This condition serves as a useful abstraction to model solidification processes involving metastable states, namely, supercooling and superheating. In contrast, the enthalpy based methods for solidification assume thermodynamic equilibrium at all points in the domain.

Keeping this in mind, we constraint local thermodynamic equilibrium to occur only along a small band of size $\Delta x$ between the solid and the liquid phase. Physically, this would signify the proximity of the liquid to nucleation sites for phase transition. This region of size $\Delta x$ will be defined as the interface. Away from the interface, we allow for the possibility of metastable states. All of this is governed by the energy phase rule described in (4).

Initially, each cell in $\Omega \times \{0\}$ is categorized as either a solid, liquid or interface. At the end of each time interval, an interface propagation step is carried out. In this step, any cell belonging to the interface that exceeds its solid fraction beyond [0,1] changes its label to either liquid or solid appropriately. This transformed cell acts as a nucleation site for its nearby cells to become a part of the interface. Figure [5] shows an example of a $\Delta x$ radial neighbourhood, also called the Von Neumann neighbourhood, used for interface propagation. In general, crystals have anisotropic surface energy, so the interface propagation may be preferred along certain directions. However, in this paper we consider the case when the crystal growth is isotropic.

The interface propagation step is carried out at the end points of the discretization scheme. Due to this, additional steps need to be taken to ensure energy is conserved when the labels on the cells
are changed. When a cell transforms from a solid or liquid phase to an interface, the temperature of the cell is updated to $T_m$ and the residual thermal energy is transferred into the solid fraction using

$$L \Delta \chi_i = c \chi_i (T_m - T_i), \quad (8)$$

where $\Delta \chi_i$ is the change in the solid fraction of cell $i$. A similar strategy is applied when the solid fraction of an interface cell exceeds $[0, 1]$ and changes to either a solid or a liquid cell.

### 3.2 Numerical Method

Applying (3) to each wall in the control volume $V_i$, the flux can be discretized using a central difference scheme and substituted in (6) and (7). Combined with the boundary conditions, the system of equations describing the evolution of the temperature and phase fields is complete and can be solved using any standard method of numerical integration. For this paper, we found the Douglas-Gunn Alternating Direction Implicit (ADI) scheme to be stable and efficient in solving the integral equations. The implementation of the ADI scheme is standard and we refer the readers to McDonough [50] for more information.

Due to the Lagrangian nature of the simulation, the domain needs to be re-centered after a fixed number of iterations to prevent the domain from leaving the area of interest. To do this effectively, we re-center the simulation domain after every $\Delta x/v \Delta t$ iterations. This restrict the choice of $v$ so that $\Delta x/v \Delta t$ is an integer. The simulation is said to reach steady-state when the solution becomes time independent within an acceptable level of tolerance.

At the initial stages of the simulation, the numerical integration starts with large step sizes, $\Delta t \approx 10 \Delta x$. The step size is then gradually decreased to $\Delta t = \Delta x$, until steady state is reached. In some situations, it was observed that the interface would oscillate for a large number of iterations and would not reach steady state. This was attributed to the explicit nature of the interface propagation step. The conversion of residual solid fraction into thermal energy based on (8) could sometimes cause the algorithm to not converge due to the large value of latent heat $L$. In this case, further decrease in the step size of the simulation or distribution of the excess solid fraction to the nearby transformed cells was found to be sufficient to stop the oscillations.
4 Application: Horizontal Ribbon Growth

To determine the boundary conditions required for our simulations, we refer to Figure 2 for a cross-sectional schematic of the horizontal ribbon growth furnace. A cooling mechanism at the top surface of the melt drives the solidification process which causes single crystal silicon to grow. Cooling takes place either through a passive mechanism, like radiation or through an active cooling system, like gas jets \[34, 51, 52, 53\]. It is unclear how one cooling mechanism may provide an advantage over the other. Therefore, we consider both mechanisms of heat removal at the top boundary condition in our simulation study.

For the case of radiation, the top surface heat loss is given by the Stefan-Boltzmann law

\[
q_t(x_1) = \epsilon \sigma (T^4 - T_c^4) F(x_1), \quad (9)
\]

where \(\sigma\) is the Stefan-Boltzmann constant, \(\epsilon = \chi \epsilon_s + (1 - \chi) \epsilon_l\) is the weighted emissivity of solid \((\epsilon_s)\) and liquid \((\epsilon_l)\) emissivities. \(T_c = 300K\) is the temperature of the water cooled walls of the furnace surrounding the crucible. \(F(x_1)\) is called the view-factor and takes into account the area exposed by an opening, like a slit, to the water cooled walls of the furnace from any point \(x_1\) on the surface of the melt. We consider the slit width to be variable and placed above the top surface of the melt at a height \(h\). The width of the slit is parameterized using the variable \(w\). The view-factor at any point \(x_1\) on the surface of the melt is given by the formula \[54\]:

\[
F(x) = \frac{\sin \phi_2 - \sin \phi_1}{2}, \quad (10)
\]

where \(\sin \phi_1\) and \(\sin \phi_2\) are

\[
\sin \phi_1 = \frac{-(w + x)}{\sqrt{(w + x)^2 + h^2}} \quad \sin \phi_2 = \frac{(w - x)}{\sqrt{(w - x)^2 + h^2}}. \quad (11)
\]

For the base case, a value of \(w = 5\text{mm}\) is chosen. A small value of \(h\), say \(h = 0.1\text{mm}\), allows a smooth transition in the radiative heat flux near the slit edges. The variable \(w\) will be used as a parameter to study the effects of radiation length on pull speed.

To model the gas cooling jet, a scaled down version of the experimental conditions in Helenbrook et al. \[43\] will be used. For gas cooling (hereon referred as Gaussian cooling), the top surface heat removal rate is modeled using a Gaussian curve, parameterized by peak intensity \(q_{\text{peak}}\) and spread \(\sigma\).

\[
q_t(x) = q_{\text{peak}} \exp \left(-\frac{x^2}{2\sigma^2}\right). \quad (12)
\]

An approximate fit to the experimental data in Helenbrook et al. \[43\] was found at \(\sigma = 0.8\). \(q_{\text{peak}}\) was chosen to be 40 W/cm², to ensure the heat removed using the Gaussian cooling profile was of the same order of magnitude as the heat removed using radiation. These values of \(\sigma\) and \(q_{\text{peak}}\) will serve as the base case for Gaussian cooling and provide us with a comparative study of the two cooling mechanisms.

A positive thermal gradient in the melt is found to provide a stable environment for crystal growth \[13\]. For this reason, a small heat flux is applied on the bottom boundary of the domain, supplied from the heaters on the underside of the crucible.

\[
q_B = 2 \ W/cm^2 \quad (13)
\]

In a reference frame moving at a constant velocity \(v\), the top and bottom boundary conditions appear to drift in the opposite direction. To account for this, we introduce a time dependent drift on the top boundary condition.

\[
q_T(x_1, t) = q_t(x_1 - vt). \quad (14)
\]
Since the bottom flux is a constant, it remains unchanged.

Preceding the growth zone is a replenishment zone that provides a constant supply of melt. This is done by means of heaters inside the crucible walls that melt silicon feed chunks. Experimental conditions maintain the temperature of the silicon melt at 1690K [43]. This bulk melt at 1690K is assumed to be 5cm away from the simulation domain. We also assume a linear temperature profile inside the replenishment zone with respect to the moving reference frame. The left boundary condition is therefore calculated to be

\[ q_L = -k \frac{\Delta T}{\Delta x} = \frac{67 \times 10^{-4}}{5 \times 10^{-2}} (1690 - T) = 0.134 \times (1690 - T) \text{ W/cm}^2 \]

(14)

As the ribbon is pulled out of the simulation domain, it exits into a stabilization zone. In this region, the temperature in the solid and liquid phases are maintained so that conduction only occurs in the vertical direction [43]. Although convective heat transport may still exist in the horizontal direction, in a moving reference frame this effect is not realized and therefore the heat flux at the right boundary will be taken to be zero.

\[ q_R = 0. \]

(15)

The initial condition for simulations was found to be fairly robust to any appropriate choice of seed crystal shape and temperature field. The first simulation was initialized using a rectangular seed crystal of width 250µm and length 5mm, covering the top half surface of the melt as shown in figure 4. The melt was initialized with a uniform temperature of 1690K and the solid was chosen to be at a 1680K. Subsequent simulation for different operating condition were initialized from the steady state solution of the previous simulation.
| Parameter                              | Symbol | Value                   |
|---------------------------------------|--------|-------------------------|
| Density of liquid silicon             | \( \rho \) | 2530 [kg/m\(^3\)]     |
| Thermal conductivity of silicon melt  | \( k_l \) | 67 [W/mK]              |
| Thermal conductivity of silicon solid | \( k_s \) | 22 [W/mK]              |
| Heat capacity of silicon melt         | \( c_l \) | 1000 [J/kgK]           |
| Heat capacity of silicon solid        | \( c_s \) | 1060 [J/kgK]           |
| Latent heat of fusion                 | \( L \)  | \( 1.8 \times 10^6 \) [J/kg] |
| Emmisivity of silicon melt            | \( \epsilon_l \) | 0.2                    |
| Emmisivity of silicon solid           | \( \epsilon_s \) | 0.6                    |

Table 1: Material properties of silicon used for simulation

4.1 Results

We begin the simulation study by applying the finite volume discretization to the base cases of radiation and Gaussian cooling. The values of the physical constants required for simulation are summarized in Table 1.

We first consider the base case when the top surface of the melt is cooled by radiation. For this case, the slit only allows the center 5 mm of the melt to radiate heat, which acts as the sole mechanism of latent heat removal. We perform simulations at pull speed increments of 0.05 mm/sec, starting from 0.3 mm/sec. Figure 6 illustrates the steady-state temperature fields at pull speeds of \( v = 0.3, 0.5, 0.7 \) and 0.9 mm/sec. The solid black line in the figures denotes the shape of the ribbon. For all pull speeds, the ribbon shape is found to approximate a wedge shape. This can be attributed to the near constant heat flux at the top surface of the solid [38]. Figure 7 illustrates the top surface heat flux for radiation and Gaussian cooling. The radiative heat flux was plotted at a steady-state pull speed of \( v = 0.5 \) mm/sec. The heat flux appears constant in solid and liquid phases and shows a jump in between due to their difference in emmisivities.

![Graph of top surface heat flux](image)

Figure 7: Comparison of top surface heat flux for radiation (\( v = 0.5 \) mm/sec) and Gaussian cooling
Figure 8: Temperature maps for gas cooling at ribbon pull speeds of 0.2, 0.4, 0.8, 1.6 mm/sec from top to bottom, respectively.

For the base case involving Gaussian cooling, simulations performed at 0.1 mm/sec increments, starting from a pull speed of 0.2 mm/sec. Unlike the radiation case, the heat removed by Gaussian cooling does not depend on the position of the ribbon tip. The temperature field and ribbon shape at pull speeds of \( v = 0.2, 0.4, 0.8 \) and 1.6 mm/sec are displayed in Figure 8. In this case, the ribbon shape is curved due to the non-linear shape of the Gaussian cooling profile.

Comparing figures 6 and 8, we observe certain similarities and differences between the two cooling mechanisms. In both cases, we observe the ribbon tip moving to the right as the pull speed increases. This creates a U-shaped pool of supercooled melt in front of the ribbon tip that grows larger in size. It is worthwhile to note the larger pool size in radiation compared to Gaussian cooling. Another important observation is the motion of the ribbon tip to the center in the Gaussian case, and to the edge of the slit in the radiation case.

The information on the pull speed and ribbon thickness for radiation and Gaussian cooling is summarized as a graph in figure 9. This relationship is governed by the total energy balance equation

\[
L \rho v t_r = Q_{tot},
\]

where \( t_r \) is the thickness of the ribbon and \( Q_{tot} \) is the total heat removed from the domain. The two curves intersect at a pull speed of \( v = 0.63 \) mm/sec. Therefore, the point where the two curves intersect denotes equal heat removal \( Q_{tot} \) for the two cases. Below this pull speed the heat removed from the radiative case is higher and above this pull speed the heat removed is lower due to the difference in emmisivities of the two phases. This causes radiation to produce thicker ribbons at lower pull speeds and thinner ribbons at higher pull speeds.

In addition, we also observe a pull speed limitation for both mechanisms. For radiation, the
Figure 9: Thickness vs pull speed plot for radiation and Gaussian cooling. The dashed lines signify the pull speed limitation observed in simulations.

limit occurs at 0.9 mm/sec as the ribbon tip reaches the end of the slit. On the other hand, the pull speed limit for Gaussian cooling occurs at 2mm/sec, as the ribbon tip reaches the center of the cooling jet.

4.1.1 Heat transfer at the triple point

To explain the pull speed limitation in our simulations, we take a closer look at the temperature profile near the ribbon tip. Figure 10 shows a close-up of the temperature contours near the ribbon tip for the two base cases at their respective pull speed limit. The isotherms become nearly vertical as they approach the ribbon tip. This implies a predominantly horizontal mode of heat removal at the ribbon tip. This is in contrast to the conventional notion of heat removal in the horizontal ribbon growth process, which was considered to be in the vertical direction. This provides an indication to the origin of pull speed limit due to heat transfer.

To explain this hypothesis, we study the variations in the temperature gradient around the ribbon tip for increasing pull speeds. Figure 11 plots the temperature profile at the top surface of the domain, \( T(x_1, 0) \) for the two base cases. The multiple curves in each plot, from left to right, denote the temperature profile for increasing pull speeds. The position of the ribbon tip in these curves can be identified by the peak at \( T_m = 1685 \text{K} \). At low pull speeds, almost all the heat removal required to maintain solidification at the ribbon tip is from the solid side. As the pull speed is increased, the ribbon tip shifts to the right. This decreases the heat removed from the solid surface and increases the heat removed form the liquid surface. The increase in the heat removed from the liquid side creates a pool of super-cooled melt in front of the ribbon tip. The negative thermal gradient in the melt provides the necessary source of heat removal to maintain growth at the tip. Moreover, the decrease in the heat removed from the solid side causes the ribbon to get thinner. Therefore, from the perspective of heat transfer, it is more efficient to remove heat from the liquid side than the solid side because some portion of the heat removed from the solid side is used to maintain the ribbon’s thickness.
Based on the above explanation we summarize the observation of pull speed limit as follows: increasing the pull speed of the ribbon requires an equal increase in the growth rate of solid at the ribbon tip. If sufficient latent heat is not removed to maintain this growth rate, the ribbon tip moves to the right. This increases the amount of heat removed from the tip—by increasing the heat removed from the liquid side—and establishes a new equilibrium position. As the pull speed is increased further, at some point the heat removed from tip is maximized and the growth rate reaches its limits. For the Gaussian case this limit occurs around the center of the cooling profile, while for the radiation case this limit occurs at the edge of the slit.
4.1.2 Parametric Study

Simulations from the previous section suggest the pull speed limit for Gaussian cooling to be higher than radiation. However, since the heat removed due to radiation varies with pull speed, it is unclear if the advantage lies in the mode of cooling or the quantity of heat removed. Figure 12 plots the total amount of heat removed $Q_{tot}$, which includes the sum of conductive and convective heat transport from all four boundaries, at different pull speeds for the two base cases. The heat removed for Gaussian cooling is nearly constant while the heat removed during radiation cooling decreases with increasing pull speed. At the limit point, the heat removed in the radiation case is significantly lower than the Gaussian case. Therefore, for a fair comparison it is reasonable to ask how radiation and Gaussian cooling compare for the same amount of heat removed.

To do this, a parametric study of the top surface cooling profiles is performed by varying the slit width $w$ in radiation cooling and $q_{peak}$ in Gaussian cooling. For the radiation case, 5 sets of simulations are performed with slit widths of $w = 2.5$ mm, $3.75$ mm, $5$ mm, $6.25$ mm, and $7.5$ mm. For Gaussian cooling, we choose $q_{peak} = 12.48$ W/cm$^2$, $18.19$ W/cm$^2$, $23.96$ W/cm$^2$, $28.94$ W/cm$^2$, and $33.91$ W/cm$^2$. These values of $q_{peak}$ were chosen to match the total top surface heat removed from the radiation case.

![Figure 12: A graph highlighting the variability in total heat removed using radiation as a function of pull speed. In contrast, the heat removed using cooling jet is almost constant.](image)

Similar to the process of finding the limit points in figure 12, we find the pull speed limit $v_{lim}$ in each case and mark them in figure 13. Interestingly, the points follow a straight line with $R^2$ value close to 1 up to 3 decimal places.

For both mechanisms, increasing the total heat removed from the system ($Q_{tot}$), leads to a proportional increase in the pull speed limit. For a given ($Q_{tot}$), Gaussian cooling achieved a higher maximum pull speed compared to radiation cooling. This can be attributed to the narrow heat removal profile in Gaussian cooling. Therefore, we find that a cooling jet provides better performance in producing high speed ribbons than radiation. The improvement is larger at higher heat removal rates.
5 Conclusions

The main goal of this paper is to provide an alternative theoretical framework for simulating crystal growth models involving non-smooth edges. We find that around non-smooth interfaces, like the triple point in a horizontally grown ribbon, the classical models do not satisfy energy conservation. Therefore, a weak formulation of the Stefan problem is needed to relax the requirements on the regularity of the interface. A modified energy-phase rule is derived to account for the existence of metastable states. We choose a finite-volume discretization scheme to maintain the conservative form of the weak formulation. This allows us to come up with an easy to implement simulation scheme, which satisfies energy conservation and provides sufficient accuracy for engineering applications.

As an application, we perform a simulation study of the horizontal ribbon growth process. Unlike the classical Stefan formulations, the weak formulation demonstrates a pull speed limitation as observed in experiments. We explain the pull speed limit based on a local heat transfer arguments. During experiments, this limitation may be compounded by other physical constraints like the formation of a stable meniscus or solidification kinetics [41, 43]. However, from the perspective of heat transfer alone, insufficient heat removal from the growth tip is shown to be the fundamental reason for pull speed limitation.

Two different mechanisms of heat removal are analyzed. We find that a diffuse cooling profile, like radiation, is less effective than a narrow cooling profile, like a cooling jet, in producing thin ribbons at high speed. A linear relationship was discovered between the total heat removed from the furnace and the maximum pull speed in both cooling mechanisms. This relationship provides an interesting insight into the heat transfer occurring in the horizontal ribbon growth furnace and would require further analysis beyond the scope of this simulation. All of this aids in our understanding of the heat transfer conditions required for the high speed operation of the horizontal ribbon growth process.
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