2-D Phase-Field Model Applied to Freezing into Supercooled Melt

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**ABSTRACT**

Cryopreservation of living cells is a necessary part of many medical procedures such as organ transplants and preservation of sperm and oocytes of endangered species. However, there is at least an apparent contradiction between the concept of cryopreservation and experimental findings that cells and tissues can be damaged by the cryopreservation process itself. A major portion of the damage is due to, and occurs during, supercooling of tissues and cells and their environment; therefore, a detailed understanding of how supercooling behaves in biological environments is important. Study of supercooled freezing is complicated by the inherit instability associated with supercooling and the presence of surface tension—a stabilizing factor—and other parameters associated with the phase-change front. The only method that successfully and effectively incorporates surface tension and many other physical phenomena of supercooling without explicit front tracking is the phase-field model in which an extra equation is introduced. The solution to this equation is an order parameter—the phase-field parameter—that varies from 0 (solid) to 1 (liquid), sharply but smoothly changing over the freezing front. Numerical results are presented for a range of supercooled and hypercooled situations. They are shown to satisfy the first law of thermodynamics,
and they exhibit dendritic morphologies. Moreover, the results are in good agreement with theoretical predictions of critical length scales for nucleation and growth rate of the solid phase, and they agree in a qualitative way with experimental findings for solidification rates in the neighborhood of unit Stefan number. We therefore conclude that phase-field models provide a potentially effective method for analyzing cryopreservation processes.

**1. INTRODUCTION**

Biological metabolism in living cells dramatically diminishes and eventually stops at low temperatures, a fact that permits long-term cryopreservation (i.e., low-temperature preservation) of living cells and tissues. With recent and rapid advances made in clinical diagnosis and treatment of diseases, there is an increasing requirement for using cell and organ transplantation to cure acquired diseases and to correct genetic defects. Coupled with this, more and more types of living cells, tissues, organs, and engineered tissues are urgently required to be cryopreserved and banked at low temperatures. Cryopreservation is not only important for modern medicine/healthcare but also for many other areas because it is indispensable for (1) banking of a large quantity of living cells/tissues for typing and matching between recipients and donors to meet greatly increased clinical needs and, sometimes, urgent needs (e.g., in war, natural disasters or other accidents); (2) facilitating transport of cells/tissues between different medical centers; and (3) allowing sufficient time for screening of transmissible diseases (e.g., HIV) in the donated cells/tissues before transplantation. In addition, (4) any engineered tissues (from tissue engineering research) need to be successfully cryopreserved before their practical use in any applications and commercialization; and (5) cryopreservation of sperm and oocytes/eggs of endangered or transgenic species are urgently needed.

However, there is at least an apparent contradiction between the concept of cryopreservation and experimental findings that cells/tissues can be killed by the cryopreservation process itself. In fact, the first successful cryopreservation of living mammalian cells became reality in 1949 when Polge et al. (1949) discovered glycerol as a cryoprotective agent (CPA), reducing cell’s injury during cryopreservation. Since then a number of glycerol-like CPAs have been discovered and used in cryopreservation. The major steps in the cryopreservation process
include: (1) adding cryoprotective agents (CPAs) to cells/tissues before cooling, (2) cooling the cells/tissues toward a low temperature (e.g., to −196 °C, liquid nitrogen temperature at 1 atm pressure) at which the cells/tissues are stored, (3) warming the cells/tissues, (4) removing the CPAs from the cells/tissues after thawing. Injury to cells has been shown to be caused by each or a combination of the above steps. One of the most important parts of ongoing research is to determine the underlying physical and biological mechanisms related to the injury of cells at low temperatures (so-called “cryoinjury”) especially associated with phase change of water in both extracellular and intracellular environments. With understanding of the mechanisms of cell cryoinjury, one may establish biophysical/mathematical models describing cell responses to environmental changes during the cryopreservation process, and use these models to develop optimal procedures/devices for the long-term cryopreservation of living cells, thus minimizing cryoinjury.

Contrary to popular belief, the challenge to cells during cryopreservation is not their ability to endure storage at low temperatures; rather, it is the cooling and warming processes (Mazur, 1963). As cells are cooled to about −5 °C, both the cells and surrounding medium remain unfrozen and supercooled. Between −5 and about −15 °C, ice forms (either spontaneously or as a result of artificially introducing ice crystals to the solution) in the external medium; but the cells’ contents remain unfrozen and supercooled, presumably because the plasma membrane blocks the growth of ice crystals into the cytoplasm. The supercooled water in the cells has a higher chemical potential than that of water in the partially frozen extracellular solution, and thus water flows out of the cells osmotically and freezes externally. The subsequent physical events in the cells depend on the cooling rate. If cells are cooled too rapidly, water is not lost fast enough to maintain equilibrium; the cells become increasingly supercooled, eventually attaining equilibrium by freezing intracellularly (Mazur, 1963, 1990). Muldrew and McGann (1994) invoked an osmotic rupture hypothesis and model of intracellular freezing injury based on solid experimental data and theoretical derivations, indicating that the water flux across the cell membrane during freezing/thawing can induce intracellular ice formation causing injury. Diller and Cravalho (1970) and Diller (1982) developed novel microscopy techniques to observe cell behavior as well as intracellular ice formation (IIF) temperatures and IIF dynamics during freezing processes. Recently, based on hetero-
geneous nucleation theory and thermodynamics, as well as experimental results, Toner et al. (1990, 1993) have developed an IIF model and equations describing the probability of IIF as a function of cooling rate, temperature and cryobiological characteristics of a specific cell type. The freezing behavior of cells can be modified by the addition of cryoprotective agents which affect the rates of water transport, nucleation, and crystal growth. Karlsson et al. (1994) further developed a model of diffusion-limited IIF in the presence of CPAs. They predicted IIF phenomena as a function of cooling rate, temperature and CPA concentration, and also predicted optimal cooling protocols preventing IIF. It was known from experiments that in most cases cells were killed by IIF (Farrant, 1970; Fujikawa, 1980; Mazur, 1977, 1984; Muldrew and McGann, 1994; Rapatz et al., 1963; Steponkus and Wiest, 1979; Stowell et al., 1965; Trump et al., 1965; Toner, et al. 1990, 1993).

Independent of the specific causes of IIF discussed above, intracellular ice formation always occurs under supercooling conditions. Therefore, one of the most important issues in the research of cryopreservation is to model/characterize and calculate/predict intracellular ice formation and ice growth inside cells in the presence of supercooling. Physically, this is actually a problem associated with solidification into supercooled liquids, which is significantly more challenging than that involving only the classical Stefan problem (without supercooling). This is because, in particular, supercooling is an inherently destabilizing process, and the effects of surface tension (which are stabilizing) must be included in the model formulation to correctly account for stable growth of the solid phase. Of the techniques currently receiving wide attention, only the phase-field method explicitly includes surface tension in its physical/mathematical formulation (Fix, 1983; Caginalp and Fife, 1986). It should also be emphasized that the traditionally-used enthalpy method (see, e.g., Shyy et al., 1996) is appropriate only in the absence of supercooling unless it is modified significantly because surface tension is not taken into account in the usual formulation of this approach.

As noted by Shyy et al. (1996), there are two general classes of numerical techniques for calculation of moving-boundary problems including phase change, namely, fixed-grid and moving-grid approaches. Of these, the fixed-grid methods are generally simpler and are preferred if they are capable of solving the given problem. Discussions in Shyy et al. (1996) imply that in the presence of supercooling the typical fixed-grid techniques perform poorly
due to the numerical effects induced by physical instabilities, while the more complicated moving-grid methods handle these effects adequately.

An exception to the fixed-grid difficulties associated with supercooling is the phase-field method that is employed herein. Because this approach automatically induces a mollification that is related to the surface tension, it correctly responds to destabilizing effects and is able to resolve the (mollified) sharp fronts typical of solidification problems (especially those involving dendrites) without difficulty, as will be apparent in the results presented below. Although other approaches have succeeded in achieving this, they are far less general than the phase-field method and thus do not possess the wide applicability of this technique. The present research has been focused on the numerical investigation of intracellular dendritic growth under supercooling conditions using the phase-field method. Due to the lack of experimental data for solidification of aqueous solutions, in the present study we have simulated solidification of supercooled nickel using the phase-field method and compared the numerical results with published experimental data to evaluate the accuracy/validity of this technique.

The purpose of the present paper is to provide a complete numerical simulation of dendritic growth into a supercooled melt via a carefully constructed, efficient numerical procedure, and to demonstrate validity of computed results by comparing them with theory and experiment. Since time-splitting methods are efficient for solving multi-dimensional problems by decomposing them into sequences of 1-D problems, a $\delta$-form Douglas and Gunn (1964) procedure is applied to the phase-field model in a rectangular region. So-called $\delta$-form quasilinearization (see, e.g., Ames, 1977) is applied to the nonlinear terms of the governing equations to complete the numerical algorithm.

The remainder of this paper is composed of the following sections. We first describe the physical underpinnings of the phase-field model, and we follow this with a section containing a fairly detailed treatment of the associated mathematics. We then present results of solving a particular problem, dendritic growth into a supercooled liquid, utilizing the phase-field approach and discuss the outcomes of these calculations in the context of known laboratory
findings. We then close with a brief summary and conclusions section.

2. BACKGROUND: PHYSICS AND MATHEMATICS OF PHASE-FIELD METHODS

The terminology “phase-field” was first introduced by Fix (1983) to describe a method including two important effects, surface tension and supercooling, not captured in classical Stefan problems. Surface tension is a stabilizing factor, while supercooling tends to amplify any perturbation introduced in the system. Presence of surface tension and supercooling imposes difficulties for numerical solution of Stefan problems, and early attempts to remove the difficulties were not very successful. Fix (1983) introduced into his model a phase variable, a so-called order parameter $\phi$, which is to be determined by an appropriate field equation and varies from one value to another sharply but smoothly. Langer (1986) presented a simple, intuitive description of the phase-field model without proposing any numerical solution approach, and Caginalp and Fife (1986) introduced a phase-field model that incorporated surface tension, anisotropy, curvature and dynamics of the interface, along with supercooling, using the Landau–Ginzburg (1950) approach. Later Penrose and Fife (1990) derived a thermodynamically consistent phase-field model using the analogous entropy functional instead of the Landau–Ginzburg free energy functional. A thermodynamically-consistent phase-field model based on the first and second laws of thermodynamics was also presented by Wang et al. (1993). In general, phase-field models provide an implicit method to solve free-boundary problems without a need for explicit front-tracking of the interface position. In phase-field models, an additional variable, phase field $\phi$, is introduced to label the solid-liquid interface. For example, $\phi = 0$ represents the solid; $\phi = 1$ represents the liquid, and any $\phi$ between zero and unity corresponds to the interface. Therefore, an extra equation, a phase equation, is to be solved in addition to the energy equation.

Caginalp and Socolovsky (1991) showed that the sharp interface problem arising from any of the major phase transition problems (classical or modified Stefan problem, etc.) can be recovered from the mathematical point of view by using the phase-field approach as a numerical method. Caginalp (1989) showed that the scaling limit of parameters in the phase-field equations can lead to the limiting behavior of the modified Stefan model. This work gave
much confidence to researchers working with the phase-field model. Initial studies focused on pure substances in the 2-D case and did not consider convection induced by a velocity field, or small-scale fluctuations. But phase transitions in binary alloys and solidification in the presence of convection have attracted increasing recent interest. Kobayashi (1993) introduced “a kind of phase-field model” to simulate directional solidification and dendritic crystal growth with and without anisotropy. He also investigated stability of the shape of interfaces against noise by introducing low-amplitude random fluctuations. Wheeler et al. (1993) applied the phase-field model to a one-dimensional spherically-symmetric geometry and a planar two-dimensional rectangular region to numerically simulate a solid front growing into a supercooled melt. Wheeler et al. (1992) also presented a phase-field model of solute trapping during solidification by introducing a species equation into the phase-field model. Murray et al. (1993) presented their computation of dendritic solidification based on the model provided in Wang et al. (1993). The numerical study of Kupferman et al. (1994) focused on the asymptotic late-stage growth in the large supercooling limit. It should also be mentioned that Juric and Tryggvason (1996) simulated dendritic solidification with a somewhat different approach to front-tracking.

3. ANALYSIS

In this section, we first present the governing equations of the phase-field model with boundary and initial conditions, followed by a description of the physics of solidification. In particular, conditions for nucleation and a theoretical discussion of crystal growth rate are discussed.

3.1 Governing Equations

In this subsection we introduce the equations of the phase-field model along with the scalings employed to render them dimensionless. Boundary and initial conditions required to formulate a well-posed mathematical problem are also prescribed.

The coupled dimensionless governing equations for phase field and temperature (Wang
et al., 1993 and Chen, 1999) can be written as:

\[
\phi_t = m \Delta \phi + \frac{m}{c^2} \phi(1 - \phi) \left[ \phi - 0.5 + 30 \epsilon a_0 S \phi(1 - \phi) \right], \tag{1a}
\]

\[
\theta_t = \Delta \theta - \frac{30 \phi^2 (1 - \phi)^2}{S} \phi_t. \tag{1b}
\]

In the above equations, \( \phi \) is the phase value to denote solid, liquid and interface; subscripts \( t \) denote partial differentiation with respect to time, and \( \Delta \) represents the Laplacian. By introducing the length scale \( w \) (the geometric size of the physical domain) and the reference time scale \( w^2/\alpha \) (the thermal diffusion time, where \( \alpha = k/\rho c_p \) is the thermal diffusivity of liquid—assumed to be a constant), dimensionless temperature \( \theta \), dimensionless spatial variable \( x \), and dimensionless time variable \( t \) are defined by

\[
\theta = \frac{T - T_m}{T_m - T_0}, \quad x = \frac{\hat{x}}{w}, \quad t = \frac{\hat{t}}{w^2/\alpha}.
\]

Here \( T \) is the temperature field of the domain, and \( T_m \) is the equilibrium melting temperature; \( T_0 \) is the initial temperature; \( \hat{x} \) and \( \hat{t} \) are the spatial and time variables, respectively.

In addition, four dimensionless parameters of the isotropic phase-field model are defined in the following forms:

\[
S = \frac{\rho c_p (T_m - T_0)}{L_0}, \quad \epsilon = \frac{\delta}{w},
\]

\[
m = \frac{\mu \sigma T_m}{\alpha \rho L_0}, \quad a_0 = \frac{\sqrt{2} w}{12 d},
\]

where \( d = c_p \sigma T_m / \rho L_0^2 \) is capillary length; \( S \) is the Stefan number indicating the intensity of supercooling; \( L_0 \) is latent heat per unit volume at the melting temperature; \( \sigma \) is surface tension; \( \mu \) is dimensionless interface kinetic coefficient, \( \epsilon \) the dimensionless interface thickness, and \( \delta \) is the length scale for interface thickness (see details in Wang et al., 1993). As \( \epsilon \to 0 \), the phase-field model approaches the modified Stefan model. Kinetic coefficient \( \mu \) is a microscopic physical parameter, and it reflects the kink density at the step and the atom exchange rate at each kink (Ueda and Mullin, 1975). Linear variation of the kinetic coefficient might be reasonable for a molecularly-rough interface. However, the kinetic co-
efficient strongly depends on the orientation of the interface for faceted interfaces (Langer, 1986). It is difficult to determine the value of this constant theoretically or experimentally; for simplicity, it will be assumed to be constant in the present study.

The boundary conditions are of Neumann type on the rectangular domain $\Omega$ with sides of length $X_0 = 4$ and $Y_0 = 4$, and are given by

$$\frac{\partial \phi}{\partial n} = 0, \quad \frac{\partial \theta}{\partial n} = 0.$$ 

Initially, a small solidified rectangle $\frac{1}{40}$ of the domain size is placed in the center of the domain to start the solidification process. Hence, prescribed initial data take the forms:

$$\theta(x, y) = 0, \quad \phi(x, y) = 0, \quad \text{in} \quad \Omega_0,$$

$$\theta(x, y) = -1, \quad \phi(x, y) = 1, \quad \text{in} \quad \Omega \setminus \Omega_0,$$

where $\Omega_0 \equiv \left[\frac{39}{80}X_0, \frac{41}{80}X_0\right] \times \left[\frac{39}{80}Y_0, \frac{41}{80}Y_0\right]$ and $\Omega \equiv [0, X_0] \times [0, Y_0]$. We apply the $\delta$-form Douglas and Gunn procedure (1964) and $\delta$-form quasilinearization (Ames, 1977) to Eqs. (1) with boundary and initial conditions specified above. Complete details of this computational procedure may be found in Xu (2003).

3.2 Conditions for Nucleation

Solidification processes typically undergo two stages: the first is nucleation controlled, and the second is growth controlled. Once nucleation has occurred, transfer of atoms (and/or molecules) to crystals must continue in order to ensure their growth, which begins the second stage. In Subsection 2.3 we will discuss the dendrite growth rate of the second stage.

A phase transition is usually initiated by a nucleation process, which occurs via rearrangement of atoms to form a new crystal structure. Nucleation of a crystal from its melt depends mainly on two processes: thermal fluctuations which lead to the creation of variously sized crystal embryos, and creation of an interface between the liquid and the solid. Hence, the critical condition for nucleation of a spherical nucleus is derived by summing the volume and interface terms for the Gibbs free energy as shown by Kurz and Fisher (1998)
and Papon et al. (2002):

\[
\Delta G = \Delta G_i + \Delta G_V \\
= 4\pi r^2 \sigma + \frac{4\pi r^3}{3} \Delta g_V,
\]

where \( r \) is the radius of a 3-D spherical nucleus, \( \sigma \) is the surface tension, and \( \Delta g_V \) designates the Gibbs free energy of formation of the new phase per unit volume. If \( \Delta h_V \) and \( \Delta s_V \) respectively denote changes in enthalpy and entropy associated with the formation of a unit volume of a new phase, with \( \Delta h_V = -L_f \) at the melting temperature \( T_m \) and the hypothesis that specific heat \( c_p \) is constant, and the same in both phases is invoked, we deduce that

\[
\Delta g_V = -L_f \frac{\Delta T}{T_m},
\]

as in Papon et al. (2002). Here \( L_f \) is the heat of fusion per unit volume, and \( \Delta T = T_m - T \) represents the degree of supercooling of liquid. Therefore, the critical radius for nucleation is

\[
r^* = \frac{2\sigma T_m}{L_f \Delta T},
\]

which means \( \Delta G \) achieves a maximum as \( r \to r^* \) when \( T < T_m \ (\Delta T > 0) \). For \( r > r^* \), formation of nuclei of increasing size results in stabilization of the solid phase. The analogous derivation applied to 2-D disk-shaped nucleus leads to the critical radius

\[
r^* = \frac{\sigma T_m}{L_f \Delta T}.
\]

### 3.3 Dendrite Growth Rate

Once a nucleus is formed, it will continue to grow. The growth rate is limited by the kinetics of atom attachment to the interface, capillarity and diffusion of heat and mass (Kurz and Fisher, 1998). In other words, the crystal growth rate depends on the net difference between the rates of attachment and detachment of the atoms at the interface. Moreover, it depends on diffusion rate in the liquid and the interface roughness on the microscopic
scale. Cahn (1960) has shown theoretically that there are two major mechanisms related to crystal growth: stepwise and continuous. The mechanism of the motion of an interface depends on the driving force, and what constitutes a sufficiently large driving force to select a particular mechanism depends on the diffuseness of the interface. Cahn et al. (1964) have identified three different regimes associated with increasing levels of driving force: classical, transitional and continuous. These correspond to low driving force (lateral mechanism), intermediate driving force (lateral spreading mechanism) and high driving force (continuous mechanism), respectively. They also derived expressions for the growth rate in the three regimes. Here, for simplicity we introduce only the expressions for classical (stepwise) and continuous regimes.

In the classical regime

\[
G = \frac{\beta(1 + 2\sqrt{g}) DL^2 \Delta T^2}{g 4\pi T^2 RT \sigma V_m},
\]

or

\[
G = \frac{\beta DL^2 \Delta T^2}{4\pi g T^2 RT \sigma V_m} \quad \text{for} \quad g \ll 1.
\]

In the continuous regime

\[
G = \frac{\beta DL \Delta T}{a RT^2},
\]

where \( g \) is the diffuseness parameter (\( g \approx 1 \) implies that the interface is sharp); \( L \) is the latent heat of fusion per mole, \( V_m \) is the molar volume of solid, \( a \) is the step height, and \( R \) is the gas constant as in Hillig (1958). The assumption that the transport process by which molecules add to the solid at the step is related to liquid diffusion introduces the parameter \( \beta \) that expresses the degree to which this simple assumption is inadequate:

\[
\beta = 6 \left( \frac{a}{\lambda} \right)^2 \left( \frac{\nu_i}{\nu_l} \right),
\]

where \( \lambda \) is the mean jump distance in the liquid and \( \nu_i, \nu_l \) are the jump frequencies at the interface and in the liquid, respectively. The growth rate equations (4) and (5) indicate a quadratic relation between the growth rate and the degree of supercooling for the lateral
mechanism and a linear relation for the continuous mechanism.

4. RESULTS AND DISCUSSION

The computations reported here were conducted on a HP SuperDome SMP operated by the University of Kentucky Computing Center. The Fortran 90 computer programming language was used with 64-bit arithmetic. In the present study, a square domain four units on a side is employed. Pure metal nickel is used, and no anisotropy is introduced. The physical properties of nickel are listed below (see, e.g., Brandes, 1983):

- Density, \( \rho = 7905 \text{ kg/m}^3 \),
- Specific heat, \( c_p = 656.19 \text{ J/(kg} \cdot \text{ K)} \),
- Thermal conductivity, \( k = 88.5 \text{ J/(m} \cdot \text{ K} \cdot \text{s)} \),
- Surface tension, \( \sigma = 0.37 \text{ N/m} \),
- Melting temperature, \( T_m = 1728 \text{ K} \),
- Heat of fusion at melting temperature, \( L_0 = 0.292 \times 10^6 \text{ J/kg} \).

For simplicity, we assume that density, specific heat and thermal conductivity are constant, and their values in the liquid are equal to those in the solid. Since there is no generally accepted strategy to set a value for the kinetic coefficient \( \mu \), we assume that it is of \( O(1) \) for pure metal, and choose \( \mu = 3.08 \text{ m/(K} \cdot \text{s)} \) such that the dimensionless kinetic coefficient \( m \) is exactly 0.05.

In phase-field models, the dimensionless interfacial thickness \( \epsilon \) strongly influences the (numerical) spatial step size. Therefore, it is important to choose a reasonable \( \epsilon \) to ensure stability of the solution process (see Xu et al., 2002 for details). In the current computations a fixed \( \epsilon = 0.004 \) is determined after a sequence of numerical tests. The length scale is \( w = 2.1 \times 10^{-6} \text{ m} \), and \( a_0 = 400 \).

The Neumann boundary condition for temperature implies that the domain \( \Omega \) is adiabatic. To verify this for our computed results, we compare the internal energies of the
initial and final states. The results show that the difference between initial and final internal energies is within the truncation error bounds of the numerical methods employed, and decreases with grid refinement, thus indicating that the energy is conserved to within numerical discretization errors.

Dendrite shapes and temperature fields at different times during the solidification process are presented for initial Stefan number $S = 0.5$ in the first subsection. The nucleation condition and crystal growth rate properties are discussed later. Finally, different dendrite structures due to different initial shape are provided.

4.1 Dendrite Structures at Different Time

![Dendrite Structures](image)

Figure 1: Dendrite structures at time $t = 0.05$, $t = 0.1$ and $t = 0.2$.

Figure 1 presents the dendrite interface locations at three different times $t = 0.05$, $0.1$ and $0.2$ for the Stefan number $S = 0.5$. The intersections of grid lines and a curve corresponding to $\phi = 0.5$ are labeled as points on the interface. The criterion that an interface point must be on a cell wall where the phase field value $\phi$ is changing from $\phi < 0.5$ to $\phi > 0.5$ is applied to determine the intersections. Figure 2 displays the temperature fields at these same times. The grid sizes for Figs. 1 and 2 are $\Delta x = \Delta y = 0.01$, and $\Delta t = 5 \times 10^{-5}$.

4.2 Critical Initial Area

In order to establish an equivalence between the computational square initial area and a theoretical 2-D circular nucleus, we introduce a “hydraulic diameter” as employed in fluid
Figure 2: Temperature fields at $t = 0.05$, $t = 0.1$ and $t = 0.2$.

mechanics analyses of duct flow (see, e.g., Wilcox, 2000):

$$D_h = \frac{4A}{P},$$

where $A$ is cross-sectional area, and $P$ is perimeter. Therefore we could rewrite Eq. (3) in the form of the side length of the square as

$$\hat{L}^* = \frac{2\sigma T_m}{L_f \Delta T}.$$  

Introducing the Stefan number leads to a dimensionless critical length of the form

$$L^* = \frac{2\sigma T_m c_p}{\rho L_f^2 Sw}.$$  \hspace{1cm} (6)

Therefore, the theoretical critical lengths are 0.059 and 0.030 corresponding to the Stefan numbers 0.01 and 0.02, respectively. To verify that the relation between the critical length and the Stefan number obeys Eq. (6), we have conducted simulations with Stefan numbers $S = 0.01$ and 0.02. The grid sizes are $\Delta x = \Delta y = 0.005$, and the time step is $\Delta t = 2.5 \times 10^{-5}$. Results shown in Figs. 3 and 4 indicate that there exists a critical length when $S$ is small, and this length decreases as $S$ increases. In Figs. 3 and 4, the left plots show that the solid area is decreasing as time increases, indicating shrinking of the nuclei; the plots on the right indicate that the nuclei are growing with time. The computed critical lengths from these figures are in the range of $0.04 \sim 0.05$ and $0.02 \sim 0.03$ corresponding to the Stefan number.
0.01 and 0.02, respectively, which are almost the same as the theoretical ones computed from Eq. (6). The consistency of the computed and theoretical critical lengths in the phase-field model indicates that the phase-field model is able to capture the physics of solidification.

![Figure 3](image1.png)  
**Figure 3:** The solid phase area as a function of time with two different initial lengths 0.04 and 0.05 at $S = 0.01$.

![Figure 4](image2.png)  
**Figure 4:** The solid phase area as a function of time with two different initial lengths 0.02 and 0.03 at $S = 0.02$.

### 4.3 Growth Rate

In this subsection, the behaviors of dendrites under various supercoolings are exhibited, and the comparison of the growth rate at different Stefan numbers is conducted. In addition, the relationship between the growth rate and the Stefan number is discussed. The domain size is enlarged to $\Omega \equiv [0, 8] \times [0, 8]$ to accommodate the rapid growth, and hence large dendrite, caused by the large Stefan number. The grid sizes are $\Delta x = \Delta y = 0.01$, and the time step is $\Delta t = 5 \times 10^{-5}$. We conduct the simulation until $t = 0.1$. The computed growth rate $V_n$ is
an averaged one; i.e., \( V_n = \frac{\Delta V}{\Delta t} \), where \( V \) is the solid phase area. According to Glicksman and Schaefer (1967), the interface can be considered to be in dendritic form in a normally supercooled melt \( (S < 1) \), and “scallops” form in a hypercooled melt \( (S > 1) \). A quasi-planar form (whose structure has irregularity between planar and “scallops”) is observed if supercooling is continuously increased. Figure 5 illustrates that computations of the phase-field model also follow this pattern. In this figure interface shapes at time \( t = 0.1 \) with three different Stefan numbers 0.5, 1.0 and 1.4 are plotted. We could also expect that as the supercooling increases, the interface becomes, from a morphological standpoint, almost indistinguishable from a smooth curve.

![Figure 5](image_url)

**Figure 5:** The interface shapes at \( t = 0.1 \) for three Stefan numbers \( S \): \( S = 0.5 \) (dendritic), \( S = 1.0 \) (scalloped) and \( S = 1.4 \) (quasi-planar).

![Figure 6](image_url)

**Figure 6:** Computational solutions of the interfacial speed as a function of time for different Stefan number: (a) \( S = 0.1 \); (b) \( S = 0.5 \).

The similarity solution of the classical Stefan problem provided in Alexiades and Solomon
(1993) and Davis (2001) shows that for one-dimensional freezing into a supercooled melt 
\( S < 1 \), interface location as a function of time is \( h \sim t^{\frac{1}{2}} \), i.e., \( V_n \sim t^{-\frac{1}{2}} \). Moreover, there 
exists no solution for \( S > 1 \) because without kinetic supercooling, the heat required to raise 
the temperature to \( T_m \) is higher than the latent heat provided, violating the energy balance. 
However, with the presence of kinetic supercooling, there are solutions for all \( S \): \( h \sim t^2 \), 
i.e., \( V_n \sim t^{-\frac{1}{2}} \) for \( S = 1 \), and \( h \sim t \), i.e., \( V_n \sim constant \) for \( S > 1 \) (Davis, 2001). Lack of 
an analytical solution for two-dimensional freezing into a supercooled melt in a rectangular 
domain implies that no analytical expression for the interfacial speed as a function of time 
can be obtained. But the computational solutions shown in Fig. 6 provide this relation as 
follows: the curves \( 0.3t^{-\frac{2}{3}} \) and \( 2t^{-\frac{2}{3}} \) are used to approximate the interfacial speeds for \( S = 0.1 \) 
and \( S = 0.5 \), respectively. We note that the power of \( t \) is essentially constant if \( S < 0.5 \) 
but increases if \( 0.5 < S < 1.0 \) (not shown in Fig. 6). This observation can be explained 
by the relation between the interfacial speed and the Stefan number shown in Fig. 7 where 
the averaged interfacial speed versus \( S \) at \( t = 0.1 \) is plotted. The existence of a quadratic 

![Graph: Relation between interfacial speed \( V_n \) and the Stefan number \( S \).](image)

Figure 7: Relation between interfacial speed \( V_n \) and the Stefan number \( S \).

relationship between \( V_n \) and \( S \) indicates the lateral mechanism for dendrite growth with 
\( S < 1 \), and the continuous mechanism (approximately linear) with \( S > 1 \) by applying Eqs. 
(4) and (5), which implies that these growth mechanisms are determined by the physical 
properties of pure nickel, and they are different for various materials. The quadratic rather 
than linear relationship for \( S < 1 \) also explains why the power of \( t \) is increasing as \( S \) increases. 
We observe that there is no apparent discontinuity in slope near \( S = 1 \) in Fig. 7, where the
system is transitioning from supercooled to hypercooled. This observation is consistent with the experimental evidence of Glicksman and Schaefer (1967).

5. SUMMARY AND CONCLUSIONS

In this paper we have presented the physical and mathematical bases for a relatively new approach to simulating freezing in the context of complex morphologies such as dendrites that may occur when the liquid phase has been supercooled, and which have been observed in cryobiology processes. This technique, termed the phase-field method, naturally lends itself to numerical implementation in the form of so-called fixed-grid methods, and within this class is the only approach to automatically incorporate the physically-stabilizing effect of surface tension in the formulation.

We have employed a very straightforward numerical implementation and presented computed results indicating the ability of the phase-field method to capture the physics of solidification in the presence of supercooling, a valuable attribute in the context of cryobiological process predictions. In particular, we have demonstrated that this approach is capable of predicting nucleation and growth rate, and in the case of pure metallic nickel, we have shown further that our computed results are in accord with theoretical predictions of several different types, and at least qualitatively with physical measurements of solidification rate as a function of Stefan number.

In light of this we believe it is reasonable to conclude that the phase-field method should be a useful tool for cryobiological simulations, especially in the presence of supercooling, provided the required physical constants can be obtained.

REFERENCES


