A SURVEY OF SUPERCOOLED STEFAN PROBLEMS

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Abstract

Supercooled Stefan problems describe the freezing of a liquid initially cooled below its freezing point. The liquid and solid phases are separated by a sharp interface that constitutes a moving boundary. Such problems are notoriously ill-posed and not only is a planar moving boundary unstable to small perturbations, but the problem is prone to so called finite time blow up if the degree of initial undercooling is too great. A number of modifications to the the isothermal phase change condition have been proposed in order to prevent finite time blow up. These include applying a Gibbs-Thomson condition and/or a kinetic undercooling condition at the free boundary. A survey of recent results for supercooled Stefan problems, including effects of these modifications, is presented.

1. Introduction

Stefan problems arise as models of freezing (or melting) processes. In deriving a Stefan problem simplifications are necessary in order to obtain a tractable problem. Typically, but not necessarily, it is assumed that the thermal properties (such as conductivity and specific heat) are constant within each phase. More drastically, it is usually assumed that the density of material is temperature independent and the same in each phase, that heat is transferred only by conduction in both liquid and solid phases and that there is a sharp, well defined, interface separating the liquid and solid phases. For a complete description of the physical derivation of the classical Stefan problem see, for example, Crank [1], Elliott & Ockendon [2], Hill & Dewynne [3], or Rubinstein [4].

As the position of the interface is not known a priori, two boundary conditions must be imposed on it; roughly, one to determine its evolution and one to provide a boundary condition for the heat flow equations in each phase. Typically, the phase change is assumed to be isothermal,

$$T = T_{\text{melt}} \quad \text{on the interface,} \tag{1.1}$$

where T is the temperature and T_{melt} is the equilibrium phase change temperature (for a planar interface and fixed pressure and density). Across the interface there is a discontinuity in heat flux, due to the release of latent heat during freezing. Energy balance across the interface gives the Stefan condition

$$\left(k\frac{\partial T}{\partial n}\right)_{\text{solid}} - \left(k\frac{\partial T}{\partial n}\right)_{\text{liquid}} = \rho L v_n \quad \text{on the interface,} \tag{1.2}$$

where k is the thermal conductivity (and k may be different in the different phases), $\partial T/\partial n$ the normal derivative of T with respect to the normal vector pointing from the solid into the liquid, ρ the density, L

the latent heat of fusion, and v_n the normal velocity of the interface. Similar boundary conditions can be derived for the crystalization of a solid from a solution, where the solute is transported by diffusion in the solution.

A supercooled Stefan problem describes the solidification of a liquid initially cooled below its freezing point (or crystalization from a supersaturated solution). There are a number of difficulties associated with supercooled Stefan problems subject to the boundary condition (1.1) Firstly, a planar interface suffers from the Mullins-Sekerka [5] instability (see [6] and Ockendon [7]), and, secondly, if the initial undercooling (or super saturation) is too great then the velocity of the interface may become infinite after a finite time (see Sherman [8], Fasano *et al* [9], Howison *et al* [10], and Fasano *et al* [11], [12]). It is known that these problems do not occur if the liquid is initially above its freezing point (or the solution is not supersaturated); the supercooled problem is ill-posed in this sense whereas the usual Stefan problem is well posed (see for example [7]). These well known results are discussed in Sections 2 and 3, together with some recent large time asymptotic results for the interface motion. The instability of the planar interface is physically acceptable, being consistent with observations of dendritic growth in supercooled melts. The isothermal boundary condition (1.1) does not, however, provide any selection mechanism for a preferred dendrite shape (see Langer [13] for a fuller discussion of selection and pattern formation in dendritic supercooled solidification) . The case in which the velocity of the interface becomes infinite in finite time is not physically acceptable. If the velocity becomes infinite at a point, the temperature becomes discontinuous at that point (through (1.2)), in general the solution cannot be continued beyond that time, and the model breaks down entirely (but see [12]). For these reasons it is felt that boundary condition (1.1) is acceptable if the liquid temperature is above its melting point, but untenable if the liquid is initially supercooled.

In order to prevent finite time blow up, and to provide a mechanism for dendrite selection, the Gibbs Thomson effect has been invoked by various authors (for example [5], [6], [13], Chadam & Ortoleva [14], Chadam, Howison & Ortoleva [15]). Thus condition (1.1) is replaced by

$$T = T_{\text{melt}} - \Gamma\kappa \quad \text{on the interface,} \tag{1.3}$$

where Γ is a positive constant and κ is the local mean curvature of the interface (relative to the solid) at a point on the interface. The idea behind this is that, firstly, it introduces a new length scale into the problem and may thus produce a preferred dendrite geometry and, secondly, that if a perturbation begins to grow rapidly then the local curvature increases so, through (1.3), the local phase change temperature decreases as does the local temperature gradient, resulting in a decreased velocity, through (1.2). This latter effect is assumed to prevent finite time blow up. As noted in Section 4, replacing (1.1) by (1.3) does not always have these effects.

In Section 5 the effect of introducing a kinetic undercooling boundary condition,

$$T = T_{\text{melt}} - \epsilon v_n \quad \text{, on the interface,} \tag{1.4}$$

is considered. Here $\epsilon > 0$ is a positive constant and v_n is the normal velocity of the interface. Such a condition arises from a sharp interface limit of the phase field model (see Caginalp [16], [17], [18], but see also Penrose & Fife [19]). Replacing (1.1) by (1.4) certainly prevents finite time blow up, by the maximum principle for the heat equation (see Section 5). Implications for the large time asymptotic behaviour of the interface and for the stability of the interface are also discussed.

2. The Classical Supercooled Stefan Problem

A typical supercooled Stefan problem is

$$\begin{aligned} u_t &= u_{xx}, && s(t) < x < \infty,\ t > 0, \\ u(s(t),t) &= 0, && t > 0, \\ u_x(s(t),t) &= -\dot{s}(t), && t > 0, \\ u(x,t) &\to u_\infty && \text{as } x \to \infty, \\ u(x,0) &= \phi(x) \le 0, && 0 = s(0) \le x < \infty, \end{aligned} \tag{2.1}$$

where $\phi(x) \le 0$ is a known, bounded function, $u_\infty = \lim_{x\to\infty} \phi(x)$, and $u(x,t)$ and $s(t)$ are to be determined.

Interpretting x, t and u as nondimensional position, time and temperature, respectively, (2.1) is a simple model for the freezing of a semi-infinite one dimensional liquid (see Fig. 1).

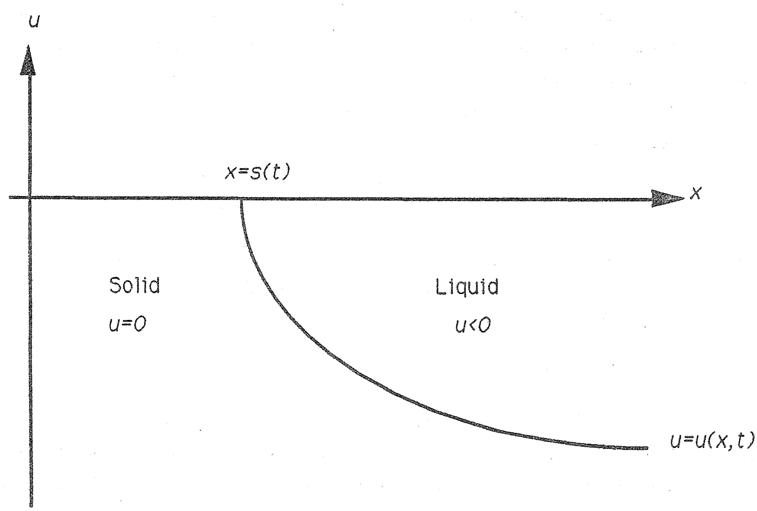

Figure 1

The freezing point is $u = 0$, the freezing front is $x = s(t)$ and, from $(2.1)_5$, the liquid is initially below its freezing point; for this reason the problem is refered to as supercooled. Condition $(2.1)_2$ asserts that the phase change is isothermal, and condition $(2.1)_3$ balances the jump in heat flux across the solid/liquid interface, $x = s(t)$, with the latent heat released at the interface. The temperature in the solid is constant, $u = 0$, so there are no thermal gradients and no heat conduction in the solid; there is only the heat flow in the liquid to consider, $(2.1)_1$. It is important to note that in (2.1) the temperature has been scaled in such a way that the latent heat released by a unit volume of liquid freezing equals the heat necessary to raise a unit volume of liquid by exactly one (nondimensional) degree. Similarly, if $-u$ is interpretted as concentration of a solute in a solution and $u = 0$ is taken as the saturation concentration then (2.1) describes crystalization from a supersaturated melt, $x = s(t)$ being the boundary between crystal and solution.

Formally, (2.1) describes the melting of a superheated solid (the temperature being $-u$ in that case). This situation does not arise in practice, in general. In broad terms, a supercooled liquid is metastable whereas a superheated solid is unstable. That is, a supercooled liquid has to overcome a potential barrier in order to reach its stable equilibrium, namely, for large scale freezing to begin small scale nucleation must occur. The Gibbs Thomson effect (c.f. (1.3) and Section 4) prevents small diameter high curvature solid particles forming until the liquid temperature falls below a threshold. There is a critical radius associated with a sphere of solid in a supercooled melt, due to the Gibbs Thomson effect, such that if the radius of the solid sphere is less than the critical radius it will melt whereas if the radius of the solid sphere is greater than the critical radius it will grow (see [5], for example). If Γ in (1.3) is large enough, significant supercooling is necessary before large scale freezing can commence.

Several exact solutions of (2.1) are known. Firstly, there are similarity solutions

$$u(x,t) = U(x/\sqrt{t}), \quad s(t) = \beta\sqrt{t}, \quad U(\xi) = -\frac{\beta}{2}e^{\beta^2/4}\int_\beta^\xi e^{-y^2/4}\,\mathrm{d}y, \tag{2.2}$$

where $u(x,0) = \phi(x) = u_\infty$ is constant and is related to β by

$$-\beta e^{\beta^2/4}\int_{\beta/2}^\infty e^{-y^2}\,\mathrm{d}y = u_\infty, \tag{2.3}$$

(see Carslaw & Jaeger [20]). It is well known ([20]) that (2.3) has real positive solutions for β if and only if $-1 < u_\infty < 0$. Moreover, if $-1 < u_\infty < 0$ then β is uniquely determined and as $u_\infty \to -1$, $\beta \to \infty$. Secondly, there are travelling wave solutions of the form

$$u(x,t) = -1 + e^{-V(x-Vt)}, \quad s(t) = Vt \tag{2.4}$$

where $V > 0$ is an arbitrary positive real number. The initial value $\phi(x)$ corresponding to (2.4) is

$$\phi(x) = -1 + e^{-Vx}, \quad 0 \le x < \infty.$$

Note that as $V \to \infty$, $\phi(x) \to -1$ uniformly on any interval $[a,\infty)$ where $a > 0$. Both of these classes of exact solutions (2.2)–(2.4) suggest that difficulties may arise if we put $\phi(x) = -1$ in (2.1). They also suggest two questions:

(i) Is it possible to obtain solutions of (2.1) with $s(t) \approx kt^\alpha$ for $1/2 < \alpha < 1$, and if so is what is the dependence of $s(t)$ on $\phi(x)$? and

(ii) What happens if $\phi(x) < -1$ at some (or all) points?

Questions (i) and (ii) have been partially answer in Dewynne *et al* [21], where the large time asymptotic behaviour of the moving boundary $s(t)$ is related to the function $\phi(x)$. By using the integral transform

$$\hat{u}(p,t) = \int_{s(t)}^\infty e^{-px}u(x,t)\,\mathrm{d}x, \quad \hat{\phi}(p) = \int_0^\infty e^{-px}\phi(x)\,\mathrm{d}x, \tag{2.5}$$

(see also Grinberg and Chekmariva [22], Crowley and Ockendon [23] and Hill [24]), it is shown in [21] that if a solution of (2.1) exists for all t then the moving boundary $s(t)$ and initial data $\phi(x)$ are related by the integral equation

$$\hat{\phi}(p) = -\frac{1}{p} + p\int_0^\infty e^{-ps(\tau)-p^2\tau}\,\mathrm{d}\tau. \tag{2.6}$$

Given some $s(t)$ with $s(0) = 0$ such that the integral on the right hand side of (2.6) exists, it is possible in princple to find $\phi(x)$ such that (2.1) has $s(t)$ as its free boundary. The calculations, however, limit this procedure to the two cases $s(t) = \beta\sqrt{t}$, (2.2)–(2.3), and $s(t) = Vt$, (2.4). By considering the limit $p \to 0$ in (2.6), it is deduced in **[21]** that, provided a solution of (2.1) exists for all t, then:

(i) If $-1 < \phi(\infty) < 0$ then $s(t) \sim \beta\sqrt{t}$ as $t \to \infty$, where β satisfies (2.3) with $u_\infty = \phi(\infty)$. The similarity solutions (2.2) are special cases of this result.

(ii) If $\phi(x) \sim -1 + cx^\gamma$ as $x \to \infty$, where $c > 0$ and $-1 < \gamma < 0$ then $s(t) \sim kt^\alpha$ as $t \to \infty$, where $1/2 < \alpha = 1/(2+\gamma) < 1$, and $k = (\Gamma(3+\gamma)/c\Gamma(1+\gamma))^\alpha$.

(iii) If $\phi(x) = -1 + \phi_1(x)$ where $0 < \int_0^\infty \phi_1(x)\,\mathrm{d}x = 1/V < \infty$ then $s(t) \sim Vt$ as $t \to \infty$. The travelling wave solutions (2.4) are particular cases of this result.

(iv) If $\hat{\phi}(p) \sim -1/p + ap^\gamma$, for $0 < \gamma < 1$, as $p \to \infty$ (that is, if $\phi(x) \sim -1 + \phi_1(x)$, where $\phi_1(x)$ is not identically zero but $\int_0^\infty \phi_1(x)\,\mathrm{d}x = 0$) then $s(t) \sim kt^\alpha$ as $t \to \infty$ where $1 < \alpha = 1/(1-\gamma)$ and $k = (\Gamma(2-\gamma)/a)^\alpha$. Anticipating the discussion in the following section, we might refer to this case as infinite time blow up, as $\dot{s}(t) \to \infty$ as $t \to \infty$. Note, however, that $\phi(x) < -1$ at some points, and this may lead to finite time blow up; the assumption of existence for all t puts extra constraints on $\phi_1(x)$ here.

(v) If $\phi(x) = -1$, then $\hat{\phi}(p) = -1/p$ and (1.6) becomes

$$\int_0^\infty e^{-ps(\tau)-p^2\tau}\,\mathrm{d}\tau = 0, \quad \forall p > 0.$$

Thus (2.1) has no solution $u(x,t)$ that is valid for all $t > 0$ and has a transform (2.5) if $\phi(x) = -1$. Again, this suggests difficulties if $\phi(x) = -1$ in (2.1).

It is known that if $\phi(x) > -1$, $\forall x$ then (2.1) has a solution for all t (see Fasano & Primicerio **[25]**). Recently Ricci & Xie **[26]** have considered the stability of solutions of (2.1) under the assumption $\phi(x) > -1$, $\forall x$ and have given necessary and sufficient conditions on $\phi(x)$ in order for $s(t) \sim \beta\sqrt{t}$ or $s(t) \sim Vt$ as $t \to \infty$. Essentially these conditions are (i) and (iii) above. The asymptotic behaviour (i) was also obtained in [14], under more restrictive assumptions.

It is widely known that the planar moving boundaries in (2.2) and (2.4) are linearly unstable ([6], [7]), in the following sense. The two dimensional equivalent of problem (2.1) is

$$\begin{aligned}
u_t = u_{xx} + u_{yy}, &\quad S(y,t) < x < \infty,\ t > 0,\\
u(S(y,t),y,t) = 0, &\quad t > 0,\\
u_x - u_y S_y = -S_t, &\quad \text{on } x = S(y,t),\ t > 0,\\
u_x,\ u_y \to 0, &\quad \text{as } x \to \infty,\\
u(x,y,0) = \Phi(x,y) < 0, &\quad S(y,0) \le x < \infty,
\end{aligned} \tag{2.7}$$

where $x = S(y,t)$ is the moving boundary and $S(y,0)$ and $\Phi(x,y)$ are given (see Fig. 2).

For the purposes of a linear stability analysis, it suffices to consider the case in which x is a function of y and t, rather than the more general relation $\hat{S}(x,y,t) = 0$. A standard linear stability analysis of (2.4) is achieved by substituting

$$S(y,t) = Vt + \delta e^{\sigma t + i\omega y},$$
$$u(x,y,t) = -1 + e^{-V(x-Vt)} + \delta e^{\sigma t + i\omega y} U(x - Vt),$$

where $\delta \ll 1$, into (2.7) and retaining only terms of $O(\delta)$ (the $O(1)$ terms cancel). The resulting $O(\delta)$ problem is

$$U'' + VU' - (\sigma + \omega^2)U = 0, \quad U(0) = V, \quad U'(0) = -(V^2 + \sigma), \quad U(\infty) = 0. \tag{2.8}$$

(The condition $U(\infty) = 0$ asserts that the perturbations are localised near the free boundary.)

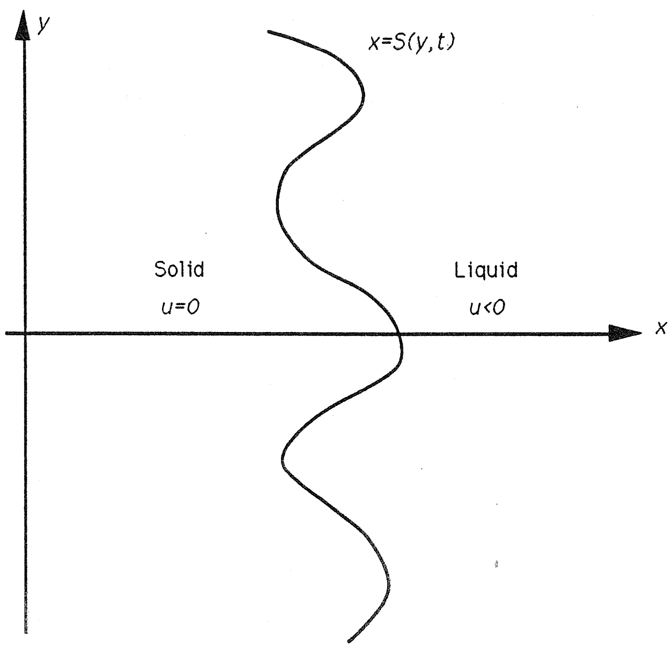

Figure 2

The case $\sigma < 0$ is uninteresting; the harmonic perturbations die away exponentially. If $\sigma > 0$ then, in order to satisfy (2.8), σ must satisfy the dispersion relation $\sigma = V|\omega|$. Thus, there are disturbance modes that grow exponentially (for small times, the linear analysis clearly fails when $\sigma t \sim -\log \delta$ and nonlinear effects must be considered). This situation is not wholly undesirable as it is not entirely inconsistent with the dendritic growth observer in supercooled melts. There is no mechanism, however, for selecting a preferred frequency, save that high frequency disturbances initially grow more rapidly than low. Similar analyses of the stability of the free boundary in a supercooled Stefan problem can be carried out for other geometries; for spherical radially symmetric problems see [5] and [**15**]; for the parabolic Ivantsov solutions (Ivantsov [**27**], Horvay & Cahn [**28**]) see [**13**]. Qualitatively, the results are the same; if an isothermal boundary condition is applied in a supercooled Stefan problem then the free boundary is unstable to perturbations of all modes, with higher mode disturbances growing more rapidly.

3. Finite Time Blow Up

Finite time blow up was first demonstrated by Sherman [8]. He considers the simple supercooled problem

$$\begin{gathered} u_t = u_{xx}, \quad 0 < x < s(t),\ t > 0, \\ u(s(t),t) = 0,\ u_x(s(t),t) = -\dot{s}(t), \quad t > 0, \\ u_x(0,t) = 0,\ t > 0, \quad u(x,0) = \phi(x) \le 0,\ 0 \le x \le s(0), \end{gathered} \tag{3.1}$$

where $\phi(x) \le 0 \in C^2[0, s(0)]$ and satisfies the compatibility conditions $\phi'(0) = \phi(s(0)) = 0$. It is shown in [8] and [30] that solutions of (3.1) must exhibit one of the following behaviours;

(i)	$u(x,t) \to 0,\ s(t) \to 0$ as $t \to \infty$	(global existence),
(ii)	$s(t_c) = 0$ for some $t_c < \infty$	(finite time extinction),
(iii)	$s(t_c) > 0,\ \dot{s}(t_c) = -\infty$ for some $t_c < \infty$	(finite time blow up).

From (3.1) Sherman derives the global energy balance condition

$$E = s(t) + \int_0^{s(t)} u(x,t)\,\mathrm{d}x = s(0) + \int_0^{s(0)} \phi(x)\,\mathrm{d}x \tag{3.2}$$

and considers the cases where $E < 0$. Assuming that (3.1) has a solution for all $t > 0$ in these cases, Sherman shows that $\dot{s}(t) \le 0$ and $\hat{u}(x,t) \le u(x,t) \le 0$ for $0 \le x \le s(t) \le s(0)$, where $\hat{u}(x,t)$ solves

$$\hat{u}_t = \hat{u}_{xx}, \quad \hat{u}_x(0,t) = 0, \quad \hat{u}(s(0),t) = 0, \quad \hat{u}(x,0) = \phi(x),$$

and hence that as $t \to \infty$, $u(x,t) \to 0$. Thus $\lim_{t\to\infty} s(t) = E < 0$ which is absurd and inconsistent with either of (i) or (ii) above. Thus, $E < 0$ implies case (iii) above and finite time blow up occurs.

It is shown in [9] that if $\phi(x_0) = -1$ for at most one $x_0 \in [0, s(0)]$ then $E > 0$, $E = 0$ and $E < 0$ imply cases (i), (ii) and (iii), respectively. In general, however, the global condition $E \ge 0$ does not preclude case (iii), see [12]. Necessary and sufficient conditions for finite time blow up have been given in [11], [12]. These conditions involve the negativity set of the function

$$c(x,t) = \int_{s(t)}^{x} (x-\xi)[1 + u(\xi,t)]\,\mathrm{d}\xi, \qquad (\text{note; } c_t = u) \tag{3.3}$$

(that is the set $N(t) = \{x : c(x,t) < 0\}$) and its intersection with the free boundary. The function (3.3) is computable, and satisfies an unconstrained Crank-Gupta problem [1], [31]; that is the problem of [31], without the constraint $c \ge 0$. Using the function $c(x,t)$, solutions of (3.1) that exhibit recoverable finite time blow up (that is, solutions of (3.1) that can sensibly be continued beyond the time t_c when $\dot{s} = -\infty$) are constructed in [12], and necessary and sufficient conditions for such continuation are given.

The physical nature of the difficulty is clear from inspection of (3.2). Problem (3.1) has the same temperature scaling as (2.1), so that E represents the total latent heat available initially minus the heat required to warm all of the supercooled liquid to its constant melting point. If E is negative, there is not enough latent heat in the system to warm the entire liquid; thermal gradients steepen as the interface proceeds towards the origin and become infinite after a finite time. As noted in [12], finite time blow up will occur in (3.1) if and only if the mean local energy

$$\hat{E}(x,t) = \frac{1}{x - s(t)} \int_{s(t)}^{x} (x - \xi)[1 + u(\xi,t)]\, \mathrm{d}\xi$$

becomes negative at some point (x,t). For problem (2.1) with $\phi(x) = -1$, $0 \leq x < \infty$, instantaneous blow up at time $t = 0$ seems likely, although it has not been proved. It is possible to achieve situations in which the right hand side of (3.2) is negative in practice; Shaefer & Glicksman [29] have reported initial undercoolings corresponding to $\phi(x) = -1.8$ in certain materials.

Identical arguments to those of Sherman [8] can be applied in radially symmetric spherical and cylindrical geometries to deduce that finite time blow up can occur. For the radially symmetric cylindrical and spherical versions of (2.1) (only the heat equation is modified) it is easy to deduce that the energy

$$E = \frac{1}{(1+n)} s(t)^{n+1} + \int_0^{s(t)} r^n u(r,t)\, \mathrm{d}r$$

is conserved (i.e. $\dot{E} = 0$). Here $n = 1$ and $n = 2$ correspond to the cylindrical and spherical cases respectively. If initially $E < 0$ then, by Sherman's argument, finite time blow up must occur. Similarly, by considering energy arguments, it can be shown that two phase supercooled Stefan problems with isothermal interfaces can exhibit finite time blow up.

In more than one spatial dimension, the problem of finite time blow up is considerably more complex; finite time blow up corresponding to the development of singularities, such as cusps, in an initially smooth free boundary. Explicit examples of two dimensional, radially asymmetric, singularity formation are given in [10]. An analysis of the multidimensional supercooled Stefan problem is given by di Benedetto & Friedman [32], who show that non-uniqueness is possible and that instability and fingering are generic.

4. The Gibbs Thomson Boundary Condition

The Gibbs Thomson condition (1.3) arises from equilibrium thermodynamic considerations near a curved interface between liquid and solid (see [5], [29]). Its effect on the stability of planar interfaces is considered in [6] and on spherical interfaces in [5]. In [5] and [6] it is assumed that the heat equation can be approximated by Laplace's equation; that is that the interface moves slowly on a diffusive time scale (in the context of supercooled solidification this means that the latent heat is very much greater than the sensible heat, in particular that the degree of supercooling can never be large on the nondimensional scale used in Sections 2 and 3). In [15] and [14] the same problems are considered, respectively, but the time derivative is retained in the heat equation. The details differ quantitatively but not qualitatively.

In the context of supercooled solidification, condition (1.3) becomes

$$u = -\gamma\kappa, \quad \text{on the interface} \tag{4.1}$$

in the nondimensional units of Section 2. In general the curvature κ will vary along the boundary, and continuity of temperature across the boundary implies thermal gradients in both liquid and solid; heat conduction must be considered in both phases. (Although a one phase problem results from considering the ablation problem where the solid is removed from the liquid as soon as it forms, or in the limit that the solid has infinite conductivity.) Even when considering the stability of a planar interface (that has zero curvature by definition), small perturbations will introduce curvature and heat flow in the solid must be taken into account. A strictly planar interface has zero curvature. A Gibbs Thomson condition can not, therefore, affect a problem with a planar interface (except to alter its stability). In particular, it can not stop finite time blow up of a problem with a planar interface. One hopes that (4.1) leaves planar boundaries unstable so that it could be argued that, while (4.1) can not stop finite time blow up of a planar interface, a planar interface is never observed in practice as it is unstable. Unfortunately this hope is not necessarily realized.

The stability of a planar interface for a single phase Stefan problem with boundary condition (4.1) is considered in [14], while [6] considers the stability of a planar interface for the two phase solidification of a binary alloy; in the latter case the usual two phase Stefan problem can be obtained from the zero impurity concentration limit. The stability of the two phase spherically symmetric Stefan problem is considered in [5]. In all cases it is shown that the effect of surface tension is to stabilize the free boundary to high frequency perturbations, although the results of [5] for the two phase spherical problem are analogous to their results for the single phase spherical problem.

The two phase Stefan problem generalizing (2.1), but with condition (4.1) on the interface is

$$\begin{array}{cc} w_t = w_{xx} + w_{yy}, \quad -\infty < x < S(y,t) & u_t = u_{xx} + u_{yy}, \quad S(y,t) < x < \infty \\ w = \gamma S_{yy}/(1+S_y^2)^{3/2}, \quad x = S(y,t) & u = \gamma S_{yy}/(1+S_y^2)^{3/2}, \quad x = S(y,t) \\ w \to w_\infty \text{ as } x \to -\infty & u \to u_\infty \text{ as } x \to \infty \\ w(x,y,0) = \psi(x,y), \quad x < S(y,0) & u(x,y,0) = \phi(x,y), \quad x > S(y,0) \\ S_t = (w_x - u_x) - (w_y - u_y)S_y \quad x = S(y,t) & \end{array} \tag{4.2}$$

where u, w denote the temperature in the liquid and solid respectively, ϕ, ψ and $S(y,0)$ are given and u, w and $S(y,t)$ are to be found for $t > 0$. For the problem to be supercooled, $\phi(x,y) \leq 0$, $u_\infty < 0$. Observe that we can generalize (2.4) to obtain a solution of (4.2);

$$w = 0, \quad x < Vt, \qquad u = -1 + e^{-V(x-Vt)}, \quad x > Vt, \qquad x = S(y,t) = Vt.$$

Here $\phi = -1 + e^{-Vx}$, $\psi = 0$ and $S(y,0) = 0$. The stability of this solution can be examined as in Section 2, by putting

$$\begin{aligned} S(y,t) &= Vt + \delta e^{\sigma t + i\omega y}, \\ u(x,y,t) &= -1 + e^{-V(x-Vt)} + \delta e^{\sigma t + i\omega y} U(x - Vt), \\ w(x,y,t) &= \delta e^{\sigma t + i\omega y} W(x - Vt), \end{aligned}$$

where $\delta \ll 1$. The resulting $O(\delta)$ problem is

$$\begin{gathered} U'' + VU' - (\sigma + \omega^2)U = 0, \quad U(0) = V - \gamma\omega^2, \quad U(\infty) = 0, \\ W'' + VW' - (\sigma + \omega^2)W = 0, \quad W(-\infty) = 0, \quad W(0) = -\gamma\omega^2, \\ \sigma + V^2 = W'(0) - U'(0). \end{gathered} \tag{4.3}$$

This can only be solved if $\sigma > -\omega^2$, in which case we obtain the dispersion relation

$$(V^2 + 2\sigma) = (V - 2\gamma\omega^2)\sqrt{V^2 + 4(\sigma + \omega^2)}. \tag{4.4}$$

Taking γ, $V > 0$, it is necessary that $0 < \omega^2 < V/2\gamma$ in order that $\sigma > 0$, showing that $\gamma > 0$ stabilizes a planar free boundary to high frequency perturbations. Assuming that $0 < \omega^2 < V/2\gamma$, then (4.4) can have positive solutions for σ only if

$$P(\omega^2) = 4\gamma^2\omega^4 + \gamma V(\gamma V - 4)\omega^2 + (1 - \gamma V)V^2 > 0.$$

Noting that $P(\omega^2)$ is quadratic in ω^2, that $P(V/2\gamma) = -\gamma V^3/2 < 0$ and that $P(0) = (1 - \gamma V)V^2$, it is clear that $\sigma > 0$ is only possible if $0 < V < 1/\gamma$. Thus if $V > 1/\gamma$, a planar interface is stable to all small harmonic perturbations.

In the context of supersaturated crystalization, it is acceptable to ignore diffusion in the crystal and consider the single phase problem for the supersaturated liquid. The analyses of [5] and [15] deal with the single phase Stefan problem for a radially symmetric crystal growing from a finite initial radius into an infinite supersaturated liquid: a problem similar to a radially symmetric three dimensional version of (2.1). In [15] it is shown that, provided $\phi(r) > -1$ (here $\phi(r)$ is the initial concentration in the solution; and $u = -1$ corresponds to critical supersaturation, $u = 0$ to no supersaturation) then there exists a solution to the problem for all time and that the free boundary $r = s(t)$ behaves asymptotically like $s(t) \sim \alpha\sqrt{t}$ as $t \to \infty$. It is also shown in [15] that if $\phi(r) < -1$ then it is possible to get finite time blow up (i.e. $\dot{s} \to \infty$ as $t \to t_c < \infty$), even with surface tension present, thus demonstrating that the Gibbs Thomson effect does not always prevent finite time blow up, even for curved boundaries.

In both [5] and [15] it is shown that a constant concentration condition on the free boundary leads to the free boundary being unstable to pertubations of all modes; if the perturbation has the form $AY_{lm}(\theta, \phi)$, where Y_{lm} is a spherical harmonic, then the initially small amplitude A will grow as $t^{(l-1)/2}$. Replacing the constant concentration boundary by the Gibbs Thomson condition has the effect of stabilizing the free boundary in the following sense. A small initial perturbation $AY_{lm}(\theta, \phi)$ will decrease in amplitude provided the radius of the crystal is less than a critical radius R_l that depends on l. If the crystal radius is greater than R_l then the amplitude of the Y_{lm} perturbation will increase. In both [5] and [15] the critical radius R_l increases as a function of l, so that large crystals are unstable to more modes than small ones. The details of the dependence of R_l on l (and other parameters) differ from [5] to [15] as [15] retains the time derivative in the diffusion equation whereas [5] does not. In both cases the critical nucleation radius R^* (i.e. the radius R^* such that a crystal of radius $R < R^*$ will dissolve rather than grow) is less than the critical radius for the first non-trivial harmonic mode. Roughly, a growing spherical crystal only becomes unstable once it is large enough. It is noted in [15], however, that the effect of retaining the time derivative in the diffusion equation can be destabilizing in that the critical radii R_l may be significantly smaller than the critical radii predicted by [5] under certain circumstances.

The argument of Sherman [8] given in Section 3 does not apply if the isothermal interface condition is replaced by the surface energy condition (4.1). Consider, for example, the growth of a spherical solid into a spherically symmetric liquid;

$$\begin{array}{ll}
(r^2 w)_t = (r^2 w_r)_r, \quad 0 < r < s(t), & (r^2 u)_t = (r^2 u_r)_r, \quad s(t) < r < 1, \\
w = -\gamma/s(t), \quad r = s(t) & u = -\gamma/s(t), \quad r = s(t) \\
w_r(0,t) = 0 & u_r(1,t) = 0, \\
w(r,0) = \psi(r), \quad 0 \le r \le s(0), & u(r,0) = \phi(r), \quad s(0) \le r \le 1,
\end{array} \tag{4.5}$$

where $w(r,t)$ denotes solid temperature, $u(r,t)$ the liquid temperature, and where $\psi \in C^2[0,s(0)]$, $\phi \in C^2[s(0),1]$ are prescribed together with $0 < s(0) < 1$ and satisfy the compatibility conditions $\psi(s(0)) = \phi(s(0)) = -\gamma/s(0)$, $\psi'(0) = \phi'(1) = 0$. It is easy to show that the energy E given by

$$E = \frac{1}{3}s(t)^3 + \int_0^{s(t)} r^2 w \, dr + \int_{s(t)}^1 r^2 u \, dr = \frac{1}{3}s(0)^3 + \int_0^{s(0)} r^2 \psi \, dr + \int_{s(0)}^1 r^2 \phi \, dr$$

is constant in time t. There is also a trivial steady state solution of (4.5), namely

$$u = w = -\gamma/s^*,$$

where $s^* > 0$ is determined uniquely by E (and, thus, by the initial conditions);

$$\frac{1}{3}\left(s^{*3} - \frac{\gamma}{s^*}\right) = E.$$

Whether or not this solution is a stable attractor for solutions of (4.5), it does prevent Sherman's argument being applied. It can no longer be asserted that one of the three cases of Section 3 must occur (allowing, of course for the possibility that $s(t) \to 1$, as well as 0, after a finite or infinite time); it may be that $s(t) \to s^*$ as $t \to \infty$. This in itself does not rule out finite time blow up; that would require a proof that $s(t) \to s^*$ as $t \to \infty$ for all reasonable initial conditions on (4.5). Although this seems likely, it has not been proved. This line of argument can be developed by noting that any supercooled two phase Stefan problem (posed on a sufficiently regular domain and with zero heat flux conditions on the boundary of that domain) will admit steady solutions consisting of one or more solid spheres, of identical radius, surrounded by liquid, both phases being at a constant temperature determined by the radius of the spheres. This radius is determined (not uniquely, unless the number of solid sphere is prescribed) by the initial energy. The locations of such spheres are not uniquely determined, and which such configurations (if any) represent attracting solutions for given initial data cannot be determined by energy arguments alone.

If, however, we consider the reverse situation where the liquid lies at the core of the sphere, $0 \leq r < s(t)$, and the solid surrounds it, $s(t) < r \leq 1$, then the curvature of the interface is negative, so $u = w = \gamma/s(t)$ at $r = s(t)$ (with u, w being, repsectively, the liquid and solid temperatures). The energy E is now given by

$$E = \frac{1}{3}(1 - s(t)^3) + \int_0^{s(t)} r^2 u \, dr + \int_{s(t)}^1 r^2 w \, dr$$

and is again constant in time, and for a steady state $u = w = \gamma/s^*$ to exist we require

$$E = \frac{1}{3}\left(1 - s^{*3} + \frac{\gamma}{s^*}\right).$$

This is impossible for $E \leq 0$ unless $s^* > 1$, and that is absurd. Finite time blow up may still occur. (The possibility that the solid and liquid rearrange themselves so that the solid occupies the core with liquid surrounding it can be discounted as being totally inconsistent with a radially symmetric solution having only one sharp interface.)

5. Kinetic Undercooling

The kinetic undercooling condition (1.4) arises from nonequilibrium thermodynamic arguments (see [**29**], [**33**]), and can be derived from a sharp interface limit of a phase field model (see [**17**], [**18**]). Unless the free boundary is moving at a constant velocity, a Stefan problem with a kinetic undercooling condition at the free boundary is inherently a two phase problem. The problem that generalizes (2.1) is

$$\begin{aligned} &w_t = w_{xx}, \quad -\infty < x < s(t), && u_t = u_{xx}, \quad s(t) < x < \infty,\\ &w(s(t),t) = -\epsilon\dot{s}, \quad t > 0, && u(s(t),t) = -\epsilon\dot{s}, \quad t > 0,\\ &w \to w_\infty, \quad x \to -\infty, && u \to u_\infty, \quad x \to \infty,\\ &w(x,0) = \psi(x), \quad -\infty < x \le s(0), && u(x,0) = \phi(x), \quad s(0) \le x < \infty, \end{aligned} \tag{5.1}$$

with suitable compatibility conditions on $\psi(x)$ and $\phi(x)$, where u, w denote liquid, solid temperatures respectively and $\epsilon > 0$ is constant. The one dimensional problem (on a finite domain) has been studied and existence, uniqueness and regularity results are known (see **[34]**, **[35]**). In particular, if ψ and ϕ in (5.1) are bounded functions, say $|\psi(x)|$, $|\phi(x)| \le M$, then from the maximum principle $|u|$, $|w| \le M$, and hence

$$|\dot{s}| \le M/\epsilon,$$

(see **[35]** for details). Thus, finite time blow up is not possible.

The single phase supercooled Stefan problem with a kinetic condition on the free boundary;

$$\begin{aligned} u_t &= u_{xx}, \quad s(t) < x < \infty,\\ u(s(t),t) &= -\epsilon\dot{s}, \quad t > 0,\\ u_x(s(t),t) &= -\dot{s}, \quad t > 0,\\ u(x,0) &= \phi(x), \quad s(0) = 0 \le x < \infty, \end{aligned} \tag{5.2}$$

is considered in **[21]**. (Note that this problem can be thought of as an ablation problem where solid is removed on formation, as a supersaturated crystalization problem with a kinetic condition or as the limit of a two phase problem in which the thermal conductivity of the solid is infinite and its heat capacity zero.) There are similarity solutions of (5.2),

$$\begin{aligned} u(x,t) &= U_1(x/\sqrt{t}) + \frac{1}{\sqrt{t}}U_2(x/\sqrt{t}), \quad s(t) = \beta\sqrt{t},\\ U_1(\xi) &= -\frac{\beta}{2}e^{\beta^2/4}\int_\beta^\xi e^{-y^2/4}\,\mathrm{d}y,\\ U_2(\xi) &= -\frac{\beta}{2}\left\{\frac{\beta}{2}e^{-\xi^2/4}\int_\beta^\xi e^{y^2/4}\,\mathrm{d}y + e^{(\beta^2-\xi^2)/4}\right\}, \end{aligned} \tag{5.3}$$

where β satisfies (2.3), and travelling wave solutions

$$u(x,t) = -(1+\epsilon V) + e^{-V(x-Vt)}, \quad s(t) = Vt, \tag{5.4}$$

that generalize (2.2) and (2.4) respectively. Note that V in (5.4) is not arbitrary, but related to the degree of undercooling as $x \to \infty$. The indeterminacy of V in (2.4) emerges from the various limits $\epsilon \to 0$, $u(\infty,t) \to -1$ of (5.4).

Using the same method outlined in Section 2, for problem (2.1), it is shown in **[21]** that for $\epsilon > 0$

(i) If $-1 < \phi(x) < 0$ for all x, then $s(t) \sim \beta\sqrt{t}$ where β satisfies (2.3) with $u_\infty = \phi(\infty) > -1$. The similarity solutions (2.2) and (5.3) are special cases, and this result is independent of $\epsilon \ge 0$.

(ii) If $\phi(x) \sim -1 + cx^{-\gamma}$ as $x \to \infty$ for $0 < \gamma < 1/2$ and $c > 0$, then $s(t) \sim kt^{\alpha}$ as $t \to \infty$ where $k = (\Gamma(3-\gamma)/c\Gamma(1-\gamma))^{\alpha}$ and $\alpha = 1/(2-\gamma)$. Note that $\phi(x) \geq -1$ as $x \to \infty$ and that $1/2 < \alpha < 2/3$.

(iii) If $\phi(x) \sim -1 + cx^{-\gamma}$ as $x \to \infty$ for $0 < \gamma < 1/2$ and $c < 0$, then $s(t) \sim kt^{\alpha}$ as $t \to \infty$ where $k = (-c(1+\gamma)/\epsilon)^{\alpha}$ and $\alpha = 1/(1+\gamma)$. Note that $\phi(x) \leq -1$ as $x \to \infty$ and that $2/3 < \alpha < 1$.

(iv) If $\phi(x) \sim -1 + cx^{-1/2}$ as $x \to \infty$ then $s(t) \sim k^* t^{2/3}$ as $t \to \infty$, where k^* is the unique real, positive, root of $(2\epsilon/3)k^{*3} + ck^{*3/2} - 3/4 = 0$.

(v) If $\phi(x) \sim -1 + cx^{-\gamma}$ as $x \to \infty$ for $1/2 < \gamma < 1$ then $s(t) \sim (9t^2/8\epsilon)^{1/3} + k_1 t^{\alpha_1}$ where $0 < \alpha_1 < 1/3$. Precise details can be found in **[21]**.

(vi) If $\phi(x) \to u_\infty < -1$ as $x \to \infty$ then $s(t) \sim Vt$ as $t \to \infty$, where $V = -(u_\infty + 1)/\epsilon$.

As $|\dot{s}|$ is bounded (given bounded initial data), there can be no finite (or infinite) time blow up.

A similar analysis for a spherically symmetric one phase Stefan problem with both Gibbs Thomson and kinetic undercooling effects on the interface is also given in **[21]**.

To examine the effect of the kinetic undercooling condition on the linear stability of a planar interface, note first that the two dimensional version of problem (5.1) is (4.2), but with conditions $(4.2)_2$ replaced by

$$w = -\epsilon S_t/(1+S_y^2)^{1/2}, \quad u = -\epsilon S_t/(1+S_y^2)^{1/2}, \quad \text{on } x = S(y,t). \tag{5.5}$$

Further, the one phase solution (5.4) generalizes to a two phase solution of (5.1), because $\dot{s} = V$ is constant, so (5.1) has the solution

$$u = -(1+\epsilon V) + e^{V(x-Vt)}, \quad w = -\epsilon V, \quad s(t) = Vt \tag{5.6}$$

Proceeding as in Sections 2 and 4, by putting

$$\begin{aligned} S(y,t) &= Vt + \delta e^{\sigma t + i\omega y}, \\ u(x,y,t) &= -(1+\epsilon V) + e^{-V(x-Vt)} + \delta e^{\sigma t + i\omega y} U(x - Vt), \\ w(x,y,t) &= -\epsilon V + \delta e^{\sigma t + i\omega y} W(x - Vt), \end{aligned}$$

we obtain the $O(\delta)$ problem (4.3), but with new boundary conditions

$$U(0) = V - \epsilon\sigma, \quad W(0) = -\epsilon\sigma,$$

leading to the dispersion relation

$$(V^2 + 2\sigma) = (V - 2\epsilon\sigma)\sqrt{V^2 + 4(\sigma + \omega^2)}. \tag{5.7}$$

Trivial graphical considerations show that (5.7) has a unique positive solution, $\sigma(\epsilon, V, \omega)$, for any given $\epsilon, V, \omega > 0$. Moreover, this unique root satisfies $0 < \sigma < V/2\epsilon$, with $\sigma \to 0$ as $\omega^2 \to 0$ and $\sigma \to V/2\epsilon$ as $\omega^2 \to \infty$. Thus the kinetic undercooling condition does not stabilize a planar interface to any frequency of disturbance. The estimate $\sigma \to V/2\epsilon$ as $\omega^2 \to \infty$ is less severe than the isothermal case where $\sigma = V|\omega|$. It seems therefore that a combination of kinetic undercooling and surface energy effects are necessary to stop finite time blow up and provide a mechanism for perturbation frequency selection.

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