Energy conservation in the one-phase supercooled Stefan problem

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Abstract
A one-phase reduction of the one-dimensional two-phase supercooled Stefan problem is developed. The standard reduction, employed by countless authors, does not conserve energy and a recent energy conserving form is valid in the limit of small ratio of solid to liquid conductivity. The present model assumes this ratio to be large and conserves energy for physically realistic parameter values. Results for three one-phase formulations are compared to the two-phase model for parameter values appropriate to supercooled salol (similar values apply to copper and gold) and water. The present model shows excellent agreement with the full two-phase model.

Keywords:

1. Introduction

When a solid forms from a liquid at the heterogeneous nucleation temperature the freezing process is relatively slow and the liquid molecules have time to rearrange into a standard crystalline configuration. However, a supercooled (or undercooled) liquid is in an unstable state, ready to solidify rapidly as soon as the opportunity arises. The solidification process may be so rapid that the liquid molecules have no time to rearrange themselves into the usual crystal structure and instead form an unorganised or amorphous solid structure that is reminiscent of the liquid phase. For this reason solids formed from a supercooled liquid have been referred to as \textit{liquids on pause}
[1]. The different molecular arrangement means that such solids may have
very different properties to the normal solid phase. Amorphous metal alloys,
formed by supercooling below the glass transition temperature can be twice
as strong and three times more elastic than steel [1]. Numerous applications
for materials formed from a supercooled liquid, such as in sport and electronic
equipment, medical and aerospace, are discussed in the article of Telford [2].

The practical importance of solids formed from a supercooled liquid mo-
tivates the need for the theoretical understanding of the associated phase
change process. Although the two-phase problem is well defined, it may be
difficult to solve, given that it involves two partial differential equations on
an \textit{a priori} unknown, moving domain. The associated one-phase problem is
a significantly less challenging prospect, particularly when dealing with com-
plex geometries. However it has been shown that the standard one-phase
reduction does not conserve energy [3]. In this paper we examine the one-
phase reduction of the one-dimensional Stefan problem. It is shown that
the energy conserving form of [3] although mathematically correct is not ap-
propriate for physically realistic problems and so we propose an alternative
reduction which shows excellent agreement with the full two-phase model.

2. Mathematical models

One of the most basic formulations of the two-phase supercooled Stefan
problem in non-dimensional form may be written

\[
\frac{\partial \theta}{\partial t} = \frac{k}{c} \frac{\partial^2 \theta}{\partial x^2}, \quad 0 < x < s(t) \quad \frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2}, \quad s(t) < x < \infty,
\]

\[
T(s, t) = \theta(s, t) = T_I(t), \quad T|_{x \to \infty} \to -1, \quad T(x, 0) = -1, \quad s(0) = 0,
\]

\[
[\beta - (1 - c) s_t] s_t = \left( k \frac{\partial \theta}{\partial x} - \frac{\partial T}{\partial x} \right) \bigg|_{x=s}
\]

where \( T, \theta \) represent the liquid and solid temperatures, \( k = k_s/k_l \) the ther-
mal conductivity ratio, \( c \) the specific heat ratio, \( \beta = L_m/(c_l \Delta T) \) the Stefan
number, \( L_m \) the latent heat and \( \Delta T \) the degree of supercooling. The above
system describes the phase change process of a supercooled semi-infinite ma-
terial which solidifies from the boundary \( x = 0 \). The phase change boundary
is at \( x = s(t) \), where \( s(0) = 0 \). The variable \( T_I(t) \) represents the temperature
at the phase change interface. If solidification occurs at the heterogeneous nucleation temperature we choose $T_I(t) = 0$. With supercooling a non-linear relation exists between $T_I$ and $s_t$ \[4, 5\]. For small levels of supercooling it is standard to choose a linear approximation $T_I(t) = -s_t$. This is often referred to as a linear kinetic undercooling model. For simplicity we will use the linear approximation throughout this paper although the methodology translates immediately to the non-linear case. The above formulation involves the assumption that the density change between liquid and solid phases is small and so may be neglected compared to other physical changes, such as the jump in specific heat. We augment this system with the initial condition $\theta(x, 0) = \theta_i$ and a boundary condition $\theta_x(0, t) = 0$: for a standard one-phase problem these extra conditions are unnecessary but they are required when looking for a reduction from a two-phase model. Note, we choose the boundary condition at $x = 0$ to match that of [6] and also because it is appropriate when working in cylindrical and spherical co-ordinates, but other boundary conditions will work in the arguments below.

The standard one-phase Stefan problem is retrieved from the above system by simply ignoring the $\theta$ equation and setting $k = 0$ in the Stefan condition, consequently

$$\frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2}, \quad s < x < \infty$$  \hspace{1cm} (4)

$$T(s, t) = -s_t, \quad T|_{x \to \infty} \to -1, \quad T(x, 0) = -1, \quad s(0) = 0$$  \hspace{1cm} (5)

$$[\beta - (1 - c)s_t] s_t = -\frac{\partial T}{\partial x}|_{x=s}. \hspace{1cm} (6)$$

In fact this is often further reduced by choosing $c = 1$. It is well-known that if supercooling is neglected, \textit{i.e.} $T_I(t) = 0$, and $c = 1$, then the well-known Neumann solution may be applied to (4)-(6), but this breaks down as $\beta \to 1^+$. Applying the linear kinetic undercooling temperature $T_I(t) = -s_t$ prevents this breakdown and so permits solutions for arbitrary undercooling.

Evans and King \[3\] point out that the above reduction does not conserve energy since the limit $\theta \to 0$ involves a singular perturbation of the two-phase system. Physically the issue is obvious: the reduction is based on setting $\theta$ constant, without the undercooling term the boundary condition determines $\theta = T_I \equiv 0$ and so the (non-dimensional) constant is zero and this satisfies the heat equation and boundary condition at $x = s$ for all time. With kinetic undercooling the temperature at $x = s$ varies with time, so
θ(s, t) is a function of time and the assumption of constant θ is no longer valid.

To determine a consistent one-phase model, Evans and King [3] investigate the limit k → 0 which is equivalent to neglecting θ in the Stefan condition. The heat equation in the solid then indicates θ_t → 0 and so θ ≈ θ(x) = θ_i, (after imposing the initial condition). However, this contradicts the condition θ(s, t) = −s_t ≠ θ_i and so indicates the need for a boundary layer. To analyse this boundary layer a new co-ordinate is introduced, x = s(t) − k̂x (where k ≪ 1), which transforms (1b) to

$$\frac{\partial \theta}{s_1 \partial x} + k \frac{\partial \theta}{\partial t} = \frac{1}{c} \frac{\partial^2 \theta}{\partial x^2}.$$ (7)

Neglecting the small term involving k allows the equation to be integrated and applying θ → θ_i as ̂x → ∞ gives

$$\frac{1}{c} \frac{\partial \theta}{\partial x} = s_t (\theta - \theta_i).$$ (8)

Noting that θ̂_x = −kθ_x we may use (8) to replace the solid temperature gradient in the Stefan condition (3) and applying θ(s, t) = −s_t gives

$$[\beta - s_t - c\theta_i] s_t = -\frac{\partial T}{\partial x}.$$ (9)

The correct reduction of the two-phase Stefan problem in the limit k → 0 is therefore specified by equations (4)-(5), with the Stefan condition given by (9). The properties and behaviour of systems of this form, with appropriate modification for different physical situations have been studied for example in [7, 8].

Heat conduction occurs on the microscopic scale due to the transfer of kinetic energy from hot, rapidly vibrating atoms or molecules to their cooler, more slowly vibrating neighbours. In solids the close, fixed arrangement of atoms means that conduction is more efficient than in fluids, which have a larger distance between atoms. Consequently, in general, the conductivity of a solid is greater than that of its corresponding liquid phase, for example with water and ice k = k_s/k_l ≈ 4, for solid and molten gold k ≈ 3. Hence the limit k → 0 has limited applicability and for practical Stefan problems it would seem more appropriate to study the large k limit.

Now we let k → ∞ and the heat equation (1b) reduces to θ_xx ≈ 0, so to leading order θ = c_0(t) + c_1(t)x = −s_t (after applying the boundary
conditions). So far this seems a reasonable result, large $k$ indicates heat travels rapidly through the solid (compared to the travel time in the liquid) which then equilibrates to the boundary temperature almost instantaneously. However, in the Stefan condition we have the term $k\theta_x$, which is zero to leading order (since $\theta = -s_t(t)$), but since the coefficient $k$ is large it is possible that the first order term plays an important role. If we write $\theta = \theta_0 + \frac{1}{k}\theta_1 + \mathcal{O}(1/k^2)$ then the leading and first order heat equations are

$$\frac{\partial^2 \theta_0}{\partial x^2} = 0, \quad c \frac{\partial \theta_0}{\partial t} = \frac{\partial^2 \theta_1}{\partial x^2}. \quad (10)$$

The appropriate temperatures are $\theta_0 = -s_t$ and $\theta_1 = -cs_{tt}(x^2 - s^2)/2$. The Stefan condition becomes

$$[\beta - (1 - c)s_t]s_t = k \left( \frac{\partial \theta_0}{\partial x} + \frac{1}{k} \frac{\partial \theta_1}{\partial x} + \mathcal{O}(1/k^2) \right) \bigg|_{x = s} - \frac{\partial T}{\partial x} \bigg|_{x = s}. \quad (11)$$

Substituting for $\theta_1$ in (11) we find that the one-phase Stefan problem in the limit of large $k$ is then specified by equations (4)-(5) and the Stefan condition

$$css_{tt} + [\beta - (1 - c)s_t]s_t = - \frac{\partial T}{\partial x} \bigg|_{x = s}. \quad (12)$$

The inclusion of the derivative $s_{tt}$ requires an extra initial condition. In the absence of supercooling, $T_I = 0$, hence $T(s, t) = T_I$ indicates $T(0, 0) = 0$. For $x > 0$ we have $T(x, 0) = -1$, hence the temperature gradient

$$T_x(x, 0) \big|_{x \to 0} = \lim_{h \to 0} \frac{T(h, 0) - T(0, 0)}{h} = \lim_{h \to 0} \left( \frac{-1 - 0}{h} \right) = -\infty. \quad (13)$$

In the one phase problem the front velocity is a function of the temperature gradient with the result that without kinetic undercooling the above initial infinite gradient indicates $s_t(0) = \infty$. This may be seen, for example, in the well-known Neumann solution where $s_t \sim 1/\sqrt{t}$. The singularity is an obvious consequence of the unphysical nature of the boundary condition: choosing $T = -1$ for all $x > 0$ and $T = 0$ at a single point $x = 0$ is not consistent with an equation based on continuum theory. Kinetic undercooling provides a mechanism for removing the unphysical behaviour. The only way to avoid the singularity is if $T(0, 0) = \lim_{h \to 0}(T(h, 0) + \mathcal{O}(h)) = \lim_{h \to 0}(-1 + \mathcal{O}(h)) = -1$. In physical terms we may think of an undercooled melt at
temperature $T = -1$ everywhere when some infinitesimally small amount of energy is input at the boundary resulting in $T(0, 0) = -1 + \mathcal{O}(h)$: this is sufficient to set off the solidification process (and it is well-known that ‘working with undercooled liquids is a bit like juggling mousetraps: they’re prone to suddenly “snap” and ruin the trick’ [1]). Since $T_I(0) = T(0, 0) = -1$ we find that in the case of linear undercooling the additional boundary condition required to close the Stefan problem is

$$s_t(0) = -T_I(0) = 1.$$  \hfill (14)

This argument also helps us with the one-phase formulation of equation (9) which requires an initial solid temperature, $\theta_i$ (despite the solid phase not entering the one-phase problem). Since the initial ‘kick’ to start solidification may be infinitesimal, and for $t$ sufficiently close to zero an infinitesimally small amount of latent heat has been released, the only physically sensible value for the solid temperature is $\theta_i = -1$. These initial conditions on $\theta_i$ and $s_t$ are obtained more formally through a short time asymptotic analysis in [9].

3. Energy conservation

The non-dimensional thermal energy in the two-phase system is given by

$$E = \int_0^s c \theta \, dx + \int_s^\infty T \, dx.$$  \hfill (15)

During the phase change the molecular rearrangement also releases (or uses) energy, namely the latent heat. So the rate of change of thermal energy, $E_t$, must balance the rate at which energy is produced by the phase change, $\beta s_t$. Differentiating the above equation we find

$$\frac{dE}{dt} = \int_0^s c \frac{\partial \theta}{\partial t} \, dx + c \theta(s, t) \frac{ds}{dt} + \int_s^\infty \frac{\partial T}{\partial t} \, dx - T(s, t) \frac{ds}{dt}.$$  \hfill (16)

The heat equations in (1) allow the time derivatives to be replaced with $x$ derivatives in the integrals, which may then be evaluated immediately. Noting that $\theta(s, t) = T(s, t) = -s$, then (16) becomes

$$\frac{dE}{dt} = k \left. \frac{\partial \theta}{\partial x} \right|_{x=0} + \left( k \left. \frac{\partial \theta}{\partial x} - \frac{\partial T}{\partial x} \right|_{x=s} + \left. \frac{\partial T}{\partial x} \right|_{x=\infty} \right) + (1 - c) \left( \frac{ds}{dt} \right)^2.$$  \hfill (17)
The temperature gradients at $x = s$ may be removed via the Stefan condition (3). The insulated boundary condition of the current study requires $\theta_x(0, t) = 0$, and as $x \to \infty$ the gradient $T_x \to 0$, so we are left with

$$
\frac{dE}{dt} = \left[ \beta - (1 - c) \frac{ds}{dt} \right] \frac{ds}{dt} + (1 - c) \left( \frac{ds}{dt} \right)^2 = \beta \frac{ds}{dt}.
$$

(18)

So the rate of change of thermal energy balances the latent heat release and the two-phase formulation conserves energy. Note, the argument follows in the same way for different boundary conditions, for example if we choose a constant flux $k\theta_x(0, t) = q$ then the rate of change of thermal energy balances the latent heat release plus the heat input at the boundary.

The energy balance for the standard one-phase problem specified by equations (4)-(5) can be obtained from the above argument by neglecting all $\theta$ terms in (16) (or equivalently setting $c = k = 0$ in (17)) and applying the Stefan condition (6) to replace $T_x(s, t)$

$$
\frac{dE}{dt} = \beta \frac{ds}{dt}.
$$

(19)

This demonstrates that energy is not conserved in this formulation. The equivalent expression in limit $k \to 0$ is obtained by replacing $\theta_x(s, t)$ via (8) and applying the Stefan condition (9) to replace $T_x(s, t)$ to equation (17) to obtain

$$
\frac{dE}{dt} = c s \frac{d^2 s}{dt^2} + \left[ \beta - (1 - c) \frac{ds}{dt} \right] \frac{ds}{dt} + (1 - c) \left( \frac{ds}{dt} \right)^2 = \beta \frac{ds}{dt}.
$$

(20)

Finally the one-phase limit with $k \to \infty$ is determined using the definition of $\theta_1$ to give $k\theta_x(s, t) = -css_t$ and $T_x(s, t)$ comes from the Stefan condition (12) to give

$$
\frac{dE}{dt} = -cs \frac{d^2 s}{dt^2} + \left[ \beta - (1 - c) \frac{ds}{dt} \right] \frac{ds}{dt} + (1 - c) \left( \frac{ds}{dt} \right)^2 = \beta \frac{ds}{dt}.
$$

(21)

Hence the large and small $k$ formulations also conserve energy.

4. Comparison of results

We now present two sets of results for the solidification of salol and water. The results were computed numerically using the boundary immobilisation
method and Keller box finite difference technique used in \cite{10, 11}. The 
\( k \to 0 \) result was rather unexpected so the computations were verified using 
an accurate heat balance method, as described in \cite{12, 13}. This provided 
solutions typically within 0.5\% of the numerics. As discussed above, the 
\( k \to 0 \) formulation requires a value for the solid temperature \( \theta_i \). At the end 
of §2 we demonstrated that \( \theta_i = -1 \). We also tried \( \theta_i = 0 \) but this did not 
improve the correspondence.

In Figure 1 we compare the position of the phase change front for the 
three one-phase formulations against the two-phase solution using parameter 
values appropriate for salol and with two values of \( \beta \). Salol was chosen 
since it was the material with the lowest value of \( k \approx 1.4 \) for which we had 
all the necessary data, see \cite{4}. The values of \( \beta \) correspond to dimensional 
temperatures of 234.8, 272.4K (the heterogeneous phase change temperature 
\( T_m \approx 314.7K \)), the value of \( c = c_s/c_l = 0.73 \). The solid line in the figure 
represents the two-phase model, the dotted line the standard one-phase model 
of equations (4)-(6), this is bounded by the two limiting cases which conserve 
energy using the Stefan conditions (9) for \( k \to 0 \) (dot-dash line) and (12) for 
\( k \to \infty \) (dashed line). Even in this case, where \( k \) is relatively small we find 
that the large \( k \) solution is extremely close to the two-phase model while the 
limit \( k \to 0 \) shows an approximately 40\% difference to the two-phase solution. 
It is also surprising that this latter energy conserving form is further from 
the two-phase solution than the form that does not conserve energy. The 
two sets of plots are for small values of \( \beta \) (in particular we wished to show 
results with \( \beta < 1 \) and \( \beta > 1 \)). In the limit of large \( \beta \) the curves all coincide 
but for the \( k \to 0 \) case the convergence is slow: for \( \beta = 40 \) the \( k \to \infty \) result 
is within 0.005\% of the 2 phase result, the \( k \to 0 \) solution is within 1.8\%.

In Figure 2 we show results for a water-ice system where \( k \approx 4, c \approx 0.49 \). 
This has a significantly lower \( c \) value than salol and a higher \( k \) value. The values \( \beta = 0.7, 1.3 \) correspond to temperatures 158.9, 211.5 (where \( T_m \approx 273K \)), 
see \cite{14}. With the larger \( k \) value we can observe that the two-phase formulation 
and the large \( k \) one-phase approximation are almost indistinguishable. 
\( k \to 0 \) formulation differs by approximately 30\% and again the result 
obtained by simply neglecting \( \theta \) is more accurate than this latter energy 
conserving form.

In addition to the results shown above we also carried out the same cal-
culations for molten and solid copper, \( k \approx 2.4, c \approx 0.72 \) and gold \( k \approx 3, c \approx 
0.79 \). In both cases the value of \( c \) is similar to that of salol and so the copper results were virtually identical to those of salol, whilst the gold results
showed a very slight decrease in the velocity $s_t$.

5. Conclusions

In summary, our simulations show that the one-phase reduction with large $k$ can provide an excellent agreement with the two-phase problem for a wide range of physically realistic parameter values and supercooling. The small $k$ formulation of [3] whilst mathematically correct is highly inaccurate for practical problems and surprisingly significantly less accurate than the non-energy conserving form. Only in the limit of large Stefan number do the solutions coincide (and in this case the supercooled formulation is unnecessary). We therefore propose that an accurate approximation to the two-phase one-dimensional Stefan problem is obtained by the simpler one-phase approximation specified by equations (4)-(5) and the Stefan condition (12). Using standard notation the dimensional form may be written

$$\frac{\partial T}{\partial t} = \frac{k_l}{\rho c_l} \frac{\partial^2 T}{\partial x^2}, \quad s(t) < x < \infty$$

$$T(s, t) = T_m - \phi s_t, \quad T|_{x \rightarrow \infty} \rightarrow T_\infty, \quad T(x, 0) = T_\infty$$

$$\rho c_s \phi s s_{tt} + \rho_l \left[ L_m - (c_l - c_s) \phi s_t \right] s_t = -k_l \frac{\partial T}{\partial x} \bigg|_{x=s},$$

$$s(0) = 0, \quad s_t(0) = 1,$$
where the constant $\phi$ is the kinetic undercooling coefficient used in the linear relation $T_I(s_t) \approx T_m - \phi s_t$. Similar reductions can no doubt be obtained for related problems and a similar analysis may be easily applied to the nonlinear undercooling case.

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**References**


