On the one-phase reduction of the Stefan problem with a variable phase change temperature

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Abstract

The one-phase reduction of the Stefan problem, where the phase change temperature is a variable, is analysed. It is shown that problems encountered in previous analyses may be traced back to an incorrectly formulated Stefan condition. Energy conserving reductions for Cartesian, cylindrically and spherically symmetric problems are presented and compared with solutions to the two-phase problem.

Keywords:

Stefan problem; Melting point depression; Energy conservation.

1. Introduction

The Stefan problem where the phase change temperature is fixed is a classical example of a moving boundary problem and has been well-studied for more than 100 years. However, with the advent of a number of new technologies, the situation where a material's phase change temperature differs from the standard value is becoming increasingly important. For example, materials made from supercooled liquids are currently used in medicine, defence and aerospace equipment, electronics and sports [8, 15]. The phase change temperature of supercooled liquids can vary because the liquid molecules have lower energy than when solidifying under normal circumstances and this affects their ability to move to the solid interface. Nanoparticles have a vast array of applications in medicine, environmental remediation, materials and energy [7]. A key factor in understanding the melting of nanoparticles is the large decrease in melt temperature with decreasing size, for example

15 a 2 nm radius gold nanoparticle will melt at approximately 500K below the
 16 bulk melt temperature [3]. In this case the high curvature of the melt inter-
 17 face leads to a large value for the surface tension induced stress which then
 18 reduces the melt temperature.

19 In order to simplify the mathematical description of the phase change
 20 process it is common to neglect one of the material phases, to produce the
 21 *one-phase Stefan problem*. When the melt temperature is the standard (or
 22 homogeneous) phase change temperature, here denoted T_m^* , then the one-
 23 phase problem is usually well-defined. However, when the phase change
 24 temperature is variable then difficulties arise (for example, energy may not
 25 be conserved) [6, 13, 19]. The issue with the one-phase formulation has been
 26 investigated by looking at asymptotic limits of low thermal conductivity in
 27 the solid (compared to that in the liquid) [6] and large conductivity in the
 28 solid [13].

29 In this paper we will demonstrate that problems with the one-phase reduc-
 30 tion may arise due to inconsistent assumptions concerning the temperature in
 31 the neglected phase. If the reduction is carried out consistently then there is
 32 no problem with the energy conservation. The one-phase reduction is invoked
 33 to simplify the analysis, another standard simplification involves assuming
 34 constant thermal properties throughout the process. If we consider the ratio
 35 of the thermal conductivity of water to ice $k = k_s/k_l \approx 4$ and the specific
 36 heat ratio $c = c_s/c_l \approx 0.5$ then it is clear that this assumption can lead to
 37 significant errors. Consequently in the following we will work with different
 38 (constant) values in each phase. The density also varies, usually to a lesser
 39 extent than conductivity and specific heat [1]. If we include density change
 40 in our analysis then the governing equations become more complex, with
 41 the addition of advection and kinetic energy, see [9]. Consequently, to keep
 42 down the number of terms in the equations and so simplify the arguments we
 43 will focus on the situation where the density, ρ , is constant throughout the
 44 process. However, the arguments may be easily adapted to include it using
 45 the equations described in [9].

46 2. Governing equations for phase change

47 We will now derive the Stefan condition and heat equations for a one-
 48 dimensional Cartesian problem via an energy balance. For simplicity we
 49 examine the case of fixed density and so avoid the velocity terms caused by
 50 the shrinkage or expansion of the material.

51 The governing equations for the Stefan problem may be obtained from
 52 the energy conservation equation

$$\frac{\partial}{\partial t} [\rho I^*] = -\nabla \cdot \mathbf{q}^*, \quad (1)$$

53 where ρ is the density, I^* the internal energy and the conductive heat flux
 54 $\mathbf{q}^* = -k\nabla T^*$. This simply states that internal energy varies with time due
 55 to heat movement through the boundary. The star superscript indicates
 56 dimensional variables. The internal energy/unit mass is

$$I_s^* = c_s(\theta^* - T_m^*) \quad I_l^* = c_l(T^* - T_m^*) + L_f, \quad (2)$$

57 where subscripts s, l denote solid and liquid, θ^*, T^* denote the respective
 58 temperatures. The heat equations may be obtained from the energy balance
 59 by simply substituting for I^* and $\mathbf{q}^*$ in (1)

$$\frac{\partial}{\partial t^*} [\rho c_s(\theta^* - T_m^*)] = \frac{\partial}{\partial x} \left(k_s \frac{\partial \theta^*}{\partial x^*} \right) \quad (3)$$

$$\frac{\partial}{\partial t^*} [\rho(c_l(T^* - T_m^*) + L_f)] = \frac{\partial}{\partial x} \left(k_l \frac{\partial T^*}{\partial x^*} \right). \quad (4)$$

60 Noting that all thermal properties and T_m^* are constant within each phase
 61 leads to the familiar form

$$\rho c_s \frac{\partial \theta^*}{\partial t^*} = k_s \frac{\partial^2 \theta^*}{\partial x^{*2}} \quad \rho c_l \frac{\partial T^*}{\partial t^*} = k_l \frac{\partial^2 T^*}{\partial x^{*2}}. \quad (5)$$

62 The Stefan condition may also be obtained from the conservation equation
 63 (1) via the Rankine-Hugoniot condition

$$\frac{\partial f}{\partial t} + \nabla \cdot \mathbf{g} = 0 \quad \Rightarrow \quad [f]_-^+ s_t = [\mathbf{g} \cdot \mathbf{n}]_-^+, \quad (6)$$

where $\mathbf{n}$ is the unit normal (in this case it is simply $\hat{\mathbf{x}}$) and $f, \mathbf{g}$ are functions evaluated on either side of the discontinuity, $x^* = s^*(t^*)$. For the case where a fluid initially occupying $x^* \geq 0$ is solidified from the boundary $x^* = 0$ we take the $+$ superscript to indicate fluid, $x^* > s^*$, and $-$ to indicate solid, $x^* < s^*$. Comparing the energy balance (1) to the Rankine-Hugoniot condition shows $f = \rho I^*$, $\mathbf{g} = \mathbf{q}^*$, and the Stefan condition follows from the second of equations (6)

$$\rho [(c_l(T^*(s^*, t^*) - T_m^*) + L_f) - c_s(\theta^*(s^*, t^*) - T_m^*)] s_{t^*}^* = -k_l \frac{\partial T^*}{\partial x^*} \Big|_{x^*=s^*} + k_s \frac{\partial \theta^*}{\partial x^*} \Big|_{x^*=s^*}. \quad (7)$$

64 The spherical and cylindrically symmetric versions are obtained from

$$\frac{\partial}{\partial t^*} [\rho c_s (\theta^* - T_m^*)] = \nabla \cdot (k_s \nabla \theta^*) \quad \frac{\partial}{\partial t^*} [\rho (c_l (T^* - T_m^*) + L_f)] = \nabla \cdot (k_l \nabla T^*) \quad (8)$$

65

$$\rho [(c_l (T^*(s^*, t^*) - T_m^*) + L_f) - c_s (\theta^*(s^*, t^*) - T_m^*)] s_{t^*}^* = -k_l \left. \frac{\partial T^*}{\partial r^*} \right|_{r^*=R^*} + k_s \left. \frac{\partial \theta^*}{\partial r^*} \right|_{r^*=R^*}, \quad (9)$$

66 where the phase change front is now located at $r^* = R^*$ and temperatures
67 depend on r^*, t^* .

68 3. Stefan problem with melting point depression

The standard two-phase, one-dimensional Cartesian Stefan problem with melting point depression is typically specified by heat equations in the solid and liquid phases and the following Stefan condition

$$\rho [(c_l - c_s) (T_I^*(t) - T_m^*) + L_f] s_{t^*}^* = -k_l \left. \frac{\partial T^*}{\partial x^*} \right|_{x^*=s^*} + k_s \left. \frac{\partial \theta^*}{\partial x^*} \right|_{x^*=s^*}, \quad (10)$$

69 where $T_I^*(t)$ is the interface temperature, see [1, 4, 6, 7, 20, 13, 18, 19]. The
70 variation of $T_I^*(t)$ may be described by a number of relations. For super-
71 cooling models an exponential relation between T_I^* and $s_{t^*}^*$ holds. This is
72 frequently linearised for small departures from the bulk phase change tem-
73 perature so $T_I^* - T_m^* \propto s_{t^*}^*$ [5, 8]. With high curvature some form of Gibbs-
74 Thomson relation is typically used [7, 8].

75 In order to follow previous asymptotic reductions we will now formulate
76 the non-dimensional version of the problem via the following scales,

$$\theta = \frac{\theta^* - T_m^*}{\Delta T^*} \quad T = \frac{T^* - T_m^*}{\Delta T^*} \quad x = \frac{x^*}{L} \quad t = \frac{t^*}{\tau} \quad (11)$$

77 where ΔT^* is a temperature scale and τ the time-scale. In the Stefan prob-
78 lem without melting point depression the length-scale L may be unknown.
79 With melting point depression L may be specified according to the equation
80 governing the phase change temperature. Choosing the time-scale for heat
81 flow in the liquid, $\tau = \rho c_l L^2 / k_l$, the heat equations now reduce to

$$\frac{\partial \theta}{\partial t} = \frac{k}{c} \frac{\partial^2 \theta}{\partial x^2} \quad \frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2}. \quad (12)$$

The Stefan condition becomes

$$[(1 - c) T_I(t) + \beta] s_t = - \left. \frac{\partial T}{\partial x} \right|_{x=s(t)} + k \left. \frac{\partial \theta}{\partial x} \right|_{x=s(t)}, \quad (13)$$

where $\beta = L_f/(c_l \Delta T)$, $k = k_s/k_l$, $c = c_s/c_l$.

These equations are often simplified via a one-phase approximation. Say, for example we neglect the solid phase, then we only need to solve the heat equation in the liquid while the Stefan condition becomes

$$[(1 - c) T_I(t) + \beta] s_t = - \left. \frac{\partial T}{\partial x} \right|_{x=s}. \quad (14)$$

The most familiar form of Stefan condition may be obtained by neglecting melting point depression, so setting $T_I = 0$ ($T_I^* = T_m^*$) in equation (14). Equation (14) may also be obtained by choosing $\theta(x, t)$ to be constant or a function of time. Wu *et al* [19] discuss papers where the solid phase is simply ignored, see [17, 21]. Many authors assume $\theta(x, t) = T_I(t)$ [4, 5, 10] or alternatively $\theta(x, t) = 0$ [11]. The first choice has the problem that it does not satisfy the heat equation, whilst the second does not satisfy the interface boundary condition. A more formal way to reduce the system is to let $k = 0$, so the liquid conducts heat infinitely faster than the solid. Then the solid temperature is removed from the Stefan condition while the heat equation in the solid becomes $\theta_t = 0$ and so θ may be set as a function of x : in practice it is usually taken as 0 or the initial temperature $\theta(x, 0) = \theta_0$.

Evans and King [6] discuss a number of papers where the Stefan problem is incorrectly formulated and discuss in detail the approximation where (14) with $T_I = 0$ is used in conjunction with melting point depression. They point out that this form is popular since it arises in the case without supercooling and is accurate in the limit of large Stefan number. It may also be derived from (13) with the common assumption that $c = 1$ and then choosing $k = 0$ to remove the contribution of the solid phase. Wu *et al* [19] discuss similar reductions in the context of spherical nanoparticle melting. They state that when the initial temperature is different to the phase change temperature then the one-phase limit may only be derived under the assumption $k \ll 0$.

In [6] it is stated that the supercooled Stefan problem using (14) with $T_I = 0$ does not conserve energy. To understand this statement consider the total heat in the system

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

108 (note, we have chosen T_m^* as the reference temperature where $E = 0$). The
 109 rate of change of energy is

$$\frac{\partial E}{\partial t} = \int_0^s c \frac{\partial \theta}{\partial t} dx + c\theta(s, t)s_t + \int_s^\infty \frac{\partial T}{\partial t} dx - T(s, t)s_t. \quad (16)$$

110 Replacing the time derivatives via the heat equations and integrating gives

$$\frac{\partial E}{\partial t} = k \left. \frac{\partial \theta}{\partial x} \right|_s - \left. \frac{\partial T}{\partial x} \right|_s - k \left. \frac{\partial \theta}{\partial x} \right|_0 + [c\theta(s, t) - T(s, t)] s_t, \quad (17)$$

111 where we have assumed $T_x \rightarrow 0$ as $x \rightarrow \infty$. The standard Stefan condition
 112 $T_x|_{x=s} = -\beta s_t$ may be obtained by setting $c = 1$, $\theta(x, t) = T_I(t)$ in (13). At
 113 the interface $\theta(s, t) = T(s, t) = T_I(t)$ and the above energy balance reduces
 114 to

$$\frac{\partial E}{\partial t} = \beta \frac{\partial s}{\partial t}. \quad (18)$$

115 This equation states that the rate of change of energy balances the heat
 116 released by the phase change, so in fact the standard Stefan condition may
 117 be consistent with energy conservation (although the choice $\theta(x, t) = T_I(t)$
 118 does not satisfy the heat equation). However, if we arrive at the standard
 119 Stefan condition by setting $c = 1$, $\theta(x, t) = 0$ in equation (13) then the energy
 120 balance gives

$$\frac{\partial E}{\partial t} = [\beta - T_I] s_t, \quad (19)$$

121 and now energy is not conserved (but the heat equation is satisfied). So in
 122 fact using the standard Stefan condition it is possible to conserve energy in
 123 the system, provided the heat equation is not satisfied, conversely the heat
 124 equation may be satisfied but then energy is not conserved.

125 4. Asymptotic solutions

126 The problem of energy conservation has been tackled in a number of pa-
 127 pers by making assumptions on the size of the conductivity ratio and seeking
 128 a series expansion in the temperature profiles. Most work has focussed on
 129 the limit of small solid to liquid conductivity ratio $k \ll 1$ [2, 6, 19]. However,
 130 in [13] it was pointed out that due to the way heat is conducted $k_s > k_l$ and
 131 so the limit $k \gg 1$ was investigated, we shall discuss both cases below.

132 *4.1. The limit of small conductivity ratio, $k \ll 1$*

The limit of small k was considered in [2, 6, 19]. In non-dimensional form the analysis of [6] simply incorporates a boundary layer in the solid, of thickness $\mathcal{O}(k)$, which allows the solid temperature to change between $T_I(t)$ at $x = s(t)$ to the initial temperature $\theta(x, 0)$ in the far-field which, for simplicity, is set to 0. Their analysis leads to the modified Stefan condition

$$[T_I(t) + \beta] s_t = - \left. \frac{\partial T}{\partial x} \right|_{x=s(t)}. \quad (20)$$

133 This is the correct form of Stefan condition for a far-field temperature $\theta = 0$
 134 and it conserves energy. However, this solution is far from ideal. For the
 135 problem considered in [6] and by many other authors on the solidification of
 136 supercooled liquids the solid does not exist at $t = 0$, hence $\theta(x, 0)$ is unde-
 137 fined. Once solidification starts the solid forms at temperature $T_I(t) \neq 0$.
 138 Since the solid is assumed to be a poor conductor (infinitely poor compared
 139 to the liquid) there is no mechanism for the far-field to attain zero temper-
 140 ature. Then, there is the physical issue that solids are better conductors of
 141 heat than liquids. Hence this condition, although mathematically correct, is
 142 not of use for thermal problems.

143 *4.2. Limit of large conductivity ratio, $k \gg 1$*

144 Noting that physically $k_s > k_l$ it makes more sense to look for a large
 145 k reduction. Unlike the $k \rightarrow 0$ limit, when $k \rightarrow \infty$ the solid reacts almost
 146 instantaneously to the boundary temperature and so $\theta(x, t) \approx T_I(t)$.

Now consider the problem where $k \gg 1$ with boundary conditions on the solid $\theta(s, t) = T_I(t)$, $k\theta_x(0, t) = -Q$. Note, previously we ignored any heat input at the boundary $x = 0$ since the solid was deemed an infinitely poor conductor. In fact previous comparisons between one-phase and two-phase approximations have often been made by imposing $\theta_x = 0$ at the boundary, see [4, 13]. Now for generality we allow a non-zero heat flux. If we assume $1/k \ll 1$ and look for a perturbation solution in terms of the small parameter $1/k$ then to first order the solid temperature is

$$\theta(x, t) = T_I(t) + \frac{1}{k} \left[\frac{\partial T_I}{\partial t} \frac{(x^2 - s^2)}{2} - Q(x - s) \right]. \quad (21)$$

Using this to determine $\theta_x(s, t)$ in the Stefan condition (13) leads to

$$-cs \frac{\partial T_I}{\partial t} + Q + [(1 - c)T_I + \beta] s_t = - \left. \frac{\partial T}{\partial x} \right|_{x=s}. \quad (22)$$

147 This is the appropriate one-phase Stefan condition, correct to first order,
 148 in the case where k is large. The version correct to leading order in $1/k$
 149 has $\theta(x, t) = T_I(t)$ and the first two terms of equation (22) are neglected
 150 (thus reducing equation (22) to (14). That is the appropriate one-phase
 151 Stefan condition, when k is infinite, is given by equation (14). The most
 152 significant difference between using the leading order and first order results
 153 is the appearance of the time derivative of T_I . In the linear undercooling
 154 case examined in [13] $T_I = -s_t$ and so the Stefan condition becomes second
 155 order in time, rather than the usual first-order equation.

156 To verify that the new form conserves energy we may substitute for θ via
 157 equation (21) and $T_x(s, t)$ via (22) into the energy equation (17) to find

$$\frac{\partial E}{\partial t} = Q + \beta s_t . \quad (23)$$

158 This equation states that the rate of change of energy balances that released
 159 by the phase change and the energy input at the boundary, *i.e.* this formula-
 160 tion conserves energy. The heat equation is also satisfied by $\theta(x, t)$. Similarly,
 161 the leading order solution $\theta(x, t) = T_I(t)$ leads to a consistent, energy con-
 162 serving solution (it satisfies the heat equation since the limit $k \rightarrow \infty$ results
 163 in $\theta_{xx} = 0$). Obviously the leading order solution will be less accurate than
 164 the first order approximation.

165 5. Formulation via equation (7)

166 In §2 we derived the dimensional Stefan formulation (7). If we compare
 167 this with the standard Stefan formulation (10), which is used in studies of
 168 melting point depression, we can see that (10) follows from equation (7) if
 169 the interface temperature of both phases is $T_I^*(t^*)$. *This implicit assumption,*
 170 *that both phases achieve the same temperature at the interface, is the root of*
 171 *the energy conservation problem.*

In non-dimensional form equation (7) may be written

$$[T(s, t) - c\theta(s, t) + \beta] s_t = - \left. \frac{\partial T}{\partial x} \right|_{x=s} + k \left. \frac{\partial \theta}{\partial x} \right|_{x=s} . \quad (24)$$

This equation should be used as the starting point for any one-phase re-
 duction. For example, to retrieve the poor solid conductor model, $k \ll 1$,
 with initial temperature θ_0 , we may impose $\theta(x, t) = \theta_0$ and so $\theta(s, t) = \theta_0$,

$\theta_x = 0$. Substituting these values together with $T(s, t) = T_I(t)$ into equation (24) gives

$$[T_I(t) - c\theta_0 + \beta] s_t = - \frac{\partial T}{\partial x} \Big|_{x=s(t)}. \quad (25)$$

172 If we choose $\theta_0 = 0$ then equation (20) is retrieved (without the need for an
173 asymptotic analysis).

In the limit of large k the solid is a good conductor and so the interface temperature is immediately transmitted through the material, hence $\theta(x, t) = T_I(t)$ and again $\theta_x = 0$. Equation (24) now reduces to

$$[(1 - c)T_I(t) + \beta] s_t = - \frac{\partial T}{\partial x} \Big|_{x=s}. \quad (26)$$

174 These constitute the final two terms on the left hand side of equation (22),
175 which are the leading order terms in the large k expansion. The first two
176 terms of equation (22) arise as a correction for finite k and come from the
177 fact that for finite k the temperature gradient $\theta_x(s, t) \neq 0$.

178 Note, the popular form specified by equation (13) may be derived from
179 equation (24) by setting $T(s, t) = \theta(s, t) = T_I(t)$. One-phase reductions must
180 be consistent with this, either by choosing the temperature of the neglected
181 phase to be $T_I(t)$ everywhere or by a boundary layer analysis to match the
182 far-field to the interface temperature, as described in [2, 6, 13, 19]. On the
183 other hand, any analysis based on equation (13) where the neglected phase
184 is assigned a constant value not equal to T_I will be inconsistent and this
185 manifests itself in the fact the energy balance is not satisfied.

186 6. Extension to cylindrical and spherically symmetric geometries

187 A common physical situation where the phase change temperature varies
188 involves the melting of nanoparticles or nanowires [7, 14, 16, 19]. In this
189 case the melting point depression is a consequence of the surface tension
190 induced pressure. The interest in nano melting for a wide variety of practical
191 applications provides us with the opportunity to investigate a different form
192 of Stefan problem to that of previous sections. In keeping with the analyses of
193 [7, 19] we will consider the radially symmetric melting of a sphere or cylinder
194 where a fixed temperature is imposed at the outer boundary $T(1, t) = 1$. The

195 appropriate nondimensional forms of (12) are

$$\frac{\partial \theta}{\partial t} = \frac{k}{c} \frac{1}{r^n} \frac{\partial}{\partial r} \left(r^n \frac{\partial \theta}{\partial r} \right), \quad \frac{\partial T}{\partial t} = \frac{1}{r^n} \frac{\partial}{\partial r} \left(r^n \frac{\partial T}{\partial r} \right), \quad (27)$$

where the solid occupies $r \in [0, R(t)]$ and the liquid $r \in [R(t), 1]$. The length-scale has been chosen as the initial radius, R_0 , and the temperature scale $\Delta T = T_H - T_m^*$ where T_H is the temperature imposed at the surface. The spherically symmetric model corresponds to $n = 2$, cylindrical to $n = 1$ and $n = 0$ gives us a one-dimensional Cartesian model. The appropriate non-dimensional form for the Stefan condition (24) is

$$[T(R, t) - c\theta(R, t) + \beta] R_t = - \left. \frac{\partial T}{\partial r} \right|_{r=R} + k \left. \frac{\partial \theta}{\partial r} \right|_{r=R}. \quad (28)$$

196 Following the arguments of §5 we may immediately write down the one
 197 phase reductions for small and large k . For $k \ll 1$, $\theta(x, t) = \theta(R, t) = \theta_0$ and
 198 equation (28) reduces to the radial form of (25) (with s replaced by R and x
 199 by r). Choosing $\theta_0 = 0$ this is exactly the one-phase limit used in the study of
 200 nanoparticle melting of [2, 19] and derived through a boundary layer analysis.
 201 For infinite k , $\theta(x, t) = \theta(R, t) = T(R, t) = T_I$ and the radial version of (14)
 202 is obtained. The correction for large but finite k requires solving the solid
 203 heat equation in (27), subject to $\theta(R, t) = T_I(t)$, $\theta_r(0, t) = 0$. This leads to

$$\theta = T_I + \frac{1}{k} \left[\frac{c}{n+1} \frac{\partial T_I}{\partial t} \left(\frac{r^2 - R^2}{2} \right) \right] + \mathcal{O}(k^{-2}). \quad (29)$$

Then the Stefan condition, correct to $\mathcal{O}(k^{-1})$, is

$$-\frac{cR}{n+1} \frac{\partial T_I}{\partial t} + [(1-c)T_I + \beta] R_t = - \left. \frac{\partial T}{\partial r} \right|_{r=R}. \quad (30)$$

Using the definition of total energy

$$E = \int_0^R c\theta r^n dr + \int_R^1 T r^n dr \quad (31)$$

204 it is a simple matter to show that the above formulae all conserve energy.

205 In [13] the accuracy of the Cartesian one-phase formulations was discussed
 206 in detail. An example was given for the material salol, which has a low value

Figure 1: Evolution of the interface $R(t)$ for the two-phase (solid line), large k (dashed), small k (dash-dotted) and standard (dotted) formulations. Plot (a) corresponds to $n = 2$ (nanoparticle) and (b) to $n = 1$ (nanowire).

207 of $k \approx 1.3$ and it was shown that the small k solution was far from the two-
 208 phase solution (with an approximately 40% slower melt rate). The standard
 209 formulation (corresponding to the infinite k limit) was more accurate than
 210 the small k solution and the large but finite k result was very accurate.
 211 With data appropriate for a water-ice system, $k \approx 4$, the same trend was
 212 observed: the small k solution gave the least accurate results, the large k
 213 solution was virtually indistinguishable from the two-phase solution. Since
 214 the accuracy of the Cartesian model has been established we now focus on
 215 the radially symmetric formulations. In Figure 1 we present two sets of
 216 results for the evolution of a particle radius for the spherical and cylindrically
 217 symmetric models. Parameter values are chosen for gold: $T_m^* = 1337\text{K}$,
 218 $L_m 6.37 \times 10^4 \text{J/kg}$, $\rho(= \rho_s) = 1.93 \times 10^4 \text{kg/m}^3$, $k = 2.9906$, $c = 0.7914$,
 219 $\sigma_{sl} = 0.27 \text{N/m}$, see [7]. The melt temperature is described by the standard
 220 Gibbs-Thomson relation, $T_I(t) = -n\Gamma/R(t)$ where $\Gamma = \sigma_{sl}T_m^*/(R_0\rho L_f\Delta T)$
 221 and σ_{sl} is the solid-liquid surface tension. Choosing an initial radius $R_0 =$
 222 20nm and temperature difference $\Delta T \approx 39 \text{K}$ we find $\Gamma = 0.3755$, $\beta = 10$.
 223 Figure 1a shows the melting of a nanosphere, Figure 1b shows a melting
 224 nanowire. The four curves in each figure represent the solution of the two-
 225 phase model of equation (28) (solid line), the large k model of equation (30)

226 (dashed line), the standard formulation (or infinite k) given by the radial
 227 version of (14) (dotted line) and the small k model, the radial version of
 228 equation (20), (dash-dot line). All curves show the expected feature that for
 229 $t \rightarrow 0^-$ and $R \rightarrow 0^+$ the velocity $R_t \rightarrow -\infty$, see [2, 7, 12, 18]. Note, the
 230 Gibbs-Thomson relation predicts a negative melt temperature for $R \approx 0.4\text{nm}$
 231 while we expect continuum theory to no longer hold below $R = 2\text{nm}$, see the
 232 discussion in [7, 9]. Consequently the graphs should only be expected to
 233 hold for $R > 0.1 = 2\text{nm}/20\text{nm}$. In the first graph, for a nanosphere, the
 234 large k solution is virtually indistinguishable from the two-phase solution.
 235 The dotted line, which represents the infinite k model is close to the two-
 236 phase solution, while the small k approximation gives the worst result. For
 237 the melting of a nanowire, Fig. 1b, again the large k solution is the most
 238 accurate but, remarkably, the small k solution shows a similar, if slightly
 239 lower, level of accuracy.

240 7. Conclusion

241 It has been noted by several authors that the standard one-phase reduc-
 242 tion to the Stefan problem in the presence of melting point depression does
 243 not conserve energy. In this paper we show two important results:

- 244 1. Depending on the assumptions made to obtain the standard reduction
 245 it may conserve energy (but then the heat equation for the neglected
 246 phase is not satisfied).
- 247 2. Difficulties encountered in writing down a one-phase reduction which
 248 satisfies both energy conservation and the heat equation stem from us-
 249 ing the wrong form of Stefan condition, which implicitly incorporates
 250 the assumption that both solid and liquid materials are at the phase
 251 change temperature at the interface. Provided the correct Stefan condi-
 252 tion is used energy conserving forms may be written down immediately.
 253 Asymptotic expansions may subsequently be used to improve accuracy.

254 In the case of melting a semi-infinite solid, in a Cartesian frame, the
 255 appropriate two-phase Stefan condition is given by equation (24) and the
 256 leading order reduction by equation (26). A reduction accurate to first-order
 257 in $1/k$ is given by equation (22). Similar equations were also derived for
 258 spherical and cylindrically symmetric problems.

259 Obviously there are many varieties of Stefan problem and we have only
 260 analysed two particular types of problem. However, their adaptation to many

261 other scenarios is straightforward. The key being to start with the correct
262 form of Stefan condition.

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