



Mathematical modelling of phase change at the nanoscale[☆]



T.G. Myers*

Centre de Recerca Matemàtica, Campus de Bellaterra, Edifici C, 08193 Bellaterra, Barcelona, Spain
 Departament de Matemàtiques, Universitat Politècnica de Catalunya, Barcelona, Spain

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ABSTRACT

Standard mathematical models for phase change at the nanoscale involve an implicit assumption that the latent heat is released at the bulk phase change temperature. They also assume the latent heat to be constant (while the melt temperature decreases with decreasing size). There is clear experimental evidence that this is not the case. In this paper, we examine the formulation of the Stefan problem at the nanoscale and present a new form of Stefan condition which correctly reflects the latent heat release, including both melt temperature and latent heat depression. We go on to show that the standard formulation can lead to melt rates up to three times slower than in reality.

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1. Introduction

Nanotechnology is a rapidly growing interdisciplinary area with a broad range of applications. Lying at the heart of nanotechnology is the nanoparticle, a unit of matter with a critical diameter between 1 and 100 nm. In many applications, including drug delivery systems, phase change memory and nanolithography, nanoparticles are subjected to relatively high temperatures. In order to understand particle behavior in these environments and so help in the future design of nanoparticles it is crucial to have the correct theoretical description. It is well-known that the thermal response of nanoparticles can be significantly different to that of macroscale particles consequently, in this paper, we develop a mathematical model for phase change at the nanoscale. The formulation is significantly different to that provided in previous studies and suggests melting rates up to three times faster than previously predicted. Earlier mathematical models lead to melting times on the order of picoseconds for 10 nm particles, see Ref. [1]. This is of the order of the relaxation time for many materials meaning that if the true melt rate is in fact more rapid than the whole mathematical formulation of the nanoscale Stefan problem may need to be altered to account for non-classical thermodynamics.

Theoretical modelling of phase change at the macroscale is relatively well understood. However, at the nanoscale it is well-known that standard models may break down or need adapting, even for sizes where continuum theory still holds. It has been demonstrated

that the heat equation based on Fourier's law may be inaccurate at the nanoscale and certainly the implicit assumption of infinite speed of heat transfer is incorrect [2]. Quantities such as the surface tension, phase change temperature and latent heat have been shown to vary significantly with size. The melt temperature variation was theoretically predicted in 1909 by Pawlow and demonstrated experimentally in 1956 by Takagi, see Ref. [3]. Lai et al. [4] point out that the thermodynamics of small systems cannot be fully understood without a detailed investigation of the heat exchange and particularly the latent heat. They use a scanning nanocalorimeter to provide the first direct measurements of latent heat for tin nanoparticles. Their results show a clear and significant decrease in both latent heat and melt temperature with particle size. Subsequently more accurate calorimetry techniques were developed to measure the latent heat release during nanoparticle melting, see Ref. [3], which confirms the findings in Ref. [4]. The results of Liu and Wang [5, Fig. 2c] show clearly that latent heat decreases are proportionally greater than those of the melt temperature.

Probably the simplest form of mathematical model which can provide insight into melting at the nanoscale involves a spherically symmetric nanoparticle. This has been studied in the context of continuum theory in Refs. [1,6–10] for example. As discussed in Refs. [1,3,11] continuum theory may be applied to heat transfer and phase change models down to diameters of the order 2–5 nm, depending on the material. In this paper, we will re-examine the standard mathematical model and show that it is incorrectly formulated. The model will be discussed in the context of tin nanoparticles, for which there exists a large amount of experimental data. For tin the melting point and latent heat depression are of the order 15% and 70% below the bulk values respectively [4]. Surface tension is also known to vary with particle size. For a sphere it may be

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* Centre de Recerca Matemàtica, Campus de Bellaterra, Edifici C, 08193 Bellaterra, Barcelona, Spain.

approximated via an expansion in terms of the reciprocal radius, $\sigma_{sl} \approx \sigma_{0,sl}(1 - 2\delta/R)$, where $\sigma_{0,sl}$ is the bulk value for surface tension and δ is the Tolman length. The Tolman length describes the deviation in surface tension between a planar and curved surface, it is unknown for most materials, however it is typically small, for water values are quoted around 0.5Å, for tin around 3.7Å [12,13]. Hence, in comparison to the melting point and latent heat variation the variation of surface tension is relatively small and will be neglected in the present study.

Now consider the spherically symmetric melting of a nanoparticle due to some external heat source. In the solid and liquid layers heat equations hold,

$$\rho_s c_s \frac{\partial \theta}{\partial t} = \nabla \cdot (k_s \nabla \theta) \quad (1)$$

$$\rho_l c_l \left(\frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T \right) = \nabla \cdot (k_l \nabla T) , \quad (2)$$

where ρ, c, k represent the density, specific heat and conductivity, T and θ are the temperatures in the liquid and solid respectively. Subscripts s and l denote solid and liquid. The central solid region, $0 \leq r \leq R(t)$, is fixed while the surrounding liquid region, $R(t) \leq r \leq R_b(t)$ moves in the radial direction with velocity \mathbf{v} due to the change in density between the phases. The position of the melt interface, $r = R(t)$, is described by the Stefan condition

$$\rho_s L(t) R_t = k_s \nabla \theta|_{r=R(t)} - k_l \nabla T|_{r=R(t)} . \quad (3)$$

Macroscale models often involve an assumption of constant thermophysical properties within each phase, a constant melt temperature and constant latent heat $L(t) = L_1(t) = L_m^*$ (L_m represents the latent heat and the star superscript indicates the bulk value). At the nanoscale, the variation of melt temperature has a significant effect on the Stefan condition, such that L is often replaced with

$$L_2(t) = L_m^* + (c_l - c_s)(T_m - T_m^*) , \quad (4)$$

where T_m denotes the melt temperature. This expression is frequently termed the ‘effective latent heat’. The melt temperature may be approximated by the standard Gibbs-Thomson relation

$$T_m(t) = T_m^* \left[1 - \frac{2\sigma_{sl}^*}{\rho_s L_m^* R} \right] . \quad (5)$$

The Stefan problem with $L_2(t)$ is the one found in theoretical investigations of nanoparticle melting [1,6–10] and also in the literature for the solidification of supercooled materials [14–18]. In all of these papers it is assumed $\rho_s = \rho_l$. Allowing density variation through the phase change introduces a kinetic energy term $v_l^2/2$ into Eq. (4). The form with kinetic energy may be found in Ref. [8] for spherically symmetric nanoparticle melting and the Cartesian version in Ref. [14].

2. Governing equations for phase change

To model the evolution of a particle we require various conservation laws. Further, to simplify the analysis we will make a number of assumptions: gravity and viscous effects are negligible; spherical symmetry is imposed; each phase is incompressible (which then fixes the solid region). Under these assumptions we may write the following system of governing equations. Firstly, mass is conserved,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 . \quad (6)$$

Conservation of mechanical energy is given by

$$\frac{\partial}{\partial t} \left(\frac{1}{2} \rho v^2 \right) + \nabla \cdot \left(\frac{1}{2} \rho v^2 \mathbf{v} + P \mathbf{v} \right) - P \nabla \cdot \mathbf{v} = 0 . \quad (7)$$

This equation states that the change in kinetic energy is balanced by the input of kinetic energy through the bulk flow, the work done by pressure, P , and the rate of reversible conversion to internal energy. Conservation of total energy is

$$\frac{\partial}{\partial t} \left(\rho \left[u + \frac{1}{2} v^2 \right] \right) + \nabla \cdot \left(\rho \left[u + \frac{1}{2} v^2 \right] \mathbf{v} + \mathbf{q} + P \mathbf{v} \right) = 0 , \quad (8)$$

where u is the internal energy/unit mass and the conductive heat flux $\mathbf{q} = -k \nabla T$. This equation states that the rate of change of total energy depends on energy flow through convection, conduction and the rate of work done by pressure. These equations are discussed in more detail in Refs. [14, §2.3E] [19, §3.3, §10.1].

The assumptions of incompressible phases, spherical symmetry and a stationary solid indicate constant ρ (within each phase), $\mathbf{v}_l = v_l(r, t) \hat{\mathbf{r}}$ and $\mathbf{v}_s = \mathbf{0}$. Mass conservation then reduces to $\nabla \cdot \mathbf{v} = 0$ and so the final term of Eq. (7) is zero. Subtracting Eq. (7) from Eq. (8) and rearranging leads to

$$\rho \left(\frac{\partial u}{\partial t} + \mathbf{v} \cdot \nabla u \right) = -\nabla \cdot \mathbf{q} , \quad (9)$$

which represents conservation of thermal energy. It is more convenient to write this equation in terms of temperature. Following Ref. [19, p.315] when the density is constant in each phase we can define the specific heat capacity at constant volume, $c_v = (du/dT)|_V$, and so express the total derivative of u as

$$\frac{du}{dt} = c_v \frac{dT}{dt} . \quad (10)$$

Substituting for \mathbf{q} , the standard form of heat equation then follows from Eq. (9)

$$\rho c_v \left(\frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T \right) = \nabla \cdot (k \nabla T) . \quad (11)$$

This equation holds in either phase, with ρ, c_v, \mathbf{v} replaced by the appropriate values for solid or liquid.

The internal energy per unit mass may be written $u = h - P/\rho$, where h is the specific enthalpy. For an incompressible material the specific heat capacity at constant pressure

$$c_p = \left. \frac{dh}{dT} \right|_p . \quad (12)$$

The difference between specific heats measured at constant volume and pressure is proportional to the thermal expansion coefficient. If the density is considered constant in each phase (and hence the volume) then we may neglect thermal expansion and set $c_v = c_p$. This is generally true for solids and liquids except for at extremely high pressures. Consequently, we denote the specific heat simply as c and may integrate Eq. (12) to give

$$\begin{aligned} h &= c_s(\theta - T_m) && \text{in the solid} \\ &= c_l(T - T_m) + L_m && \text{in the liquid.} \end{aligned} \quad (13)$$

The definition of latent heat is key to the present derivation: it is the *jump in specific enthalpy at the phase change temperature*, that is $L_m(t) = (h_l - h_s)|_{\theta=T=T_m(t)}$. We discuss this apparently obvious statement in more detail in the subsequent section.

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