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Mathematical Modelling of Nanoparticle Melting

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Abstract—Many physical properties of materials, especially the melting point, change when the physical size of the material approaches the micro and nano scales. The problem considered in this paper is the inward melting of nanoparticles with a spherical geometry, and which initially are in a solid state with low temperature. For the nanoparticles, whose melting (freezing) point has been reported to decrease with decreasing particle radius, the numerical enthalpy method is used to solve the melting problem for an idealized two phase Stefan problem. The behaviour of the nanoparticle melting process compared with a particle melting process at the macro scale is also discussed. The numerical results show that the interfacial tension increases the melting rate of the nanoparticle.

Keywords—nanoparticles; Stefan problem; variable melting point; enthalpy method

I. INTRODUCTION

Stefan problems, involving phase change with moving boundaries, occur in a great many engineering applications, such as melting and solidification of alloys, freezing and thawing foods, production of ice, solidification of steel and chemical reactions, and so on. Ever since Gabriel Lamé and Benoit Clapeyron [1] first considered the Stefan problem, a great deal of work has been done by many authors [1-8]. Because the moving boundary is unknown and is to be determined, it adds much complexity to the solution of these kind of problems. Hence only a few analytical solutions exist for simple cases, for example the famous Neumann similarity solutions which consider the melting or freezing process of the ice in a semi-infinite region in Carslaw et al's work [2]. And Hill [3] also proposed to utilize the Fourier series, pseudo steady state and heat-balance method to get the analytical or approximate analytical solutions. Dewynne [4] used the integral formulation and obtained good results of the melting of solid spheres.

Except for the few analytical solutions, many numerical schemes have been developed in order to solve most of the Stefan problems. In the books written by Crank [1] and Hill and Dewynne [3], some numerical approaches are discussed in detail. The methods can be classified into three types: the front tracking methods, the front-fixing method and the fixed-domain methods. For the front tracking method, which computes the position of the moving boundary at each time step, fixed finite-difference grid and modified grids [1] are used. The second type adopts new space coordinates by the

Landau transformation [5] which avoids considering the unknown region at the same time. Wu et al. [6] uses this transformation and a small-time series expansion technique to get an analytical expression for the phase growth rate of liquid solidification. What should be noticed in the fixed-domain methods is the enthalpy scheme proposed by Eyres [7]; the great advantage of this method is that it avoids explicit reference to the moving boundary. With this method, Voller and Cross [8] obtain accurate solutions of moving boundary problems.

However, most of the above problems are analyzed with constant physical properties at the macro scale, and there are few reports about the melting of nanoparticles. But some physical properties of materials, especially the melting point, change when the physical size of the material approaches the micro scale. It has been observed in both experiments and theoretical simulations that nanoparticles melt at temperatures lower than those of the bulk material. There are many proposed models for the melting temperature of nanoparticles. Buffat and Borel [9] used the scanning electron-diffraction technique to investigate the effects of the interfacial tension and particle size on the melting point of gold nanoparticles, showing that the melting point is proportional to the reciprocal of the particle radius, provided that the physical constants of gold are the known values appropriate to the massive metal. Qi and Wang [10] discuss both the shape and size effect on the melting temperature of metallic nanoparticles, indicating that the nanoparticle melting point is a function of the radius of the atom and the nanoparticle. A theory based on Laplace's equation and the Gibbs-Duhem equation gave the homogeneous melting and growth model, the liquid shell model and the liquid nucleation and growth model under different melting mechanisms when taking account of the interfacial tensions between the solid and liquid phases [11]. There are several models for the melting point of nanoparticles referred to in [12]. The form of these models can be described by

$$T_f(R) = T_o \left(1 - \frac{\omega}{R} \right), \quad (1)$$

where $\omega = 2\gamma/L$. The parameter γ is related to the interfacial (solid/liquid phase) tensions. T_o is the bulk melting point and $T_f(R)$ is the melting point of a particle with radius R . L is latent heat per unit mass at the equilibrium temperature T_o . For

isolated nanoparticles we can assume the temperature on the surface is higher than the bulk melting point, and then the melting will begin and continue, while the liquid phase will not flow away.

The objective of this work, based on the model for the melting point of nanoparticles, is to investigate the melting behaviour of the nanoparticle melting process, including determination of the temperature distribution and the behaviour of the moving boundary which varies with time.

Figure 1. Problem Geometry.

II. MODEL, PROBLEM AND FORMULATION

A. Problem

The problem domain consists of a nanoparticle whose size is in the range of several nanometers to several hundreds of nanometers. Its melting process under the spherical coordination is illustrated in Fig. 1. Suppose that the nanoparticle is initially frozen at the constant temperature T_i^* and the initial radius of nanoparticle is a^* and the moving boundary is at $R^*(t^*)$, which is a function of time t^* . The temperatures in the liquid and solid phases are $T_l^*(r^*, t^*)$ and $T_s^*(r^*, t^*)$, respectively. The thermal conductivities and mass density of the two phases are assumed to be equal. The specific heat capacities of the two phases are c_l and c_s , respectively. L denotes the latent heat per unit mass at the equilibrium temperature T_o . The bulk melting temperature and nanoparticle melting temperature are T_o and $T_f(R)$, which is dependent on the size of the nanoparticle as described in (1). We assume perfect thermal contact at the surface and the temperature remains at T_a^* , and the inner boundary at $r^*=0$ is insulated.

The temperature profile in the liquid and solid can be determined by solving the heat conduction equations in the domain

$$\rho c_l r^{*2} \frac{\partial T_l^*}{\partial t^*} = \frac{\partial}{\partial r^*} \left(k r^{*2} \frac{\partial T_l^*}{\partial r^*} \right), \quad R^*(t^*) \leq r^* \leq a^*, \quad (2)$$

$$\rho c_s r^{*2} \frac{\partial T_s^*}{\partial t^*} = \frac{\partial}{\partial r^*} \left(k r^{*2} \frac{\partial T_s^*}{\partial r^*} \right), \quad 0 \leq r^* \leq R^*(t^*), \quad (3)$$

here ρ , c_l , c_s , and k are assumed constants. The initial conditions are

$$R^*(0) = a^*, \quad T_s^*(r^*, 0) = T_i^*, \quad (4)$$

and the boundary conditions are

(i) temperature continuity at the moving boundary

$$T_l^*(R^*(t^*), t^*) = T_s^*(R^*(t^*), t^*) = T_o \left(1 - \frac{\omega}{R^*(t^*)} \right), \quad (5)$$

(ii) the fixed boundary conditions

$$T_l^*(a^*, t^*) = T_a^*, \quad \frac{\partial T_s^*}{\partial r^*}(0, t^*) = 0, \quad (6)$$

(iii) a discontinuity in heat flux due to the liberation of the latent heat L across the phase change at the location $R^*(t^*)$

$$k \frac{\partial T_l^*}{\partial r^*}(R^*(t^*), t^*) - k \frac{\partial T_s^*}{\partial r^*}(R^*(t^*), t^*) = -\rho_s L \frac{dR^*}{dt^*}. \quad (7)$$

B. Nondimensionalization

To simplify the governing equations, we introduce the following nondimensional variables

$$r = \frac{r^*}{a^*}, \quad R(t) = \frac{R^*(t^*)}{a^*}, \quad t = \frac{k}{\rho c_l a^{*2}} t^*, \quad \alpha = \frac{L}{c_l \Delta T}, \quad c = \frac{c_s}{c_l}, \quad (8)$$

$$T_l(r, t) = \frac{T_l^*(r^*, t^*) - T_o(1 - \omega/r^*)}{\Delta T}, \quad T_s(r, t) = \frac{T_s^*(r^*, t^*) - T_o(1 - \omega/r^*)}{\Delta T}, \quad (9)$$

$$T_i(r, 0) = \frac{T_i^* - T_o(1 - \omega/r^*)}{\Delta T}, \quad \Delta T = T_a^* - T_o(1 - \omega/a^*), \quad (10)$$

where $T(r, t)$ represents the nondimensional temperature, c denotes the specific heat capacity, the subscript l refers to the liquid phase and the subscript s refers to the solid phase. $R(t)$ denotes the nondimensional position of the moving boundary. With the nondimensional variables, the one dimensional two-phase Stefan problem becomes

$$r^2 \frac{\partial T_l(r, t)}{\partial t} = \frac{\partial}{\partial r} \left(r^2 \frac{\partial T_l(r, t)}{\partial r} \right), \quad R(t) \leq r \leq 1, \quad (11)$$

$$c r^2 \frac{\partial T_s(r, t)}{\partial t} = \frac{\partial}{\partial r} \left(r^2 \frac{\partial T_s(r, t)}{\partial r} \right), \quad 0 \leq r \leq R(t). \quad (12)$$

The initial and fixed boundary conditions become

$$R(0) = 1, \quad T_s(r, 0) = T_i(r, 0), \quad (13)$$

and

$$T_i(1,t)=1, \quad \frac{\partial T_s(0,t)}{\partial r}=0, \quad (14)$$

and the conditions related to the moving boundary become

$$T_l(R(t),t)=T_s(R(t),t)=0, \quad (15)$$

with the Stefan condition

$$\frac{\partial T_l(R,t)}{\partial r} - \frac{\partial T_s(R,t)}{\partial r} = -\alpha \frac{dR}{dt}, \quad (16)$$

where α is the Stefan number which is defined in (8), and $R(t)$ is the nondimensional moving boundary position.

III. ENTHALPY METHOD, RESULTS AND DISCUSSION

The enthalpy scheme is an attractive fixed-domain method for solving Stefan problems. One of its major advantages is that no explicit reference to the moving boundary is required, and the problem can be simplified to a fixed boundary problem. To introduce the scheme, we define a nondimensional enthalpy function $H(T)$ as a function of temperature which is also nondimensional

$$H(T) = \begin{cases} \alpha + T, & \text{if } T > 0 \\ [0, \alpha], & \text{if } T = 0 \\ cT, & \text{if } T < 0 \end{cases}, \quad (17)$$

where α and c are the nondimensional constants defined in the previous section. It is easy to define the temperature T in terms of the enthalpy H

$$T(H) = \begin{cases} H - \alpha, & \text{if } H > \alpha \\ 0, & \text{if } H \in [0, \alpha] \\ H / c, & \text{if } H < 0 \end{cases}, \quad (18)$$

and the enthalpy scheme describing the heat flow (11) and (12) become

$$r^2 \frac{\partial H}{\partial t} = \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right), \quad (19)$$

with the initial and fixed boundary conditions

$$R(0)=1, \quad H(r,0)=cT_i(r,0), \quad (20)$$

$$T_l(1,t)=1, \quad \frac{\partial T_s(0,t)}{\partial r}=0. \quad (21)$$

We obtain the explicit difference representation of (22) by using the forward difference approximation in time and central difference approximations in space following the enthalpy method described by Hill [3]

$$H_{i,j+1} = H_{i,j} + \delta \left[\left(1 + \frac{\Delta r}{r_i} \right) T_{i+1,j} + \left(1 - \frac{\Delta r}{r_i} \right) T_{i-1,j} - 2T_{i,j} \right], \quad (22)$$

where $2 \leq i \leq N-1$, $j \geq 0$ and $\delta = \Delta t / (\Delta r)^2$. We apply the central difference approximations at the end point

$$H_{1,j+1} = H_{1,j} + 2\delta[(T_{2,j} - T_{1,j})], \quad H_{N,j+1} = \alpha + 1, \quad (23)$$

where N is the number of nodes.

In this example, we use the model for melting of gold nanoparticles referred to in [13]. In this model, the bulk

TABLE I. INPUT PARAMETERS FOR PRESENT MODEL

T_i^*	T_a^*	ω	α	t_{c1}	t_{c2}
500	2000	0.20	0.4441	0.2098	0.2170
500	2000	0.10	0.4494	0.2126	
500	2000	0.01	0.4542	0.2151

Figure 2. Temperature profiles for $\omega = 0.2$.

Figure 3. Temperature profiles for $\omega = 0.01$.

Figure 4. Temperature profiles for $\omega = 0$.

Figure 5. Comparison of the melting of nanoparticles with constant and variable melting temperatures.

melting point T_o is 1090 K, the latent heat L is 53800 J/kg and ω is about 0.2. The initial temperature T_i^* is 500 K and the surface temperature T_a^* is 2000 K. Table 1 shows some parameters for present modeling. t_{c1} and t_{c2} are the time for complete melting of particles with variable and constant melting point, respectively. We obtain the temperature profiles under $\omega=0.2$, $\omega=0.01$ and $\omega=0$, shown in Figs. 2, 3 and 4.

Fig. 5 gives the comparison of the moving boundary behaviour under different ω . When $\omega=0.01$, the $R(t)$ curve for the moving boundary position is very close to the one for constant melting point. But when $\omega=0.2$, given the same original radius of the nanoparticle, the time for complete melting is much smaller than that of the particle with constant melting points. The results indicate that the ω plays an important role in nanoparticle melting, that is the decrease of the melting point increases the moving rate of the moving boundary.

It should be noted that in the present work we make an assumption that the model for the melting point will become

invalid when the particle radius approaches zero and that the melting point of the region near the origin is equal to the bulk melting temperature. Thus, we can take the temperature gradient with respect to the radius at the origin to be zero, and then simplify the problem. And it is understandable that the temperature profiles near the origin show an abnormal behaviour. So, strictly speaking, to obtain more accurate results we should know the melting properties when the radius become close to zero. Another assumption is that the melting temperature of the particle will never be negative. So must make sure that the smallest size of the element does not let the melting point become zero.

IV. CONCLUSION

In this study, the effect of the interfacial (solid/liquid) tensions (reflected by ω) on the melting of nanoparticles has been examined by the numerical enthalpy method. It is found that when ω is increased it greatly increases the melting rate of nanoparticles, and that when ω is sufficiently small, the effect is negligible.

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