Quasi-approximation for Stefan problem of nearly spherical phase change materials

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Abstract. Phase change occurs when a phase change material exchanges its energy with the external environment. In this paper, we investigate the solidification of nearly spherical materials, which is famously known as Stefan problem and is of practically important. When the material solidifies, the inner moving boundary (see Figure 1) can be determined by solving the elliptic-typed partial differential equation, equipped with the outer fixed and the inner moving boundary conditions, derived from the Newton cooling law and the latent heat, respectively. Since the shape of materials induces a huge impact on the retreating speed of the moving boundary. To demonstrate this idea, we consider the perfect spherical object and certain irregular objects, such as an ellipse. We derive the analytical solutions for both cases and find that the shape of the moving boundary changes from the ellipse into the sphere during the solidification process.

1. Introduction
In recent years, increasing attention has been paid to micro manufacture, which has shaped almost every sector in health care, telecommunication and energy, just to name a few. Especially, in the medical field, new drug-loaded materials have already generated intensive research activities. These new drug carriers are usually manufactured using phase change techniques. In particular, the shape of carriers affects the (un)loading rate for the embedded drug. Such phase change problem is known as Stefan problems. Usually, they are highly non-linear so that it is inconceivable to obtain exact solutions, except in some very simple cases. In particular, the exact solution of one-dimensional Stefan problems has been surveyed by Hill [1]. Due to its huge impact, a large number of experiments and simulations has been performed to investigate the shape effect of drug carriers [2]. Here, we adopt the elliptic-typed partial differential equation, equipped with some thermal boundary conditions to determine the speed of solidification for nearly spherical phase change materials. To simplify our model, we ignore the heat carried away by the liquid flow outside the material, and adopt the linearization technique to simplify the tedious moving boundary condition. We also assume that the drug temperature is as same as the temperature of the molten material due to the tiny size of the drug carrier.

2. Methods
Here, we do not take into account the convective effect induced by the surface air flow so that the external temperature is constant. The shape effect of the material is investigated for the case of a spherical shape and other irregular shapes. We determine the speed of solidification for such materials.
While the heat transfer between the solid and the surrounding environment can be modeled by the Newton's law of cooling, the heat transfer between the liquid phase and the solid phase is driven by the latent heat, resulting in a moving boundary. Thus, the equilibrium heat equation, Newton cooling law and the latent heat are used to form a mathematical basis for analyzing the present problem. We note that drug is loaded inside \( r \leq \varepsilon \), the liquid phase lies between \( \varepsilon \leq r < a_i \), where \( a_i \) is the radius for the molten domain and the solid phase lies between \( a_i \leq r \leq R \) (see the schematic in Figure 1).

![Figure 1](image-url)

**Figure 1.** This is a schematic for the present problem, where it shows the different radio of three domains. In particular, \( f(\theta) \) is the shape function of the outside boundary and \( g(\theta) \) is the shape function of the inside boundary. \( T_s \) is the solid temperature, \( T_L \) is the liquid temperature, \( T_\infty \) is the external temperature, \( R \) is the outer shape radius, \( \varepsilon \) is the inner drug radius, \( a_i \) is the radius of the moving boundary and \( i \) represents the time step.

### 2.1. Perfect sphere

In this paper, we firstly solve the perfect spherical case, followed by a case of irregular shapes. For the perfect sphere, the boundary conditions for the solid and liquid phases are given by

\[
T_s = T_L \quad (1)
\]

\[
\rho \lambda v = -k \left. \frac{\partial T_s}{\partial r} \right|_r \quad (2)
\]

Equation (1) reveals that the solid temperature and the liquid temperature are equal at the moving boundary. We comment that Equation (2) is the Stefan condition, which deduces the moving boundary/Stefan problem [3], and \( \rho, \lambda, v, k, T_s, \) and \( r \) denote the mass density of the liquid, latent heat, the retreating velocity of the moving boundary, heat constant, the temperature in the solid/liquid phase and the usual radial coordinate, respectively. In addition, the boundary condition caused by the heat exchange between the solid phase and the surrounding environment [4] is modelled by the Newton cooling law, which is given by

\[
k \frac{\partial T_s}{\partial n} + \Gamma (T_s - T_\infty) = 0 \quad (3)
\]

where \( \Gamma \) is a constant, called the surface heat transfer coefficient. We set \( \varepsilon \ll a_i \ll r \ll R \), and solve the following equilibrium heat equation, where the heat is conducted through the solid. Due to the radial symmetry, we obtain

\[
\nabla^2 T_s = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T_s}{\partial r} \right) = 0 \quad (4)
\]

\[
r^2 \frac{dT_s}{dr} = B
\]
\[ T_S = \frac{C}{r} + D, \]  

(5)

where \( B, C \) and \( D \) are integration constants. In order to obtain a unique solution for \( T_S \), \( T_S \) is solved with the boundary conditions, i.e. Equation (1) and Equation (3). By boundary equation 1, i.e. Equation (1):

\[ T_S(a_i) = \frac{C}{a_i} + D = T_L \]  

(6)

By boundary equation 2, i.e. Equation (2):

\[ k \frac{d}{dr} \left( \frac{C}{r} + D \right) \bigg|_{r=R} + \Gamma \left( \frac{C}{R} + D - T_e \right) = 0 \]  

(7)

By subtraction, we get

\[ C = \frac{\Gamma \Delta T}{\gamma_1} \]  

(8)

By addition, we get

\[ D = \frac{T_e + T_L}{2} - \frac{\gamma_2}{2\gamma_1} \Delta T \]  

(9)

where \( \Delta T = T_L - T_e, \gamma_1 = \frac{\Gamma}{a_i} - \frac{k}{R}, \gamma_2 = \frac{\Gamma}{a_i} - \frac{k}{R^2} \). Substituting Equation (8) and Equation (9) into Equation (5), gives

\[ T_S = \frac{\Gamma \Delta T}{\gamma_1} \frac{1}{r} + \left\{ \frac{T_e + T_L}{2} - \frac{\gamma_2}{2\gamma_1} \Delta T \right\} \]  

(10)

We remain to find the location of the moving boundary \( a \), which can be determined by the remaining Stefan condition. Upon substituting Equation (5) into the latent heat, i.e. Equation (2), we get

\[ \rho \lambda \nu = -k \frac{\partial T_S}{\partial r} \bigg|_{r=a_i} = -k \left\{ -\frac{C}{a_i^2} \right\} \]  

(11)

When \( a_i = R, \nu = \frac{\Gamma \Delta T}{\lambda \rho \gamma} \), which is dependent from the heat conductivity of the material in the solid phase. Now by setting the solidification time \( S_n \), and \( \Delta x_i = R - a_i \), we obtain

\[ S_n = \sum_{i=1}^{n} \frac{\Delta x_i}{v_i} = -\frac{\lambda \rho}{k \Gamma \Delta T} \sum_{i=1}^{n} \left\{ \Gamma a_i - \frac{\Gamma a_i^2}{2} + k a_i \right\} \Delta x_i \]  

(12)

Take \( n \to \infty \), we can convert the summation into an integration in order to obtain the total solidification time, \( S_{sol} \):

\[ S_{sol} = \frac{\lambda \rho}{k \Gamma \Delta T} \left[ \frac{\Gamma a_i^2}{2} - \frac{\Gamma a_i^3}{3R} + k a_i \right]_{\epsilon}^{\infty} \]  

(13)

Take \( \epsilon \to 0 \), Equation (13) can be approximated as follow,
$$\sim \frac{\lambda \rho}{k \Gamma \Delta T} \left\{ \frac{\Gamma R^2}{6} + kR \right\}$$  

(14)

Hence, \( S_{tot} \propto \frac{1}{\Delta T} \propto \lambda \) and \( S_{tot} \propto R^n \), where \( 1 \leq n \leq 2 \). The actual value of \( n \) depends on the competition between \( k \) and \( \Gamma \).

2.2. Irregular shape

It is worthy to notice that the governing equation for the case of the irregularly shaped material still satisfies the above three boundary conditions. Since the irregular shape induces an inconsistency in the speed of solidification at different angles, the boundary condition for latent heat is angular dependent. Firstly, we discretize the angles by

$$\theta = \frac{2\pi}{N_{\theta}} j \pi \quad j=1\ldots N_{\theta}$$  

(15)

We then linearize the moving boundary about the perfect sphere to get:

Boundary equation 1:

$$T_s \left|_{\hat{a}_{i,j} = \varepsilon \theta} = T_L(\theta) + \varepsilon T_\infty \right. \quad \text{where \ldots donates higher order term}$$  

(16)

$$\rho \lambda \mathbf{v}(a_{i,j}) = -k \left( \frac{\partial T_s(r, \theta)}{\partial a_{i,j}} \right)_{r=a_{i,j}} + \frac{1}{r} \frac{\partial T_s(r, \theta)}{\partial \theta} \bigg|_{r=a_{i,j}}$$  

(17)

where \( a_{i,j} \) denotes the minimum radius for the liquid domain at the time \( t = i \cdot \Delta t \) (\( \Delta t \) is the unit interval time). The angle \( \theta \) can be computed in Equation (15).

Boundary equation 2:

$$k n \cdot \nabla T_s + \Gamma \left\{ T_s - T_{\infty} \right\}_{\theta + \varepsilon \theta} = 0$$  

(18)

From the Laplace Equation \( \Delta T_s = 0 \), we obtain

$$T_s(r, \theta) = \frac{A_0}{2} + \sum_{n=1}^{\infty} r^n (A_n \cos n\theta + B_n \sin n\theta)$$  

(19)

where \( A_n \) and \( B_n \) are the Fourier coefficients. From B1, i.e. Equation (16), by comparing coefficients, we obtain the zero order term

$$\frac{A_0}{2} + \sum_{n=1}^{\infty} a_{i,j} (A_n \cos n\theta + B_n \sin n\theta) = T_L(\theta)$$  

(20)

From B2, we obtain the other zero order term

$$\frac{A_0}{2} + \sum_{n=1}^{\infty} (n \gamma_3 R^{n-1} + R^n) A_n \cos n\theta + (n \gamma_3 R^{n-1} + R^n) B_n \sin n\theta = T_L(\theta) \quad \text{where} \quad \gamma_3 = \frac{k}{\Gamma}$$  

(21)

Since the temperature difference between the external and liquid temperatures is significant in the present problem, we introduce a new variable for the temperature difference \( \Delta T(\theta) \) by subtracting Equation (20) by Equation (21),
Using the Fourier technique [5] to determine \( A_n, B_n \) from Equation (22) as functions of \( \Delta T(\theta) \):

\[
A_n = \frac{1}{(a_{i,j}^n - n\gamma R^{n-1} - R^n)} \int_{-\pi}^{\pi} \Delta T(\theta) \cos n\theta d\theta
\]

\[
B_n = \frac{1}{(a_{i,j}^n - n\gamma R^{n-1} - R^n)} \int_{-\pi}^{\pi} \Delta T(\theta) \sin n\theta d\theta
\]

and \( A_0 \) is given by

\[
A_0 = \frac{1}{\pi} \int_{-\pi}^{\pi} T_L(\theta) d\theta
\]

Next, we determine the speed of solidification using the Latent heat equation (17). The radial velocity \( \nu \) is then given by

\[
\rho \lambda \cdot \nu(a_{i,j}) = -k \left( \frac{\partial T}{\partial a_{i,j}} \right)_{a_{i,j}} = -k \left\{ \sum_{n=1}^{\infty} n a_{i,j}^n (A_n \cos n\theta + B_n \sin n\theta) \right\}
\]

\[
\nu(a_{i,j}) = \frac{\rho \lambda}{-k \left\{ \sum_{n=1}^{\infty} n a_{i,j}^n (A_n \cos n\theta + B_n \sin n\theta) \right\}}
\]

From which, we can compute the total solidification time \( S_n \),

\[
S_n = \sum_{i=1}^{n} \frac{\Delta x_{i,j}}{\nu(a_{i,j})} = \sum_{i=1}^{n} \frac{\rho \lambda \Delta x_{i,j}}{-k \left\{ \sum_{n=1}^{\infty} n a_{i,j}^n (A_n \cos n\theta + B_n \sin n\theta) \right\}},
\]

where \( \Delta x_{i,j} = R - a_{i,j} \).

3. Numerical results and discussion

In this section, we take an ellipse as the irregular shape to present some numerical solutions. The polar coordinate is used, where \( \theta \) is determined in Equation (15).

\[
\begin{align*}
  x_{i,j} &= a_{i,j} \cos \theta \\
  y_{i,j} &= a_{i,j} \sin \theta
\end{align*}
\]

It turns out that the location of the moving boundary \( a_{i,j} \) can be calculated iteratively. Upon setting \( a_{0,j} = R = 1, \nu(a_{0,j}) = 0, \Delta t = 0.01 \), \( \varepsilon = 0.1 \), the simplest iteration is given below:

\[
a_{i+1,j} = a_{i,j} - \nu(a_{i,j}) \Delta t \quad \text{when} \quad a_{i,j} \leq 0.1 \quad \text{stops.}
\]

We assume unit parameters, i.e. \( \rho = 1, k = 1, \lambda = 1 \). For each time step, we compute the partial sum of the retreating speed \( v_k \) and the convergence of the series, i.e. \( n \) is determined by the following algorithm;

\[
v_k(a_{i,j}) = \sum_{n=1}^{k} n a_{i,j}^n (A_n \cos n\theta + B_n \sin n\theta), \quad \text{when} \quad |v_{k+1} - v_k| < 0.01 \quad \text{stops.}
\]
Due to the symmetry of the ellipse, we can take $N_\theta = 4$, where \( \theta = \frac{\pi}{2} j - \pi \). To map the numerical results into the 2D elliptic surface, we use \( \frac{y^2}{a^2} + \frac{x^2}{b^2} = 1 \) (a, b are constants and \( a > b > 0 \)), where \( j = 0 \) corresponds to \( \theta = -\pi \) and \( j = 1 \) corresponds to \( \theta = -\frac{\pi}{2} \) in order to deduce the points \((-a_{i,0}, 0)\) and \((0, -a_{i,1})\), i.e. Equation (28). The plot for the moving boundary is then given in Figure 2.

![Figure 2. Moving Boundary $a_{i,j}$ at different time.](image)

As we can be seen from Figure 2, the moving boundary retreats with time, where the original elliptic shape appears to approach into the spherical shape. We notice that such phenomenon occurs in numerical natural melting process. We securitize such phenomenon by looking into the retreating velocities. We explore two specific angles, namely \(-\pi\) and \(-\frac{\pi}{2}\), which correspond exactly to the major axis and the minor axis, respective, and the numerical solution is given in Figure 3.
As we can be seen from the Figure 3, $v(a_{i,0}) \geq v(a_{i,1})$ happens only at the beginning of the solidification. However, after approximately 0.0166 s, $v(a_{i,1})$ exceeds $v(a_{i,0})$, and the trend remains intact afterwards. The magnitude of the retreating speeds for both major and minor axis decreases with time, explaining the increasingly compact inner rings as seen in Figure 2. Moreover, the retreating speed for the major axis outreaches that for the minor axis partially explains the shape transition from the ellipse into the sphere. In order to verify such phenomenon, we introduce a new variable $y = \frac{b}{a}$, where $a, b$ are the length of the minor axis and the major axis, respectively and check if the value of $y$ approaches 1 with time, which is given in Figure 4.

From Figure 4, we observe that the value of $b/a$ decrease remarkably before 0.05s. But after 0.05s, the ratio reveals a good linear relationship so that we can fit the data points in Figure 4 using a linear regression, gives
\[ y = \frac{b}{a} = 0.2319t + 0.8455, \quad R^2 = 0.995, \]  
(31)

where \( R^2 \) is coefficient of determination. It shows that the regression function can explain 99.5% of the variation. Here, we obtain \( R^2 = 0.995 \approx 1 \), which means that the correlation between \( y \) and time is very strong. The spherical shape attains at \( t = 0.666 \) s upon letting \( y = 1 \) in Equation (31). We take \( i = 67 \) to compute \( a_{67,0}, a_{67,1} \), and the result shows as follow;

\[ a_{67,0} = 0.13126, \quad a_{67,1} = 0.13096, \]

within the error \( 10^{-3} \). We deem \( a_{67,0} = a_{67,1} \) after 0.666 s so that the ellipse will become the spherical shape in the reasonable range of \( 0.1 = \varepsilon \leq a_{i,j} < R = 1 \).

4. Conclusions

In this paper, we have determined the semi-analytical solutions for the moving boundary problem for nearly spherical objects, where we take an ellipse as an example. We have found that the moving boundary retreats slower with time. On the other hand, we discover that due to the curvature effect, the shape of the moving boundary changes from the ellipse into the sphere owing to the fact that the speed of solidification for major axis exceeds that of the minor axis. The present outcomes open up a new research direction for studying solidification for more irregular shapes, such as 8-shaped shapes, pommel horse shapes, etc.

References

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