A MODEL FOR MELTING OF A PURE MATERIAL DURING MODULATED TEMPERATURE DIFFERENTIAL SCANNING CALORIMETRY*

C. NIKOLOPOULOS †

Abstract. We model the melting of a pure material during Modulated Temperature Differential Scanning Calorimetry (MTDSC) as a one-dimensional two-phase Stefan problem. For the case that the latent heat is large, we obtain an analytical approximate solution using perturbation methods. For latent heat small we solve numerically the problem by the enthalpy method. Also we analyse the solution for small times. Finally the results are used to simulate MTDSC signal during the melting.

Key words. Modulated Temperature Differential Scanning Calorimetry (MTDSC), Heat Equation, Free boundary problems, Perturbation methods

AMS subject classifications. 35K05, 35R35, 58J37.

1. Introduction. Modulated Temperature Differential Scanning Calorimetry or MTDSC is a method introduced by Reading and collaborators for measuring thermal properties of materials ([15] - [18]). In this method, conventional DSC is used with the modification that the usual programme of a linearly increasing temperature is modulated by a periodic perturbation.

During an experiment, a sample of material under investigation is placed in one of two pans, the other of which is empty but otherwise identical, and these pans are positioned symmetrically within the calorimeter. Heat is supplied to (or removed from) the calorimeter in a controlled (and spatially) symmetric way so that the sample's temperature follows a preset programme. The temperature difference between the sample and the reference pan is monitored. This gives a measure of the rate of heat intake (or output) by the sample and allows quantities such as the heat capacity to be determined. More precisely the furnace is heated so that the temperature rise is linear with an addition of sinusoidal modulation (controlled in such a way so that the sample's temperature has the required form) and the response, i.e. the release or absorption of heat due to temperature variation, of the sample and the reference material (which the latter is of known heat capacity) to this heating rate is measured; the heat flows are determined by the temperature difference between the two pans. Measuring the temperature difference between the two pans enables to measure purely the response, to the preset temperature program, of the sample. Then the sample's thermal properties can be deduced.

This measure of heat transfer is split into a slowly varying part, the 'underlying signal', and an oscillatory part (or at least the first harmonic) the 'cyclic signal'. These two signals can both used in an experiment.

MTDSC measurements can be used to deduce both qualitative and quantitative information about the sample's nature, e.g. its consistency, measurements of specific heat, latent heat, in general the behaviour of the sample under a transition etc. Also it is useful for thermal characterization of the sample by identifying the sample's thermal response with already existing data. Therefore there is need of rigorous theoretical analysis of MTDSC operation in order to optimize interpretation of the measurements.

*This work was supported by the State Scholarship Foundation

† Department of Mathematics, Faculty of Sciences, National Technical University of Athens, Zografou Campus, 15780 Athens, Greece

In standard MTDSC, heating/cooling is done sinusoidally. Provided the amplitude is small enough, the sample to behaves linearly. This means that every quantity $f(T_s)$, depending on temperature $T_s = bt + B\sin(\omega t)$, can be linearized and written as $f(T_s) = f(bt) + B\sin(\omega t)f'(bt)$. There will also be sinusoidal heat intake/output and all temperatures can be thought of as consisting of an underlying and cyclic part, the latter having negligible higher harmonics.

Both the underlying and cyclic parts of the temperature are fixed by controlling heat supply. The amplitude B can be increased/reduced by varying the amplitude of the heating. There will, in general, be a phase difference between the heat supply and the temperature of the sample, and this phase will normally vary during the course of an experiment. The actual phase of the temperature is not particularly important for an analysis of the results, and we shall generally take the sample temperature oscillations to be simply $B\sin(\omega t)$.

The simplest model for the calorimeter (see [9]) is given by neglecting its internal heat capacity and, without loss of generality, a pair of ordinary differential equations represents the heat flows into the pans with their associated changes of temperature:

$$\frac{dQ_s}{dt} = (C_r + C_s)\frac{dT_s}{dt} + f = K_0(T_r - T_s); \tag{1.1}$$

$$\frac{dQ_r}{dt} = C_r\frac{dT_r}{dt} = K_0(T_s - T_r). \tag{1.2}$$

Here K_0 is the heat transfer coefficient between the pans and with the exterior of the calorimeter, C_r is the heat capacity of the pan, C_s is the heat capacity of the actual sample, and f is the rate of heat absorption by the sample by any chemical reaction, phase transition, etc. The temperature of the furnace T_F has been eliminated because of symmetry (see [9]).

The temperature difference of the reference and the sample, $\Delta T = (T_r - T_s)$, satisfies the equation

$$C_r\frac{d\Delta T}{dt} + K\Delta T = C_s\frac{dT_s}{dt} + f,$$

with $K = 2K_0$. For B small enough to allow linearization we have $\Delta T = \Delta\overline{T} + \Delta\widetilde{T}$ and $f = \bar{f} + \tilde{f} = \bar{f} + Re\{\hat{f}\exp i\omega t\}$ so that

$$\Delta\overline{T} = \frac{1}{K}(C_s b + \bar{f})$$

while

$$\Delta\widetilde{T} = B\omega Re\left\{\frac{C_s + i\hat{f}/B\omega}{K + i\omega C_r}\, e^{i\omega t}\right\}.$$

During an MTDSC operation $\Delta\overline{T}$ and $\Delta\widetilde{T}$ are measured and experimental measurements, of the underlying and cyclic heat capacity, are calculated by the formulas $\overline{C} = K\Delta\overline{T}/b$ and $\widetilde{C} = \sqrt{(K^2 + \omega^2 C_R^2)}|\Delta\widetilde{T}|/\omega B$ respectively, where by $|\cdot|$ we denote the amplitude of a quantity (see [8], [9], [17], [23], [24]). For an inert sample, $f = 0$, in an experiment, we have $\overline{C} = \widetilde{C} = C_s$. Using now the above expressions for $\Delta\overline{T}$ and $\Delta\widetilde{T}$, we have finally that the underlying and cyclic measurements of heat capacity, $\overline{C}$ and $\widetilde{C}$ respectively, will be simulated by the following formulas:

$$\overline{C} = C_s + \bar{f}/b. \tag{1.3}$$

$$\widetilde{C} = |C_s + \hat{f}/\omega B|. \tag{1.4}$$

The main problem studied in this work, is the modeling of the melting process inside the sample pan for the case of the sample being a pure material. In this way we can determine the heat absorption f for this specific process. Then we can use the ODE model, presented above, about the calorimeter as a whole, to simulate the MTDSC signal for this case. Therefore to see how the melting of a pure material affects the output from an MTDSC run, the underlying and cyclic rate of heat absorption $\bar{f}$ and $\tilde{f}$ have to be calculated. Knowledge of $\overline{f}$ and $\widetilde{f}$ allows to use formulas (1.3) and (1.4) and to simulate underlying and cyclic measurements.

We first formulate the problem as a one-dimensional two-phase Stefan problem and we find an approximate analytical solution for the case when the latent heat is large. The relative sizes of dimensionless latent heat, $1/\epsilon$, and frequency, ω_0, have an important role in the perturbation expansion as regards the cyclic output, and we examine separately the cases $\epsilon \ll 1/\omega_0$ (part of this analysis as well as the formulation of the problem can be found in [9] and it is presented here for completeness), and where $\epsilon \sim O(\omega_0)$ or larger. For the case, the latent heat is not large ($\epsilon \sim O(1)$), we cannot use an approximate analytical solution so we solve the problem numerically using the enthalpy method. Using these solutions, we investigate the output of the signal. Also we examine the behaviour of the interface in these cases for small times. Conclusions and further work is presented in the discussion of this paper.

Similar problems have been treated also in [6], [22] and [26]. In [26] the problem that it is studied is subject to radiative and convection boundary conditions. A perturbation expansion is applied in terms of the dimensionless Stefan number. In [22] a two phase Stefan problem is treated but with constant temperature or heat flux at the boundary. A perturbation expansion is applied again in terms of the dimensionless Stefan number. In both works quantities are scaled in a similar way as in the present work and the quasi steady approximation is valid to leading order terms. The same result is found here for the underlying part of temperature. The major difference in the present work is the modulation added in the linear rise in temperature and therefore there is a need to use multiple scales in order to have a valid asymptotic solution for frequency very large. Also in section 4 we need to investigate the problem for a short time scale due to the transient diffusion and a long time scale due to the interface motion. Similar approach is applied in [22]. Finally a more extended numerical treatment of the same problem , as the one in Section 5, can be found in [6]. Here we use a fairly simple approach by using the enthalpy method in order to obtain the underlying part of temperature, and based on this, to calculate the modulated part of temperature analytically.

2. Formulation of the problem. A model for the melting process inside the pan should take into account a temperature gradient inside the sample. This can be appropriate for modelling the melting of a pure material where experimental evidence of a significant temperature gradient exists ([14], [25]). The sample will be taken to be a slab (such as a thin disc) and essentially one-dimensional. The disc is symmetric so we need to study only one half of it. The surfaces of the disc are taken to have temperature T_s which is controlled in the usual way, $T_s = T_o + bt + B\sin(\omega t)$.

In real experiments the method of control is likely to be different. During a melting run the control of the sample pan's temperature is in practice difficult, because of the existence of the significant temperature gradient inside the sample and instead the reference pan's temperature is programmed. This is controlled in the usual feed-back process i.e. by controlling the heat flow in the furnace so that the reference pan's temperature takes the required form. In the present work we assume for simplicity that T_s is controlled to concentrate on the melting of the sample. For a more accurate model the actual method of control in the experiments should be taken into account.

The centre of the disc is at the point $x = L_s$, and, because of symmetry, here there will be a zero temperature gradient, $\frac{\partial T}{\partial x} = 0$.

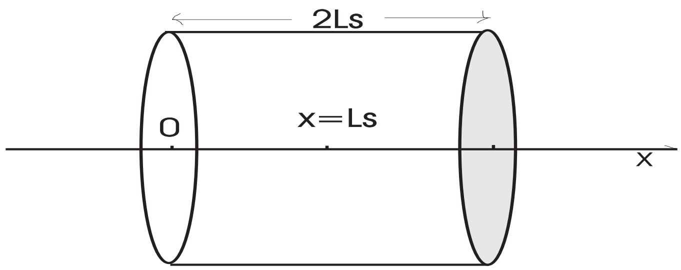

FIG. 2.1. *Schematic representation of a sample*

While the material is changing phase, there will be a free boundary, say at $x = S(t)$, separating the solid phase, $S < x < L_s$, from the liquid phase, $0 < x < S$. In the two parts of the sample we have the heat equation

$$\rho c \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} \quad , \quad 0 < x < S \quad \text{and} \quad S < x < L_s,$$

with ρ the density, c the specific heat and k the thermal conductivity. These are, in the present work, assumed to be constant and the same for both parts of the sample.

Before the melting starts, heat is absorbed inside the sample only because of the specific heat and this effect is small (compared with the heat needed to cause melting). So at the instant that melting is about to start, at the time $t = \frac{T_m - T_o}{b}$ (when T_s reaches T_m, the phase-change temperature), the temperature inside the sample, $T = T_1(x,t)$, comes from solving the heat equation. For simplicity we take $T_o = T_m$ so that at $t = 0$, $T_s = T_m$. We assume that T_1 has the form $T_1(x) = \bar{T}_1(x) + bt + BIm\{\hat{T}_1(x)e^{i\omega t}\}$ for $t < 0$ (while the sample remains solid). This gives that for $t = 0$, $T_1(x)$ is approximately $T_1(x) \simeq -\frac{\rho c b}{2k}\left[L_s^2 - (L_s - x)^2\right]$. Also $S = 0$ at $t = 0$, i.e the boundary of the two phases is at the edge of the disc when melting begins.

On the free boundary, conservation of heat will give the Stefan condition

$$T = T_o \quad \text{at} \quad x = S \quad , \quad k\left[\frac{\partial T}{\partial x}\right]_{s_-}^{s_+} = \rho \mathcal{L} \frac{dS}{dt},$$

where $\mathcal{L}$ is the latent heat. Thus the full Stefan problem will be

$$\rho c \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} \quad , \quad 0 < x < S \quad \text{and} \quad S < x < L_s, \tag{2.1}$$

$$T = T_o, \quad k\left[\frac{\partial T}{\partial x}\right]_{S_-}^{S_+} = \rho \mathcal{L} \frac{dS}{dt} \quad \text{at} \quad x = S \quad , \tag{2.2}$$

$$T = T_s = T_o + bt + B\sin(\omega t) \quad \text{at} \quad x = 0, \tag{2.3}$$

$$\frac{\partial T}{\partial x} = 0 \quad \text{at} \quad x = L_s, \tag{2.4}$$

$$T \simeq T_1(x) \left(\simeq -\frac{\rho c b}{2k} \left[L_s^2 - (L_s - x)^2 \right] \leq 0 \right) \text{at} \quad t = 0. \tag{2.5}$$

In order to identify the important terms of the problem, we scale the variables. We scale distance with the obvious choice L_s, $x = L_s y$, so y is the dimensionless space variable, time with t_o, $t = t_o \tau$, so τ is the dimensionless time, and temperature with T_T, $T = T_T \theta + T_o$, where θ is the dimensionless temperature. The values t_o and T_T are fixed below. Also we scale S with the length of the half disc, L_s, so that for the dimensionless position of the moving boundary s we have the relation $sL_s = S$. The Stefan condition then becomes

$$\frac{kT_T}{L_s} \left[\frac{\partial \theta}{\partial y} \right]_{s_-}^{s_+} = \frac{\rho \mathcal{L} L_s}{t_o} \frac{ds}{d\tau}.$$

The values of t_o and T_T are chosen to get balances at the driving boundary ($x = 0$) and at the free boundary ($x = S$). This ensures that constants can be eliminated for the normalized versions of (2.2) and (2.3). The choices are $t_o = L_s \sqrt{\frac{\rho \mathcal{L}}{kb}}$, $T_T = L_s \sqrt{\frac{\rho \mathcal{L} b}{k}}$, and the non-dimensional Stefan problem takes the form

$$\epsilon \frac{\partial \theta}{\partial \tau} = \frac{\partial^2 \theta}{\partial y^2} \quad , \quad 0 < y < s \quad \text{and} \quad s < y < 1, \tag{2.6}$$

$$\theta = 0 \quad \text{at} \quad y = s \quad , \quad \left[\frac{\partial \theta}{\partial y} \right]_{s^-}^{s^+} = \frac{ds}{d\tau}, \tag{2.7}$$

$$\theta = \theta_s = \tau + l \sin(\omega_0 \tau) \quad \text{at} \quad y = 0, \tag{2.8}$$

$$\frac{\partial \theta}{\partial y} = 0 \quad \text{at} \quad y = 1, \tag{2.9}$$

$$\theta = \theta_{o1}(y) = \frac{T_1}{T_T} \leq 0 \quad \text{at} \quad t = 0. \tag{2.10}$$

Here $\epsilon = \frac{T_T c}{\mathcal{L}} = \frac{\rho c L_s^2}{t_o k} = c L_s \sqrt{\frac{\rho b}{k \mathcal{L}}}$ is the Stefan number which for the sample sizes of interest, is very small. Some typical numbers found in [10] are $c = 2 \times 10^3$ J kg^{-1}^{o}K^{-1}, $L_s = 10^{-4}$m, $\rho = 10^3$Kg m^{-3}, $k = 0.2$W m^{-1}^{o}K^{-1}, $\mathcal{L} = 6 \times 10^4$J kg^{-1}, so then $\epsilon = 10^{-3}$ which is indeed tiny. Also we have that the dimensionless frequency is $\omega_0 = \omega t_o = \omega L_s \sqrt{\frac{\rho \mathcal{L}}{kb}}$ and the dimensionless amplitude, $l = \frac{B}{T_T} = \frac{B}{L_s} \sqrt{\frac{k}{\rho \mathcal{L} b}}$. These quantities are very important for the analysis of the problem. The small size of l allows linearization of quantities and separation of them to its underlying and modulated part while the large size of ω_0, related to the size of $1/\epsilon$, play an important role in the perturbation expansion applied in the problem. Note also that for the initial condition θ_{o1} we have : $\theta = \theta_{o1}(y) = \frac{T_1}{T_T} = -\frac{\rho c b}{2kL_s} \sqrt{\frac{k}{\rho \mathcal{L} b}} \left(L_s^2 - (L_s - x)^2 \right) = -\frac{\epsilon}{2} \left(1 - (1 - y)^2 \right)$.

Now we will consider the case that $\frac{1}{\omega_0} \gg \epsilon$ which indicates that the temperature is approximately harmonic, even allowing for the sinusoidal forcing .

3. Case of $\frac{1}{\omega_0} \gg \epsilon$. Because of the small size of the Stefan number, we can drop the time derivative in the heat equation, and this will indicate that to leading order θ is linear for both sides of the sample. Motivated by this we apply a regular perturbation expansion in the problem employing the small Stefan number ϵ. Therefore we seek solutions of the form $\theta \simeq \theta_0 + \epsilon\theta_1 + \epsilon^2\theta_2 + \dots$ for the temperature θ and $s \simeq s_0 + \epsilon s_1 + \epsilon^2 s_2 + \dots$ for the position of the moving boundary s. The initial condition, which expresses only the effect of the specific heat, is of order ϵ and so to order one we have that $T(x,0) = T_m$ or $\theta(y,0) = 0$. Now using the condition on $y = 0$, we have that

$$\theta_0 = [\tau + l\sin(\omega_0\tau)]\,(1 - \frac{y}{s_0}),$$

in the liquid part. In the solid part $\theta_0 = 0$ at $y = s_0$ and $\frac{\partial\theta_0}{\partial y} = 0$ at $y = 1$ thus $\theta_0 = 0$ in $s_0 < y < 1$. This means that to leading-order the temperature in the solid is equal to the melting temperature during the transition. Then, using the Stefan condition, we have

$$-\left[\frac{\partial\theta_0}{\partial y}\right]_{s_0-} = \frac{\tau + l\sin(\omega_0\tau)}{s_0} = \frac{ds_0}{d\tau}.$$

Integrating this and using the fact that $s = 0$ at $\tau = 0$, we obtain

$$s_0^2 = \tau^2 + \frac{l}{\omega_0}\left[1 - \cos(\omega_0\tau)\right],$$

which gives, as long as l is sufficiently small for us to be able to linearize the above expression,

$$s_0 = \sqrt{\tau^2 + \frac{l}{\omega_0}\left[1 - \cos(\omega_0\tau)\right]} \simeq \tau + \frac{l}{2\omega_0\tau}\left[1 - \cos(\omega_0\tau)\right]. \tag{3.1}$$

Returning to dimensional variables, we get that the temperature is simply $T = T_m$ for $S \leq x \leq L_s$ and

$$T = T_m + bt + B\sin(\omega t) - \frac{x}{S}(bt + B\sin(\omega t)) \quad \text{in} \quad 0 < x < S,$$

while the position of the free boundary, to leading-order, is given by

$$S \simeq \sqrt{\frac{kb}{\rho\mathcal{L}}}\left[t + \frac{B}{\omega bt}\left(1 - \cos(\omega t)\right)\right]. \tag{3.2}$$

For the linearization to be valid, we need B "small". (Also for the time derivative to be negligible, we need $\epsilon\omega_0$ to be small as well. Note that for $\omega = 0.1s^{-1}$ we have that $\epsilon\omega_0 = \frac{\omega c\rho L_s^2}{k} = 10^{-2} \ll 1$).

In Figure (3.1) we can see a schematic representation of the temperature profile. The temperature in the liquid part is linear and the effect of the specific heat can be seen only in the solid part; the role of specific heat is very small compared with that of the latent heat.

However, there is a singularity at $t = 0$ in (3.2) which results from $\frac{B}{\omega}$ not being small compared with bt^2 at the start of the melting. In other words the decomposition of the signal into its underlying and cyclic parts at the start of the event does not make sense because there are not yet enough cycles completed.

Second Term in the Expansion. We see that the dimensionless cyclic measurement is small (of order $\frac{1}{\omega_0}$), so in order to have a more accurate estimation of the cyclic measurement, we have to include the effect of the specific heat in the measurement by finding the second term of the expansion in the approximate solution.

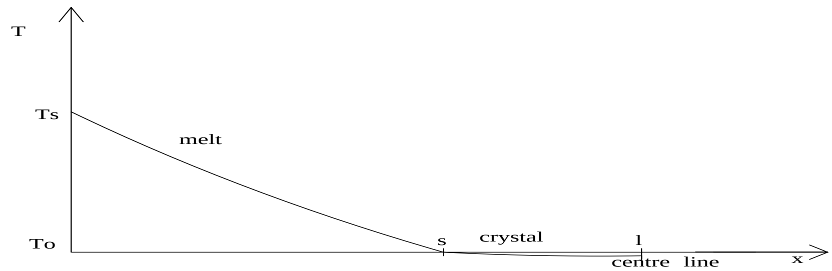

FIG. 3.1. *Temperature profile inside the pan*

The problem for the O(ϵ) terms is

$$\frac{\partial \theta_0}{\partial \tau} = \frac{\partial^2 \theta_1}{\partial y^2} \quad , \qquad 0 < y < s_0 \quad \text{and} \quad s_0 < y < 1,$$

$$s_1 \frac{\partial \theta_0}{\partial y}(s_0, \tau) + \theta_1(s_0, \tau) = 0, \qquad \left[\frac{\partial \theta_1}{\partial y}\right]_{s_0^-}^{s_0^+} = \frac{ds_1}{d\tau} \quad \text{at} \quad y = s_0,$$

$$\theta_1 = 0 \quad \text{at} \quad y = 0, \qquad \frac{\partial \theta_1}{\partial y} = 0 \quad \text{at} \quad y = 1,$$

$$\theta(y, 0) = \theta_{o1} = \frac{T_1}{T_T} \quad \text{at} \quad t = 0,$$

where $\theta_0 = \theta_S \left(1 - \frac{y}{s_0}\right)$ for $y < s_0$, $\theta_0 = 0$ for $y > s_0$,

with $\theta_S = \tau + l \sin(\omega_0 \tau)$ and $s_0 = \sqrt{\tau^2 + \frac{l}{\omega_0}\left[1 - \cos(\omega_0 \tau)\right]}$.

Note that the equation $\theta \simeq \theta_0(s_0 + \epsilon s_1) + \epsilon\theta_1(s_0 + \epsilon s_1) = 0$, if we expand θ_0 and θ_1 for ϵ small takes the form $\theta_0(s_0) + \epsilon s_1 \frac{\partial \theta_0}{\partial y}(s_0) + \epsilon\theta_1(s_0) + O(\epsilon^2) = 0$, so our first condition on the free boundary is as written. The second is achieved likewise.

For $y \geq s_0$, i.e. in the solid region, we have that the problem for $O(\epsilon)$ terms is

$$\frac{\partial \theta_0}{\partial \tau} = \frac{\partial^2 \theta_1}{\partial y^2} \quad , \qquad s_0 < y < 1,$$

$$s_1 \frac{\partial \theta_0}{\partial y}(s_0, \tau) + \theta_1(s_0, \tau) = 0, \quad \text{at} \quad y = s_0,$$

$$\frac{\partial \theta_1}{\partial y} = 0 \quad \text{at} \quad y = 1.$$

Because $\theta_0 = 0$, these equations will give that $\frac{\partial^2 \theta_1}{\partial y^2} = 0$. So $\theta_1 = \theta_1(\tau)$ due to $\frac{\partial \theta_1}{\partial y} = 0$ at $y = 1$. Therefore the gradient for θ_1 in the solid region will not contribute to the Stefan condition at $y = s_0$ because it is purely a function of time. (Note also for a short time of order $O(\epsilon)$, or even smaller, after the melting starts, the temperature in the solid region depends upon the initial condition $\theta(y, 0)$. For larger times the effect of this initial condition decays exponentially to zero.)

Now, in the liquid zone, by the heat equation we have for O(ϵ) terms that

$$\frac{\partial^2 \theta_1}{\partial y^2} = y\left(\theta_S \frac{s_0'}{s_0^2} - \frac{\theta_S'}{s_0}\right) + \theta_S'.$$

where $\theta_S' = \frac{\partial \theta_S}{\partial \tau} = 1 + l\omega_0 \cos(\omega_0 \tau)$. Integrating this we obtain

$$\theta_1 = \frac{y^3}{6}\left(\theta_S \frac{s_0'}{s_0^2} - \frac{\theta_S'}{s_0}\right) + \frac{y^2}{2}\theta_S' + y\alpha(\tau) + \beta(\tau),$$

for some functions of time $\alpha(\tau)$ and $\beta(\tau)$. The boundary condition at $y = 0$ in this problem is $\theta_1 = 0$ and this will give $\beta(\tau) = 0$.

Using the equation for θ_1 at s_0, we finally obtain for $\alpha(\tau)$:

$$\alpha(\tau) = \theta_S\left(\frac{s_1}{s_0^2} - \frac{s_0'}{6}\right) - \theta_S' \frac{s_0}{3}.$$

Therefore we have that θ_1 takes the form

$$\theta_1 = \frac{y^3}{6}\left(\theta_S \frac{s_0'}{s_0^2} - \frac{\theta_S'}{s_0}\right) + \frac{y^2}{2}\theta_S' + y\left(\theta_S\left(\frac{s_1}{s_0^2} - \frac{s_0'}{6}\right) - \theta_S'\frac{s_0}{3}\right). \tag{3.3}$$

We now apply the Stefan condition for $O(\epsilon)$ terms at the moving boundary, (bear in mind that $\frac{\partial^2 \theta_0}{\partial y^2} = 0$ at $y = s_0$) and we have

$$\left[\frac{\partial \theta_1}{\partial y}\right]_{s_0^-}^{s_0^+} = -\frac{\partial \theta_1}{\partial y}(s_0^-) = \frac{ds_1}{d\tau}.$$

Substitution of the expression given for θ_1 in the liquid region from equation (3.3) in the Stefan condition results in a differential equation for s_1,

$$s_1' + \frac{\theta_S}{s_0^2}s_1 = -\theta_S'\frac{s_0}{6} + \theta_S\left(\frac{s_0^2}{6} - \frac{s_0'}{2}\right).$$

We write $s_1 = \bar{s}_1 + l\tilde{s}_1$, separating the underlying and the cyclic parts of s_1, and the resulting equation for $\bar{s}_1$ is

$$\bar{s}_1' + \frac{1}{\tau}\bar{s}_1 = \frac{\tau^3}{6} - \frac{2\tau}{3}.$$

The solution of this equation, for $\bar{s}_1(0) = 0$, is

$$\bar{s}_1 = \frac{\tau^2}{3}\left(\frac{\tau^2}{10} - \frac{2}{3}\right). \tag{3.4}$$

The equation for the modulated part of s_1, $\tilde{s}_1$, is

$$\begin{aligned}\tilde{s}_1' + \frac{\tau}{\bar{s}_0^2}\tilde{s}_1 = &-\frac{\omega_0}{6}\bar{s}_0\cos(\omega_0\tau) + \left(\frac{1}{6}\bar{s}_0 - \frac{1}{2}\bar{s}_0' - \frac{\bar{s}_1}{\bar{s}_0^2}\right)\sin(\omega_0\tau)\\ &+ \frac{1}{6}\tilde{s}_0 + \tau\left(\frac{1}{3}\bar{s}_0\tilde{s}_0 - \frac{1}{2}\tilde{s}_0' + 2\frac{\bar{s}_1\tilde{s}_0}{\bar{s}_0^2}\right),\end{aligned}$$

with $\tilde{s}_1(0) = 0$.

The dominant term in the solution of this equation comes from the term $\frac{\omega_0}{6}\bar{s}_0\cos(\omega_0\tau)$. Therefore dropping the $O(1)$ or smaller terms, we obtain

$$\tilde{s}_1 = \frac{\tau}{6}\sin(\omega_0\tau). \tag{3.5}$$

The O(ϵ) terms of the heat flow will be proportional to the corresponding contributions to the temperature gradient at the point $y = 0$. The underlying part is then

$$\frac{\partial \bar{\theta}_1}{\partial y}(0,\tau) = \frac{\tau}{3}\left(\frac{\tau^2}{10} - \tau - \frac{7}{18}\right),$$

while the cyclic part is

$$\frac{\partial \tilde{\theta}_1}{\partial y}(0,\tau) = \left(\frac{\tau^2}{30} - \frac{\tau}{3} - \frac{2}{9}\right)\sin(\omega_0\tau).$$

It is important to note that the above analysis is applicable as long as we ensure that we have a single interface between the solid and the liquid phase. Having the temperature always nondecreasing obviously suffices. If there is cooling during the cycle, i.e. having $B\omega > b$, there should still be a single stable interface provided that $\frac{1}{\omega_0} \gg \epsilon$. This means that because the Stefan number is very small, the temperature is approximately harmonic even with the small time scale of the oscillations. In the case that the frequency is very large, $\frac{1}{\omega_0} = O(\epsilon)$, then the sample is cooled and heated in the time scale that the heat is being transferred inside the sample. In such a case it is likely that temperature is not harmonic in the time scale of a period, and this situation is analysed in the next Section.

4. Case of $\frac{1}{\omega_0} \simeq \epsilon$ or $\frac{1}{\omega_0} \ll \epsilon$. We may assume that $\frac{1}{\omega_0} \simeq \epsilon$ i.e. that $\omega_0\epsilon = \frac{\rho^2 L_s^2 \omega c}{k} = O(1)$. By the discussion in the previous Section, in such a case the perturbed expansion breaks down because the temperature is no longer harmonic (diffusion time $\simeq \frac{1}{\omega_0}$). We now introduce two time scales: a slow one, $\tau = O(1)$, and a fast one $\tau = \omega_0\sigma$, $\sigma/\tau = O(\frac{1}{\omega_0})$, so that the time derivative is replaced by

$$\omega_0\frac{\partial}{\partial\sigma} + \frac{\partial}{\partial\tau}.$$

We consider a perturbation expansion in powers of $\frac{1}{\omega_0}$ for temperature $\theta = \theta(y,\tau,\sigma)$ and the free boundary $s = s(\tau,\sigma)$ so that $\theta \simeq \theta_0 + \frac{1}{\omega_0}\theta_1 + \frac{1}{\omega_0^2}\theta_2 + ...$ and $s \simeq s_0 + \frac{1}{\omega_0}s_1 + \frac{1}{\omega_0^2}s_2 + ...$ Therefore we have as regards the heat equation, taking $\delta = 1/\omega_0\epsilon$,

$$\frac{1}{\delta\omega_0}\left(\omega_0\frac{\partial}{\partial\sigma} + \frac{\partial}{\partial\tau}\right)\theta = \frac{\partial^2\theta}{\partial y^2}$$

and using the expansion for θ we have

$$\frac{\partial\theta_0}{\partial\sigma} + \frac{1}{\omega_0}\frac{\partial\theta_0}{\partial\tau} + \frac{1}{\omega_0}\frac{\partial\theta_1}{\partial\sigma} + ... \simeq \delta\frac{\partial^2\theta_0}{\partial y^2} + \frac{\delta}{\omega_0}\frac{\partial^2\theta_1}{\partial y^2} + ...$$

Similarly as regards the Stefan condition we have

$$\left[\frac{\partial\theta}{\partial y}\right]_{s^-}^{s^+} = \omega_0\frac{\partial s}{\partial\sigma} + \frac{\partial s}{\partial\tau} + ... \quad ,$$

which, after the substitution of the expansion for θ and s, becomes

$$\left[\frac{\partial\theta_0}{\partial y}\right]_{s^-}^{s^+} + \frac{1}{\omega_0}\left[\frac{\partial\theta_1}{\partial y}\right]_{s^-}^{s^+} + ... = \omega_0\frac{\partial s_0}{\partial\sigma} + \frac{\partial s_0}{\partial\tau} + \frac{\partial s_1}{\partial\sigma} + \frac{1}{\omega_0}\frac{\partial s_1}{\partial\tau} + \frac{1}{\omega_0}\frac{\partial s_2}{\partial\sigma}... \quad ,$$

at $y = s_0$. Also $\theta_0 = 0$ at $y = s_0$ and $\theta_0 = \tau + \frac{\lambda}{\omega_0}\sin(\sigma)$ at $y = 0$ while $\frac{\partial \theta}{\partial y} = 0$ at $y = 1$. Here we make use of the assumption that l is small so that we can write $l = \frac{\lambda}{\omega_0}$ for $\lambda = O(1)$. (In practical situations, l and $\frac{1}{\omega_0}$ are of the same size).

Then from the equation of $O(\omega_0)$ terms we have

$$\frac{\partial s_0}{\partial \sigma} = 0 \quad \text{so} \quad s_0 = s_0(\tau)$$

and to $O(1)$ terms we get

$$\frac{\partial \theta_0}{\partial \sigma} = \delta \frac{\partial^2 \theta_0}{\partial y^2}, \quad 0 < y < s_0, \quad \text{and} \quad s_0 < y < 1, \tag{4.1}$$

$$\left[\frac{\partial \theta_0}{\partial y}\right]_{s_0^-}^{s_0^+} = \frac{\partial s_0}{\partial \tau} + \frac{\partial s_1}{\partial \sigma}, \quad \text{and} \quad \theta_0 = 0 \quad \text{at} \quad y = s_0, \tag{4.2}$$

$$\theta_0 = \tau \quad \text{at} \quad y = 0. \tag{4.3}$$

$$\frac{\partial \theta_0}{\partial y} = 0 \quad \text{at} \quad y = 1. \tag{4.4}$$

Especially as regards the solid region i.e $s_0 < y < 1$, note that the problem is

$$\frac{\partial \theta_0}{\partial \sigma} = \delta \frac{\partial^2 \theta_0}{\partial y^2} \quad , \quad s_0 < y < 1, \tag{4.5}$$

$$\theta_0 = 0 \quad \text{at} \quad y = s_0, \quad \text{and} \quad \frac{\partial \theta_0}{\partial y} = 0 \quad \text{at} \quad y = 1, \tag{4.6}$$

and initially $\theta(y, 0) = O(\epsilon)$. This gives $\theta_0(y, 0) = 0$ and the temperature, $\theta(y, \tau, \sigma) = 0$, for this region to leading order terms. Therefore we have no contribution by the temperature gradient in the solid region to the Stefan condition.

Looking at the equation for the liquid region, $0 < y < s_0$ and taking the average over a cycle by writing $\bar{\theta}_0 = \frac{1}{2\pi}\int_0^{2\pi} \theta_0 d\sigma$, we have, from the heat equation

$$\frac{\partial^2 \bar{\theta}_0}{\partial y^2} = 0,$$

while the Stefan condition becomes

$$-\frac{\partial \bar{\theta}_0}{\partial y} = \frac{\partial s_0}{\partial \tau}.$$

Also $\bar{\theta}_0 = \tau$ at $y = 0$ and $\bar{\theta}_0 = 0$ at $s_0 = 0$. Therefore the problem for the underlying part of the temperature is the same as before, and the solution of this is $\bar{\theta}_0 = \tau(1 - \frac{y}{s_0})$, with $\bar{s}_0 = \tau$.

As regards the cyclic part of θ_0, we have $\tilde{\theta}_0 = \theta_0 - \bar{\theta}_0$, and for this we get the following set of equations :

$$\frac{\partial \tilde{\theta}_0}{\partial \sigma} = \delta \frac{\partial^2 \tilde{\theta}_0}{\partial y^2} \quad , \quad 0 < y < s_0,$$

$$\tilde{\theta}_0 = 0 \quad \text{at} \quad y = s_0,$$

$$-\frac{\partial \tilde{\theta}_0}{\partial y} = \frac{\partial \tilde{s}_1}{\partial \sigma} \quad \text{at} \quad y = s_0,$$

$$\tilde{\theta}_0 = 0 \quad \text{at} \quad y = 0,$$

and this gives $\tilde{\theta}_0 = 0$ and $\tilde{s}_1 = 0$.

To see the cyclic part of the moving boundary, we have to take higher order terms. Equating terms of order $O(\frac{1}{\omega_0})$, we obtain

$$\frac{\partial \theta_0}{\partial \tau} + \frac{\partial \theta_1}{\partial \sigma} = \delta \frac{\partial^2 \theta_1}{\partial y^2} \quad , \quad 0 < y < s_0,$$
$$s_1 \frac{\partial \theta_0}{\partial y} + \theta_1 = 0 \quad \text{at} \quad y = s_0,$$
$$-\frac{\partial \theta_1}{\partial y} = \frac{\partial s_1}{\partial \tau} + \frac{\partial s_2}{\partial \sigma} \quad \text{at} \quad y = s_0,$$
$$\theta_1 = \lambda \sin(\sigma) \quad \text{at} \quad y = 0.$$

Taking the average as before, we have for $\bar{\theta}_1 = \frac{1}{2\pi}\int_0^{2\pi} \theta_1 d\sigma$, and the problem for $\bar{\theta}_1$ becomes

$$\frac{\partial \bar{\theta}_0}{\partial \tau} = \delta \frac{\partial^2 \bar{\theta}_1}{\partial y^2} \quad , \quad 0 < y < s_0,$$
$$\bar{s}_1 \frac{\partial \bar{\theta}_0}{\partial y} + \bar{\theta}_1 = 0 \quad \text{at} \quad y = s_0,$$
$$-\frac{\partial \bar{\theta}_1}{\partial y} = \frac{\partial \bar{s}_1}{\partial \tau} \quad \text{at} \quad y = s_0,$$
$$\bar{\theta}_0 = 0 \quad \text{at} \quad y = 0.$$

This will give the same result for $\bar{\theta}_1$ and $\bar{s}_1$ as above (see (3.3) and (3.4)). Also again $\bar{\theta}_1$ in the solid region, being purely a function of time, will not contribute in the Stefan condition. The same applies for $\tilde{\theta}_1$ satisfying the same set of equations as (4.5) and (4.6), with $\tilde{\theta}_1(y,0,0) = 0$, and this will give $\tilde{\theta}_1 = 0$ for all times in the solid region. That is because the effect of the initial condition decays exponentially to zero. For $\tilde{\theta}_1 = \theta_1 - \bar{\theta}_1$ we get the problem

$$\frac{\partial \tilde{\theta}_1}{\partial \sigma} = \delta \frac{\partial^2 \tilde{\theta}_1}{\partial y^2} \quad , \quad 0 < y < s_0, \tag{4.7}$$
$$\tilde{\theta}_1 = 0 \quad \text{at} \quad y = s_0, \tag{4.8}$$
$$-\frac{\partial \tilde{\theta}_1}{\partial y} = \frac{\partial \tilde{s}_2}{\partial \sigma} \quad \text{at} \quad y = s_0, \tag{4.9}$$
$$\tilde{\theta}_1 = \lambda \sin(\sigma) \quad \text{at} \quad y = 0. \tag{4.10}$$

We assume that $\tilde{\theta}_1$ has the form $Im\{\lambda \hat{\theta}_1(y) e^{i\sigma}\}$. Substituting this into the above set of equation, we get the boundary value problem

$$\delta\, \hat{\theta}_1''(y) = i\hat{\theta}_1, \tag{4.11}$$
$$\hat{\theta}_1 = 1 \quad \text{at} \quad y = 0, \quad \text{and} \quad \hat{\theta}_1 = 0, \quad \text{at} \quad y = s_0. \tag{4.12}$$

This gives

$$\hat{\theta}_1 = A \left[\exp(\frac{1}{\sqrt{2\delta}}(i+1)(s_0 - y)) - \exp(\frac{1}{\sqrt{2\delta}}(i+1)(s_0 - y)) \right]$$

with

$$A=\frac{1}{2}\left[\sinh(\frac{s_0}{\sqrt{2\delta}})\cos(\frac{s_0}{\sqrt{2\delta}})+i\cosh(\frac{s_0}{\sqrt{2\delta}})\sin(\frac{s_0}{\sqrt{2\delta}})\right].$$

Finally we have for $\tilde{\theta}_1$

$$\tilde{\theta}_1=\frac{\lambda}{Q_0}\left[(Q_1+Q_2)\sin(\sigma)+(Q_4-Q_3)\cos(\sigma)\right]$$

where

$$\begin{aligned}
Q_0 &= \sinh^2(\frac{s_0}{\sqrt{2\delta}})\cos^2(\frac{s_0}{\sqrt{2\delta}})+\cosh^2(\frac{s_0}{\sqrt{2\delta}})\sin^2(\frac{s_0}{\sqrt{2\delta}})\\
Q_1 &= \sinh(\frac{s_0}{\sqrt{2\delta}})\cos(\frac{s_0}{\sqrt{2\delta}})\sinh(\frac{(s_0-y)}{\sqrt{2\delta}})\cos(\frac{(s_0-y)}{\sqrt{2\delta}}),\\
Q_2 &= \cosh(\frac{s_0}{\sqrt{2\delta}})\sin(\frac{s_0}{\sqrt{2\delta}})\cosh(\frac{(s_0-y)}{\sqrt{2\delta}})\sin(\frac{(s_0-y)}{\sqrt{2\delta}}),\\
Q_3 &= \cosh(\frac{s_0}{\sqrt{2\delta}})\sin(\frac{s_0}{\sqrt{2\delta}})\sinh(\frac{(s_0-y)}{\sqrt{2\delta}})\cos(\frac{(s_0-y)}{\sqrt{2\delta}}),\\
Q_4 &= \sinh(\frac{s_0}{\sqrt{2\delta}})\cos(\frac{s_0}{\sqrt{2\delta}})\cosh(\frac{(s_0-y)}{\sqrt{2\delta}})\sin(\frac{(s_0-y)}{\sqrt{2\delta}}).
\end{aligned}$$

In order to see the behaviour of the cyclic part of the moving boundary, $\tilde{s}$, we use the Stefan condition, $-\tilde{\theta_1}_y=\frac{\partial\tilde{s}_2}{\partial\sigma}$, and after simplifying the resulting expression for $\tilde{s}_2$, we obtain

$$\tilde{s}_2=\frac{\lambda}{Q_0}\left[(q_1+q_2)(\cos(\sigma)-1)+(q_1-q_2)\sin(\sigma)\right], \tag{4.13}$$

$$\text{with}\qquad q_1=\sinh(\frac{s_0}{\sqrt{2\delta}})\cos(\frac{s_0}{\sqrt{2\delta}})\quad\text{and,}\quad q_2=\cosh(\frac{s_0}{\sqrt{2\delta}})\sin(\frac{s_0}{\sqrt{2\delta}}).$$

Finally the amplitude of cyclic signal will be proportional to the amplitude of the gradient of the cyclic part of temperature, $|\frac{\partial\tilde{\theta}}{\partial y}|$, at $y=0$. Therefore

$$|\frac{\partial\tilde{\theta}}{\partial y}|_{y=0}=\left[q_1^2(q_4-q_3)^2+q_2^2(q_4+q_3)^2\right]^{\frac{1}{2}}, \tag{4.14}$$

$$\text{with}\quad q_3=\cosh(\frac{s_0}{\sqrt{2\delta}})\cos(\frac{s_0}{\sqrt{2\delta}})\quad\text{and,}\quad q_4=\sinh(\frac{s_0}{\sqrt{2\delta}})\sin(\frac{s_0}{\sqrt{2\delta}}).$$

We see that the amplitude of the cyclic signal, proportional to the amplitude of $\frac{\partial\tilde{\theta}}{\partial y}$ at $y=0$, starts with a singularity at zero and then increases exponentially as $s_0=s_0(\tau)=\tau$ increases. Since δ is small, i.e. $\frac{1}{\omega_0}\ll\epsilon$, the same results hold, and the rate of change of $|\frac{\partial\tilde{\theta}}{\partial y}|_{y=0}$ for later times is even larger.

Behaviour of the cyclic signal for $\tau=\mathbf{O}(\frac{1}{\omega_0})$. In order to get an understanding of the behaviour of the signal for small times in the previous cases, where dimensionless latent heat is large, we have to look at the problem for using a time scale of order $\frac{1}{\omega_0}$. We start by scaling time in the dimensionless problem (2.6)-(2.10). We write $\sigma=\omega_0\tau$. We scale also distance y and the moving boundary position, s, with $\frac{1}{\omega_0}$ because for this time scale the position of the moving boundary is also of order $\frac{1}{\omega_0}$. So we have a boundary layer in an inner region of order $O(\frac{1}{\omega_0})$ at $y = 0$, and an outer region of order one. We take $z = \omega_0 y$ and $\xi = \omega_0 s$, and then the problem for the inner region becomes:

$$\frac{1}{\omega_0^2}\theta_\sigma = \delta\theta_{zz}, \quad \text{for} \quad 0 < z < \xi, \tag{4.15}$$

$$\omega_0 [\theta_z]_-^+ = \frac{d\xi}{d\sigma}, \quad \text{at} \quad z = \xi, \tag{4.16}$$

$$\theta = \frac{\sigma}{\omega_0} + \frac{\lambda}{\omega_0}\sin(\sigma) \quad \text{at} \quad z = 0. \tag{4.17}$$

We take again a perturbation expansion, $\theta(\sigma, z) = \frac{1}{\omega_0}\theta_0 + \frac{1}{\omega_0^2}\theta_1 + ...$, $\xi(\sigma) = \xi_0 + \frac{1}{\omega_0}\xi_1 + \frac{1}{\omega_0^2}\xi_2 + ...$, and after equating terms of order one, we obtain for θ_0

$$\theta_{0zz} = 0, \quad \text{for} \quad 0 < z < \xi, \quad \xi < z, \tag{4.18}$$

$$[\theta_{0z}]_-^+ = \frac{d\xi_0}{d\sigma}, \quad \text{at} \quad z = \xi_0, \tag{4.19}$$

$$\theta = \sigma + \lambda\sin(\sigma) \quad \text{at} \quad z = 0. \tag{4.20}$$

This means that the quasi-steady approximation is valid for this time scale with $\theta_0 = (\sigma + \lambda\sin(\sigma))(1 - \frac{z}{\xi_0})$ in the liquid region and $\theta_0 = A_0(\sigma)(z - \xi_0)$ in the solid region. Here $A_0(\sigma)$ is a function of time which will be determined by the solution of the outer region.

In the outer region we want to see the behaviour of the solution in the whole interval, so we need to scale only time as we did for the inner region, $\sigma = \omega_0\tau$. The problem with this scaling becomes :

$$\check{\theta}_\sigma = \delta\check{\theta}_{yy}, \quad \text{for} \quad 0 < y < 1 \tag{4.21}$$

$$\check{\theta} = \begin{cases} 0 & \check{\theta} \geq 0 \\ \sigma + \lambda\sin(\sigma) & \check{\theta} < 0 \end{cases} \quad \text{at} \quad y = 0, \tag{4.22}$$

$$\check{\theta}_y = 0 \quad \text{at} \quad y = 1, \tag{4.23}$$

where $\check{\theta}$ is the solution of the problem in the outer region. After taking again $\check{\theta} = \frac{1}{\omega_0}\check{\theta}_0 + \frac{1}{\omega_0^2}\check{\theta}_1 + ...$, the solution of the resulting Dirichlet problem for $\check{\theta}_0$ is:

$$\check{\theta}_0 = 2\sum_{m=0}^{\infty} e^{-\delta b_m^2\sigma}\cos(b_m(1-y))\,(I_1 + I_2) \tag{4.24}$$

where

$$I_1 = -\frac{1}{2\delta}\int_0^1 (1 - (1-y)^2)\cos(b_m(1-y))dy = -\frac{\sin(b_m)}{b_m}(\frac{2}{\delta^2 b_m} + \frac{3}{\delta} - 1),$$

and

$$I_2 = \sum_{i=1}^{K}\left[e^{-\delta b_m^2\sigma}\left(\frac{\lambda}{1+\delta^2 b_m^2}(\delta b_m\sin(\sigma) - \cos(\sigma)) + \sigma + \frac{1}{\delta^2 b_m^2}\right)\right]_{\sigma_-^\mu}^{\sigma_+^\mu},$$

for $b_m = \frac{(2m+1)\pi}{2}$ and having temperature being negative at the intervals $[\sigma_-^\mu, \sigma_+^\mu]$, $\mu = 1, 2, ...M$. We have to note here that temperature $\check{\theta}_0 = \sigma + \lambda\sin(\sigma)$ can become negative for some times (for M time intervals $[\sigma_-^\mu,\sigma_+^\mu]$, $\mu=1,2,...M$) if $\lambda>1$ until σ becomes large enough so that $\check{\theta}(\sigma,0)>0$ for all later times. In case that $\lambda\leq 0$ then temperature is always positive and $I_2=0$.

We need now to combine the results of the inner and outer region. We have at the inner region in the solid part of it that $\theta_0=A_0(\sigma)(z-\xi)$, $\theta_1=A_1(\sigma)(z-\xi)$, $\theta_2=A_0'(\sigma)z^3/6+(A_0'\xi_0-A_0\xi_0')z^2/2+cz+d$, for c, d being some functions of σ. The functions A_0 and A_1 will be determined by using the fact that away from the moving boundary in the solid region the solution of the inner problem, θ^+, should match with the solution of the outer problem. This means that taking $z=y\omega_0$ we have:

$$\theta^+(z,\sigma)=\theta^+(y\omega_0,\sigma)=\frac{1}{\omega_0}A_0(\sigma)(y\omega_0-\xi)+\frac{1}{\omega_0^2}A_1(\sigma)(y\omega_0-\xi)+\frac{1}{\omega_0^3}+$$
$$+\big(A_0'(\sigma)(y\omega_0)^3/6(A_0'\xi_0-A_0\xi_0')(y\omega_0)^2/2+c(y\omega_0)+d\big)+...\quad .$$

Therefore we have

$$\theta^+(y,\sigma)=A_0(\sigma)y+A_0'(\sigma)y^3/6+\frac{1}{\omega_0}(A_1y-A_0\xi_0+(A_0'\xi_0-A_0\xi_0')y^2/2)+...\quad .$$

This gives that $A_0(\sigma)=0$ because the solution of the outer region to order one is zero, and that $A_1(\sigma)=\frac{\partial\check{\theta}_0}{\partial y}$ at $y=0$. Thus in the inner region the moving boundary to first order terms, ξ_0, solves the equation

$$\frac{\sigma+\lambda\sin(\sigma)}{\xi_0}=\frac{d\xi_0}{d\sigma},$$

and this gives $\xi_0=[\frac{\sigma^2}{2}+\lambda(\cos(\sigma)-1)]^{\frac{1}{2}}$, while the temperature at the solid region contributes only to higher order terms. This result in terms of variables τ and s is given by equation (3.1). This result could be also obtained by taking the limit of $\tilde{s}_2$ for s_0 and s_0-y being small. Therefore for times of $O(\frac{1}{\omega_0})$, the quasi-steady approximation is valid, and the temperature in the solid region tends exponentially to zero as it can be seen from (4.24).

5. Numerical Solution. We solve numerically this Stefan problem by using the enthalpy method (see [1], [3]). We define the enthalpy H by

$$H=\begin{cases}\theta+\frac{1}{\epsilon} & \theta\geq 0,\\ \theta & \theta<0,\end{cases}$$

where $\frac{1}{\epsilon}$ is the dimensionless latent heat. Therefore the field equation becomes

$$\frac{\partial H}{\partial\tau}=\frac{1}{\epsilon}\frac{\partial^2\theta}{\partial y^2}. \qquad (5.1)$$

Initially the temperature is $\theta(y,0)=\frac{\epsilon}{2}(1-(1-y)^2)$ and we compute the evolution of the temperature by using an explicit in time scheme.

$$H_j^{i+1}=H_j^i+r(\theta_{j-1}^i-2\theta_j^i+\theta_{j+1}^i) \qquad (5.2)$$

where H_j^i and θ_j^i are the enthalpy and temperature respectively at the jth space grid and at the ith time level. Also $r=\frac{dt}{\epsilon(dx)^2}$ (we need $r<1/2$ for the scheme to be

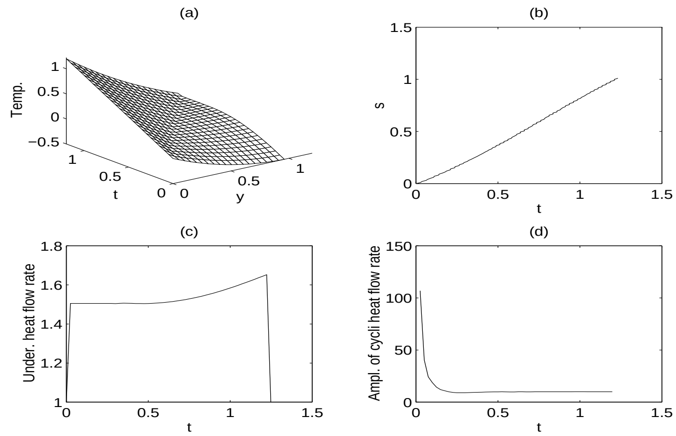

FIG. 5.1. *Numerical solution of problem (2.6)-(2.10). θ is plotted against time and space variables in (a). In (b) s is plotted against time. In (c) the underlying part of temperature gradient, $-\frac{\partial\bar{\theta}}{\partial y}|_{y=0}$ and in (d) the amplitude of modulation of temperature $|\frac{\partial\tilde{\theta}}{\partial y}|_{y=0}$, given by equation (5.9), are plotted against time for $\epsilon = 1$, $\omega_0 = 100$ and $l = 0.033$.*

stable). Now knowing the enthalpy θ_j^i at the ith time level the temperature at this level is given by

$$\theta = \begin{cases} H - \frac{1}{\epsilon} & H \geq \frac{1}{\epsilon}, \\ 0 & 0 < H < \frac{1}{\epsilon}, \\ H & H < 0, \end{cases} \tag{5.3}$$

This method will give a step-like solution for the free boundary, so we need an algorithm to compute the free boundary position more accurately. Assuming that at the jth space grid, the enthalpy is $0 < H_j^i < \frac{1}{\epsilon}$, we expect the enthalpy to be $H_j^i = \frac{1}{2\epsilon}$ at a time given by the condition

$$dt_s = dt \left(\frac{H_j^i - \frac{1}{2\epsilon}}{H_j^{i+1} - H_j^i} \right). \tag{5.4}$$

These results are demonstrated in Figure (5.1)where the temperature profile is plotted after solving numerically the problem for $\epsilon = 1$ and $\omega_0 = 100$ (5.1 a) and s is plotted against time (5.1 b). The result is similar as in [6].

The numerical results should be separated in its underlying and cyclic parts. In order to be able to do this we can solve the problem numerically without the modulation in the boundary condition , i.e. $\theta(0,\tau) = \tau$. In this way we can compute the underlying part of the temperature $\bar{\theta}$ and the moving boundary $\bar{s}$. Then writing $\theta = \bar{\theta} + l\tilde{\theta} = \bar{\theta} + lIm\{\hat{\theta}e^{i\omega\tau}\}$ and $s = \bar{s} + l\tilde{s} = \bar{s} + lIm\{\hat{s}e^{i\omega\tau}\}$ we obtain for $\hat{\theta}$ and $\hat{s}$ the following problem :

$$i\epsilon\omega_0\hat{\theta} = \hat{\theta}_{yy}, \quad \text{for} \quad 0 < y < \bar{s}, \quad \bar{s} < y < 1 \tag{5.5}$$

$$\hat{\theta} = 1, \quad \text{at} \quad y = 0, \tag{5.6}$$

$$\hat{\theta} = -\hat{s}\bar{\theta}_y^- = -\hat{s}\bar{\theta}_y^+, \quad \text{at} \quad y = \bar{s}, \tag{5.7}$$

$$\hat{\theta}_y = 0, \quad \text{at} \quad y = 1. \tag{5.8}$$

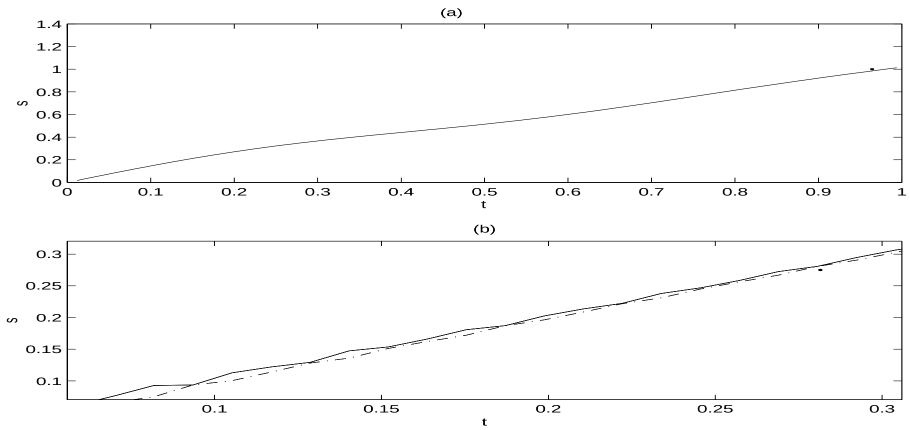

FIG. 5.2. *Comparison of numerical results with analytic approximations of Sections 3 and 4. In (a) the numerical solution (dotted line) and the approximation by equation (3.1), (solid line) are plotted against time with* $\epsilon = .01$ *and* $\omega_0 = 10$. *In (b) the numerical solution (dotted line), the approximation by equation (3.1) in Section 3 (solid line), together with the approximation by equation (4.13) in Section 4 (dashed line) are plotted against time.*

Note that the condition $\hat{\theta} = -\hat{s}\bar{\theta}_y^-$ at $y = \bar{s}$ comes from linearizing θ for l small, i.e. $\theta(\tau, s) \sim \bar{\theta}(\bar{s}) + l\tilde{s}\bar{\theta}_y + l\tilde{\theta} + ...$, so to $O(l)$ terms we have $\tilde{s}\bar{\theta}_y + \tilde{\theta} = 0$ or equivalently $\hat{\theta} = -\hat{s}\bar{\theta}_y^-$ where $\bar{\theta}_y^-$ is the gradient of $\bar{\theta}$ at $y = \bar{s}$ for $y < \bar{s}$ (for $y > \bar{s}$ we have $\hat{\theta} = -\hat{s}\bar{\theta}_y^+$).

Solving this for the liquid region, $0 < y < \bar{s}$ we obtain

$$\hat{\theta} = \exp\left((i+1)\sqrt{\frac{\epsilon\omega_0}{2}}y\right) - \left[\hat{s}\bar{\theta}_y^- + \exp\left((i+1)\sqrt{\frac{\epsilon\omega_0}{2}}\bar{s}\right)\right]\left[\frac{\sinh\left((i+1)\sqrt{\frac{\epsilon\omega_0}{2}}y\right)}{\sinh\left((i+1)\sqrt{\frac{\epsilon\omega_0}{2}}\bar{s}\right)}\right].$$

Similarly in the solid region we have that

$$\hat{\theta} = -\hat{s}\bar{\theta}_y^+\left[\frac{\exp\left((i+1)\sqrt{\frac{\epsilon\omega_0}{2}}(y-2)\right) + \exp\left(-(i+1)\sqrt{\frac{\epsilon\omega_0}{2}}y\right)}{\exp\left((i+1)\sqrt{\frac{\epsilon\omega_0}{2}}(\bar{s}-2)\right) + \exp\left(-(i+1)\sqrt{\frac{\epsilon\omega_0}{2}}\bar{s}\right)}\right].$$

We use now the Stefan condition, and we get that

$$i\omega_0\hat{s} = \left[\hat{\theta}_y\right]_-^+ + \hat{s}\left[\bar{\theta}_{yy}\right]_-^+,$$

then from the obtained expressions for $\hat{\theta}$ for the liquid and solid region we can solve the resulting algebraic equation for $\hat{s}$ and obtain the following formula:

$$\hat{s} = \frac{P_0}{i\omega_0 + \bar{\theta}_y^+ P_1 - \bar{\theta}_y^- P_2 - [\bar{\theta}_{yy}]_-^+},$$

where

$$P_0 = (i+1)\sqrt{\frac{\epsilon\omega_0}{2}}\exp\left((i+1)\sqrt{\frac{\epsilon\omega_0}{2}}\bar{s}\right)\left[1 - \coth\left((i+1)\sqrt{\frac{\epsilon\omega_0}{2}}\bar{s}\right)\right],$$

$$P_1 = (i+1)\sqrt{\frac{\epsilon\omega_0}{2}}\left[\frac{\exp\left((i+1)\sqrt{\frac{\epsilon\omega_0}{2}}(\bar{s}-2)\right) - \exp\left(-(i+1)\sqrt{\frac{\epsilon\omega_0}{2}}\bar{s}\right)}{\exp\left((i+1)\sqrt{\frac{\epsilon\omega_0}{2}}(\bar{s}-2)\right) + \exp\left(-(i+1)\sqrt{\frac{\epsilon\omega_0}{2}}\bar{s}\right)}\right],$$

$$P_2 = (i+1)\sqrt{\frac{\epsilon\omega_0}{2}}\coth\left((i+1)\sqrt{\frac{\epsilon\omega_0}{2}}\bar{s}\right).$$

By these formulas we can calculate the quantity $-\frac{\partial\tilde{\theta}}{\partial y}$ at $y=0$ by taking $-\frac{\partial\tilde{\theta}}{\partial y} \sim -Im\{l\frac{\partial\hat{\theta}}{\partial y}e^{i\omega_0\tau}\}$ at $y=0$. More precisely

$$\text{(5.9)} \qquad \frac{\partial\hat{\theta}}{\partial y} = (i+1)\sqrt{\frac{\epsilon\omega_0}{2}}\left[1 - \frac{\hat{s}\bar{\theta}_y^- - \exp\left(-(i+1)\sqrt{\frac{\epsilon\omega_0}{2}}\bar{s}\right)}{\sinh\left(-(i+1)\sqrt{\frac{\epsilon\omega_0}{2}}\bar{s}\right)}\right] \quad \text{at} \quad y=0.$$

Applying a similar analysis as in Section 4 regarding the behaviour of the system for small times we can see that for this initial stage temperature is harmonic so that the underlying signal is constant and the cyclic behaves like $\frac{1}{\tau}$. This can be seen in Figure (5.1 c) and (5.1 d). Note that this analysis based on l being small is valid when $\epsilon = O(1)$ or larger. If this is not the case, the approach followed in sections 3 or 4, depending the case, should be applied.

Also in Figure (5.2) we compare the numerical solution of problem (2.6)-(2.10) with the approximate analytical results of Section 3 and 4. In Figure (5.2 a) the problem is solved numerically with $\epsilon = .01$ and $\omega_0 = 10$. The position of the moving boundary is plotted with a dotted line. The solid line corresponds to the position of the moving boundary given by equation (3.1). We see that equation (3.1) is a very good approximation to the numerical solution for the case that $\frac{1}{\omega_0} \gg \epsilon$. In Figure (5.2 b) the problem is solved numerically, again with $\epsilon = .1$ and $\omega_0 = 100$. The position of the moving boundary given by the numerical solution of the problem is plotted with the dotted line. It appears to have a good fit with the approximate solution (dashed line) given by the analysis in Section 4. In this case $s = s_0 + \frac{1}{\omega_0}s_1 + \frac{1}{\omega_0^2}s_2$ where and $\tilde{s}_2$ is given by equation (4.13). The expression in equation (3.1), plotted with the solid line, is not valid any more because $\frac{1}{\omega_0} \ll \epsilon$. (The range of the plot is the interval [0 0.3], so that the difference of the two approximations can be obvious in the graph.)

6. Effects of the melting process at the signal. We will examine the behaviour of the signal initially for the case that $\epsilon \ll \frac{1}{\omega_0} \ll 1$. During the melting the rate of intake of heat will be approximately

$$\frac{dQ_s}{dt} = 2\rho S_c \mathcal{L} L_s \frac{dS}{dt} \simeq 2S_c\sqrt{kb\rho\mathcal{L}}\left[1 + \frac{B}{bt}\left(\sin(\omega t) - \frac{1}{\omega t}(1-\cos(\omega t))\right)\right],$$

where S_c is the cross-sectional area of the sample pan. Note here that in this case the quasi-steady approximation is valid so that the heat intake in the sample is $f = -\left[\frac{\partial T}{\partial t}\right]_{x=0} = -\left[\frac{\partial T}{\partial t}\right]_{x=s} = \frac{dS}{dt}$. The only important contribution comes only from the latent heat term while those representing the effect of specific heat (of order ϵ and smaller) are neglected. In Figure (6.1a) the heat flow Q_s is plotted against time t.

Using the assumption of the large frequency, $\omega_0 = \omega t_o \gg 1$, we can neglect the $\frac{1}{\omega}$ term in the brackets of the previous equation, and the expression for the heat intake can be written more simply as

$$\frac{dQ_s}{dt} = 2\rho S_c \mathcal{L} L_s \frac{dS}{dt} \simeq 2S_c\sqrt{kb\rho\mathcal{L}}\left[1 + \frac{B\sin(\omega t)}{bt}\right].$$

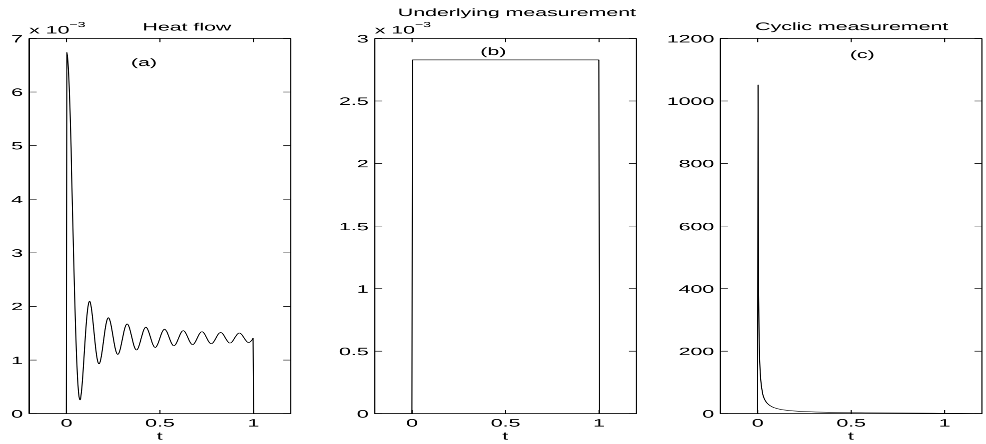

FIG. 6.1. *a)Total heat flow rate* $\frac{dQ_s}{dt}$, *b) Underlying measurement* $\bar{C}$, *c)Cyclic measurement* $\tilde{C}$

We use this in the basic ordinary-differential-equation model for the calorimeter, and we obtain, approximately,

$$C_R \frac{\Delta T}{dt} + K\Delta T = 2S_c\sqrt{kb\rho\mathcal{L}}\left[1 + \frac{B\sin(\omega t)}{bt}\right].$$

Solving this equation in the usual way, and separating the underlying and cyclic parts of the solution, we obtain

$$\Delta T = \Delta\bar{T} + \Delta\tilde{T},$$

with

$$\Delta\bar{T} = 2S_c\sqrt{\frac{kb\rho\mathcal{L}}{K}} \quad \text{and} \quad \Delta\tilde{T} = \frac{2BS_c}{t}\sqrt{\frac{k\rho\mathcal{L}}{b}}\frac{K\sin(\omega t) - \omega C_R\cos(\omega t)}{K^2 + \omega^2 C_R^2}.$$

The heat capacity measurements are

$$\overline{C} = 2S_c\sqrt{\frac{k\rho\mathcal{L}}{b}} \quad \text{and} \quad \widetilde{C} = \frac{2S_c}{\omega t}\sqrt{\frac{k\rho\mathcal{L}}{b}}. \tag{6.1}$$

Plots of these underlying and cyclic measurements are shown here in Figures (6.1 b) and (6.1 c) respectively. The size of the peak in the underlying measurement is $2S_c\sqrt{\frac{k\rho\mathcal{L}}{b}}$, and it starts at time $t = 0$ and drops to zero when the melting is completed at time $L_s\sqrt{\frac{\rho\mathcal{L}}{bk}}$. The cyclic measurement takes place at the same range of time and behaves like $\frac{1}{t}$. Including the second term in the regular perturbation expansion will give for the measurements

$$\overline{C} = 2S_c\sqrt{\frac{k\rho\mathcal{L}}{b}}\left\{1 + \frac{cb}{3\mathcal{L}}\left(\frac{kb}{10L_s^2\rho\mathcal{L}}t^3 - \frac{1}{L_s}\sqrt{\frac{kb}{\rho\mathcal{L}}}t^2 - \frac{7}{18}t\right)\right\},$$

$$\widetilde{C} = \frac{2S_c}{\omega}\sqrt{k\rho\mathcal{L}b}\left\{\frac{1}{bt} - \frac{c}{\mathcal{L}}\left(\frac{1}{30L_s}\frac{kb}{\rho\mathcal{L}}t^2 - \frac{1}{3L_s}\sqrt{\frac{kb}{\rho\mathcal{L}}}t - \frac{2}{9}\right)\right\}.$$

The sample is inert for $t < 0$ and for $t > t_o = L_s\sqrt{\frac{\rho\mathcal{L}}{kb}}$, which is the time needed for the whole material to melt, so before and after the melting takes place, we have $\bar{C} = \tilde{C} = C_S$. This is of course small compared with the cyclic and underlying measurements in equation (6.1).

Considering now the case that the frequency is very large and using the results of Section 4 we obtain for the cyclic measurement

$$\widetilde{C} = \frac{2S_c}{\omega t}\sqrt{k\mathcal{L}\rho b}\left[q_1^2(q_4 - q_3)^2 + q_2^2(q_4 + q_3)^2\right]^{\frac{1}{2}},$$

for δ being of order $O(1)$ and the q's are $q_i = q_i(\frac{s_0}{\sqrt{2\delta}}) = q_i(\sqrt{\frac{\rho c k \omega b}{2\mathcal{L}}}t)$. In the case that δ is small we have the same measurement i.e. initially the signal behaves like $\frac{1}{t}$ and for larger times it modulates as it can be seen according to Figure (6.2)

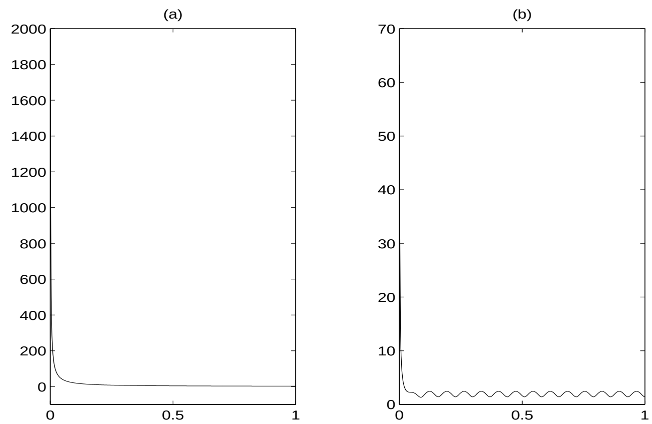

FIG. 6.2. *Cyclic signal is plotted in (a) for $\delta = 1$ and in (b) for $\delta = 0.001$*

Finally for the case that the enthalpy is of same size as the specific heat the cyclic signal has the same form i.e. initially behaves like $\frac{1}{t}$ as in Figure (5.1 d) while the underlying appears to have the form of a small bump proportional to $\frac{\partial\bar{\theta}}{\partial y}|_{y=0}$ as in Figure (5.1 c). This happens because heat is not transferred instantly and we need an extra amount of heat for the final part of the sample to melt.

According to the experiment presented in [14] of the melting of a pure lead sample, the results illustrated from the above analysis are in qualitative agreement with those of the experiment. The underlying measurement remains constant during the transition while the amplitude of the modulation decays with time during the melting. When the melting is completed there is a sharp change in the amplitude and central value of the signal.

7. Discussion. The melting of a pure material has been modelled as a one-dimensional two-phase Stefan problem. The assumption of having a large latent heat allows us to obtain an asymptotic approximate solution. Without this assumption the problem is solved numerically.

In the former case the quasi-steady approximation for temperature is valid for the underlying part, and for the cyclic part, the relative sizes of dimensionless frequency and latent heat play an important role in the solution.

If ϵ is very small, the underlying signal is constant, because the quasi-steady approximation is valid, and this is irrelevant to the relative size of ω_0 and ϵ. As regards the cyclic signal for the case that $\omega_0\epsilon \ll 1$, again the quasi-steady approximation is valid during the experiment, and the signal is proportional to $\frac{1}{t}$. For $1/\delta = \omega_0\epsilon = O(1)$ we have that the signal has the form of a combination of elementary trigonometric functions of $\frac{s_0}{\sqrt{2\delta}} = \tau\sqrt{\omega_0\epsilon/2}$. Initially again it is proportional to $\frac{1}{t}$. Taking δ to be small, we observe modulations of the cyclic signal during the experiment, due to the fact that the hyperbolic trigonometric functions become large with δ small.

Finally for the case where both latent heat and specific heat play an important role in the melting process i.e. $\epsilon = O(1)$, we can simulate both the underlying and cyclic signal of the device. The underlying signal, computed numerically, initially is constant because the quasi-steady approximation is valid, and then it increases with time. The cyclic signal behaves like $\frac{1}{t}$.

In all cases the size of the cyclic heat capacity decreases with increasing frequency and for small times the deconvolution of the signal has no meaning so the cyclic signal behaves like $1/t$. Also the moving boundary for this kind of problem is stable (we have no mechanism causing instability).

These results are in qualitative agreement with the experimental results presented in [14].

A two or three-dimensional model would be an aspect for future work in order to have a more accurate simulation of the signal. In such a case asymmetries and artifacts of the device could be involved in the model.

Another possible idea for future work is to review the problem with the more realistic assumption that the reference pan's temperature is controlled as is likely in practice in order to be able to have a quantitative comparison with real experiments.

Acknowledgment. The author wants to thank Prof. A.A. Lacey for his support and valuable advise on this work. Part of this work (Section 2) has been done while the author was doing his Ph.D thesis under the supervision of Prof. A.A. Lacey. The author wish also to thank Prof. D. E. Tzanetis for valuable discussions about the subject. This work was completed in NTUA with the financial support of I.K.Y. (State Scholarship Foundation).

REFERENCES

[1] J. Crank. *Free and Moving Boundary Problems.* Oxford University Press, 1973.

[2] J. Cole and P. Kevorkian. *Perturbation Methods in Applied Mechanics.* Springer Verlag, New York 1981.

[3] C.M. Elliott and J.R. Ockendon. *Weak and Variational Methods for Free and Moving Boundary Problems.* Pitman, London, 1982.

[4] J. Hatta. *Compatibility of Differential Scanning Calorimetry and AC Calorimetry,* Jpn. J. Appl. Phys., 1994, **33**, 686-688.

[5] E.J. Hinch. *Perturbation Methods.* Cambridge University Press, 1991.

[6] C. K. Hsieh and Chang-Yong Choi. *Solutions of one - and Two - Phase Melting and Solidification Problems Imposed With Constant or Time - Variant Temperature and Flux Boundary Conditions,*J. Heat Transfer, 1992,**114**, 524-528.

[7] A.A. Lacey et al. *ICI. Paints: Modulated Differential Scanning Calorimetry.* Report from the European Study Group with Industry, Nottingham, 1992.

[8] A.A. Lacey et al. *The origin and Interpretation of the Signals of MTDSC.* Thermochemica Acta, 1997, **304/305**, 187-199.

[9] A.A. Lacey, C. Nikolopoulos, and M. Reading. *A Mathematical Model for Modulated Differential Scanning Calorimetry.* J. Therm. Anal. 1997, **50**, 279-333.

[10] S.M. Marcus and M. Reading. *Method and Apparatus for Thermal Conductivity Measurements.* U.S. Patent 5335933, 1994

[11] J.D. Murray. *Asymptotic Analysis.* Oxford University Press, 1973.
[12] A. Nayfeh. *Perturbation Methods.* Wiley, New York, 1973.
[13] J.R. Ockendon A.A.Lacey et al. *Applied Partial Differential Equations* . Oxford University Press, London, 1999.
[14] K.A.Q. O'Reilly and B Cantor. *Cyclic Differential Scanning Calorimetry and the Melting and Solidification of Pure Metals.* Proc. Roy. Soc. Lon., 1996, **452**, 2141-2160.
[15] M. Reading, D.Elliot and L. Hill. *Some Aspects of the Theory and Practice of Modulated Differential Scanning Calorimetry.* Proc. 21st North American Thermal Analysis Society Conference, 1992, 145-150.
[16] M. Reading. *Modulated Differential Scanning Calorimetry - A New Way Forward in Materials Characterization.* Trends in Polymer Sci., 1993, **1**, 248-253.
[17] M. Reading, A. Luget and R. Wilson. *Modulated Differential Scanning Calorimetry*, Thermochim. Acta, 1994, 238.
[18] M. Reading, R Wilson and H.M. Pollock. In Proccedings of the 23rd North American Thermal Analysis Society Conference, 1994, 2-10.
[19] L.I. Rubinstein. *The Stefan Problem.* American Mathematical Society, 1971.
[20] G.D. Smith. *Numerical Solution of Partial Differential Equations: Finite Difference Methods.* Oxford University Press, 1985.
[21] A.B. Tayler. *Mathematical Models in Applied Mechanics.* Oxford University Press, 1986.
[22] S. Welnbaum and L. M. Jiji. *Singular Perturbation Theory for Melting or Freezing in Finite Domains Initially Not at the Fusion Temperature* ,J. Appl. Mech., 1977,**44**, 25-30.
[23] B. Wunderlich and A. Boller. *Modulated Differential Scanning Calorimetry Capabilities and Limits*, preprint.
[24] B. Wunderlich, A. Boller, I Okazaki and S Kreitmeier. *Linearity, Steady State, and Complex Heat Hapacity in Modulated Differential Scanning Calorimetry.* Thermochim. Acta, 1996, **283**, 143-155.
[25] B. Wunderlich. *Macromolecular Physics, Vol 3, Crystal Melting.* Academic press, New York,1980.
[26] M. M. Yan and P. N. S. Huang. *Perturbation Solutions to Phase Change Problem Subject to Convection and Radiation*,J. Heat Transfer, 1979,**101**, 96-100.