Thermochimica Acta 336 (1999) 1–15

thermochimica acta

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Derivation of temperature variation rule and variation rules of temperature lag, heat flows, internal energy and effective specific heat of platelike sample in temperature modulated differential scanning calorimetry☆

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Received 4 January 1999; received in revised form 2 June 1999; accepted 7 June 1999

Abstract

In this paper, the temperature variation rule of platelike sample in temperature modulated differential scanning calorimetry (TMDSC) has been drawn with strict mathematical derivation. The obtained analytical result reveals the total variation rule of the platelike sample from its initial equilibrium state to its steady state. With this temperature variation rule, the variation rules of both reversible and irreversible heat flows, temperature lag, internal energy and effective specific heat of the platelike sample have been derived and studied as well. If the thermal conductivity of the sample is so great that the temperature gradients within the sample can be neglected, in this case the temperature variation rule derived from the fundamental equation of the temperature distribution of our TMDSC is the same as the current TMDSC theories. If the modulated amplitude A_{T_s} or modulated frequency ω equals zero, it reverts to the conventional DSC situation, so all the results in the TMDSC model derived in this article are automatically suitable for the conventional DSC situation and current TMDSC theories. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Temperature modulated differential scanning calorimetry; Platelike sample; Temperature distribution; Heat flow; Effective specific heat

1. Introduction

Temperature modulated differential scanning calorimetry (TMDSC) is a powerful thermal analysis tool, which finds much use in various regions. The study and manufacture of new and effective thermal analysis apparatus have drawn much attention internationally. Since Reading [1,18] invented the TMDSC, the apparatus of TMDSC has been successfully commercialized [2–6]. The non-linear heating rate in TMDSC causes many difficulties in handling the data. How to use TMDSC to measure the characteristics of matter effectively, how to solve the difficult problems in dealing data and how to expand the application of TMDSC are the focuses of studying in thermal analysis theoretical society.

If the real temperature gradients within the sample are omitted, the measured sample can be taken as the sample with a uniform temperature. Under this

☆Presented at the Ninth Chinese Conference on Chemical Thermodynamics and Thermal Analysis (CTTA), Beijing, China, August 1998.

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PII: S0040-6031(99)00143-4

approximate condition, there are some articles dealing with sample heat capacities, glass-transition temperature, etc. in TMDSC [7–12]. Just as in the conventional DSC, if the temperature gradients within the sample are omitted, the measuring errors in TMDSC will occur unavoidably, which are sometimes rather large in some case [13]. To minimize the measuring errors, and to explain the physical meanings of each eigen point and each eigen curve correctly, it is necessary to consider the temperature gradients within the sample [14]. Thus, the variation rule can be revealed correctly between the temperature distribution within the sample and the heating form of stove, and much valuable information can be effectively obtained from the real thermal analysis curve.

For simplicity, in this paper we assume that the pan's thermal resistor are so small that can be neglected. This assumption will not influence the universality of our following theory.

To enhance the measuring precision and decrease the measuring error caused by the temperature gradients within the sample, the sample is generally made in the platelike form and the quantity of sample is as small as possible within the sensitivity of the apparatus. Because in the general thermal apparatus, temperature detector (e.g., thermocouple) is placed in the central position under the sample box, the measured temperature actually is the sample temperature in the center of outer surface, so the real sample can be taken as a plate, and the boundary effect caused by the finite sample size can be rationally omitted.

In this article, we will use strict mathematical tools to solve the temperature distribution rule of platelike sample in TMDSC model. Then, we will use this temperature variation rule to obtain the strict mathematical expressions of reversible and irreversible heat flows, temperature lag, internal energy and effective specific heat of the platelike sample.

2. Mathematical derivation of temperature variation rule of platelike sample in TMDSC model

Assume the sample shape studied in TMDSC is flat, it can be taken as a plate. For a platelike sample, we only need to study the temperature distribution in the plate depth direction. In this condition, there is a thermal transference equation

$$\frac{\partial T(x,t)}{\partial t} = a^2 \frac{\partial^2 T(x,t)}{\partial x^2}, \tag{1}$$

where $T(x,t)$ is the sample temperature at the depth x and at the time t, $a^2 = \kappa/\rho c_p$, κ is the thermal conductivity of the sample at temperature T, ρ the mass density of sample at temperature T, c_p is the specific heat capacity of sample at temperature T. Here, for simplicity, the value of κ, ρ and c_p are assumed as constants in the studied temperature interval.

Almost all the existing popular theories of TMDSC are based on the approximate assumptions that the values of κ, ρ and c_p of the sample are assumed as constants in the studied temperature interval, and the temperature gradients within the sample are omitted which actually implies that the thermal conductivity of the sample is infinite. In most situations, the assumptions that the κ, ρ and c_p of the sample are constant in the studied temperature interval can be rationally accepted which may cause little error, but the assumption that the temperature gradients within the sample are omitted may cause obvious errors, and may cause rather big errors in some cases. Although there are some thermal analysis theories dealing with conventional DSC [15] and TMDSC [16,17] in which the temperature gradients in the sample are considered, there are also some obvious approximations in these theories. In our TMDSC theory, by considering the temperature gradients within the sample we will try to obtain the exact temperature distribution within the sample and its variation rule. Using the obtained temperature variation rule we can obtain the variation rule of some physical quantities, so we can improve the existing analytical theory of TMDSC and obtain more precise values of physical quantities by TMDSC experiments.

The sample can be taken as a total depth $2l$ with two surfaces exposed to the heating surrounding, or equivalently a total depth l with one adiabatic surface and another surface exposed to the heating surrounding, so we get boundary condition:

$$\left(T - \frac{\kappa}{K}\frac{\partial T}{\partial x}\right)\Bigg|_0 = T_s,$$

$$\frac{\partial T}{\partial x}\Bigg|_l = 0. \tag{2}$$

where $T_s = T_0 + qt + A_{T_s}\sin\omega t$, T_s is the program-controlled stove temperature in TMDSC model, T_0 the initial temperature of stove, q the linear heating rate of stove, and A_{T_s} and ω are, respectively, amplitude and frequency of modulated heating rate.

Sample's initial condition is

$$T(x,0) = T_0, \tag{3}$$

i.e., at the initial time, whole sample's temperature is T_0.

Define

$$T(x,t) = T_0 + qt + A_{T_s}\sin\omega t + \Delta(x,t), \tag{4}$$

where $\Delta(x,t)$ is a correction function. Only in the extremely ideal situation that the thermal conductivity of the sample is infinite, the correction function $\Delta(x,t)$ is equal to zero. In the general situation $\Delta(x,t)$ is not equal to zero, so Eq. (1) can be changed into the following form:

$$\frac{\partial\Delta(x,t)}{\partial t} - a^2\frac{\partial^2\Delta(x,t)}{\partial x^2} = -q - A_{T_s}\omega\cos\omega t. \tag{5}$$

The boundary condition (2) becomes

$$\left.\left(\Delta - \frac{\kappa}{K}\frac{\partial\Delta}{\partial x}\right)\right|_0 = 0,$$
$$\left.\frac{\partial\Delta}{\partial x}\right|_l = 0, \tag{6}$$

and the initial condition (3) becomes

$$\Delta(x,0) = 0. \tag{7}$$

By using the method of impulse theorem and defining $\Delta(x,t) = \int_0^t v(x,t;\tau)\,\mathrm{d}\tau$, Eq. (5) becomes

$$\frac{\partial v(x,t)}{\partial t} - a^2\frac{\partial^2 v(x,t)}{\partial x^2} = 0. \tag{8}$$

The boundary condition (6) becomes:

$$\left.\left(v - \frac{\kappa}{K}\frac{\partial v}{\partial x}\right)\right|_0 = 0,$$
$$\left.\frac{\partial v}{\partial x}\right|_l = 0, \tag{9}$$

and the initial condition (7) becomes

$$v(x, t = \tau + 0) = -q - A_{T_s}\omega\cos\omega\tau. \tag{10}$$

By using variable separation method and defining $v(x,t)=U(t)X(x)$, we have

$$\frac{1}{U}\frac{\mathrm{d}U}{\mathrm{d}t} = \frac{a^2}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}. \tag{11}$$

The left side of Eq. (11) is the function of time t, but the right side is the function of place x. Because the equation is valid, both side of the equation must be equal to a constant. Defining this constant $-\lambda^2 a^2$, we get:

$$\frac{1}{U}\frac{\mathrm{d}U}{\mathrm{d}t} = \frac{a^2}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} = -\lambda^2a^2. \tag{12}$$

From these, the obtained solutions are

$$U = U(0)\mathrm{e}^{-\lambda^2a^2t}, \tag{13}$$
$$X(x) = A\sin\lambda x + B\cos\lambda x. \tag{14}$$

From a recent boundary condition $\left(X - \frac{\kappa}{K}\frac{\partial X}{\partial x}\right)|_0 = 0$, we can obtain

$$B = \frac{\kappa}{K}A\lambda. \tag{15}$$

From another boundary condition $\frac{\mathrm{d}X(x)}{\mathrm{d}x}|_l = 0$, we get

$$A\lambda\cos\lambda l - B\lambda\sin\lambda l = 0. \tag{16}$$

Combining Eq. (15) with Eq. (16), if follows

$$\lambda_n = \frac{K}{\kappa}ctg\lambda_n l, \quad n = 0,1,2,\ldots, \tag{17}$$

i.e., to satisfy the boundary conditions, λ must be the roots of Eq. (17).

So we have a general solution

$$v(x,t;\tau) = \sum_{n=0}^{+\infty} C_n(\tau)\mathrm{e}^{-\lambda_n^2a^2(t-\tau)} \times \left[\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right]. \tag{18}$$

From initial condition $\sum_{n=0}^{+\infty} C_n(\tau)[\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x] = -q - A_{T_s}\omega\cos\omega\tau$, we get

$$C_n(\tau) = -\frac{2K^2}{\lambda_n(K^2l + l\kappa^2\lambda_n^2 + \kappa K)} \times (q + A_{T_s}\omega\cos\omega\tau), \tag{19}$$

where we have used orthogonal relation of the intrinsic function

$$C_n(\tau)\int_0^l |X_n(x)|^2\,\mathrm{d}x = -(q + A_{T_s}\omega\cos\omega\tau)\int_0^l X_n(x)\,\mathrm{d}x, \tag{20}$$

$$\int_0^l |X_n(x)|^2\,\mathrm{d}x = \frac{K^2 l + l\kappa^2\lambda_n^2 + \kappa K}{2K^2},$$
$$\int_0^l X_n(x)\mathrm{d}x = \frac{1}{\lambda_n}. \tag{21}$$

So we have

$$v(x,t;\tau) = -(q + A_{\mathrm{T_s}}\omega\cos\omega\tau)\sum_{n=0}^{+\infty} \times \frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)}\mathrm{e}^{-\lambda_n^2 a^2 (t-\tau)} X_n(x). \tag{22}$$

Thus, we can obtain the correction function

$$\Delta(x,t) = \int_0^t v(x,t;\tau)\mathrm{d}\tau = \sum_{n=0}^{+\infty}\Delta_n(A,\omega,x,t)$$
$$= -\sum_{n=0}^{+\infty}\frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} \times \left(\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right) \times \left\{\frac{q}{\lambda_n^2 a^2}(1-\mathrm{e}^{-\lambda_n^2 a^2 t}) + \frac{A_{\mathrm{T_s}}\omega}{\lambda_n^4 a^4 + \omega^2} \times \left[\lambda_n^2 a^2(\cos\omega t - \mathrm{e}^{-\lambda_n^2 a^2 t}) + \omega\sin\omega t\right]\right\},$$
$$(0 \le x \le l,\ t \ge 0). \tag{23}$$

Δ_n is defined as follows:

$$\Delta_n(A,\omega,x,t) = -\frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} \times \left(\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right) \times \left\{\frac{q}{\lambda_n^2 a^2}(1-\mathrm{e}^{-\lambda_n^2 a^2 t}) + \frac{A_{\mathrm{T_s}}\omega}{\lambda_n^4 a^4 + \omega^2} \times \left[\lambda_n^2 a^2(\cos\omega t - \mathrm{e}^{-\lambda_n^2 a^2 t}) + \omega\sin\omega t\right]\right\},$$
$$(0 \le x \le l, t \ge 0), \tag{24}$$

where Δ_n is the nth temperature distribution correction item of the sample.

Finally, we have

$$T(x,t) = T_0 + qt + A_{\mathrm{T_s}}\sin\omega t + \Delta(x,t)$$
$$= T_0 + qt + A_{\mathrm{T_s}}\sin\omega t - \sum_{n=0}^{+\infty} \times \frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} \times \left(\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right) \times \left\{\frac{q}{\lambda_n^2 a^2}(1-\mathrm{e}^{-\lambda_n^2 a^2 t}) + \frac{A_{\mathrm{T_s}}\omega}{\lambda_n^4 a^4 + \omega^2} \times \left[\lambda_n^2 a^2(\cos\omega t - \mathrm{e}^{-\lambda_n^2 a^2 t}) + \omega\sin\omega t\right]\right\}, \tag{25}$$

$$T(x,t) = T_0 + qt + A_{\mathrm{T_s}}\sin\omega t + \Delta(x,t)$$
$$= T_0 + qt + A_{\mathrm{T_s}}\sin\omega t - \sum_{n=0}^{+\infty} \times \frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} \times \left(\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right) \tag{25A}$$
$$\left\{\frac{q}{\lambda_n^2 a^2}(1-\mathrm{e}^{-\lambda_n^2 a^2 t}) + \frac{A_{\mathrm{T_s}}\omega}{\sqrt{\lambda_n^4 a^4 + \omega^2}}\sin(\omega t + \alpha_n) \times -\frac{A_{\mathrm{T_s}}\omega\lambda_n^2 a^2 \mathrm{e}^{-\lambda_n^2 a^2 t}}{\lambda_n^4 a^4 + \omega^2}\right\}, \quad (0 \le x \le l,\ t \ge 0),$$

where α_n is defined as

$$\alpha_n \equiv \arcsin\frac{\lambda_n^2 a^2}{\sqrt{\lambda_n^4 a^4 + \omega^2}}. \tag{26}$$

Eqs. (25) and (25A) are the temperature distribution rule within the platelike sample in TMDSC model, and this is the fundamental and most important equation of our TMDSC theory.

If the time is long enough, the item $\mathrm{e}^{-\lambda_n^2 a^2 t}$ becomes so small that it can be neglected. In this case the sample is in the steady state, and Eqs. (25) and (25A) can be rewritten as

$$T^{(s)}(x,t) = T_0 + qt + A_{T_s}\sin\omega t - \sum_{n=0}^{+\infty} \times \frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} \times \left(\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right) \tag{25B}$$

$$\left\{\frac{q}{\lambda_n^2 a^2} + \frac{A_{T_s}\omega}{\lambda_n^4 a^4 + \omega^2}\left[\lambda_n^2 a^2\cos\omega t + \omega\sin\omega t\right]\right\},$$

$$T^{(s)}(x,t) = T_0 + qt + A_{T_s}\sin\omega t - \sum_{n=0}^{+\infty} \times \frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} \times \left(\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right) \times \left[\frac{q}{\lambda_n^2 a^2} + \frac{A_{T_s}\omega}{\sqrt{\lambda_n^4 a^4 + \omega^2}}\sin(\omega t + \alpha_n)\right], \quad (0\le x\le l,\ t\ge 0). \tag{25C}$$

From Eqs. (25) and (25A) it can be known that the temperature distribution function $T(x,t)$ is related to the experimental conditions, such as heating rate of surrounding, Newton's Law Constant of the sample box, sample's initial temperature, its specific heat, its thermal conductivity and other factors. When A_{T_s} or ω equals zero, it reverts to the conventional DSC situation, so the temperature distribution rule within the sample in the TMDSC model derived in this article automatically suits the conventional DSC situation.

The temperature gradients within the sample can be derived from the basic Eqs (25) and (25A):

$$\frac{dT(x,t)}{dx} = -\sum_{n=0}^{+\infty}\frac{2K^2}{K^2 l + l\kappa^2\lambda_n^2 + \kappa K} \times \left(\cos\lambda_n x - \frac{\kappa\lambda_n}{K}\sin\lambda_n x\right) \times \left\{\frac{q}{\lambda_n^2 a^2}(1 - e^{-\lambda_n^2 a^2 t}) + \frac{A_{T_s}\omega}{\lambda_n^4 a^4 + \omega^2} \times \left[\lambda_n^2 a^2(\cos\omega t - e^{-\lambda_n^2 a^2 t}) + \omega\sin\omega t\right]\right\}, \tag{27}$$

$$\frac{dT(x,t)}{dx} = -\sum_{n=0}^{+\infty}\frac{2K^2}{K^2 l + l\kappa^2\lambda_n^2 + \kappa K}\left(\cos\lambda_n x - \frac{\kappa\lambda_n}{K}\sin\lambda_n x\right) \times \left\{\frac{q}{\lambda_n^2 a^2}(1 - e^{-\lambda_n^2 a^2 t}) + \frac{A_{T_s}\omega}{\sqrt{\lambda_n^4 a^4 + \omega^2}}\sin(\omega t + \alpha_n) - \frac{A_{T_s}\omega\lambda_n^2 a^2 e^{-\lambda_n^2 a^2 t}}{\lambda_n^4 a^4 + \omega^2}\right\}. \tag{27A}$$

3. Discussion on the temperature distribution rule

To verify Eqs. (25) and (27), now we study a very special example.

Example 1. Assume that in the studied temperature interval the sample's thermal conductivity κ is 1, its mass density ρ is 1, its specific heat c_p is 1.5, so we get $a^2 = \kappa/\rho c_p = 0.6667$. We also assume that sample' depth l is 0.1. From Eq. (17) we can get the roots, λ_0=8.6033357, λ_1=34.25618387, λ_2=64.3729811, λ_3=95.29334263, λ_4=126.45287025, λ_5=157.71284669, etc.

Assume the Newton's constant K is 10, the modulated amplitude and frequency, A_{T_s} and ω are 1 and π, respectively. We can get a relation between the temperature of stove T_s and the time t as shown in Fig. 1.

From Fig. 2, we can know that Δ_0 is the dominant item, the sum of other items is just only the 2% of the value of Δ_0. For simplicity, in this special example we only need to consider the influence of the Δ_0 and the error caused by this approximation will be less than 2%.

In this special situation, Eqs. (25) and (25A) can be rewritten as follows:

$$T(x,t) \approx T_0 + qt + A_{T_s}\sin\omega t + \Delta_0(A,\omega,x,t) = T_0 + qt + A_{T_s}\sin\omega t - \frac{2K^2}{\lambda_0(K^2 l + l\kappa^2\lambda_0^2 + \kappa K)} \times \left(\sin\lambda_0 x + \frac{\kappa\lambda_0}{K}\cos\lambda_0 x\right) \times \left\{\frac{q}{\lambda_0^2 a^2}(1 - e^{-\lambda_0^2 a^2 t}) + \frac{A_{T_s}\omega}{\lambda_0^4 a^4 + \omega^2} \times \left[\lambda_0^2 a^2(\cos\omega t - e^{-\lambda_0^2 a^2 t}) + \omega\sin\omega t\right]\right\}, \tag{25D}$$

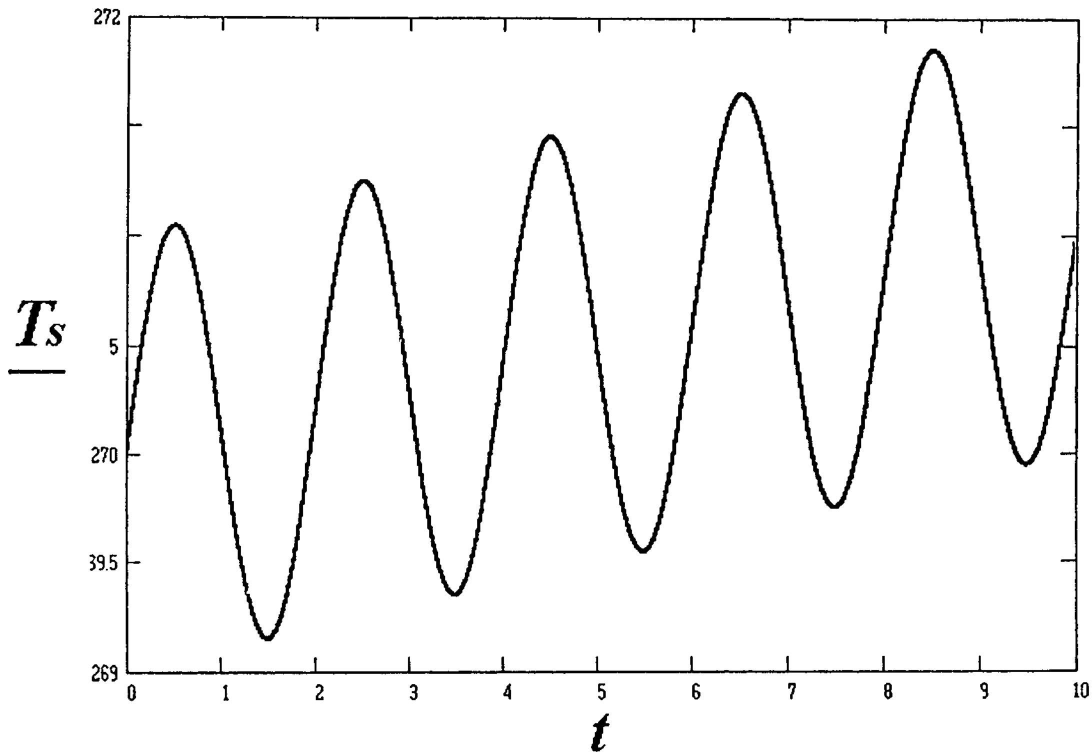

Fig. 1. Heating rate in a TMDSC experiment.

$$
\begin{aligned}
T(x,t) &\approx T_0 + qt + A_{T_s}\sin\omega t + \Delta_0(A,\omega,x,t) \\
&= T_0 + qt + A_{T_s}\sin\omega t \\
&\quad - \frac{2K^2}{\lambda_0(K^2 l + l\kappa^2\lambda_0^2 + \kappa K)} \\
&\quad \times \left(\sin\lambda_0 x + \frac{\kappa\lambda_0}{K}\cos\lambda_0 x\right) \\
&\quad \times \left\{ \frac{q}{\lambda_0^2 a^2}(1 - \mathrm{e}^{-\lambda_0^2 a^2 t}) \right. \\
&\quad + \frac{A_{T_s}\omega}{\sqrt{\lambda_0^4 a^4 + \omega^2}}\sin(\omega t + \alpha) \\
&\quad \left. - \frac{A_{T_s}\omega\lambda_0^2 a^2 \mathrm{e}^{-\lambda_0^2 a^2 t}}{\lambda_0^4 a^4 + \omega^2} \right\}, \quad (0 \le x \le l,\ t \ge 0),
\end{aligned} \tag{25E}
$$

where α is defined as

$$\alpha \equiv \arcsin\frac{\lambda_0^2 a^2}{\sqrt{\lambda_0^4 a^4 + \omega^2}}.$$

Now, we study the relationship between the modulated temperature of the stove and the 0th temperature distribution correction item of the sample Δ_0. From Fig. 3, we know there is a phase shift, $\pi+\alpha$, between them. In this example, we have $\alpha = 1.507$. The main cause of this phase shift is the sample's limited thermal conductivity.

Now, we study the temperature gradients within the sample. Fig. 4(a) shows us the temperature distributions within the sample at the different time. To obviously observe the temperature gradients within the sample and its variation rules, at first, we derive the

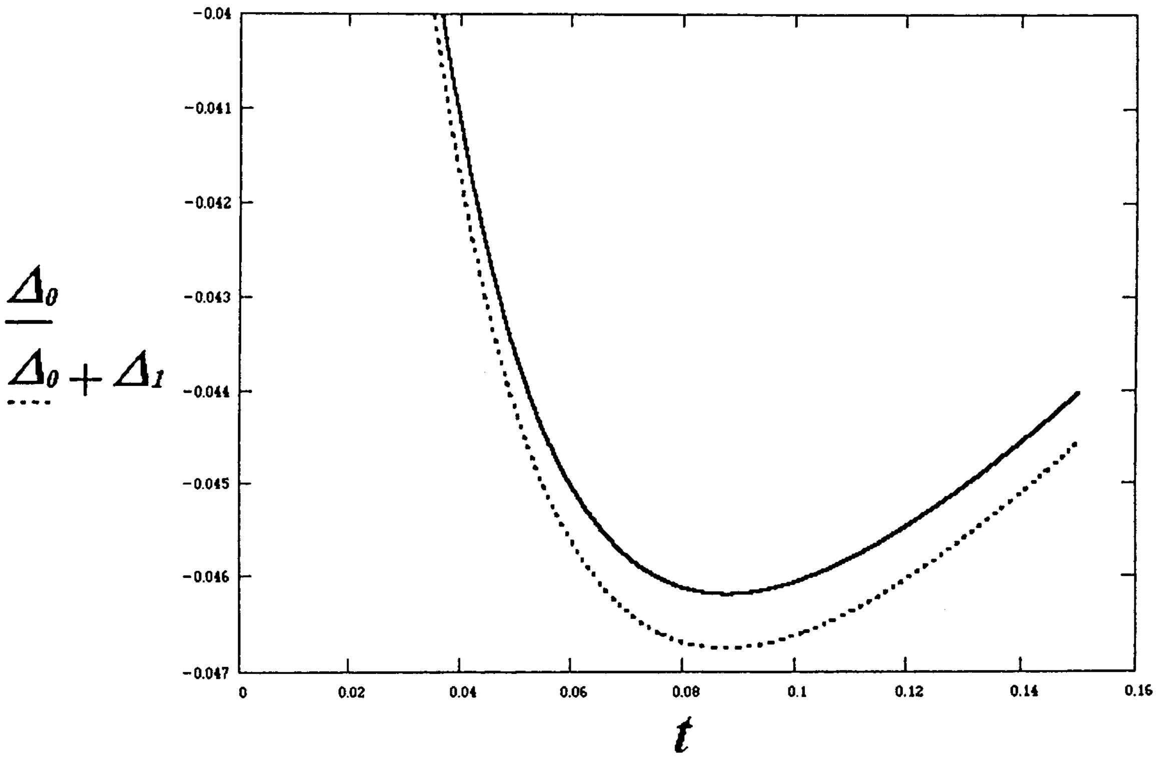

Fig. 2. Compare between 0th and 1st correction items.

relationship between the temperature gradient and the depth x. From Eq. (27A), it is easy that the temperature gradients within the sample can be derived

$$\frac{\mathrm{d}T(x,t)}{\mathrm{d}x} = -\frac{2K^2}{K^2 l + l\kappa^2\lambda_0^2 + \kappa K} \times \left(\cos\lambda_0 x - \frac{\kappa\lambda_0}{K}\sin\lambda_0 x\right) \times \left\{\frac{q}{\lambda_0^2 a^2}(1-\mathrm{e}^{-\lambda_0^2 a^2 t}) + \frac{A_{\mathrm{T_s}}\omega}{\sqrt{\lambda_0^4 a^4 + \omega^2}}\sin(\omega t + \alpha) \times -\frac{A_{\mathrm{T_s}}\omega\lambda_0^2 a^2 \mathrm{e}^{-\lambda_0^2 a^2 t}}{\lambda_0^4 a^4 + \omega^2}\right\}, \qquad (27\mathrm{B})$$

$$\frac{\mathrm{d}T(x,t)}{\mathrm{d}x} = -\frac{2K^2}{K^2 l + l\kappa^2\lambda_0^2 + \kappa K} \times \left(\cos\lambda_0 x - \frac{\kappa\lambda_0}{K}\sin\lambda_0 x\right) \times \left\{\frac{q}{\lambda_0^2 a^2}(1-\mathrm{e}^{-\lambda_0^2 a^2 t}) + \frac{A_{\mathrm{T_s}}\omega}{\sqrt{\lambda_0^4 a^4 + \omega^2}}\sin\omega(t+\tau) - \frac{A_{\mathrm{T_s}}\omega\lambda_0^2 a^2 \mathrm{e}^{-\lambda_0^2 a^2 t}}{\lambda_0^4 a^4 + \omega^2}\right\}, \quad (0 \le x \le l,\ t \ge 0), \qquad (27\mathrm{C})$$

where $\tau \equiv \alpha/\omega$, in this example, $\tau = 0.48$.

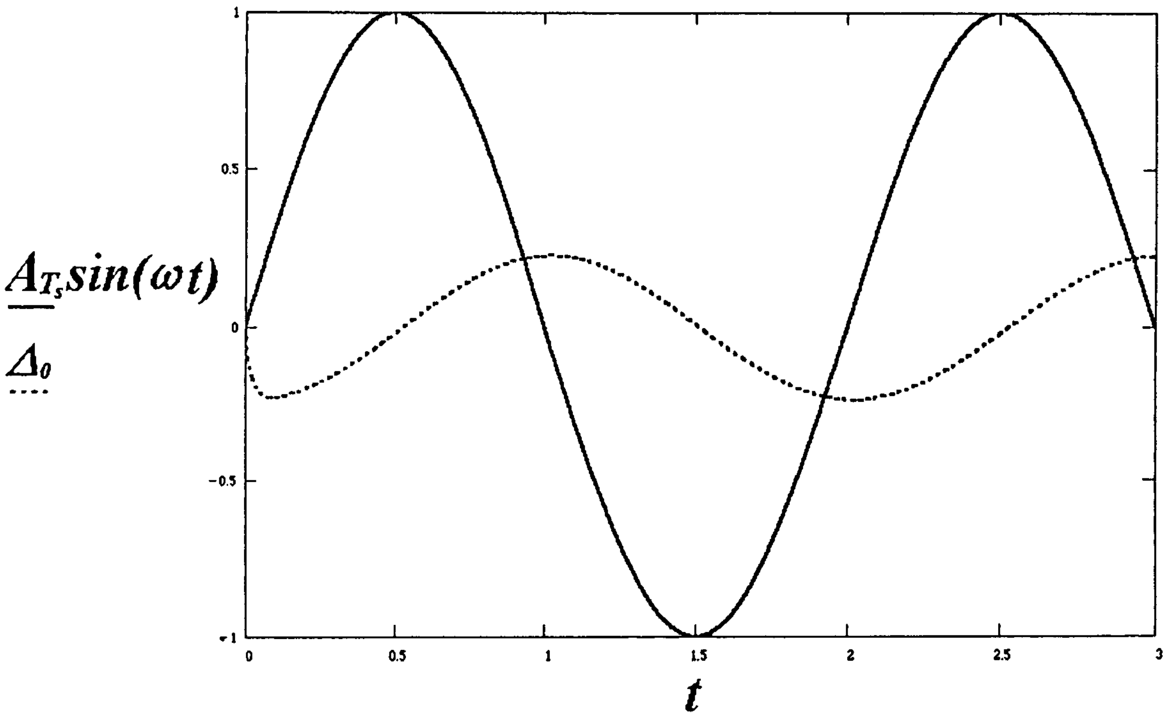

Fig. 3. Variation of modulated temperature and sample's surface temperature.

From Fig. 4(b) we can obviously know that there is really temperature gradient within the sample which varies periodically with the time. In Fig. 4(b), we can discover the temperature gradient in depth l is zero, which is the inexorable result obeying the boundary condition. We also can find out another interesting phenomenon, i.e., the temperature gradients variation in a periodic time is asymmetric to the abscissa. This phenomenon is reasonable, in the heating process the equivalent heat flowing direction is from stove to sample in a periodic time so the total temperature gradients within the sample must be negative.

In Fig. 5, we can find out the influences of the modulated amplitude and frequency on the 0th temperature distribution correction item of the sample. From these calculation results, it can be easily known that bigger the modulated amplitude or the frequency, the bigger is the variation extent of the 0th temperature distribution correction item.

If we draw a figure about the relationship between the sample's surface temperature and the time, we can get an almost the same curve as shown in Fig. 1. But if we amplify the curve, we can discover the temperature difference (i.e. temperature lag) between the sample's surface and the stove (as shown in Fig. 6).

From above brief discussion we find out that the temperature variation rule of platelike sample is self-satisfied, and the obtained results in all these figures conform to our previous experiences about the thermal analysis.

Now, we discuss another representative example.

Example 2. From above discussion, we know that in the general situation if the thermal conductivity of the sample is big enough, that is $\kappa \rightarrow +\infty$, in Eq. (25), we only need to study the dominant item Δ_0 and neglect other correction items. So Eq. (25) can be simplified as follows:

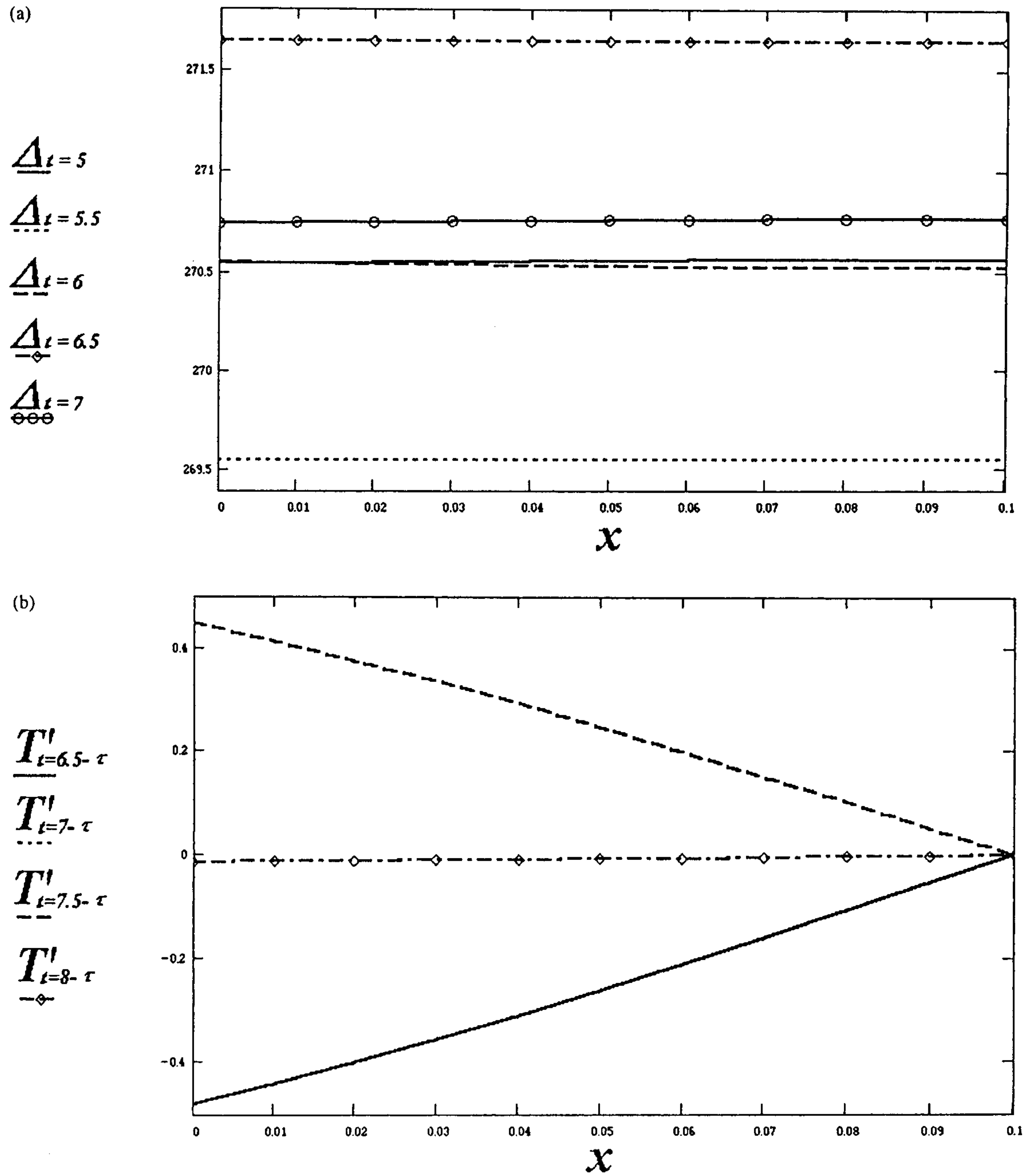

Fig. 4. Temperature distribution within the sample: (a) temperature distribution within the sample at different time; (b) temperature gradients within in a periodic time.

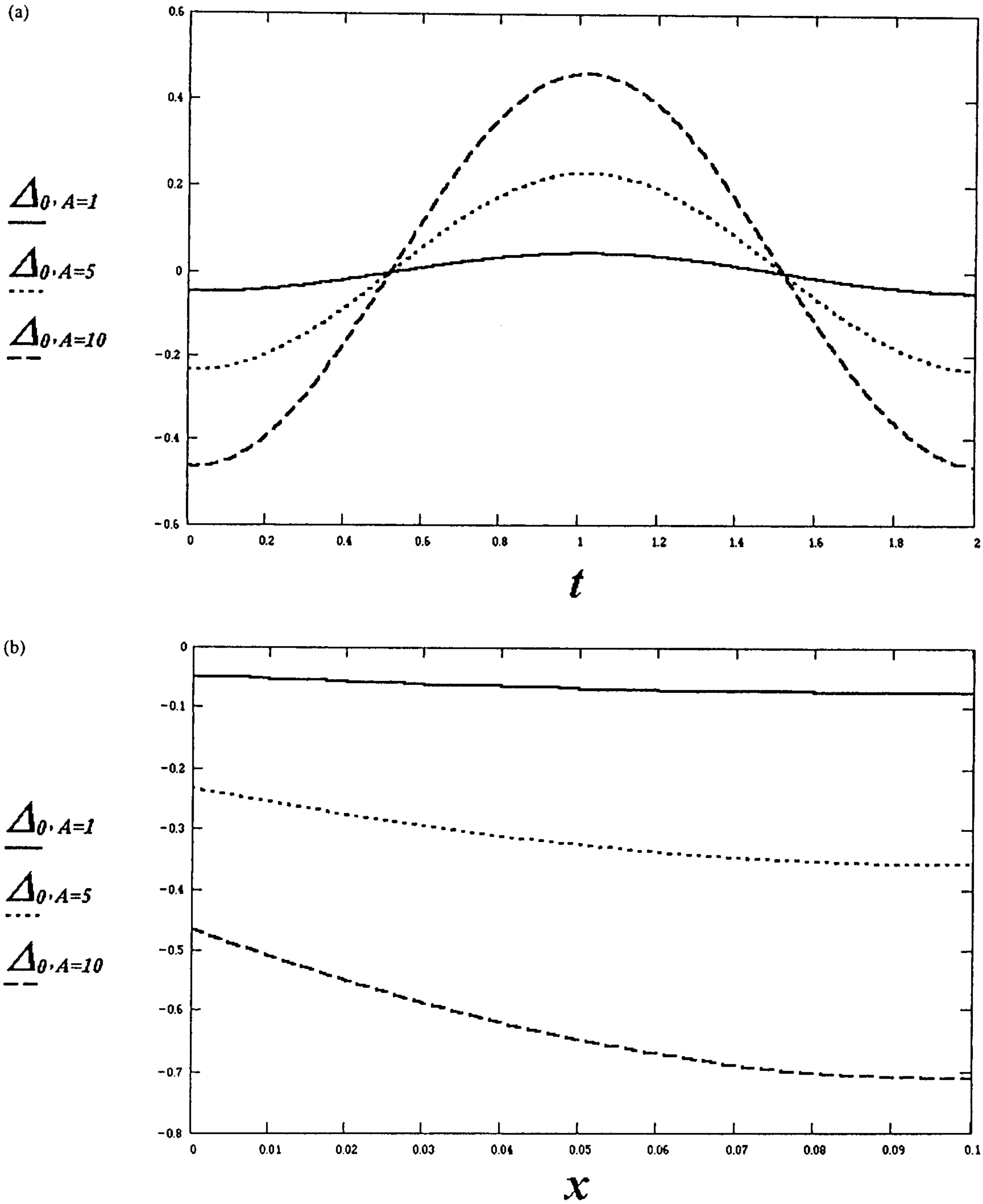

Fig. 5. Inference of the modulated amplitude and frequency: (a) the relation between the modulated amplitude and sample's surface temperature; (b) the relation between the modulated amplitude and sample's temperature distribution; (c) the relation between the modulated frequency and sample's surface temperature; (d) the relation between the modulated frequency and sample's temperature distribution.

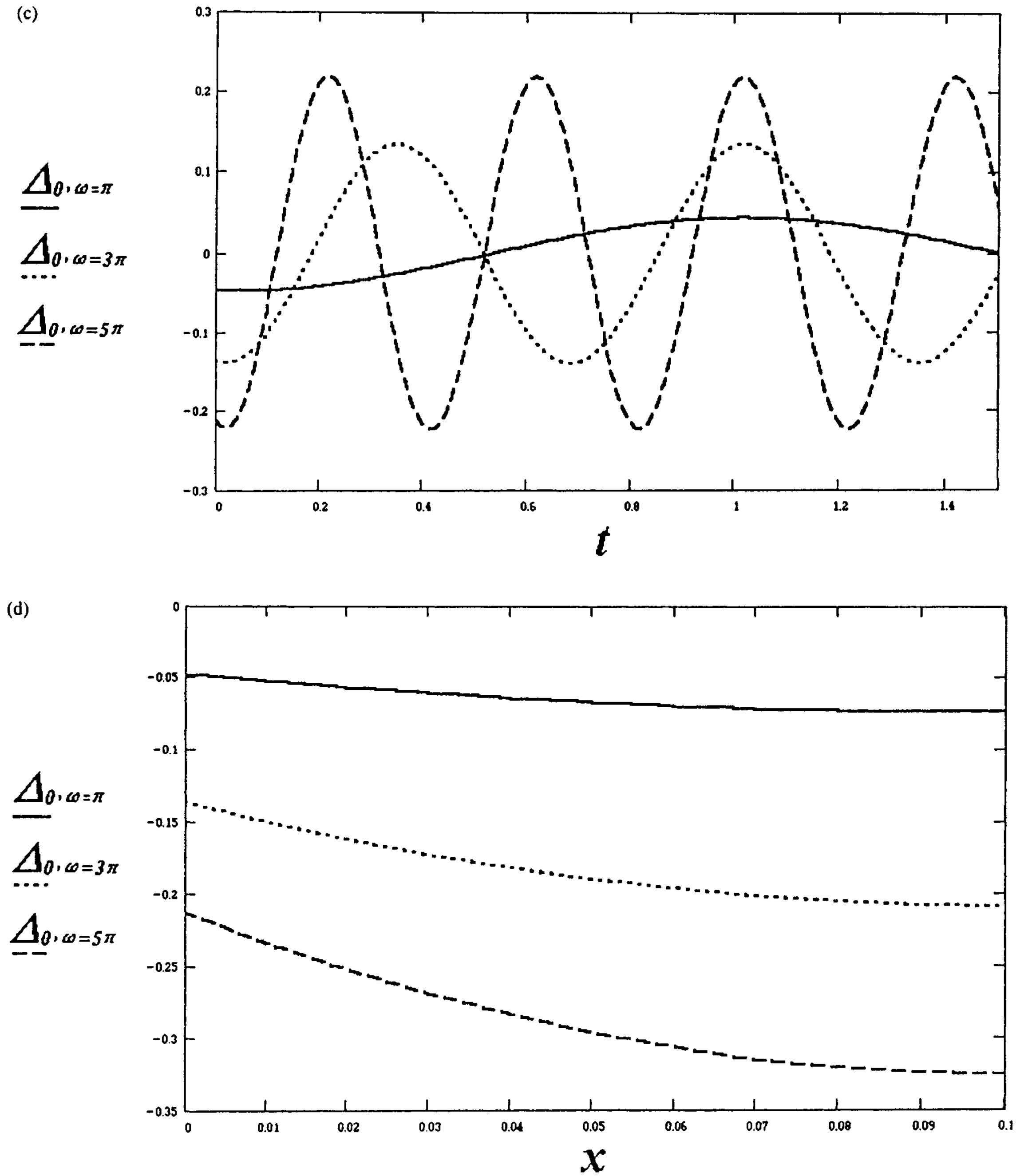

Fig. 5. (*Continued*)

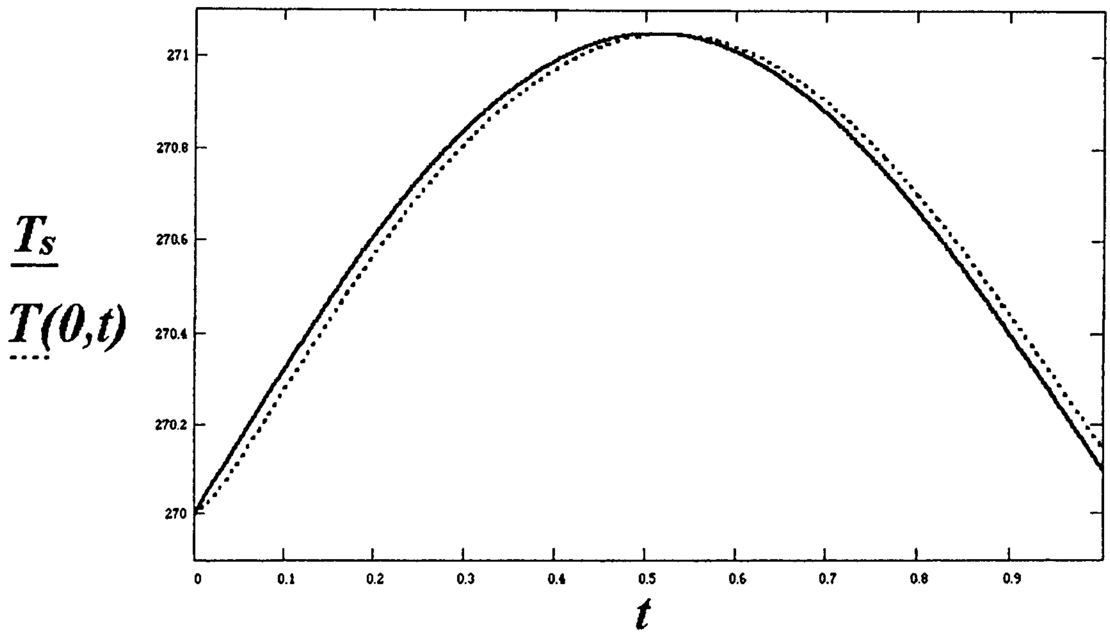

Fig. 6. Temperature of stove and sample's surface temperature.

$$
\begin{aligned}
T(x,t) \approx\; & T_0 + qt + A_{T_s}\sin\omega t \\
& - \frac{2K^2}{\lambda_0(K^2 l + l\kappa^2\lambda_0^2 + \kappa K)} \\
& \times \left(\sin\lambda_0 x + \frac{\kappa\lambda_0}{K}\cos\lambda_0 x\right) \\
& \times \left\{ \frac{q}{\lambda_0^2 a^2}(1 - \mathrm{e}^{-\lambda_0^2 a^2 t}) + \frac{A_{T_s}\omega}{\lambda_0^4 a^4 + \omega^2} \right. \\
& \left. \times \left[\lambda_0^2 a^2(\cos\omega t - \mathrm{e}^{-\lambda_0^2 a^2 t}) + \omega\sin\omega t\right] \right\} \\
=\; & T_0 + qt + A_{T_s}\sin\omega t - \chi q\tau\left(1 - \mathrm{e}^{-t/\tau}\right) \\
& - \frac{\chi A_{T_s}\omega\tau}{1 + \omega^2\tau^2}\left[(\cos\omega t - \mathrm{e}^{-t/\tau}) + \omega\tau\sin\omega t\right].
\end{aligned} \tag{25F}
$$

where some definitions are used

$$\tau \equiv \lambda_0^2 a^2, \tag{28}$$

$$\chi \equiv \frac{2K\kappa}{K^2 l + l\kappa^2\lambda_0^2 + \kappa K}, \tag{29}$$

If the sample's thermal conductivity is sufficiently great, the temperature gradients within the sample can be rationally omitted. In the situation $\kappa \to +\infty$, from $\lambda_0 = \frac{K}{\kappa} ctg\lambda_0 l$, we can get $\lambda_0^2 = K/\kappa l$ and $\tau = (\rho c_p l/K) = (C/KS)$, so we obtain $\chi = 1$. Thus, we get

$$
\begin{aligned}
T(0,t) =\; & T_0 + qt - q\tau(1 - \mathrm{e}^{-t/\tau}) \\
& + \frac{A_{T_s}}{1 + \omega^2\tau^2}\left[\sin\omega t - \omega\tau(\cos\omega t - \mathrm{e}^{-t/\tau})\right] \\
=\; & T_0 + qt - q\tau(1 - \mathrm{e}^{-t/\tau}) + \frac{A_{T_s}\omega\tau}{1 + \omega^2\tau^2}\mathrm{e}^{-t/\tau} \\
& + \frac{A_{T_s}}{\sqrt{1 + \omega^2\tau^2}}\sin(\omega t - \omega\tau), \quad (t \geq 0)
\end{aligned} \tag{30}
$$

This equation is exactly the same as the basic equation of the current TMDSC theories in which the temperature gradients are omitted [7]. So it can be seen that the current TMDSC theories in which temperature gradients are omitted are only special examples of our general theory.

4. Derivation of the variation rules of temperature lag, heat flows, internal energy and effective specific heat of platelike sample

Further discussion of Eqs. (25) and (25B) will give rise to many new subjects, such as the variation rules of sample's internal energy, the energy flow within the sample, the temperature lag, the reversible heat flow and the irreversible heat flow within the sample, etc., so we will discuss them in the following.

4.1. Temperature lag rule of the platelike sample

First of all, we study the temperature lag δT of the sample surface temperature with the variation of surrounding temperature. δT is defined as follows:

$$\delta T \equiv T(0,t) - T_s(t) = T(0,t) - T_0 - qt - A_{T_s}\sin\omega t. \tag{31}$$

According to Eq. (25), Eq. (31) has the form

$$\delta T = -2K\kappa \sum_{n=0}^{+\infty} \frac{1}{K^2 l + l\kappa^2\lambda_n^2 + \kappa K} \times \left\{ \frac{q}{\lambda_n^2 a^2}(1 - e^{-\lambda_n^2 a^2 t}) + \frac{A_{T_s}\omega}{\lambda_n^4 a^4 + \omega^2} \times \left[\lambda_n^2 a^2(\cos\omega t - e^{-\lambda_n^2 a^2 t}) + \omega \sin\omega t\right] \right\}. \tag{32}$$

To simplify the form of Eq. (32), we make the following definitions:

$$h_n \equiv \frac{2K\kappa}{K^2 l + l\kappa^2\lambda_n^2 + \kappa K}, \tag{33}$$

$$f_n(t) \equiv \frac{q}{\lambda_n^2 a^2}(1 - e^{-\lambda_n^2 a^2 t}) + \frac{A_{T_s}\omega}{\lambda_n^4 a^4 + \omega^2} \times [\lambda_n^2 a^2(\cos\omega t - e^{-\lambda_n^2 a^2 t}) + \omega \sin\omega t]. \tag{34}$$

Thus Eq. (32) can be written as

$$\delta T = -\sum_{n=0}^{+\infty} h_n f_n(t). \tag{35}$$

This is the generalized temperature lag rule of the platelike sample in TMDSC.

Under the steady-state condition, i.e. the term $e^{-\lambda_n^2 a^2 t}$ can be omitted, we have

$$f_n^{(s)}(t) \equiv \frac{q}{\lambda_n^2 a^2} + \frac{A_{T_s}\omega}{\lambda_n^4 a^4 + \omega^2}(\lambda_n^2 a^2 \cos\omega t + \omega \sin\omega t). \tag{34A}$$

Thus, under the steady-state condition, there is temperature lag rule of the platelike sample

$$\delta T^{(s)} = -\sum_{n=0}^{+\infty} h_n f_n^{(s)}(t). \tag{35A}$$

4.2. Variation rule of reversible and irreversible heat flows in the platelike sample

Under the general-state condition, the ideal reversible Newton's heat flow HF_{rev} which is flowing into the sample through the boundary of sample within a unit area and in a unit time is

$$HF_{rev} = \frac{dQ_s}{dt} = -K\delta T = K\sum_{n=0}^{+\infty} h_n f_n(t), \tag{36}$$

where Q_s is the heat energy absorbed by the sample.

Irreversible heat flow is

$$HF_{n.r.} = \langle HF \rangle - HF_{rev}, \tag{37}$$

where $\langle HF \rangle$ is the standard heat flow detected practically with the experiment.

Under the steady-state condition, the ideal reversible Newton's heat flow $HF_{rev}^{(s)}$ which is flowing into the sample through the boundary of sample within a unit area and in a unit time is

$$HF_{rev}^{(s)} = \frac{dQ_s^{(s)}}{dt} = -K\delta T^{(s)} = K\sum_{n=0}^{+\infty} h_n f_n^{(s)}(t). \tag{36A}$$

Irreversible heat flow is

$$HF_{n.r.}^{(s)} = \left\langle HF^{(s)} \right\rangle - HF_{rev}^{(s)}, \tag{37A}$$

where $\left\langle HF^{(S)} \right\rangle$is the standard heat flow detected practically in the steady state in the experiment.

4.3. Variation rule of internal energy of platelike sample

In the general situation, there is an equation about internal energy of sample at time t in a unit volume

$$\begin{aligned} \mathrm{E}(t) &\equiv \frac{\rho c_p}{l}\int_0^l T(x,t)\,\mathrm{d}x \\ &= \rho c_p\left[(T_0+qt+A_{\mathrm{T_s}}\sin\omega t) - \sum_{n=0}^{+\infty}\frac{2K^2}{\lambda_n^2 l(K^2 l + l\kappa^2\lambda_n^2+\kappa K)}f_n(t)\right] \\ &= \rho c_p\left[(T_0+qt+A_{\mathrm{T_s}}\sin\omega t) - \sum_{n=0}^{+\infty}\frac{K}{\kappa\lambda_n^2 l}h_n f_n(t)\right]. \end{aligned} \tag{38}$$

In the steady-state situation, there is an equation about internal energy of sample at time t in a unit volume

$$\begin{aligned} \mathrm{E}^{(\mathrm{s})}(t) &\equiv \frac{\rho c_p}{l}\int_0^l T^{(\mathrm{s})}(x,t)\,\mathrm{d}x \\ &= \rho c_p\left[(T_0+qt+A_{\mathrm{T_s}}\sin\omega t) - \sum_{n=0}^{+\infty}\frac{K}{\kappa\lambda_n^2 l}h_n f_n^{(\mathrm{s})}(t)\right] \end{aligned} \tag{38A}$$

4.4. Variation rule of effective specific heat of platelike sample

Because of the thermal resistance of the sample and the non-linear heating or cooling rate in the TMDSC model, there is a sample's temperature lag effect that takes place with the variation of surrounding environmental temperature. Because the temperature measured in the real TMDSC experiment is the temperature of the sample's outer surface, the measured specific heat in TMDSC is not the same as the real specific heat of the sample. We use equivalent specific heat or effective specific heat to obtain the exact value of the measured sample's specific heat in TMDSC.

The definition of effective specific heat is

$$c_{\mathrm{eff}} \equiv \frac{1}{\rho}\frac{\mathrm{dE}(t)}{\mathrm{d}T(0,t)}. \tag{39}$$

Eq. (39) can also be written

$$c_{\mathrm{eff}} = \frac{1}{\rho}\frac{\mathrm{dE}(t)}{\mathrm{d}t}\frac{1}{\mathrm{d}T(0,t)/\mathrm{d}t}. \tag{40}$$

In the general situation, from Eq. (38) , there is a following relation:

$$\frac{\mathrm{dE}(t)}{\mathrm{d}t} = \rho c_p\left[(q + A_{\mathrm{T_s}}\omega\cos\omega t) - \sum_{n=0}^{+\infty}\frac{K}{\kappa\lambda_n^2 l}h_n g_n(t)\right], \tag{41}$$

where $g_n(t)$ is defined as follows:

$$\begin{aligned} g_n(t) \equiv \frac{\mathrm{d}f_n(t)}{\mathrm{d}t} &= q\mathrm{e}^{-\lambda_n^2 a^2 t} + \frac{A_{\mathrm{T_s}}\omega}{\lambda_n^4 a^4+\omega^2} \\ &\times [\lambda_n^2 a^2(\lambda_n^2 a^2 \mathrm{e}^{-\lambda_n^2 a^2 t} - \omega\sin\omega t) + \omega^2\cos\omega t]. \end{aligned} \tag{42}$$

Because there is a relation

$$\frac{\mathrm{d}T(0,t)}{\mathrm{d}t} = q + A_{\mathrm{T_s}}\omega\cos\omega t - \sum_{n=0}^{+\infty} h_n g_n(t), \tag{43}$$

from Eq. (40), there is a relation as follows:

$$c_{\mathrm{eff}} = c_p\frac{q + A_{\mathrm{T_s}}\omega\cos\omega t - \sum_{n=0}^{+\infty}\frac{K}{\kappa\lambda_n^2 l}h_n g_n(t)}{q + A_{\mathrm{T_s}}\omega\cos\omega t - \sum_{n=0}^{+\infty}h_n g_n(t)}. \tag{44}$$

Under steady-state condition, there is a similar expression of sample's effective specific heat

$$c_{\mathrm{eff}}^{(\mathrm{s})} = c_p\frac{q + A_{\mathrm{T_s}}\omega\ \cos\ \omega t - \sum_{n=0}^{+\infty}\frac{K}{\kappa\lambda_n^2 l}h_n g_n^{(\mathrm{s})}(t)}{q + A_{\mathrm{T_s}}\omega\ \cos\ \omega t - \sum_{n=0}^{+\infty}h_n g_n^{(\mathrm{s})}(t)}, \tag{44A}$$

where the used definition $g_n^{(\mathrm{s})}(t)$ is as follows:

$$\begin{aligned} g_n^{(\mathrm{s})}(t) \equiv \frac{\mathrm{d}f_n^{(s)}(t)}{\mathrm{d}t} &= \frac{A_{\mathrm{T_s}}\omega^2}{\lambda_n^4 a^4+\omega^2} \\ &\times (\omega\cos\omega t - \lambda_n^2 a^2\sin\omega t). \end{aligned} \tag{42A}$$

The expression in Eq. (44) is the effective specific heat of sample in TMDSC. With this expression, the exact value of real specific heat of sample can be obtained from the effective specific heat measured in TMDSC. From the expression of effective specific heat of sample, it is obvious that the effective specific heat of sample can vary with the variation of the modulate amplitude and modulated frequency.

Now, let us reconsider the example two. Considering an imaginary situation in which the thermal conductivity of the sample is infinite, i.e. $\kappa \rightarrow +\infty$. In this ultimate situation, the temperature gradients within the sample can be neglected. From the Eqs. (33) and (42) we know when κ tends to infinite, the value of h_n tends to zero and the value of $g_n\ (t)$ is a finite quantity, so we can easily obtain the relation $c_{\text{eff}} = c_p$ from Eq. (44). Only in the ultimate situation that the sample's thermal conductivity is so high that the temperature gradients within the sample can be neglected, the value of sample's effective specific heat in TMDSC equals to that of real specific heat.

From the above derivation, it is not difficult to know that if the sample's thermal conductivity is not so high that the temperature gradients within the sample cannot be neglected. In this general situation, the temperature gradients within the sample must be considered. The analytical theory here is far more complex in form than the current theories and we can anticipate that our analytical theory of TMDSC is more precise.

All these equations derived here will be verified by both TMDSC experiments and computer simulations. The detailed results will be offered in other articles.

5. Conclusion

The strict analytical temperature variation rule of platelike sample in TMDSC model derived here reveals the total variation rule of the platelike sample from its initial equilibrium state to its steady state. This theory is more general than the current TMDSC theories. Both current TMDSC theories and conventional DSC theories are included in our theory. The variation rules of some sample's physical quantities can be derived from this fundamental temperature variation rule. The obtained results show that reversible and irreversible heat flows, temperature lag, internal energy and effective specific heat of the platelike sample are functions of experimental conditions, such as modulated amplitude and modulated frequency. So if we use TMDSC to obtain the characteristics of the matter we must deal with the experimental data according to corresponding physical rules. In the general situation, the sample's thermal conductivity is not great enough, so the effects caused by temperature gradients cannot be omitted. All the experimental data obtained in the TMDSC must be dealt carefully with appropriate calibration methods such as considering the temperature gradients within the sample.

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