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Theory of general temperature modulated differential scanning calorimetry☆

En-Yong Ding[a,b,*], Rong-Shi Cheng[a]

[a]College of Material Science and Engineering, South China University of Technology, Guangzhou 510640, PR China
[b]Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, PR China

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Abstract

In the theory of general temperature modulated differential scanning calorimetry (GTMDSC), the modulated temperature of furnace accords with a random cyclically modulated rule and even a random non-cyclic rule. In this paper, the temperature variation rule of platelike sample in GTMDSC 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. Sinusoidal rule of modulated temperature is only a very special example of general cyclic modulated rules. 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 GTMDSC is the same as the current TMDSC theories. If the modulated part in temperature equals 0, it reverts to the conventional DSC situation, so all the results in the GTMDSC model derived in this article are automatically suitable for the conventional DSC situation and current TMDSC theories.

Keywords: General temperature modulated differential scanning calorimetry; Platelike sample; Temperature distribution; Random modulation of furnace temperature

1. Introduction

Since Reading invented the TMDSC [1,2], the apparatus of TMDSC has been commercialized successfully by TA instruments. Many apparatus companies developed their own TMDSC apparatus with various modulated rules, such as square wave, triangle wave and other sawtooth waves, etc. The non-linear heating rate in TMDSC causes many difficulties in the handling of data [3–14]. In this paper, we will develop a general temperature modulated differential scanning calorimetry (GTMDSC) theory, which can be applied to any TMDSC apparatus for data handling.

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 [15]. There

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* Corresponding author. Tel.: +86-20-8523-1035;
fax: +86-20-8523-1119.
E-mail address: dingey@mail.gic.ac.cn (E.-Y. Ding).

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are some TMDSC theories, in which the temperature-modulating modes are random cyclically modulated rules, such as sawtooth modulation [16,17]. But the temperature gradients within the sample are omitted in all these theories, so the approximate extents are rather large. Although there are some thermal analysis theories dealing with conventional DSC [18] and TMDSC [19,20] in which the temperature gradients in the sample are considered, there are also some obvious approximations in these theories. To minimize the measuring errors, and to explain the physical meanings of each eigen point and each eigen curve correctly, it is necessary to develop a GTMDSC theory in which the temperature gradients within the sample and random modulation of furnace temperature are considered.

For the 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 if the TMDSC apparatus is ideal. So the real sample can be taken as a plate, and the boundary effect caused by the finite sample size can be rationally omitted.

It must be pointed here that in the real TMDSC apparatus there are additional heat conducting paths between the measuring system and the sample pan [21,22]. So if the quantity of sample is too small, the measuring precision of current TMDSC apparatus will decrease. To enhance the measuring precision, it is necessary to calibrate the apparatus influence. In this article, we will focus on the theory of ideal heat-flux type TMDSC. The further theory of GTMDSC will be proposed later, in which the apparatus influence will be calibrated.

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

Because the sample shape studied in GTMDSC 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 the thermal conductivity of the sample at temperature T, ρ the mass density of sample at temperature T, c_p the specific heat 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.

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

$$\left(T - \frac{\kappa}{K}\frac{\partial T}{\partial x}\right)\bigg|_0 = T_s, \qquad \frac{\partial T}{\partial x}\bigg|_l = 0 \tag{2}$$

where K is the Newton's law constant, and where

$$T_s = T_0 + qt + T_{\text{Modulated}}(t) \tag{3}$$

$$T_{\text{Modulated}}(t) = \sum_{m=1}^{+\infty} A_m \sin m\omega_0 t + \sum_{m=0}^{+\infty} B_m \cos m\omega_0 t \tag{4}$$

where T_s is the program-controlled furnace temperature in GTMDSC model, T_0 the initial temperature of furnace, q the linear heating rate of furnace, ω_0 is the basic angular frequency, other modulated angular frequencies are $2\omega_0$, $3\omega_0$, $4\omega_0$, etc. which are, respectively, called double frequency, triple frequency, and fourfold frequency, etc. A_m and B_m are modulated amplitudes, respectively, corresponding to sine and cosine functions of various modulated angular frequencies. From the expression of $T_{\text{Modulated}}(t)$ it can be found clearly that any cyclic function can be taken as a linear overlap of sine and cosine functions of various modulated angular frequencies. Assume $T_{\text{Modulated}}(t)$ is a cyclic function in which the interval from $-p/2$ to $p/2$ is a modulation period, the radical angular frequency ω_0 is $2\pi/p$. Each coefficient in Eq. (4) can be decided as follows

$$A_m = \frac{\omega_0}{\pi}\int_{-\pi/\omega_0}^{\pi/\omega_0} T_{\text{Modulated}}(\tau) \sin m\omega_0 \tau \, d\tau \tag{4A}$$

$$B_0 = \frac{\omega_0}{2\pi}\int_{-\pi/\omega_0}^{\pi/\omega_0} T_{\text{Modulated}}(\tau)\,\mathrm{d}\tau \tag{4B}$$

$$B_m = \frac{\omega_0}{\pi}\int_{-\pi/\omega_0}^{\pi/\omega_0} T_{\text{Modulated}}(\tau)\cos m\omega_0\tau\,\mathrm{d}\tau, \quad (m \neq 0) \tag{4C}$$

Sample's initial condition is

$$T(x,0) = T_0 \tag{5}$$

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

Define :

$$T(x,t) = T_0 + qt + \sum_{m=1}^{+\infty} A_m \sin m\omega_0 t + \sum_{m=0}^{+\infty} B_m \cos m\omega_0 t + \Delta(x,t) \tag{6}$$

where $\Delta(x, t)$ is a correction function. Only in the extremely ideal situation that the thermal conductivity of the sample is infinite and the Newton's law constant is sufficiently large, the correction function $\Delta(x, t)$ is equal to 0. In the general situation, $\Delta(x, t)$ is not equal to 0, so the Eq. (1) can be changed into the following form:

$$\frac{\partial\Delta(x,t)}{\partial t} - a^2\frac{\partial^2\Delta(x,t)}{\partial x^2} = -q - \sum_{m=1}^{+\infty} m\omega_0 A_m \cos m\omega_0 t + \sum_{m=1}^{+\infty} m\omega_0 B_m \sin m\omega_0 t \tag{7}$$

The boundary condition (2) becomes

$$\left(\Delta - \frac{\kappa}{K}\frac{\partial\Delta}{\partial x}\right)\bigg|_0 = 0, \qquad \frac{\partial\Delta}{\partial x}\bigg|_l = 0 \tag{8}$$

and the initial condition (5) becomes

$$\Delta(x,0) = 0 \tag{9}$$

By using the method of impulse theorem and defining $\Delta(x,t) = \int_o^t v(x,t;\tau)\,\mathrm{d}\tau$, Eq. (7) becomes

$$\frac{\partial v(x,t)}{\partial t} - a^2\frac{\partial^2 v(x,t)}{\partial x^2} = 0 \tag{10}$$

The boundary condition (8) becomes

$$\left(v - \frac{\kappa}{K}\frac{\partial v}{\partial x}\right)\bigg|_0 = 0, \qquad \frac{\partial v}{\partial x}\bigg|_l = 0 \tag{11}$$

and the initial condition (9) becomes

$$v(x, t=\tau+0) = -q - \sum_{m=1}^{+\infty} mA_m\omega_0 \cos m\omega_0\tau + \sum_{m=1}^{+\infty} mB_m\omega_0 \sin m\omega_0\tau \tag{12}$$

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

$$\frac{1}{U}\frac{\mathrm{d}U}{\mathrm{d}t} = \frac{a^2}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} \tag{13}$$

The left side of Eq. (13) 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 $-\lambda^2a^2$, we get

$$\frac{1}{U}\frac{\mathrm{d}U}{\mathrm{d}t} = \frac{a^2}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} = -\lambda^2a^2 \tag{14}$$

In Eq. (14), the value of λ must have a positive real value. The reason is as follows:

$$X(x) = A\mathrm{e}^{\lambda\mathrm{i}x} + B\mathrm{e}^{-\lambda\mathrm{i}x}$$

To satisfy the boundary condition shown in Eq. (11), the parameters A and B must be equal to 0 at the same time. So the assumption λ being an imaginary number is wrong.

From these, the obtained solutions are

$$U = U(0)\mathrm{e}^{-\lambda^2a^2t} \tag{15}$$

$$X(x) = A\sin\lambda x + B\cos\lambda x \tag{16}$$

From a recent boundary condition $(X - (\kappa/K)(\partial X/\partial x))|_0 = 0$, we can obtain

$$B = \frac{\kappa}{K}A\lambda \tag{17}$$

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

$$A\lambda\cos\lambda l - B\lambda\sin\lambda l = 0 \tag{18}$$

Combine Eq. (17) with Eq. (18), we get

$$\lambda_n = \frac{K}{\kappa}ctg\lambda_n l, \quad n = 0, 1, 2, \ldots \tag{19}$$

that is to satisfy the boundary conditions, λ must be the roots of Eq. (19).

So we have a general solution

$$v(x,t;\tau) = \sum_{n=0}^{+\infty} C_n(\tau) e^{-\lambda_n^2 a^2 (t-\tau)} \left[\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right] \quad (20)$$

From initial condition

$$\sum_{n=0}^{+\infty} C_n(\tau)\left[\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right] = -q - \sum_{m=1}^{+\infty} mA_m\omega_0\cos m\omega_0\tau + \sum_{m=1}^{+\infty} mB_m\omega_0 \sin m\omega_0\tau$$

we get

$$C_n(\tau) = -\frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} \times \left(q + \sum_{m=1}^{+\infty} mA_m\omega_0\cos m\omega_0\tau - \sum_{m=1}^{+\infty} mB_m\omega_0\sin m\omega_0\tau\right) \quad (21)$$

where we have used orthogonal relation of the intrinsic function

$$C_n(\tau)\int_0^l ||X_n(x)||^2\,dx = -\left(q + \sum_{m=1}^{+\infty} mA_m\omega_0\cos m\omega_0\tau - \sum_{m=1}^{+\infty} mB_m\omega_0\sin m\omega_0\tau\right)\int_0^l X_n(x)\,dx \quad (22)$$

$$\int_0^l ||X_n(x)||^2\,dx = \frac{K^2 l + l\kappa^2\lambda_n^2 + \kappa K}{2K^2}, \quad \int_0^l X_n(x)\,dx = \frac{1}{\lambda_n} \quad (23)$$

So we have

$$v(x,t;\tau) = -\left(q + \sum_{m=1}^{+\infty} mA_m\omega_0\cos m\omega_0\tau - \sum_{m=1}^{+\infty} mB_m\omega_0\sin m\omega_0\tau\right) \times \sum_{n=0}^{+\infty}\frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} e^{-\lambda_n^2 a^2(t-\tau)} X_n(x) \quad (24)$$

Thus, we can obtain the correction function

$$\begin{aligned}\Delta(x,t) &= \int_0^t v(x,t;\tau)\,d\tau = \sum_{n=0}^{+\infty}\Delta_n(A,\omega,x,t) \\ &= -\sum_{n=0}^{+\infty}\frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} \times \left(\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right) \\ &\quad\times\left\{\frac{q}{\lambda_n^2 a^2}(1 - e^{-\lambda_n^2 a^2 t}) + \sum_{m=1}^{+\infty}\frac{mA_m\omega_0}{\lambda_n^4 a^4 + m^2\omega_0^2} \times [\lambda_n^2 a^2(\cos m\omega_0 t - e^{-\lambda_n^2 a^2 t}) + m\omega_0\sin m\omega_0 t] \right. \\ &\quad\left. + \sum_{m=1}^{+\infty}\frac{mB_m\omega_0}{\lambda_n^4 a^4 + m^2\omega_0^2} \times [m\omega_0(\cos m\omega_0 t - e^{-\lambda_n^2 a^2 t}) - \lambda_n^2 a^2 \sin m\omega_0 t]\right\}, \quad (0 \le x \le l, t \ge 0)\end{aligned} \quad (25)$$

Δ_n is defined as follows:

$$\begin{aligned}\Delta_n(A,\omega,x,t) &= -\frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)}\left(\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right) \\ &\quad\times\left\{\frac{q}{\lambda_n^2 a^2}(1 - e^{-\lambda_n^2 a^2 t}) + \sum_{m=1}^{+\infty}\frac{mA_m\omega_0}{\lambda_n^4 a^4 + m^2\omega_0^2} \times [\lambda_n^2 a^2(\cos m\omega_0 t - e^{-\lambda_n^2 a^2 t}) + m\omega_0\sin m\omega_0 t] \right. \\ &\quad\left. + \sum_{m=1}^{+\infty}\frac{mB_m\omega_0}{\lambda_n^4 a^4 + m^2\omega_0^2}[m\omega_0(\cos m\omega_0 t - e^{-\lambda_n^2 a^2 t}) - \lambda_n^2 a^2 \sin m\omega_0 t]\right\}, \quad (0 \le x \le l, t \ge 0)\end{aligned} \quad (26)$$

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

Finally, we have

$$\begin{aligned}T(x,t) &= T_0 + qt + \sum_{m=1}^{+\infty} A_m \sin m\omega_0 t + \sum_{m=0}^{+\infty} B_m\cos m\omega_0 t + \Delta(x,t) \\ &= T_0 + qt + \sum_{m=1}^{+\infty} A_m\sin m\omega_0 t\end{aligned}$$

$$+\sum_{m=0}^{+\infty} B_m \cos m\omega_0 t - \sum_{n=0}^{+\infty} \frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} \times \left(\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right) \times \left\{ \frac{q}{\lambda_n^2 a^2}(1 - e^{-\lambda_n^2 a^2 t}) + \sum_{m=1}^{+\infty} \frac{mA_m\omega_0}{\lambda_n^4 a^4 + m^2\omega_0^2} \times [\lambda_n^2 a^2(\cos m\omega_0 t - e^{-\lambda_n^2 a^2 t}) + m\omega_0 \sin m\omega_0 t] + \sum_{m=1}^{+\infty} \frac{mB_m\omega_0}{\lambda_n^4 a^4 + m^2\omega_0^2}[m\omega_0(\cos m\omega_0 t - e^{-\lambda_n^2 a^2 t}) - \lambda_n^2 a^2 \sin m\omega_0 t] \right\} \tag{27}$$

$$T(x,t) = T_0 + qt + \sum_{m=1}^{+\infty} A_m \sin m\omega_0 t + \sum_{m=0}^{+\infty} B_m \cos m\omega_0 t - \sum_{n=0}^{+\infty} \frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} \times \left(\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right) \tag{27A}$$

where $\alpha_{n,m}$ is defined as

$$\alpha_{n,m} \equiv \arcsin\frac{\lambda_n^2 a^2}{\sqrt{\lambda_n^4 a^4 + m^2\omega_0^2}} \tag{28}$$

and $\beta_{n,m}$ is defined as

$$\beta_{n,m} \equiv \arccos\frac{m\omega}{\sqrt{\lambda_n^4 a^4 + m^2\omega_0^2}} \tag{28A}$$

Eqs. (27) and (27A) is the temperature distribution rule within the platelike sample in GTMDSC model, and this is the fundamental and most important equation of our GTMDSC theory.

If the time is long enough, the item $e^{-\lambda_n^2 a^2 t}$ becomes so small that it can be neglected. In this case the sample is in the steady state, and the Eqs. (27) and (27A) can be rewritten as

$$T^{(s)}(x,t) = T_0 + qt + \sum_{m=1}^{+\infty} A_m \sin m\omega_0 t + \sum_{m=0}^{+\infty} B_m \cos m\omega_0 t - \sum_{n=0}^{+\infty} \frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} \times \left(\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right) \times \left\{ \frac{q}{\lambda_n^2 a^2}(1 - e^{-\lambda_n^2 a^2 t}) + \sum_{m=1}^{+\infty} \frac{mA_m\omega_0}{\lambda_n^4 a^4 + m^2\omega_0^2} \times [\lambda_n^2 a^2 \cos m\omega_0 t + m\omega_0 \sin m\omega_0 t] + \sum_{m=1}^{+\infty} \frac{mB_m\omega_0}{\lambda_n^4 a^4 + m^2\omega_0^2} \times [m\omega_0 \cos m\omega_0 t - \lambda_n^2 a^2 \sin m\omega_0 t] \right\} \tag{27B}$$

$$T^{(s)}(x,t) = T_0 + qt + \sum_{m=1}^{+\infty} A_m \sin m\omega_0 t - \sum_{n=0}^{+\infty} \frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} \times \left(\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right) \times \left\{ \frac{q}{\lambda_n^2 a^2}(1 - e^{-\lambda_n^2 a^2 t}) + \sum_{m=1}^{+\infty} \frac{mA_m\omega_0}{\sqrt{\lambda_n^4 a^4 + m^2\omega_0^2}} \times \sin(m\omega_0 t + \alpha_{n,m}) + \sum_{m=1}^{+\infty} \frac{mB_m\omega_0}{\sqrt{\lambda_n^4 a^4 + m^2\omega_0^2}} \times \cos(m\omega_0 t + \beta_{n,m}) \right\}, \quad (0 \le x \le l, t \ge 0) \tag{27C}$$

From Eqs. (27) and (27A), 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. If ω_0 and A_1 are not 0 but all other modulated amplitudes are 0, it reverts to the situation that the modulated mode is sinusoidal, i.e. common TMDSC [23]. When all modulated amplitudes equal 0, it reverts to the conventional DSC situation, so the temperature distribution rule within the sample in the GTMDSC model derived in this article is automatically suitable for the conventional DSC situation and common TMDSC.

The temperature gradients within the sample can be derived from the basic Eqs. (27) and (27A)

$$\frac{dT(x,t)}{dx} = -\sum_{n=0}^{+\infty} \frac{2K^2}{K^2 l + l\kappa^2\lambda_n^2 + \kappa K} \times \left(\cos\lambda_n x - \frac{\kappa\lambda_n}{K}\sin\lambda_n x\right) \times \left\{ \frac{q}{\lambda_n^2 a^2}(1 - e^{-\lambda_n^2 a^2 t}) + \sum_{m=1}^{+\infty} \frac{mA_m\omega_0}{\lambda_n^4 a^4 + m^2\omega_0^2} \times [\lambda_n^2 a^2(\cos m\omega_0 t - e^{-\lambda_n^2 a^2 t}) + m\omega_0 \sin m\omega_0 t] + \sum_{m=1}^{+\infty} \frac{mB_m\omega_0}{\lambda_n^4 a^4 + m^2\omega_0^2} \times [m\omega_0(\cos m\omega_0 t - e^{-\lambda_n^2 a^2 t}) - \lambda_n^2 a^2 \sin m\omega_0 t] \right\} \quad (29)$$

$$\frac{dT(x,t)}{dx} = -\sum_{n=0}^{+\infty} \frac{2K^2}{K^2 l + l\kappa^2\lambda_n^2 + \kappa K} \times \left(\cos\lambda_n x - \frac{\kappa\lambda_n}{K}\sin\lambda_n x\right) \times \left\{ \frac{q}{\lambda_n^2 a^2}(1 - e^{-\lambda_n^2 a^2 t}) + \sum_{m=1}^{+\infty} \frac{mA_m\omega_0}{\sqrt{\lambda_n^4 a^4 + m^2\omega_0^2}} \sin(m\omega_0 t + \alpha_{n,m}) - \sum_{m=1}^{+\infty} \frac{mA_m\omega_0\lambda_n^2 a^2 e^{-\lambda_n^2 a^2 t}}{\lambda_n^4 a^4 + m^2\omega_0^2} + \sum_{m=1}^{+\infty} \frac{mB_m\omega_0}{\sqrt{\lambda_n^4 a^4 + m^2\omega_0^2}} \cos(m\omega_0 t + \beta_{n,m}) - \sum_{m=1}^{+\infty} \frac{m^2 B_m\omega_0^2 e^{-\lambda_n^2 a^2 t}}{\lambda_n^4 a^4 + m^2\omega_0^2} \right\}, \quad (0 \le x \le l, t \ge 0) \quad (29A)$$

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

The further discussion of Eqs. (27) and (27B) will give rise to many interesting 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.

3.1. 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:

$$\delta T \equiv T(0,t) - T_s(t) = T(0,t) - T_0 - qt - A_{T_s}\sin\omega t \quad (30)$$

According to Eq. (27), Eq. (30) has the form

$$\delta T \equiv T(0,t) - T_s(t) = -\sum_{n=0}^{+\infty} h_n f_n(t) \quad (31)$$

where some definitions are made in the following

$$h_n \equiv \frac{2K\kappa}{K^2 l + l\kappa^2\lambda_n^2 + \kappa K} \quad (32)$$

$$f_n(t) \equiv \frac{q}{\lambda_n^2 a^2}(1 - e^{-\lambda_n^2 a^2 t}) + \sum_{m=1}^{+\infty} \frac{mA_m\omega_0}{\lambda_n^4 a^4 + m^2\omega_0^2} \times [\lambda_n^2 a^2(\cos m\omega_0 t - e^{-\lambda_n^2 a^2 t}) + m\omega_0 \sin m\omega_0 t] + \sum_{m=1}^{+\infty} \frac{mB_m\omega_0}{\lambda_n^4 a^4 + m^2\omega_0^2} [m\omega_0(\cos m\omega_0 t - e^{-\lambda_n^2 a^2 t}) - \lambda_n^2 a^2 \sin m\omega_0 t] \quad (33)$$

Eq. (31) is the generalized temperature lag rule of the platelike sample in GTMDSC.

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

$$f_n^{(s)}(t) \equiv \frac{q}{\lambda_n^2 a^2} + \sum_{m=1}^{+\infty} \frac{mA_m\omega_0}{\lambda_n^4 a^4 + m^2\omega_0^2} [\lambda_n^2 a^2 \cos m\omega_0 t + m\omega_0 \sin m\omega_0 t] + \sum_{m=1}^{+\infty} \frac{mB_m\omega_0}{\lambda_n^4 a^4 + m^2\omega_0^2} \times [m\omega_0 \cos m\omega_0 t - \lambda_n^2 a^2 \sin m\omega_0 t] \quad (33A)$$

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

$$\delta T^{(s)} = -\sum_{n=0}^{+\infty} h_n f_n^{(s)}(t) \tag{34A}$$

3.2. 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

$$HF_{rev} = \frac{dQ_s}{dt} = -K\delta T = K\sum_{n=0}^{+\infty} h_n f_n(t) \tag{35}$$

where Q_s is the heat energy absorbed by the sample.

Irreversible heat flow is

$$HF_{n.r.} = \langle HF \rangle - HF_{rev} \tag{36}$$

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

$$HF_{rev}^{(s)} = \frac{dQ_s^{(s)}}{dt} = -K\delta T^{(s)} = K\sum_{n=0}^{+\infty} h_n f_n^{(s)}(t) \tag{35A}$$

Irreversible heat flow is

$$HF_{n.r.}^{(s)} = \langle HF^{(s)} \rangle - HF_{rev}^{(s)} \tag{36A}$$

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

3.3. 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

$$E(t) \equiv \frac{\rho c_p}{l}\int_0^l T(x,t)\,dx$$

$$E(t) = \rho c_p\left[\left(T_0 + qt + \sum_{m=1}^{+\infty} A_m \sin m\omega_0 t + \sum_{m=0}^{+\infty} B_m \cos m\omega_0 t\right) - \sum_{n=0}^{+\infty} \frac{2K^2}{\lambda_n^2 l(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} f_n(t)\right]$$

$$E(t) = \rho c_p\left[\left(T_0 + qt + \sum_{m=1}^{+\infty} A_m \sin m\omega_0 t + \sum_{m=0}^{+\infty} B_m \cos m\omega_0 t\right) - \sum_{n=0}^{+\infty} \frac{K}{\kappa\lambda_n^2 l} h_n f_n(t)\right] \tag{37}$$

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

$$E^{(s)}(t) \equiv \frac{\rho c_p}{l}\int_0^l T^{(s)}(x,t)\,dx = \rho c_p\left[\left(T_0 + qt + \sum_{m=1}^{+\infty} A_m \sin m\omega_0 t + \sum_{m=0}^{+\infty} B_m \cos m\omega_0 t\right) - \sum_{n=0}^{+\infty} \frac{K}{\kappa\lambda_n^2 l} h_n f_n^{(s)}(t)\right] \tag{37A}$$

3.4. 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 GTMDSC 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 GTMDSC experiment is the temperature of the sample's outer surface, the measured specific heat in GTMDSC is not as 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 GTMDSC.

The definition of effective specific heat is

$$c_{eff} \equiv \frac{1}{\rho}\frac{dE(t)}{dT(0,t)} \tag{38}$$

Eq. (38) can also be written as

$$c_{eff} = \frac{1}{\rho}\frac{dE(t)}{dt}\frac{dt}{dT(0,t)} \tag{39}$$

In the general situation, from Eq. (37), there is a following relation:

$$\frac{\mathrm{d}E(t)}{\mathrm{d}t} = \rho c_p\left[q + \sum_{m=1}^{+\infty} m\omega_0(A_m\cos m\omega_0 t - B_m\sin m\omega_0 t) - \sum_{n=0}^{+\infty}\frac{K}{\kappa\lambda_n^2 l}h_n g_n(t)\right] \qquad (40)$$

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

$$g_n(t) \equiv \frac{\mathrm{d}f_n(t)}{\mathrm{d}t} = q\mathrm{e}^{-\lambda_n^2 a^2 t} + \sum_{m=1}^{+\infty}\frac{mA_m\omega_0}{\lambda_n^4 a^4 + m^2\omega_0^2}[\lambda_n^2 a^2(\lambda_n^2 a^2 \mathrm{e}^{-\lambda_n^2 a^2 t} - m\omega_0 \sin m\omega_0 t) + m^2\omega_0^2\cos m\omega_0 t] + \sum_{m=1}^{+\infty}\frac{m^2 B_m\omega_0^2}{\lambda_n^4 a^4 + m^2\omega_0^2}[\lambda_n^2 a^2 \mathrm{e}^{-\lambda_n^2 a^2 t} - m\omega_0 \sin m\omega_0 t - \lambda_n^2 a^2 \cos m\omega_0 t] \qquad (41)$$

Because there is a relation

$$\frac{\mathrm{d}T(0,t)}{\mathrm{d}t} = q + \sum_{m=1}^{+\infty} m\omega_0(A_m\cos m\omega_0 t - B_m\sin m\omega_0 t) - \sum_{n=0}^{+\infty} h_n g_n(t) \qquad (42)$$

from Eq. (39), there is a relation as follows:

$$= +\sum_{m=1}^{+\infty}\frac{m^2 A_m\omega_0^2}{\lambda_n^4 a^4 + m^2\omega_0^2}\times[m\omega_0\cos m\omega_0 t - \lambda_n^2 a^2 \sin m\omega_0 t] - \sum_{m=1}^{+\infty}\frac{m^2 B_m\omega_0^2}{\lambda_n^4 a^4 + m^2\omega_0^2}\times[m\omega_0\sin m\omega_0 t + \lambda_n^2 a^2 \cos m\omega_0 t] \qquad (41A)$$

The expression in Eq. (43) is the effective specific heat of sample in GTMDSC. With this expression, the exact value of real specific heat of sample can be obtained from the effective specific heat measured in GTMDSC. 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 modulated mode.

Now, let us reconsider an imaginary situation in which the thermal conductivity of the sample is infinite, i.e. $\kappa \to +\infty$. In this ultimate situation, the temperature gradients within the sample can be neglected. From the Eqs. (32) and (41) we know when κ tends to infinite, the value of h_n tends to 0 and the value of $g_n(t)$ is a finite quantity, so we can easily obtain the relation $c_{\mathrm{eff}} = c_p$ from Eq. (43). 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 GTMDSC equals to that of real specific heat.

$$c_{\mathrm{eff}}(t) = c_p\frac{q + \sum_{m=1}^{+\infty} m\omega_0(A_m\cos m\omega_0 t - B_m\sin m\omega_0 t) - \sum_{n=0}^{+\infty}(K/\kappa\lambda_n^2 l)h_n g_n(t)}{q + \sum_{m=1}^{+\infty} m\omega_0(A_m\cos m\omega_0 t - B_m\sin m\omega_0 t) - \sum_{n=0}^{+\infty} h_n g_n(t)} \qquad (43)$$

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

$$c_{\mathrm{eff}}^{(\mathrm{s})}(t) = c_p\frac{q + \sum_{m=1}^{+\infty} m\omega_0(A_m\cos m\omega_0 t - B_m\sin m\omega_0 t) - \sum_{n=0}^{+\infty}(K/\kappa\lambda_n^2 l)h_n g_n^{(\mathrm{s})}(t)}{q + \sum_{m=1}^{+\infty} m\omega_0(A_m\cos m\omega_0 t - B_m\sin m\omega_0 t) - \sum_{n=0}^{+\infty} h_n g_n^{(\mathrm{s})}(t)} \qquad (43\mathrm{A})$$

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

$$g_n^{(\mathrm{s})}(t) \equiv \frac{\mathrm{d}f_n^{(\mathrm{s})}(t)}{\mathrm{d}t}$$

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.

4. Discussion on the GTMDSC theory

To verify the generality of GTMDSC theory, now we study following very special examples.

Example 1. Square wave modulation

Assume there is a square wave frequency diagram of the furnace temperature

$$T_{\text{Modulated}}(t) = \begin{cases} +T_A & (2kt_0, (2k+1)t_0), \\ -T_A & ((2k-1)t_0, 2kt_0), \end{cases}$$

where $k = 0, \pm 1, \pm 2, \pm 3, \ldots$

In the whole time from $-\infty$ to $+\infty$, the square wave is an odd cyclic function of time t as shown in Fig. 1. So it can be evolved into Fourier series, in which each coefficient B_m is 0.

The real time of research or study is $t \geq 0$, above treatment will not influence the validity of the final result.

From Fig. 1, it can be known that $2t_0$ is a period, so

$$\omega_0 \equiv \frac{2\pi}{2t_0} = \frac{\pi}{t_0}$$

The modulation of temperature can be evolved into

$$T_{\text{Modulated}}(t) = \sum_{m=1}^{+\infty} A_m \sin m\omega_0 t$$

where the efficient A_m is decided in the following:

$$\begin{aligned} A_m &= \frac{2\omega_0}{\pi} \int_0^{\pi/\omega_0} T_{\text{Modulated}}(\tau) \sin m\omega_0\tau \, d\tau \\ &= \frac{2\omega_0 T_A}{\pi} \int_0^{\pi/\omega_0} \sin m\omega_0\tau \, d\tau \\ &= -\frac{2T_A}{m\pi} [\cos m\omega_0\tau]_0^{\pi/\omega_0} = -\frac{2T_A}{m\pi} [(-1)^m - 1] \\ &= \begin{cases} 0 & (m \text{ is even}) \\ \dfrac{4T_A}{m\pi} & (m \text{ is odd}) \end{cases} \end{aligned}$$

The Fourier series of square wave as shown in Fig. 1 is as follows:

$$T_{\text{Modulated}}(t) = \frac{4T_A}{\pi}\left(\sin \omega_0 t + \frac{1}{3}\sin 3\omega_0 t + \frac{1}{5}\sin 5\omega_0 t + \frac{1}{7}\sin 7\omega_0 t + \ldots\right)$$

Fig. 2 shows composite waves of the Fourier series, curves of tiny lines represent the waves, respectively, composed by first item, the first two series items, ..., the first five series items, and the curve of bold line represents the wave composed by the first six series items. From Fig. 2 we know that with the increase of series item, the composed wave gradually approaches the real square wave.

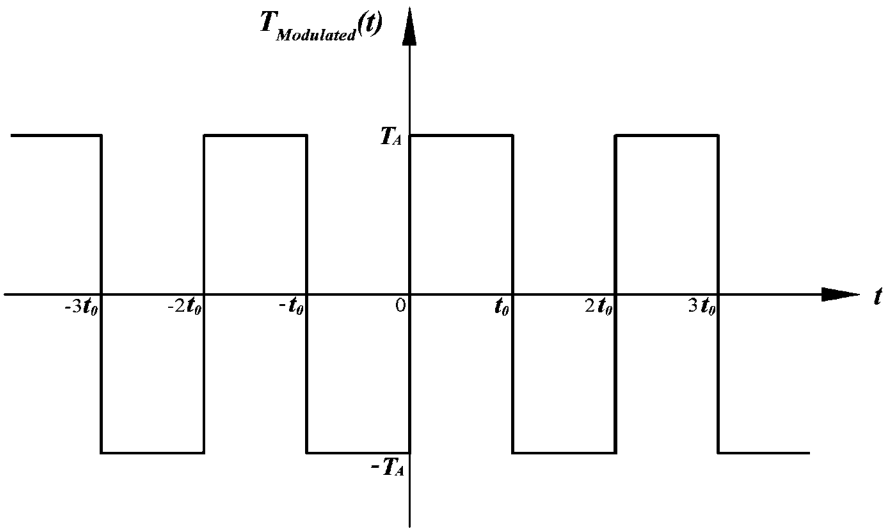

Fig. 1. Square wave modulation.

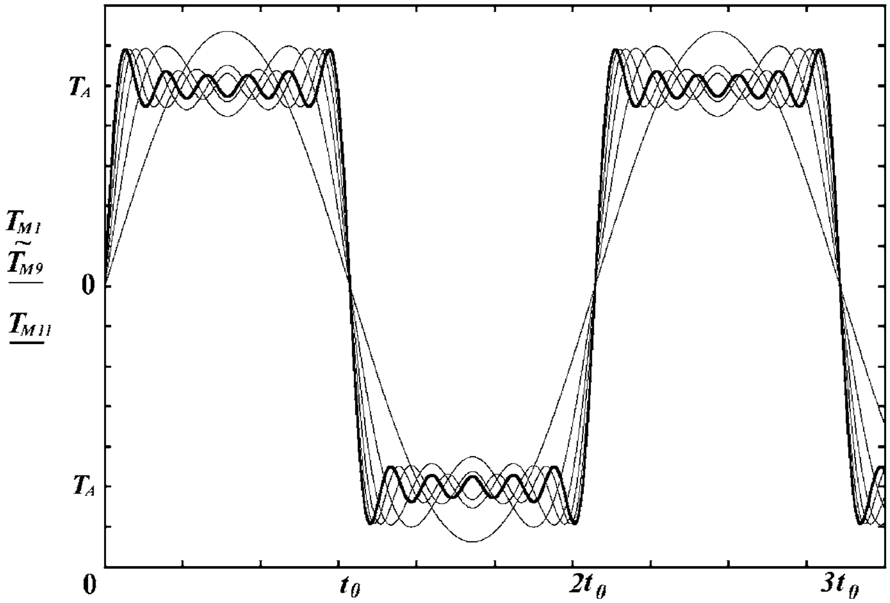

Fig. 2. Waves of the Fourier series composed by front series items.

The frequency diagram of square wave is composed of basic harmonic wave and odd harmonic waves. The amplitudes of harmonic waves are inversely proportional to their ranks, so the convergency speed of this series is very slow. In the real usage, sufficient items should be remained to ensure the composite wave is not distorted.

Substituting coefficients A_m and B_m into corresponding expressions, the temperature variation rule and the variation rules of other physical parameters of platelike sample can be obtained.

Example 2. Sawtooth (triangle) wave modulation

In a period $[-t_0, t_0]$, $T_{\text{Modulated}}(t)$ can be expressed

$$T_{\text{Modulated}}(t) = \xi|t|, \quad \xi > 0$$

In the whole time from $-\infty$ to $+\infty$, the sawtooth wave is an even cyclic function of time t as shown in Fig. 3. So it can be evolved into Fourier series, in which each coefficient A_m is 0. The real time of research or study is $t \geq 0$, above treatment will not influence the validity of the final result.

From Fig. 3, it can be known that $2t_0$ is a period, so

$$\omega_0 \equiv \frac{2\pi}{2t_0} = \frac{\pi}{t_0}$$

$$T_{\text{Modulated}}(t) = \sum_{m=0}^{+\infty} B_m \cos m\omega_0 t$$

$$B_0 = \frac{\xi}{t_0}\int_0^{t_0} \tau \, d\tau = \frac{\pi}{2\omega_0}$$

$$\begin{aligned} B_m &= \frac{\omega_0}{\pi}\int_{-(\pi/\omega_0)}^{(\pi/\omega_0)} T_{\text{Modulated}}(\tau)\cos m\omega_0\tau \, d\tau \\ &= \frac{2\xi\omega_0}{\pi}\int_0^{(\pi/\omega_0)} \tau \cos m\omega_0\tau \, d\tau \\ &= \frac{2\xi}{m^2\omega_0\pi}[\cos m\omega_0\tau + m\omega_0\tau \sin m\pi\tau]|_0^{\pi/\omega_0} \\ &= \frac{2\xi}{m^2\omega_0\pi}[(-1)^m - 1] \\ &= \begin{cases} 0 & (m \text{ is a non-zero even}) \\ -\dfrac{4\xi}{m^2\omega_0\pi} & (m \text{ is a odd } 2k+1, k \geq 0) \end{cases} \end{aligned}$$

So the Fourier series of sawtooth wave shown in Fig. 3 is as follows:

$$T_{\text{Modulated}}(t) = \frac{\pi\xi}{2\omega_0} - \frac{4\xi}{\omega_0\pi}\sum_{k=0}^{+\infty}\frac{1}{(2k+1)^2} \times \cos(2k+1)\omega_0 t$$

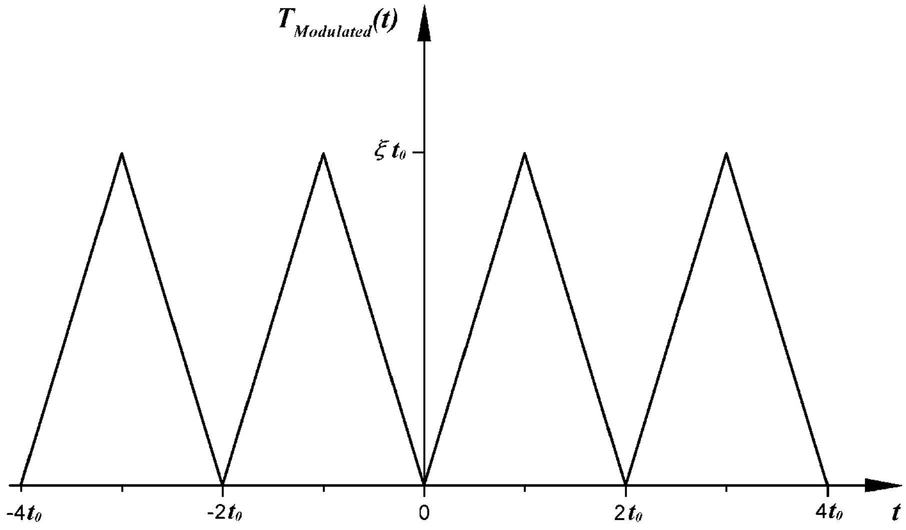

Fig. 3. Sawtooth (triangle) wave modulation.

Fig. 4 shows composite waves of the above Fourier series, curves of tiny lines represent the waves composed by first item, the first two items, . . ., the first five items, and the curve of bold line represents the wave composed by the first six series items. From Fig. 4 we know that with the increase of series items, the composed wave gradually approaches the real sawtooth wave.

The shape of the sawtooth wave is much similar to that of cosine function. The amplitudes of harmonic waves are inversely proportional to the square of their ranks, so the convergence speed of this series is very

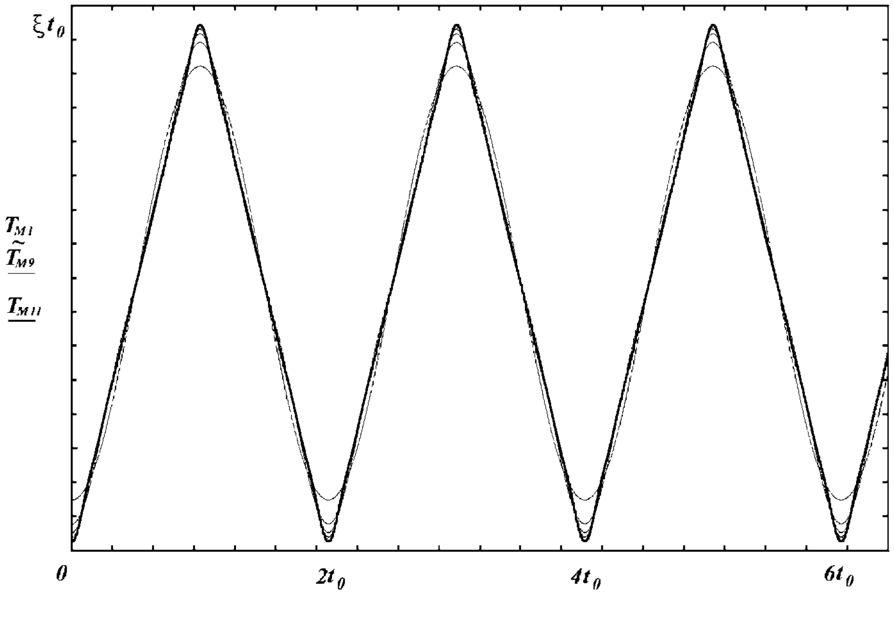

Fig. 4. Sawtooth waves of the Fourier series composed by front series items.

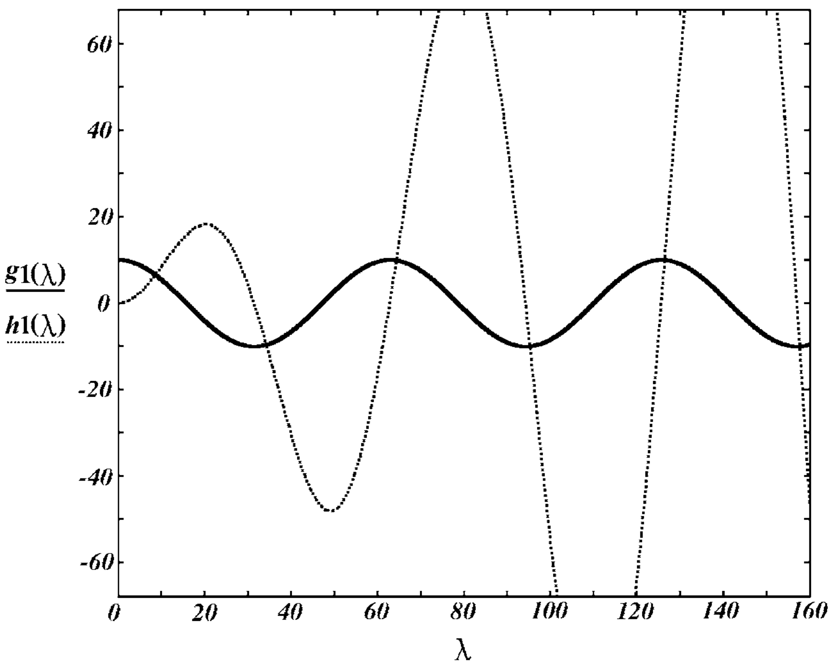

Fig. 5. The distribution of front six roots of Eq. (19).

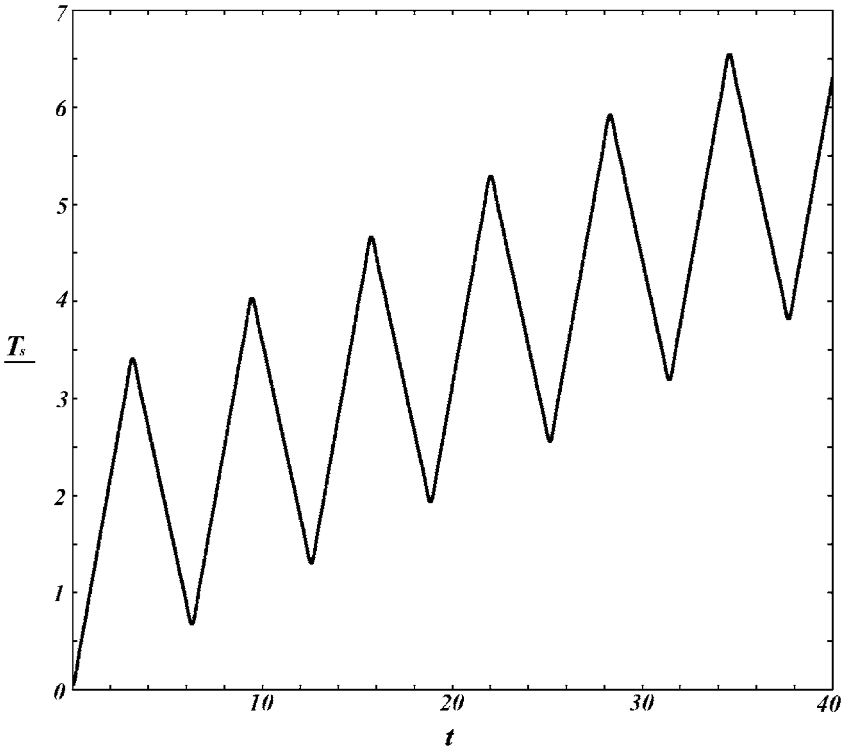

Fig. 6. The variation rule of furnace temperature.

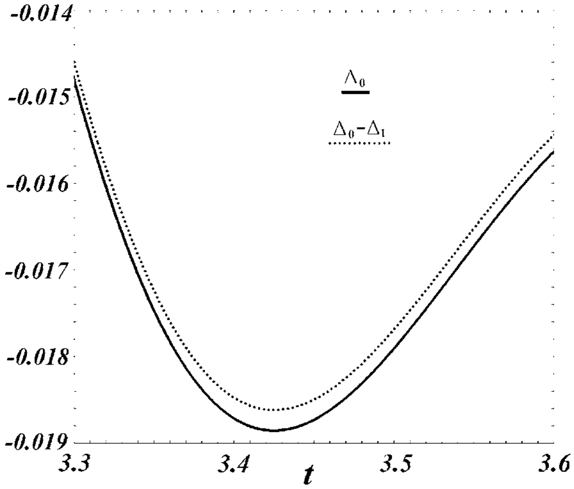

Fig. 7. Variation rule of 0th correction item and its difference to 1th item.

fast. In the real usage, the front six items are sufficient to ensure that the composite wave is not distorted.

Substituting coefficients A_m and B_m into corresponding expressions, the temperature variation rule and the variation rules of other physical parameters of platelike sample can be obtained.

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 samples depth l is 0.1.

Assume $g1(\lambda) = (K/\kappa)\cos(\lambda l)$, $h1(\lambda) = \lambda \sin(\lambda l)$, in the same figure we, respectively, draw the lines $g1(\lambda)$ and $h1(\lambda)$ for λ, shown in Fig. 5. The values of λ corresponding to the intersecting points are the roots of Eq. (19). So we can get the roots: $\lambda_0 = 8.6033357$, $\lambda_1 = 34.25618387$, $\lambda_2 = 64.3729811$, $\lambda_3 = 95.29334263$, $\lambda_4 = 126.45287025$, $\lambda_5 = 157.71284669$, etc.

Assume the Newton's law constant K is 10, ξ is 1, and the modulated basic frequency ω_0 is 1, which means the semi-period t_0 is π. We can get a relation between the temperature of furnace T_s and the time t as shown in Fig. 6.

Fig. 7 shows the variation rule of 0th correction item and its difference to 1th correction item with time t. From Fig. 7 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 the 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%.

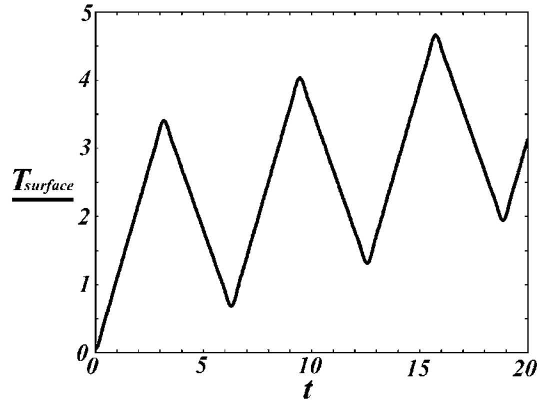

Fig. 8. Variation rule of sample's surface temperature lag.

Thus, using Eq. (31) we can obtain the variation rule of sample's surface temperature lag, as shown in Fig. 8.

Contrasting Figs. 6 and 8, it seems that the sample's surface temperature varies synchronously with the variation of furnace temperature. But after detailed study, we still can find differences. Drawing the variation of furnace temperature and sample's surface temperature in the same figure and amplifying the local part, shown in Fig. 9, it can be observed that there is an obvious temperature lag of sample's surface. The main cause of this temperature lag is the limited value of sample's thermal conductivity. If the thermal conductivity of sample is infinite and the pan's Newton's law constant is sufficient large, form Eq. (25) it can be known the correction function is 0, so the temperature of sample is equal to that of furnace, i.e. there is no temperature lag phenomenon.

Increasing the value of sample's thermal conductivity and remaining other physical quantities constant, in Fig. 10 we can find that the sample's surface temperature lag can be diminished obviously. The number denoted in the brackets in Fig. 10 is corresponding to sample's thermal conductivity.

Similarly, increasing the value of the pan's Newton's law constant and remaining other physical quantities constant, in Fig. 11 we can find that the sample's surface temperature lag can also be diminished obviously. The number denoted in the brackets in Figs. 11 and 12 is corresponding to pan's Newton's law constant.

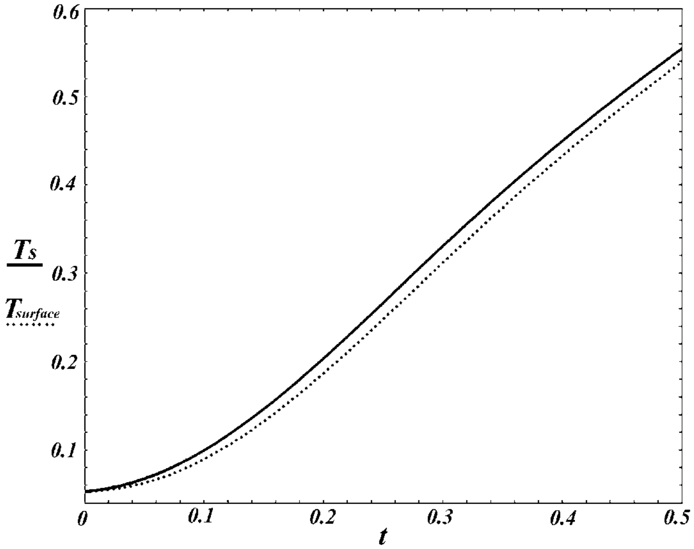

Fig. 9. Variation of sample's surface temperature and furnace temperature.

5. GTMDSC theory for any modulated functions of temperature

At above, we have studied the GTMDSC theory for any random cyclically modulated function of temperature. The obtained theory is rather general. But there is a more general situation, in which the modulated function of temperature is random and may be non-cyclic. This is a more challenging project, to which we often face in the real thermal

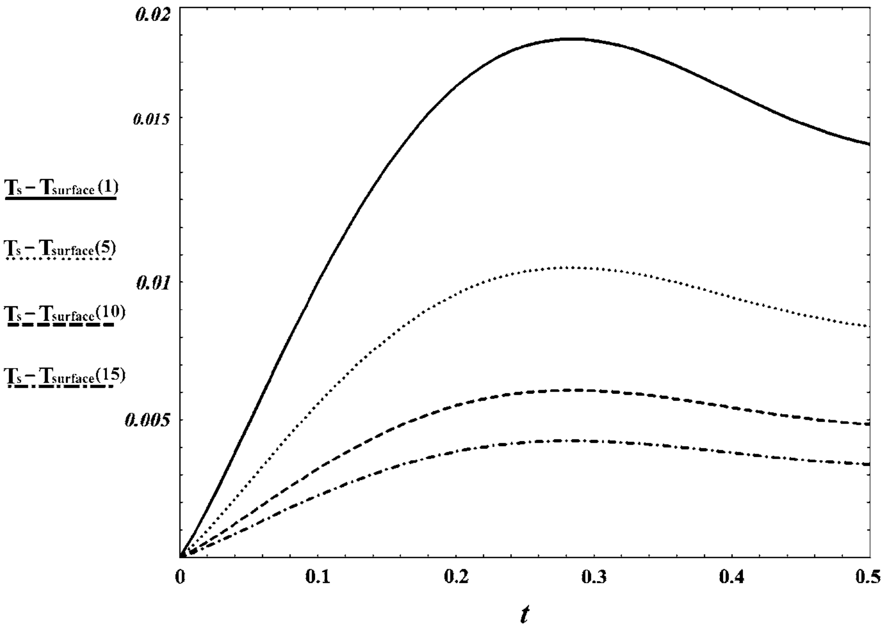

Fig. 10. Relationship between the sample's temperature lag and its thermal conductivity.

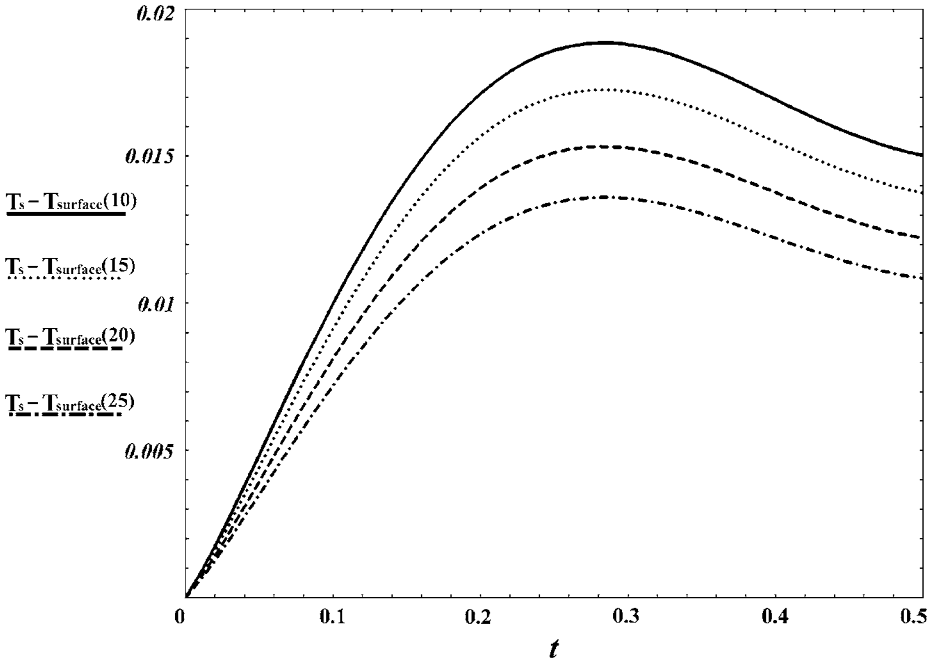

Fig. 11. Relationship between the sample's temperature lag and its pan's Newton's law constant.

analysis process. Because of lacking corresponding theory, this difficult project has always been shunned. For example, in the experimental process of traditional DSC, the furnace temperature is controlled by program. Theoretically, the furnace temperature should rise with perfect linear rule. But, actually, to all the DSC apparatus, the precision will not be so high. Especially, in the initial time of heating process, because of the thermal inertia of furnace, the heating rate is not exactly the same. Sometime in the initial heating stage, there is a fluctuation in heating rate, which results in the obvious protuberance in the

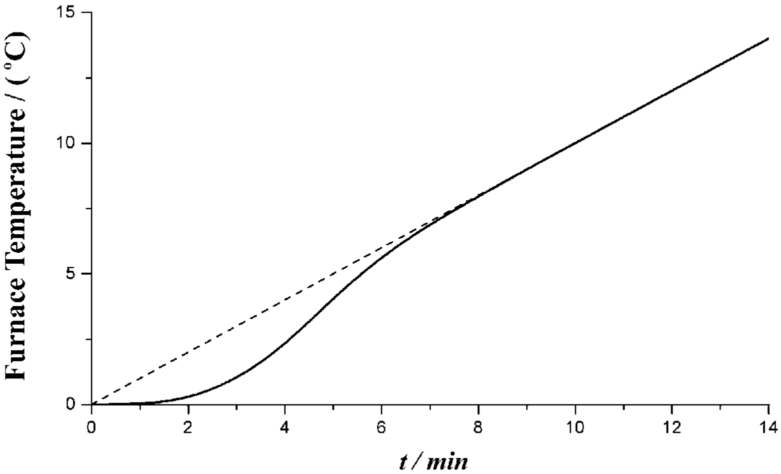

Fig. 12. Real heating rule of furnace temperature.

initial curve of DSC diagram. The nicer the thermal analysis apparatus, the smaller the protuberance. Actually, almost no apparatus can totally eliminate this protuberance. In the current DSC apparatus, this protuberance phenomenon is still serious. Many experienced thermal analyzers discard this protuberance part of the thermal diagram and only use the posterior part of diagram, which corresponds to the stable heating rate. If someone want to detect the physical properties at low temperature, to avoid the disturbance of initial protuberance, he must cool the sample to lower temperature which cause high cost and inconvenience in real operation process. The most serious result is that the discard of the initial curve of thermal diagram will result in the loss of important information, which is contained in the initial curve.

Based on our previous study of GTMDSC theory, through appropriate treatment, now we are totally possible to develop a universal thermal theory, which refers to the random temperature modulation, and to obtain strict analytical expression of the temperature variation rule of platelike sample.

Now, we deal with a representative example.

Without losing generality, assume the programmed heating rate of furnace is 1 K/min.

The Fig. 13 shows the variation rule of furnace temperature in a popular DSC experimental process in the whole time interval, 0 to t_{max}. From this diagram we know the variation rule of furnace temperature is non-linear and non-cyclic.

We also can obtain the real heating rate of furnace temperature (shown in Fig. 13) and non-linear modulation of furnace temperature (shown in Fig. 14).

In following we will make some technical treatments on the non-linear modulation of furnace temperature. At first, analytical continuation can be made on the whole time axis, as shown in Fig. 15. From Fig. 15, the non-linear modulation rule of furnace temperature is only taken as part of a cyclic modulation function in the whole time. In principle, if a part of the cyclic modulation function is the same as the real modulation rule of temperature, the various cyclic modulation functions can be right. Figs. 15 and 16, respectively, show two simplest cyclic functions, in which only one period wave is depicted. In Fig. 15 it is an odd cyclic function and in Fig. 16 it is an even cyclic function.

After above technical treatment, for a former random non-linear modulation of temperature, the whole theory of random cyclically modulated temperature also can be used. So we can obtain strict analytical solution for any modulation of temperature. Thus, this difficult problem of DSC can be solved satisfactorily. The method described here is very important to the calibration of DSC apparatus. Our GTMDSC theory makes it possible from whole thermal diagram to obtain useful information as much as possible.

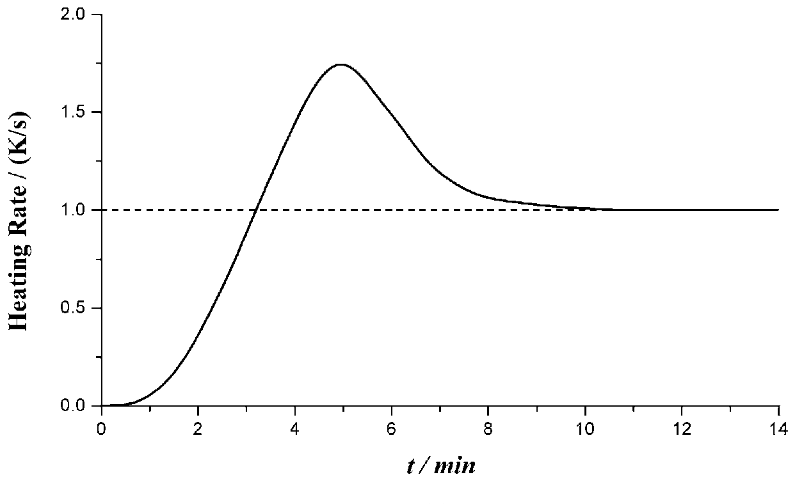

Fig. 13. Real heating rate of furnace temperature.

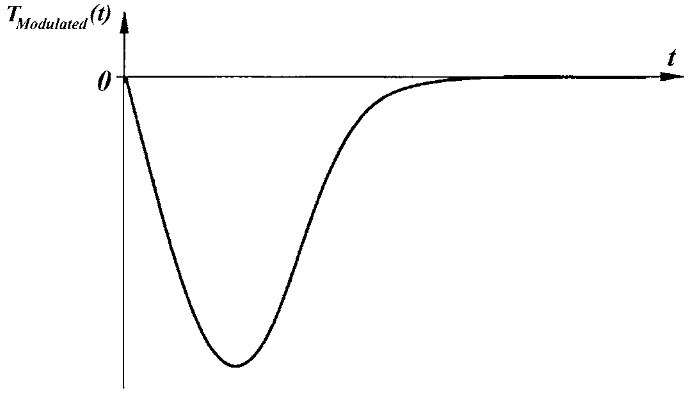

Fig. 14. Non-linear modulation of furnace temperature.

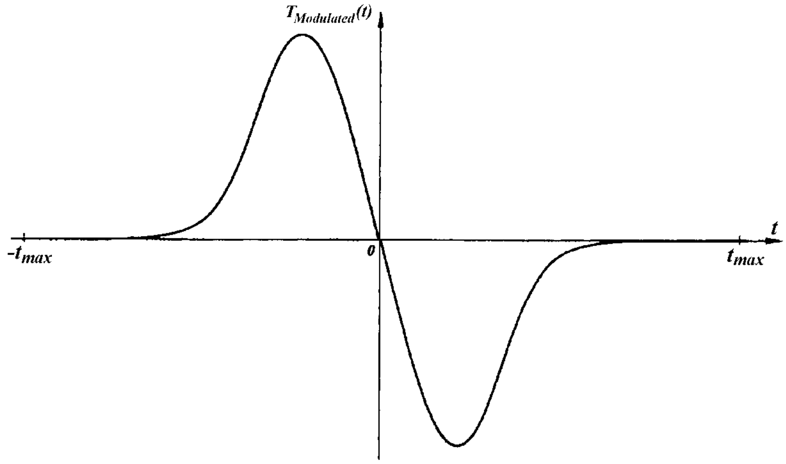

Fig. 15. Odd continuation of non-linear modulation of furnace temperature.

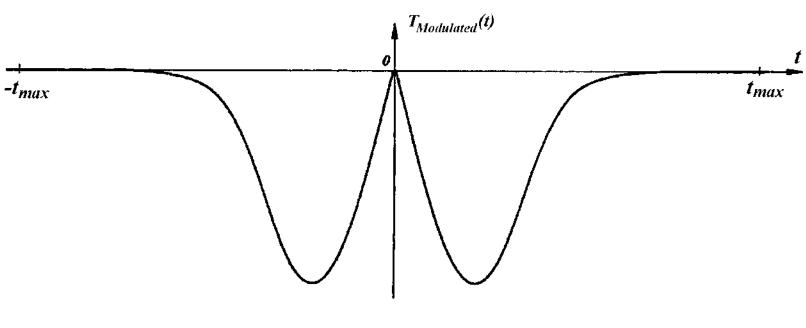

Fig. 16. Even continuation of non-linear modulation of furnace temperature.

6. Conclusion

The strict analytical temperature variation rule of platelike sample in GTMDSC model derived here reveals the total variation rule of the platelike sample from its initial equilibrium state to its steady state. In the GTMDSC theory, the modulated temperature of furnace accords with a random cyclically modulated rule and even a random non-cyclic rule. 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, in which much useful information such as sample's thermal conductivity and specific heat capacity, etc. is included. 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 modulation mode of furnace temperature. So if we use GTMDSC 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 GTMDSC must be dealt with carefully with appropriate calibration methods such as considering the temperature gradients within the sample.

Although the analytical theory of GTMDSC here is far more complex in form than the current TMDSC theories, we can anticipate that our analytical theory of GTMDSC is more precise and more general.

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