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Novel quasi-isothermal method of measuring heat capacity in temperature modulated differential scanning calorimetry☆

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Abstract

In this paper, a novel quasi-isothermal method of measuring sample's specific heat capacity in temperature modulated differential scanning calorimetry (TMDSC) has been studied. With the strict temperature variation rule of plate-like sample in TMDSC model, the expression of the sample's surface temperature lag in quasi-isothermal state has been obtained. With this temperature lag rule, sample's specific heat capacity and its thermal conductivity can be determined at the same time by quasi-isothermal experiment of TMDSC.

It has been pointed out here that the obtained heat capacity value of the sample with the quasi-isothermal method is only the average value within the measured temperature interval, and it is true that the bigger the modulated amplitude, the smother the value of heat capacity obtained. In the situation that the specific heat capacity of sample is approximately constant within the measured temperature interval, the quasi-isothermal method of TMDSC is better. If within the measured temperature interval the specific heat capacity of sample is apparently the function of temperature, the best tool to measure the sample's specific heat capacity is traditional DSC. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Temperature modulated differential scanning calorimetry (TMDSC); Quasi-isothermal; Specific heat capacity; Thermal conductivity

1. Introduction

Temperature modulated differential scanning calorimetry (TMDSC) is a novel thermal analysis tool. Since Reading invented the TMDSC [1], the apparatus of TMDSC has been successfully commercialized [2–6]. How to use TMDSC to measure the characteristics of matter effectively, how to solve the difficult problems in the dealing of data and how to expand the application of TMDSC are the focuses of studying in the thermal analysis theoretical society [7–12].

Specific heat capacity is a very important physical parameter of matter. How to use TMDSC to measure sample's specific heat capacity exactly is an urgent and basic problem to be solved.

Wunderlich proposed a quasi-isothermal theory of TMDSC to survey sample's specific heat capacity [7,8]. In this article, at first, we study this representative method, and then compare it with the method of

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conventional DSC for measuring specific heat capacity of sample.

In the steady state, the basic equations of temperature variation rules of TMDSC furnace, sample and reference are as follows [7]:

$$T_s(t) = T_0 + qt + A_{T_s} \sin \omega t \quad (1)$$

$$T(t) = T_0 + qt - \frac{qC_{sp}}{K} + A_{sp} \sin(\omega t - \varepsilon) \quad (2)$$

$$T_r(t) = T_0 + qt - \frac{qC_r}{K} + A_{T_r} \sin(\omega t - \phi) \quad (3)$$

where T_0 is the initial temperature of furnace, reference and sample, $T_s(t)$, $T(t)$ and $T_r(t)$ are, respectively, the temperature of furnace, sample and reference at time t, q, A_{T_s} and ω, respectively, represent the underlying heating rate, the amplitude and the angular frequency of modulation of furnace, $A_{sp}(t)$ and $A_{T_r}(t)$ are, respectively, amplitudes of modulation of sample and reference, C_{sp} and C_r are, respectively, heat capacity of sample and reference, ε and ϕ are, respectively, the phase lag of sample and reference.

In the derivation of above three equations, the assumption that the heat gradients within the sample and reference are omitted is used.

In the quasi-isothermal state, the furnace changes its temperature in sinusoidal rule around the average temperature $\overline{T}$. In this situation, Wunderlich proposed a relation

$$mc_p = \frac{A_\Delta}{A_{T_r}} \sqrt{\frac{K}{\omega} + C'^2} \quad (4)$$

with C' representing the pan heat capacity (equal for reference and sample), c_p, the specific heat capacity of the sample, m the sample mass, and A_Δ is the modulation amplitude of the temperature difference ΔT.

From Eq. (4) we know that the bigger A_{T_s}, the smoother the value of sample's specific heat. It seems that the bigger A_{T_s}, the more accurate the value of sample's specific heat.

We have different point of view. As a matter of fact, when A_{T_s} and ω are not zero at the same time, the sample changes its temperature around $\overline{T}$ with the extent of $2A_{T_s}$, where $A_{sp} \approx A_{T_s}$. Because the Newton's law constant K is impossible to be infinite, there always is temperature lag of sample relative to furnace.

On the one side, Newton's cooling rule must be obeyed

$$\frac{dQ_{sp}}{dt} = -K[T(t) - T_s(t)] \quad (5)$$

where dQ_{sp}/dt is the heat energy absorbed from surrounding by sample in a unit time.

On the another side, after absorbing heat from surrounding, sample must enhance its temperature, so we have

$$C_{sp}(T)\frac{dT}{dt} = \frac{dQ_{sp}}{dt} \quad (6)$$

According to energy conservation law, the basic equation can be obtained

$$C_{sp}(T)\, dT = -K[T(t) - T_s(t)] \quad (7)$$

To reach Eq. (4) form Eq. (7), we must assume the heat capacity of sample is constant in the temperature interval $\overline{T} \pm A_{sp}$. If in the general situation in which the heat capacity is a function of temperature, the heat capacity $C_{sp}(T)$ must be replaced by the average heat capacity $\overline{C_{sp}(T)}$ in this temperature interval to ensure the validity of Eq. (4). So if heat capacity is a function of temperature, the heat capacity obtained from Eq. (4) is only an average value of heat capacity in the temperature interval $\overline{T} \pm A_{sp}$.

From traditional DSC theory, the heating rates of surrounding influence the experimental curve greatly. If the heating rate is zero, for a sufficiently long time, the temperatures of sample and reference are the same. The bigger the heating rate, the bigger the temperature differences between sample and reference, and the higher the detecting sensitivity. In the quasi-isothermal situation of TMDSC, the instantaneous heating or cooling rate is not always equal to zero. The biggest value of heating or cooling rate is proportional to the multiple of modulation amplitude and angular frequency. Because the envelope line of TMDSC curve in the quasi-isothermal situation is just corresponding to the extremum of heating or cooling rate, so the detecting sensitivity and precision are enhanced greatly. Thus, if in a temperature interval the heat capacity of the sample is constant or a slow changing function of temperature, the heat capacity obtained in TMDSC can be anticipated more accurate than that in conventional DSC.

In the general situation that the variation of heat capacity with temperature cannot be omitted, because the quasi-isothermal method of TMDSC only can obtain the average value of heat capacity of sample, much important information included in the heat capacity may be lost. In this situation, conventional DSC precedes TMDSC.

On account of the actuality that almost all TMDSC theories of detecting sample's heat capacity, including Wunderlich's theory [7,8], neglected the influence of an important factor, temperature gradients within the sample and reference, it is difficult to obtain the exact value of sample's heat capacity, although some calibrations are made [13,14]. To exert the advantage of TMDSC sufficiently, it is necessary to develop a novel quasi-isothermal theory of TMDSC in which temperature gradients in the sample are fully considered. The following is a general quasi-isothermal method of TMDSC.

2. Novel quasi-isothermal theory of TMDSC

In general situation in which the temperature gradients in the sample are considered, the temperature variation rule of plate-like sample in TMDSC has been drawn with strict mathematical derivation [10]. The temperature variation rule is as follows:

$$\begin{aligned} T(x,t) &= T_0 + qt + A_{T_s}\sin\omega t + \Delta(x,t) \\ &= T_0 + qt + A_{T_s}\sin\omega t \\ &\quad - \sum_{n=0}^{+\infty} \frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} \\ &\quad \times \left(\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right) \\ &\quad \times \left\{ \frac{q}{\lambda_n^2 a^2}(1 - \mathrm{e}^{-\lambda_n^2 a^2 t}) + \frac{A_{T_s}\omega}{\lambda_n^4 a^4 + \omega^2} \right. \\ &\quad \left. \times [\lambda_n^2 a^2(\cos\omega t - \mathrm{e}^{-\lambda_n^2 a^2 t}) + \omega\sin\omega t] \right\} \end{aligned} \tag{8}$$

$$\begin{aligned} &T(x,t) \\ &= T_0 + qt + A_{T_s}\sin\omega t - \sum_{n=0}^{+\infty} \frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} \\ &\times \left(\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right) \left\{ \frac{q}{\lambda_n^2 a^2}(1 - \mathrm{e}^{-\lambda_n^2 a^2 t}) \right. \\ &\left. + \frac{A_{T_s}\omega}{\sqrt{\lambda_n^4 a^4 + \omega^2}}\sin(\omega t + \alpha_n) - \frac{A_{T_s}\omega\lambda_n^2 a^2 \mathrm{e}^{-\lambda_n^2 a^2 t}}{\lambda_n^4 a^4 + \omega^2} \right\}, \\ &(0 \le x \le l, t \ge 0) \end{aligned} \tag{8A}$$

where $a^2 = \kappa/\rho c_p$, ρ is the mass density of sample, κ the thermal conductivity of sample, α_n is defined as

$$\alpha_n \equiv \arcsin \frac{\lambda_n^2 a^2}{\sqrt{\lambda_n^4 a^4 + \omega^2}} \tag{9}$$

and λ_n is the root of following equation:

$$\lambda_n = \frac{K}{\kappa} ctg\lambda_n l, \quad n = 0, 1, 2, \ldots \tag{10}$$

In the quasi-isothermal situation, the temperature variation rule of plate-like sample is

$$\begin{aligned} T(x,t) &= \overline{T} + A_{T_s}\sin\omega t + \Delta(x,t) \\ &= \overline{T} + A_{T_s}\sin\omega t - \sum_{n=0}^{+\infty} \frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} \\ &\quad \times \left(\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right) \frac{A_{T_s}\omega}{\lambda_n^4 a^4 + \omega^2} \\ &\quad \times [\lambda_n^2 a^2\cos\omega t + \omega\sin\omega t] \end{aligned} \tag{11}$$

$$\begin{aligned} T(x,t) &= \overline{T} + A_{T_s}\sin\omega t - \sum_{n=0}^{+\infty} \frac{2K^2}{\lambda_n(K^2 l + l\kappa^2\lambda_n^2 + \kappa K)} \\ &\quad \times \left(\sin\lambda_n x + \frac{\kappa\lambda_n}{K}\cos\lambda_n x\right) \\ &\quad \times \frac{A_{T_s}\omega}{\sqrt{\lambda_n^4 a^4 + \omega^2}}\sin(\omega t + \alpha_n) \end{aligned} \tag{11A}$$

where $\overline{T}$ is the average temperature of surrounding. In the quasi-isothermal situation, the initial temperature influence can be rationally omitted, so in the Eq. (11) the item $\mathrm{e}^{-\lambda_n^2 a^2 t}$ is neglected.

We have testified that for a general sample the dominant item of correction function is sufficient [10]. So Eq. (11) can be written as

$$\begin{aligned} T(x,t) &= \overline{T} + A_{T_s}\sin\omega t - \frac{2K^2}{\lambda_0(K^2 l + l\kappa^2\lambda_0^2 + \kappa K)} \\ &\quad \times \left(\sin\lambda_0 x + \frac{\kappa\lambda_0}{K}\cos\lambda_0 x\right) \frac{A_{T_s}\omega}{\lambda_0^4 a^4 + \omega^2} \\ &\quad \times [\lambda_0^2 a^2\cos\omega t + \omega\sin\omega t] \end{aligned} \tag{12}$$

$$\begin{aligned} T(x,t) &= \overline{T} + A_{T_s}\sin\omega t - \frac{2K^2}{\lambda_0(K^2 l + l\kappa^2\lambda_0^2 + \kappa K)} \\ &\quad \times \left(\sin\lambda_0 x + \frac{\kappa\lambda_0}{K}\cos\lambda_0 x\right) \\ &\quad \times \frac{A_{T_s}\omega}{\sqrt{\lambda_0^4 a^4 + \omega^2}}\sin(\omega t + \alpha_0) \end{aligned} \tag{12A}$$

In the general thermal apparatus the temperature detector (e.g. thermocouple) is placed in the central position under the sample support. If the thermal conductivities of sample support and sample pan are much bigger than that of sample, the temperature gradients within the sample pan and its support can be rationally omitted. In this situation the measured temperature actually is the sample's surface temperature $T(0, t)$, so Eq. (12) can be rewritten as

$$T(0,t) = \overline{T} + A_{T_s}\sin\omega t - \frac{2K\kappa}{K^2 l + l\kappa^2\lambda_0^2 + \kappa K} \times \frac{A_{T_s}\omega}{\lambda_0^4 a^4 + \omega^2}[\lambda_0^2 a^2 \cos\omega t + \omega\sin\omega t] \quad (13)$$

$$T(0,t) = \overline{T} + A_{T_s}\sin\omega t - \frac{2K\kappa}{K^2 l + l\kappa^2\lambda_0^2 + \kappa K} \times \frac{A_{T_s}\omega}{\sqrt{\lambda_0^4 a^4 + \omega^2}}\sin(\omega t + \alpha_0) \quad (13A)$$

The average temperature of furnace $\overline{T}$, the modulation amplitude A_{T_s} and angular frequency ω are programmed, and they are known. Now, let us analyze the very important information included in the signal of sample's surface temperature lag to furnace. The format of Eq. (13A) is more suitable for the study of this project, so we will accept it in the following.

The signal of sample's surface temperature lag to furnace is

$$\delta T(t) \equiv T(0,t) - T_s = -\frac{2K\kappa}{K^2 l + l\kappa^2\lambda_0^2 + \kappa K}\frac{A_{T_s}\omega}{\sqrt{\lambda_0^4 a^4 + \omega^2}}\sin(\omega t + \alpha_0) = -A'\sin(\omega t + \alpha_0) \quad (14)$$

where A' is defined as

$$A' \equiv \frac{2K\kappa}{K^2 l + l\kappa^2\lambda_0^2 + \kappa K}\frac{A_{T_s}\omega}{\sqrt{\lambda_0^4 a^4 + \omega^2}} \quad (15)$$

In the real quasi-isothermal experiments of TMDSC, the sample's temperature lag signal can be detected. This temperature lag signal satisfies the Eq. (14), so by using Eq. (14) the parameters of sample's physical properties can be obtained. From Eq. (14), it is easy to know that this temperature lag signal gives two useful items at the same time, amplitude A' and phase lag α_0. From definitions Eqs. (9) and (15), A' and α_0 are, respectively, related to the Newton's law constant of pan, sample's thermal conductivity, mass density, depth, specific heat capacity and angular frequency of modulation, and A' is also related to modulation amplitude of furnace. Thus, with the temperature lag signal detected in the quasi-isothermal experiment, two physical quantities of sample can be obtained at the same time.

For a given TMDSC apparatus, the Newton's law constant of pan is known in order of magnitude. For an actual experiment, the average temperature of furnace $\overline{T}$, the modulation amplitude A_{T_s} and angular frequency ω are programmed, and they are known. The depth and mass density of sample can be determined with other methods. Thus, in the quasi-isothermal experiment the specific heat capacity and thermal conductivity of sample can be determined at the same time. So, the novel quasi-isothermal theory greatly broadens the application area of TMDSC, and takes full advantage of the useful information included in the thermal diagram.

If turning our quasi-isothermal theory of TMDSC into appropriate software to deal with the real time experimental data, it will become very convenient to obtain sample's specific heat capacity and thermal conductivity at the same time.

3. Discussion on the quasi-isothermal theory of TMDSC

To verify above theory, we will deal with two special examples.

3.1. 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. For the simplicity, the dimension in this example is missing purposedly. From Eq. (10) we can get the root: $\lambda_0 = 8.6033357$.

Assume the Newton's constant of pan, K, is 10, average temperature of furnace $\overline{T}$ 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 furnace T_s and the time t as shown in Fig. 1.

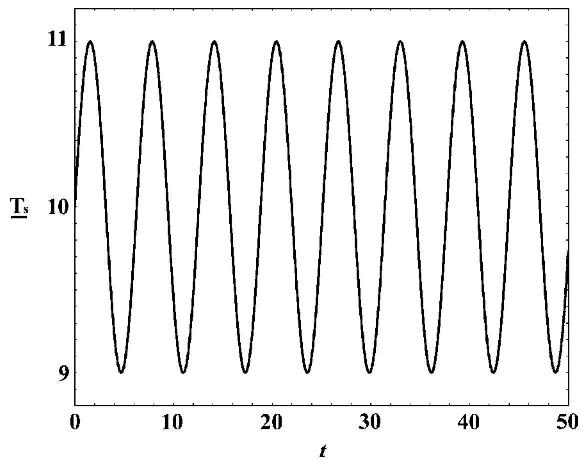

Fig. 1. Variation rule of furnace with time t in quasi-isothermal state.

Fig. 2 shows the variation rule of sample's surface temperature lag with time t in quasi-isothermal state, from which the information included in the amplitude and phase lag can be obtained.

Increasing the value of sample's specific heat capacity and remaining other physical quantities constant, in Fig. 3 we can find the variation rule of phase lag with sample's specific heat capacity. Contrarily, from the value of phase lag, we also can obtain the sample's specific heat capacity.

Similarly, increasing the value of sample's thermal conductivity and remaining other physical quantities constant, in Fig. 4 we can find the variation rule of phase lag with sample's thermal conductivity. Contrarily, from the value of phase lag, we also can obtain the sample's thermal conductivity.

3.2. Example 2

If the thermal conductivity of the sample is big enough, that is $\kappa \to +\infty$, the Eqs. (9) and (15) can be simplified as follows:

$$A' \equiv \frac{A_{T_s}\omega}{\sqrt{(K/\rho c_p l)^2 + \omega^2}} \tag{16}$$

$$\alpha_0 \equiv \arcsin\frac{K/\rho c_p l}{\sqrt{(K/\rho c_p l)^2 + \omega^2}} \tag{17}$$

In the derivation process of above two equations, the following relations are used [10]:

$$\lambda_0^2 = \frac{K}{\kappa l} \tag{18}$$

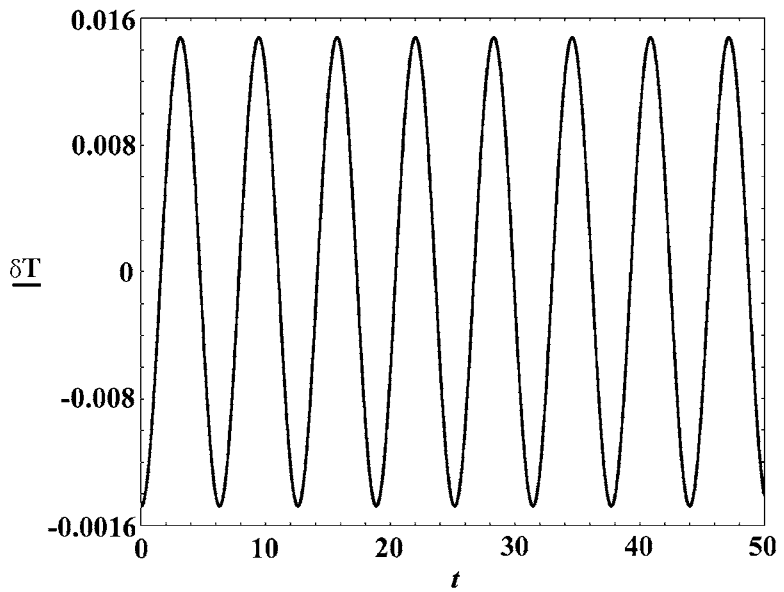

Fig. 2. Variation of sample's temperature lag with time t in quasi-isothermal state.

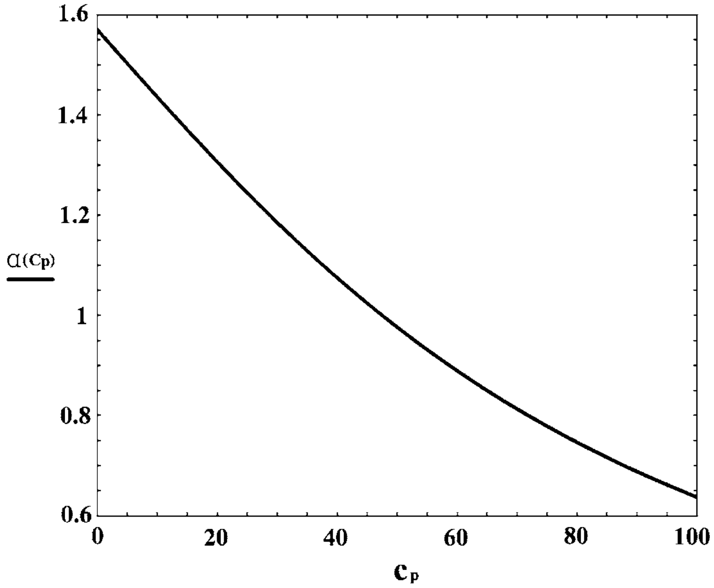

Fig. 3. Variation of sample's temperature lag with the specific heat capacity of sample in quasi-isothermal state.

$$\chi \equiv \frac{2K\kappa}{K^2 l + l\kappa^2\lambda_0^2 + \kappa K} = 1 \quad (19)$$

$$\lambda_0^2 a^2 = \frac{K}{\rho c_p l} \quad (20)$$

In this situation, from Eqs. (16) and (17), the amplitude and phase lag of temperature lag signal, only one unknown parameter, specific heat capacity of sample, can be obtained. So if the temperature gradients within the sample are omitted, the approximate degree of corresponding TMDSC theories is serious, that will inevitably result in the loss of some useful information.

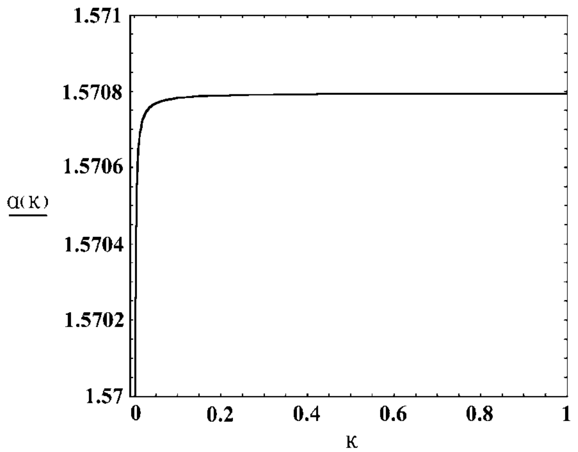

Fig. 4. Variation of sample's temperature lag with the thermal conductivity of sample in quasi-isothermal state.

4. Conclusion

With the strict temperature variation rule of plate-like sample in TMDSC model, in which the temperature gradients within the sample are considered fully, the expression of the sample's surface temperature lag in quasi-isothermal state can be obtained. Important information is included in the signal of sample's temperature lag, so sample's specific heat capacity and its thermal conductivity can be determined at the same time by quasi-isothermal experiment of TMDSC. If the temperature gradients within the sample are omitted in the general situation, it will inevitably result in the loss of some useful information.

In the quasi-isothermal experiment of TMDSC, the obtained specific heat capacity of sample is only its average value within the measured temperature interval. If the specific heat capacity of sample is approximately constant within the measured temperature interval, the quasi-isothermal method of TMDSC is better. But if within the measured temperature interval the specific heat capacity of sample is apparently the function of temperature, the best tool to measure sample's heat capacity is traditional DSC.

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