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Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

GENERAL THEORY OF STEADY STATE OF tm-DSC AND ITS APPLICATION TO COMPLEX HEAT CAPACITY MEASUREMENTS

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Abstract

For complex heat capacity measurements, steady state of various types of temperature modulated DSC is theoretically investigated by a set of common comprehensive fundamental equations of heat balance. Heat capacities of heat paths, heat loss to the environment and mutual heat exchange between the sample and the reference material are taken into accounts together with thermal contact effect between the cell and its holder plate. Rigorous and general solutions have been obtained, and useful relations for complex heat capacity measurements have been derived for each type of DSC. They are compared with each other to elucidate unique features of each type of DSC.

Keywords: complex heat capacity measurement, heat flux DSC, photo-modulated DSC, power compensation DSC, steady state, temperature modulated DSC

Introduction

Since publication of temperature-modulated differential scanning calorimetry (tm-DSC) in 1992 [1, 2], various types have been invented. Modulation by direct temperature control was first applied to heat flux DSC (hf-DSC) [1, 2], and then to power compensation DSC (pc-DSC) [3]. Indirect modulation was tried by modulated light irradiation for hf-DSC (photo-modulated DSC; pm-DSC) [4]. They are classified in Table 1. We investigated theoretically the steady state of these types of tm-DSC and discussed complex heat capacity measurement by them in previous papers [5–8].

To compare these types of tm-DSC, a set of comprehensive fundamental equations of heat balance has been formulated taking into accounts of the heat flows and heat capacities in the apparatus, and it is commonly applicable to all of these types of tm-DSC. By solving this set of equations for the steady state, general and rigorous equations for the temperature oscillations have been derived and a new insight into tm-DSC has been given by these comprehensive solutions. For each variety of tm-DSC, solutions have been derived from these comprehensive solutions. The solutions can be used in heat capacity measurements, in which the heat capacity is com-

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plex heat capacity consisting of the real and imaginary parts. Thus various types of tm-DSC have been compared for the complex heat capacity measurements on the same base and their unique features have been elucidated. These results are reported in this paper.

Model and fundamental equations

Generalized model

In DSC apparatuses there are a few heat flows. They are (1) the main heat flow from the furnace to the sample and the reference material, (2) the heat loss to the environment by purge gas and through the temperature sensor leads, and (3) the mutual heat exchange between the sample side and the reference material side. In addition to these, micro-heaters are attached beneath the sample cell and the reference material cell to control their temperatures in pc-DSC. Besides, in pm-DSC thermal power input is supplied to the sample side (and the reference material side) by modulated light irradiation from above in one type and from below in the other type. These heat flows are all considered in the following comprehensive fundamental equations of heat balance. The heat paths for these heat flows have heat capacities, which have influence on the temperature oscillations by reducing the amplitudes and shifting the phase angle. Although the heat capacities are distributed along the paths, they are approximated to be concentrated at a few points in the model. The temperature distribution within the sample and its cell is also assumed to be negligibly small, and it is the same for the reference material side.

Another important factor influencing the temperature oscillation is thermal contacts between the cell and its holder. To take this factor into accounts, the cell and the holder are separated in the model and thermal resistance is inserted between them.

Thus general comprehensive model has been made, and it is commonly applicable to the various types of tm-DSC. It is shown in a form of electrical equivalent circuits, as seen in Fig. 1. In this figure, PS and MPS mean the power source (the furnace) and the micro-power source (the micro-heater or the light source), respectively. Following this general model, a set of the fundamental equations has been formulated and solved. To derive the equations for the steady state in each type of tm-DSC, some unnecessary factors should be deleted.

Table 1 Classification of temperature modulated DSC

- (1) Direct temperature modulation
  - Power compensation DSC
  - Heat flux DSC
    - Sample temperature control mode
    - Furnace temperature control mode
    - (Reference material temperature control mode)
- (2) Indirect temperature modulation by light irradiation
  - Heat flux DSC
    - Irradiation from above
    - Irradiation from below

Fundamental equations of heat balance

First a set of comprehensive fundamental equations is formulated for the model, as follows. This is commonly applicable to all existing types of tm-DSC in Table 1.

$$C_K \mathrm{d}T_{fs}/\mathrm{d}t = 2K_K\,(T_f - T_{fs}) + 2K_K\,(T_{ps} - T_{fs}) \tag{1}$$

$$C_s^* \mathrm{d}T_s/\mathrm{d}t = K_s\,(T_{ps} - T_s) + P_s^* \exp(i\omega t) + P_{0s} \tag{2}$$

$$C_{ps} \mathrm{d}T_{ps}/\mathrm{d}t =$$

$$2K_K\,(T_{fs} - T_{ps}) + 3K_h\,(T_{hs} - T_{ps}) + K_o\,(T_o - T_{ps}) + K_s\,(T_s - T_{ps}) + P_{ps}^* \exp(i\omega t) + P_{0ps} \tag{3}$$

$$C_h \mathrm{d}T_{hs}/\mathrm{d}t = 3K_h\,(T_{ps} - T_{hs}) + 3K_h\,(T_{hr} - T_{hs}) \tag{4}$$

$$C_h \mathrm{d}T_{hr}/\mathrm{d}t = 3K_h\,(T_{pr} - T_{hr}) + 3K_h\,(T_{hs} - T_{hr}) \tag{5}$$

$$C_{pr} \mathrm{d}T_{pr}/\mathrm{d}t =$$

$$2K_K\,(T_{fr} - T_{pr}) + 3K_h\,(T_{hr} - T_{pr}) + K_o\,(T_o - T_{pr}) + K_r\,(T_r - T_{pr}) + P_{pr}^* \exp(i\omega t) + P_{0pr} \tag{6}$$

$$C_r^* \mathrm{d}T_r/\mathrm{d}t = 2K_r\,(T_{pr} - T_r) + P_r^* \exp(i\omega t) + P_{0r} \tag{7}$$

and

$$C_K \mathrm{d}T_{fr}/\mathrm{d}t = 2K_K\,(T_f - T_{fr}) + 2K_K\,(T_{pr} - T_{fr}) \tag{8}$$

where C (C^*), T, t, P^*, P_0 and K are respectively the heat capacity (the complex heat capacity), the temperature, the time, the complex amplitude of the oscillating thermal power input, the constant (non-oscillating) thermal power input, and the heat transfer coefficient. The asterisks mean that the quantities are complex to express the amplitude and the phase difference. The absolute value of P^* is equal to or less than P_0 for each combination, because the sum of P^* and P_0 expresses the thermal power input and it must be not minus but zero or plus.

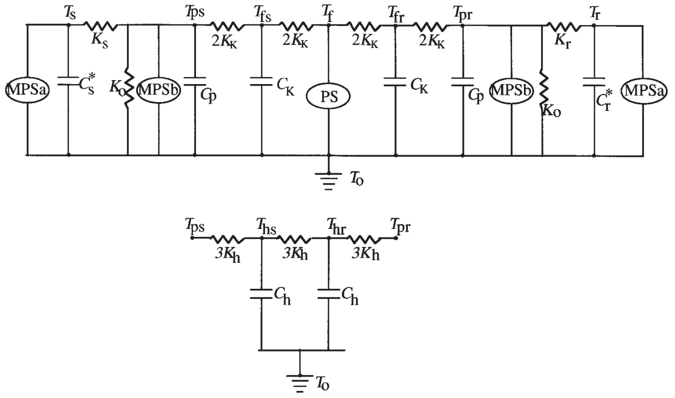

Fig. 1 Equivalent electrical circuits for main heat flows (upper) and mutual heat exchange (lower) in usual apparatus. PS, MPSa and MPSb are the heat source (the furnace, the power source), the light source (the micro-power source) from above and the micro-heater or the light source (the micro-power source) from below, respectively

The subscripts for the temperatures T and the power inputs P are as follows; *f*, the furnace; *fs*, the midpoint between the furnace and the sample; *s*, the sample; *r*, the reference material; *ps*, the sample cell holder plate; *pr*, the reference material cell holder plate; *fr*, the midpoint between the furnace and the reference material; *hs*, a point in the heat path for the mutual heat exchange; *hr*, another similar point near the reference material, and *o*, the environment. The subscripts for the power inputs P indicate the points to which the power is supplied.

The subscripts for the heat transfer coefficients K mean K, the heat paths from the furnace to the sample and the reference material; *h*, the mutual heat exchange; *s*, the thermal contact between the sample cell and its holder plate; *r*, that between the reference material cell and its holder and *o*, the heat loss to the environment through the temperature sensor leads and/or by the purge gas, respectively.

The subscripts for the heat capacities C (and C^*) denote K, the heat path between the furnace and the sample or the reference material; *s*, the sample; *r*, the reference material; *p* the cell holder plate and *h*, the heat path for the mutual heat exchange, respectively.

These symbols are also shown in Fig. 1 of the equivalent electrical circuits. As seen in this figure and the set of fundamental equations, the DSC apparatus in this model is of perfect symmetry, but the heat capacities of the sample and the reference material are different, and the power inputs are not necessarily symmetric.

The asterisks for C_s^* and C_r^* mean that these heat capacities are assumed to be complex heat capacities consisting of the real and the imaginary parts as follows;

$$C^* = C' - iC'' \tag{9}$$

where i, C^*, C' and C'' are the unit of imaginary numbers, the complex heat capacity, its real part and its imaginary part, respectively. As the reference material, substance without the imaginary heat capacity is usually used, however the heat capacity of the reference material is assumed to be complex heat capacity to investigate various possibility of the heat capacity measurement.

In the steady state, any temperature, T_i, changes at a fixed frequency, an amplitude and a constant underlying heating rate, so that

$$T_i = T_b + A_i^* \exp(i\omega t) + \beta t - \beta_i' t - B_i \tag{10}$$

where T_b, A_i^*, ω, β, β_i' and B_i are the initial temperature, the complex amplitude expressing the amplitude and the phase angle, the angular frequency, the programmed underlying heating rate, the decrease of the underlying heating rate due to the heat loss to the environment and the constant temperature lag, respectively. The subscript i is one of the subscripts for the temperatures (*f*, *fs*, *s*, *r*, *ps*, *pr*, *fr*, *hs* or *hr*). In this equation

$$\exp(i\omega t) = \cos(\omega t) + i\sin(\omega t) \text{ [Euler equation]} \tag{11}$$

and

$$A^* \exp(i\omega t) = A' \cos(\omega t) - A'' \sin(\omega t) + iA'' \cos(\omega t) + iA' \sin(\omega t) \tag{12}$$

where

$$A^* = A' + iA'' \tag{13}$$

In these equations related with the temperatures, only the real part has physical meaning and the imaginary part should be neglected. This is the same for the temperatures and the temperature differences below.

Derivation of comprehensive solutions

Introducing Eq. (10) for $i=s$ and ps into Eq. (2) and comparing the coefficient, as was done previously [6–8], we get three sets of linear simultaneous equations from the coefficients of the terms relating with the time, t, those of constants and the coefficients of the oscillating terms, $\exp(i\omega t)$, respectively. Solving these simultaneous equations, we can easily derive the following relations between the cell holder temperature and the sample temperature;

$$T_s = T_{ps} + (P_s^*/K_s - i\omega\tau_s^* A_{ps}^*)\exp(i\omega t)/(1 + i\omega\tau_s^*) - \{C_s'(\beta - \beta_{ps}') - P_{0s}\}/K_s \tag{14}$$

and similarly for the reference material temperature, by introducing Eq. (10) for $i=r$ and pr into Eq. (7),

$$T_r = T_{pr} + (P_r^*/K_r - i\omega\tau_r^* A_{pr}^*)\exp(i\omega t)/(1 + i\omega\tau_r^*) - \{C_r'(\beta - \beta_{pr}') - P_{0r}\}/K_r \tag{15}$$

where

$$\tau_s^* = C_s^*/K_s \tag{16}$$

and

$$\tau_r^* = C_r^*/K_r \tag{17}$$

The heat transfer from the sample or the reference material to their cell holder can be calculated as follows;

$$K_s(T_s - T_{ps}) = (P_s^* - i\omega C_s^* A_{ps}^*)\exp(i\omega t)/(1 + i\omega\tau_s^*) - \{C_s'(\beta - \beta_{ps}') - P_{0s}\} \tag{18}$$

and

$$K_r(T_r - T_{pr}) = (P_r^* - i\omega C_r^* A_{pr}^*)\exp(i\omega t)/(1 + i\omega\tau_r^*) - \{C_r'(\beta - \beta_{pr}') - P_{0r}\} \tag{19}$$

These four equations express the effect of thermal contact.

Because the temperatures follow Eq. (10) in the steady state, the next equation is derived for the temperature differences ΔT_i between symmetric points.

$$\Delta T_i = A_i^* \exp(i\omega t) - \Delta\beta_i' t - \Delta B_i \tag{20}$$

where

$$\Delta T_f = T_{fs} - T_{fr} = \Delta A_f^* \exp(i\omega t) - \Delta\beta_f' t - \Delta B_f \tag{21}$$

$$\Delta T_{\mathrm{p}} = T_{\mathrm{ps}} - T_{\mathrm{pr}} = \Delta A^*_{\mathrm{p}} \exp(i\omega t) - \Delta\beta'_{\mathrm{p}} t - \Delta B_{\mathrm{p}} \tag{22}$$

and

$$\Delta T_{\mathrm{h}} = T_{\mathrm{hs}} - T_{\mathrm{hr}} = \Delta A^*_{\mathrm{h}} \exp(i\omega t) - \Delta\beta'_{\mathrm{h}} t - \Delta B_{\mathrm{h}} \tag{23}$$

Similarly from the set of equations of heat balance, we have

$$C_{\mathrm{K}} \mathrm{d}\Delta T_{\mathrm{f}}/\mathrm{d}t = 2K_{\mathrm{K}}\Delta T_{\mathrm{p}} - 4K_{\mathrm{K}}\Delta T_{\mathrm{f}} \tag{24}$$

$$C_{\mathrm{h}} \mathrm{d}\Delta T_{\mathrm{h}}/\mathrm{d}t = 3K_{\mathrm{h}}\Delta T_{\mathrm{p}} - 9K_{\mathrm{h}}\Delta T_{\mathrm{h}} \tag{25}$$

and

$$\begin{gathered} C_{\mathrm{p}} \mathrm{d}\Delta T_{\mathrm{p}}/\mathrm{d}t = \\ 2K_{\mathrm{K}}\Delta T_{\mathrm{f}} + 3K_{\mathrm{h}}\Delta T_{\mathrm{h}} - (2K_{\mathrm{K}} + 3K_{\mathrm{h}} + K_{\mathrm{o}})\Delta T_{\mathrm{p}} + \{K_{\mathrm{s}}(T_{\mathrm{s}} - T_{\mathrm{ps}}) - K_{\mathrm{r}}(T_{\mathrm{r}} - T_{\mathrm{pr}})\} + \\ \Delta P^*_{\mathrm{p}} \exp(i\omega t) + \Delta P_{0\mathrm{p}} \end{gathered} \tag{26}$$

where

$$\Delta P_0 = P_{0\mathrm{s}} - P_{0\mathrm{r}} \tag{27}$$

and

$$\Delta P^*_{\mathrm{p}} = P^*_{\mathrm{ps}} - P^*_{\mathrm{pr}} \tag{28}$$

Introducing Eqs (18), (19) and (20) into Eqs (24), (25) and (26) and comparing the coefficients, as done in the above, we have similarly three sets of linear simultaneous equations and finally the next comprehensive solutions.

From the non-oscillating terms, we have

$$\Delta C' = \{(\Delta P_0 + \Delta P_{\mathrm{p}0}) + \Delta B_{\mathrm{p}}(K_{\mathrm{K}} + 2K_{\mathrm{h}} + K_{\mathrm{o}})\}/(\beta - \beta'_{\mathrm{ps}}) \tag{29}$$

and from the oscillating terms

$$\Delta C^*_{\mathrm{sr}} = \{\Delta P^*_{\mathrm{p}} + \Delta P^*_{\mathrm{sr}} - (S_1 + iS_2)\,\Delta A^*_{\mathrm{p}}\}/i\omega A^*_{\mathrm{ps}} \tag{30}$$

where

$$\begin{gathered} S_1 = (2K_{\mathrm{K}} + 3K_{\mathrm{h}} + K_{\mathrm{o}}) - K_{\mathrm{K}}/(1 + \omega^2\tau^2_{\mathrm{K}}) - \\ K_{\mathrm{h}}/(1 + \omega^2\tau^2_{\mathrm{h}}) + \{\omega C''_{\mathrm{r}} + \omega^2(\tau'_{\mathrm{r}}C'_{\mathrm{r}} + \tau''_{\mathrm{r}}\, C''_{\mathrm{r}})\}/\{(1 + \omega\tau''_{\mathrm{r}})^2 + \omega^2\tau'^2_{\mathrm{r}}\} \end{gathered} \tag{31}$$

$$S_2/\omega = C_{\mathrm{K}}/4(1 + \omega^2\tau^2_{\mathrm{K}}) + C_{\mathrm{h}}/9(1 + \omega^2\tau^2_{\mathrm{h}}) + C'_{\mathrm{r}}/\{(1 + \omega^2\tau''^2_{\mathrm{r}}) + \omega^2\tau'^2_{\mathrm{r}}\} + C_{\mathrm{p}} \tag{32}$$

$$\Delta P^*_{\mathrm{sr}} = P^*_{\mathrm{s}}/(1 + i\omega\tau^*_{\mathrm{s}}) - P^*_{\mathrm{r}}/(1 + i\omega\tau^*_{\mathrm{r}}) \tag{33}$$

$$\Delta P_0 = P_{0\mathrm{s}} - P_{0\mathrm{r}} \tag{34}$$

and

$$\Delta C^*_{\mathrm{sr}} = C^*_{\mathrm{s}}/(1 + i\omega\tau^*_{\mathrm{s}}) - C^*_{\mathrm{r}}/(1 + i\omega\tau^*_{\mathrm{r}}) \tag{35}$$

Eqs (29) and (30) are the comprehensive solutions for the generalized model. Eq. (29) is the fundamental relation for the underlying constant rate heating, so that it is applicable to the conventional DSC and also to the average temperature or the average power input discussed below, and only the real part of heat capacity can be measured by this relation. On the other hand, Eq. (30) is that for the oscillating temperature, and the both of the real and imaginary parts of complex heat capacity are involved in this relation. As seen in Eq. (35), the heat capacities of the sample and the reference material are effectively changed to $C_s^*/(1+i\omega\tau_s^*)$ and $C_r^*/(1+i\omega\tau_r^*)$ due to the thermal contact effect. Therefore, what we can directly measure is not the difference in complex heat capacity $(C_s^*-C_r^*)$ but the difference in the effective complex heat capacity $[C_s^*/(1+i\omega\tau_s^*)-C_r^*/(1+i\omega\tau_r^*)]$.

It should also be noted in Eq. (30) that ΔP_p^*, ΔP_{sr}^* and $-(S_1+iS_2)\,\Delta A_p^*$ are mutually interchangeable, so that they are equivalent to each other in its role. This relation expresses the difference among the varieties of tm-DSC.

Solutions for heat capacity measurements by each type of DSC

First of all it should be pointed out that the thermal contact effects have serious effect on the heat capacity measurements, and that the factors, τ_s^* and τ_r^*, cause errors in the actual experiments, because they are experimentally uncontrollable and can not be estimated. Therefore, the reference material is not desirable to be used for avoiding the error caused by the latter, τ_r^*, at least. It should also be mentioned that the heat capacity of the reference material is involved in another way as shown in Eqs (31) and (32).

Hereafter, solutions for heat capacity measurements by each type of DSC will be given for the cases that the reference material is not used. For these cases, the comprehensive equation for the complex heat capacity measurements is as follows;

$$C_s^*/(1+i\omega\tau_s^*) = \{\Delta P_p^* + \Delta P_{sr}^* - (S_1+iS_2)\,\Delta A_p^*\}/i\omega A_{ps}^* \qquad (36)$$

where the parameters S_1 and S_2 are changed, and they become not functions of the experimental parameters but the parameters characteristic of the apparatus;

$$S_1 = (2K_K + 3K_h + K_o) - K_K/(1+\omega^2\tau_K^2) - K_h/(1+\omega^2\tau_h^2) \qquad (37)$$

and

$$S_2/\omega = C_K/4(1+\omega^2\tau_K^2) + C_h/9(1+\omega^2\tau_h^2) + C_p \qquad (38)$$

These parameters can be measured by measuring the standard materials such as α-alumina, in which the imaginary part of heat capacity does not occur.

(1) tm-hf-DSC

By deleting some factors in the above equation (36), we can derive useful relations for each type of tm-DSC. For instance, all power inputs except the heat flow from the furnace do not occur in tm-hf-DSC, so that

$$P_{s0} = P_{r0} = \Delta P_0 = 0 \tag{39}$$

$$P_s^* = P_r^* = \Delta P_{sr}^* = 0 \tag{40}$$

$$P_{ps0} = P_{pr0} = \Delta P_{p0} = 0 \tag{41}$$

and

$$P_{ps}^* = P_{pr}^* = \Delta P_p^* = 0 \tag{42}$$

Therefore, we have the following relations;

$$C_s' = \Delta B_p(K_K + 2K_h + K_o)/(\beta - \beta'_{ps}) \tag{43}$$

$$C_s'/(1 + i\omega\tau_s^*) = -(S_1\Delta A_p'' + S_2\Delta A_p')/\omega A_{ps} \tag{44}$$

and

$$C_s''/(1 + i\omega\tau_s^*) = (S_1\Delta A_p' - S_2\Delta A_p'')/\omega A_{ps} \tag{45}$$

where $\Delta A_p'$ and $\Delta A_p''$ are respectively the real part and the imaginary part of ΔA_p^*. Because the temperature oscillation of the sample cell holder (A_{ps}) is the reference oscillation and the temperature difference oscillation to be measured is given as a function of this reference oscillation, the real part of the temperature difference oscillation ($\Delta A_p'$) is in the same phase with the sample cell holder temperature (A_{ps}). This is independent on the temperature to be controlled (the sample temperature, the furnace temperature or the reference material temperature) (Table 1).

The former relation [Eq. (43)] is the same as that for heat capacity measurements by conventional hf-DSC. The latter relations [Eqs (44) and (45)] are for complex heat capacity measurements by tm-hf-DSC. When the thermal contact between the sample cell and its holder plate is good enough and its thermal resistance is negligibly small,

$$C_s^* =(S_1\Delta A_p'' + S_2\Delta A_p')/\omega A_{ps} \tag{46}$$

and

$$C_s'' = (S_1\Delta A_p' - S_2\Delta A_p'')/\omega A_{ps} \tag{47}$$

(2) tm-pc-DSC

For tm-pc-DSC the light is not irradiated, but the power inputs are supplied to the cell holder plate, i.e.,

$$P_{s0} = P_{r0} = \Delta P_0 = 0 \tag{39}$$

$$P_s^* = P_r^* = \Delta P_{sr}^* = 0 \tag{40}$$

and the temperature difference is controlled to be zero by adjusting P_{ps0}, P_{pr0}, P_{ps}^* and P_{pr}^*. Namely,

$$\Delta T = 0 \tag{48}$$

and hence

$$\Delta A_{\mathrm{p}}^{*} = 0 \tag{49}$$

Thus,

$$C_{\mathrm{s}}' = \Delta P_{\mathrm{p0}}/(\beta - \beta_{\mathrm{ps}}') \tag{50}$$

$$C_{\mathrm{s}}'/(1 + i\omega\tau_{\mathrm{s}}^{*}) = \Delta P_{\mathrm{p}}''/\omega A_{\mathrm{ps}} \tag{51}$$

and

$$C_{\mathrm{s}}''/(1 + i\omega\tau_{\mathrm{s}}^{*}) = \Delta P_{\mathrm{p}}'/\omega A_{\mathrm{ps}} \tag{52}$$

For the case that the thermal contact effect can be neglected, the simple relations are derived;

$$C_{\mathrm{s}}' = \Delta P_{\mathrm{p}}''/\omega A_{\mathrm{ps}} \tag{53}$$

and

$$C_{\mathrm{s}}'' = \Delta P_{\mathrm{p}}'/\omega A_{\mathrm{ps}} \tag{54}$$

(3) pm-DSC

For pm-DSC, in which the light is irradiated from below

$$P_{\mathrm{s0}} = P_{\mathrm{r0}} = \Delta P_{0} = 0 \tag{38}$$

$$P_{\mathrm{s}}^{*} = P_{\mathrm{r}}^{*} = \Delta P_{\mathrm{sr}}^{*} = 0 \tag{39}$$

Then we have

$$C_{\mathrm{s}}' = \{\Delta P_{\mathrm{p0}} + \Delta B_{\mathrm{p}}(K_{\mathrm{K}} + 2K_{\mathrm{h}} + K_{\mathrm{o}})\}/(\beta - \beta_{\mathrm{ps}}') \tag{55}$$

$$C_{\mathrm{s}}'/(1 + i\omega\tau_{\mathrm{s}}^{*}) = \{\Delta P_{\mathrm{p}}'' - S_{1}\Delta A_{\mathrm{p}}'' - S_{2}\Delta A_{\mathrm{p}}'\}/\omega A_{\mathrm{ps}} \tag{56}$$

and

$$C_{\mathrm{s}}''/(1 + i\omega\tau_{\mathrm{s}}^{*}) = \{\Delta P_{\mathrm{p}}' + S_{1}\Delta A_{\mathrm{p}}' - S_{2}\Delta A_{\mathrm{p}}''\}/\omega A_{\mathrm{ps}} \tag{57}$$

where S_1 and S_2 are the same as Eqs (37) and (38). When the power inputs for the sample and the reference material side are equal to each other [$\Delta P_{\mathrm{p}}^{*}=0$], Eqs (56) and (57) are reduced to those for tm-hf-DSC [Eqs. (44) and (45)], and the relations for the case without the thermal contact effect are equal to Eqs (46) and (47).

For pm-DSC in which the light is irradiated from above,

$$P_{\mathrm{ps0}} = P_{\mathrm{pr0}} = \Delta P_{\mathrm{p0}} = 0 \tag{41}$$

$$P_{\mathrm{ps}}^{*}=P_{\mathrm{pr}}^{*}=\Delta P_{\mathrm{p}}^{*}=0 \tag{42}$$

so that we have

$$C_{\mathrm{s}}'=\{\Delta P_0+\Delta B_{\mathrm{p}}(K_{\mathrm{K}}+2K_{\mathrm{h}}+K_{\mathrm{o}})\}/(\beta-\beta_{\mathrm{ps}}') \tag{58}$$

$$C_{\mathrm{s}}'/(1+i\omega\tau_{\mathrm{s}}^{*})=\{\Delta P_{\mathrm{sr}}''-S_1\Delta A_{\mathrm{p}}''-S_2\Delta A_{\mathrm{p}}'\}/\omega A_{\mathrm{ps}} \tag{59}$$

and

$$C_{\mathrm{s}}''/(1+i\omega\tau_{\mathrm{s}}^{*})=\{\Delta P_{\mathrm{sr}}'+S_1\Delta A_{\mathrm{p}}'-S_2\Delta A_{\mathrm{p}}''\}/\omega A_{\mathrm{ps}} \tag{60}$$

These equations for the temperature oscillation [Eqs (59) and (60)] can not be used practically, because we do not have any mean to know the quantity, either $\Delta P_{\mathrm{sr}}^{*}$ ($\Delta P_{\mathrm{sr}}'$ and $\Delta P_{\mathrm{sr}}''$) or τ_{s}^{*}. A simple method to decrease error due to this fact is to make the thermal contact good enough. Then we can estimate $\Delta P_{\mathrm{sr}}'$ and $\Delta P_{\mathrm{sr}}''$ exactly. By equalizing the thermal input to the sample side with that to the reference material side and keeping the thermal contact good enough, we can realize the next condition.

$$\Delta P_{\mathrm{sr}}^{*}=0 \tag{39}$$

Then solutions for pm-DSC of this type are reduced to those for tm-hf-DSC;

$$C_{\mathrm{s}}'=-\{S_1\Delta A_{\mathrm{p}}''+S_2\Delta A_{\mathrm{p}}'\}/\omega A_{\mathrm{ps}} \tag{46}$$

and

$$C_{\mathrm{s}}''=\{S_1\Delta A_{\mathrm{p}}'-S_2\Delta A_{\mathrm{p}}''\}/\omega A_{\mathrm{ps}} \tag{47}$$

However, the error by neglecting the thermal contact effect may still exist in double points; one in the above equalization of the power inputs and the other in the propagation of the temperature oscillation from the sample to its holder plate. Therefore, this type of pm-DSC is not so recommendable as the other.

Discussion

For easy comparison, these results are tabulated in Table 2. As clearly seen in this table, when we do not estimate the thermal contact effect (τ_{s}^{*}) exactly, we can only measure the effective heat capacity (or apparent heat capacity), $C_{\mathrm{s}}^{*}/(1+i\omega\tau_{\mathrm{s}}^{*})$. This is a quite different point from the conventional DSC. It can be understood by considering that the heat capacity is measured as the thermal inertia against the temperature oscillation and that the thermal resistance, such as the thermal contact, plays a role of resistance against the propagation of the oscillation. But in the conventional DSC either the heat flow itself or the temperature difference for the heat flow is directly measured to estimate the heat capacity. This difference causes difference in the influence of the thermal contact. Thus, the thermal contact effect is the most important point in

Table 2 Comparison among various types of tm-DSC

Type	tm-hf-DSC	tm-pc-DSC	pm-DSC[#]
Furnace Temp. Control			
$T_f=$	$T_b+\beta t+A_f\exp(i\omega t)$	T_o or $T_b+\beta t$	$T_b+\beta t$
Other Operation Modes			
	$P_{s0}=P_{r0}=\Delta P_0=0$ $P_s^*=P_r^*=\Delta P_{sr}^*=0$ $P_{ps0}=P_{pr0}=\Delta P_{p0}=0$ $P_{ps}^*=P_{pr}^*=\Delta P_p^*=0$	$P_{s0}=P_{r0}=\Delta P_0=0$ $P_s^*=P_r^*=\Delta P^*=0$	$P_{s0}=P_{r0}=\Delta P_0=0$ $P_s^*=P_r^*=\Delta P^*=0$ or $P_{ps0}=P_{pr0}=\Delta P_{p0}=0$ $P_{ps}^*=P_{pr}^*=\Delta P_p^*=0$
From Base Line			
$\Delta C'=$	$\Delta B_p(K_K+2K_h+K_o)/(\beta-\beta'_{ps})$	$\{\Delta P_{p0}+\Delta B_p(K_K+2K_h+K_o)\}(\beta-\beta'_{ps})$	$\{\Delta P_{p0}+\Delta B_p(K_K+2K_h+K_o)\}/(\beta-\beta'_{ps})$ or $\{\Delta P_0+\Delta B_p(K_K+2K_h+K_o)\}/(\beta-\beta'_{ps})$
From Oscillation			
$C'_s/(1+i\omega\tau_s^*)=$	$-(S_1\Delta A''_p+S_2\Delta A'_p)/\omega A_{ps}$	$\Delta P''_p/\omega A_{ps}$	$\{\Delta P''_p-S_1\Delta A''_p-S_2\Delta A'_p\}/\omega A_{ps}$ or $\{\Delta P''_{sr}-S_1\Delta A''_p-S_2\Delta A_p{}'\}/\omega A_{ps}$
$C''_s/(1+i\omega\tau_s^*)=$	$S_1\Delta A'_p-S_2\Delta A''_p)/\omega A_{ps}$	$\Delta P'_p/\omega A_{ps}$	$(\{\Delta P'_p+S_1\Delta A'_p-S_2\Delta A''_p\}/\omega A_{ps}$ or $\{\Delta P'_{sr}+S_1\Delta A'_p-S_2\Delta A''_p\}/\omega A_{ps}$

[#] The equations below are shown for pm-DSC irradiated from below or that from above.

complex heat capacity measurements by any type of tm-DSC [6, 9–11], and it should be discussed first.

When the thermal contact is not negligible, additional phase shift, which is equivalent to the imaginary part of the heat capacity, can be detected as an apparent imaginary part in a region where the imaginary part of the sample heat capacity does not occur. Therefore, this additional procedural phase shift can be used for checking the thermal contact effect. Thus, another possible way to measure the complex heat capacity precisely is to make the thermal contact good enough, for instance by using grease, and to observe the above procedural phase shift for checking the thermal contact effect. After confirming that the additional phase shift is not detectable in a region where the imaginary part does not occur, we can measure the complex heat capacity by neglecting the thermal contact effect.

We can also measure the real part of sample heat capacity independently from the base line in the conventional DSC or from the average temperature difference, $<\Delta T>$ in tm-hf-DSC and pm-DSC or the average power input difference, $<\Delta P_{p0}>$, in tm-pc-DSC. They can be obtained by integrating the oscillating differences for n cycles,

$$<\Delta T> = (\omega/2n\pi)\int \Delta T\,\mathrm{d}t \tag{61}$$

and

$$<\Delta P_{p0}> = (\omega/2n\pi)\int \Delta P_{p0}\,\mathrm{d}t \tag{62}$$

By using these quantities and Eq. (43) or Eq. (50), we can measure C'_s. However, this is not necessarily equal to C'_s estimated from the equations of the oscillation, because the latter is dependent on the frequency [12].

Another point to be discussed is easiness or precision of the temperature modulation. The following consideration seems valid as a general tendency. In pm-DSC, modulation is given by light irradiation and the furnace temperature is simply increasing at the constant rate, so that it is the easiest way for modulation and the precision of the modulation seems the highest. Thus, higher frequency modulation can be done in comparison with the other types. On the other hand, in tm-hf-DSC, the modulation is made by direct temperature control of the furnace, and its heat capacity is larger than those of the components of the apparatus, in general. Therefore, the thermal response time is larger than in the other types and the temperature control for the modulation is not so easy as in the others. In tm-pc-DSC the temperature control for the modulation is done for each side, the sample and the reference material, separately with each micro-heater, and the furnace temperature, if it occurs, is controlled at a constant rate heating. Therefore, the thermal response time is small, and the direct temperature control at high frequency modulation seems rather easier than in tm-hf-DSC.

The following point should also be considered in relation to precision of the temperature control. That is deformation of the sinusoidal temperature oscillation in the steady state. It may cause some error, but precisely repeated deformation causes higher harmonics in the oscillation, so that it does not cause so severe errors as occasional deformations, which cause deviation from the steady state.

As it was discussed in relation with the thermal contact effect, the temperature oscillation is propagating through the thermal path, which has the heat capacity and the definite thermal resistance, and the phase is changing while the amplitude is decreasing along the path. The same situation occurs within the sample itself and between the sample and the sample pan. This is another cause of error, so that the amount or the thickness of the sample should be considered [13]. However, in the general model of this paper, the sample temperature is assumed to be uniform, and it should be considered in another way.

Appendix

Furnace temperature and reference material temperature as reference oscillation

In tm-hf-DSC, the furnace temperature is controlled as seen in Table 2, and relation between the furnace temperature oscillation and the temperature difference oscillation or the input difference oscillation to be measured might be useful, so that it is interesting to derive this relation. This has been done as below.

In the steady state the temperatures change as described in Eq. (10). These equations for the furnace temperature, the sample temperature, the sample cell holder temperature and other temperatures are introduced into Eqs (1), (2), (3) and (4), and from these four equations three sets of simultaneous equations are obtained by comparing the coefficients respectively from the terms relating the underlying constant rate heating, the constant terms and the terms expressing the oscillation, as was done before. For solving these simultaneous equations, we use the following relations, which was obtained in the course of deriving the above comprehensive solutions;

$$\Delta A_\mathrm{h}^* = \Delta A_\mathrm{p}^*/3(1+i\omega\tau_\mathrm{h}) \tag{A-1}$$

$$\Delta B_\mathrm{p} = 3\Delta B_\mathrm{h} \tag{A-2}$$

and

$$\Delta\beta_\mathrm{i} = 0 \tag{A-3}$$

From these simultaneous equations, we finally have

$$\begin{aligned} A_\mathrm{ps}^*(g_1 + ig_2) = {} & K_\mathrm{K}A_\mathrm{f}^*/(1 + \mathrm{i}\omega\tau_\mathrm{K}) + P_\mathrm{s}^*/(1 + i\omega\tau_\mathrm{s}^*) + \\ & P_\mathrm{ps}^* - (\Delta P_\mathrm{p}^* + \Delta P_\mathrm{sr}^*)K_\mathrm{h}/(1 + i3\omega\tau_\mathrm{h})(1 + i\omega\tau_\mathrm{h})(S_1 + iS_2) \end{aligned} \tag{A-4}$$

where

$$\begin{aligned} g_1 + ig_2 = {} & 2K_\mathrm{K} + 3K_\mathrm{h} + K_\mathrm{s} + K_\mathrm{o} + i\omega C_\mathrm{p} - K_\mathrm{K}/(1 + i\omega\tau_\mathrm{K}) - K_\mathrm{s}/(1 + i\omega\tau_\mathrm{s}^*) - \\ & 3K_\mathrm{h}\{1 + (i\omega C_\mathrm{s}^*)/3(1 + i\omega\tau_\mathrm{h})(S_1 + iS_2)\}/(1 + i3\omega\tau_\mathrm{h}) \end{aligned} \tag{A-5}$$

Because in tm-hf-DSC

$$P_\mathrm{s}^* = P_\mathrm{ps}^* = \Delta P_\mathrm{p}^* = \Delta P_\mathrm{sr}^* = 0 \tag{A-6}$$

we have

$$A^*_{\mathrm{ps}}(g_1 + ig_2) = K_{\mathrm{K}}A^*_{\mathrm{f}}/(1 + i\omega\tau_{\mathrm{K}}) \tag{A-7}$$

By introducing this equation into Eqs (44) and (45), we obtain the relation between the furnace temperature oscillation and the temperature difference oscillation, and these are the general and rigorous solutions for tm-hf-DSC. These soulutions was tried to be obtained but could not be derived in our previous paper [5]. However, they are not useful, because it is very complicated and, moreover, the complex sample heat capacity is involved in the parameters, $(g_1{+}ig_2)$. Thus, the sample temperature oscillation should be the reference oscillation, and its relations with the temperature difference oscillation, i.e., Eqs (44) and (45), are the useful relations for the heat capacity measurement by tm-hf-DSC.

Similarly, the temperature difference oscillation or the input difference oscillation can be obtained as a function of the reference material temperature oscillation. This relation can be derived by exchanging ΔC^*_{s}, C'_{s} and C''_{s} by ΔC^*_{r}, C'_{r} and C''_{r}, respectively, in Eqs (30)–(32). The average temperature difference and the input difference (or the conventional DSC method) does not change by this exchange [Eq. (29)], but the unknown sample heat capacity is involved in the proportionality coefficient in the oscillating temperature difference for tm-hf-DSC and pm-DSC by the exchange [Eqs (31) and (32)]. Therefore, it is not practical and useful.

Thus the furnace temperature and the reference material temperature are both not suitable for the reference oscillation.

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