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A theoretical approach to steady state of photo-modulated heat flux DSC and its application to complex heat capacity measurements

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Abstract

Modulation of heat flux DSC can be made by modulated light irradiation to the cells or the cell holders. For this type of temperature-modulated DSC, a theoretical approach has been tried to study steady state and hence its application to heat capacity measurement. In this approach, additional heat flows, such as mutual heat exchange between the sample and the reference material and heat loss to the environment, are taken into account together with heat capacities in the heat paths, which have the effect of amplitude decrement and phase shift of the oscillation. The effect of thermal contact between the cell and the cell holder is also considered. The results are compared with the results for other types of temperature-modulated DSC made by similar approaches to make clear the features of this type of temperature-modulated DSC.

Keywords: Temperature-modulated DSC; Photo-modulated DSC; Heat flux DSC; Steady state; Complex heat capacity measurement

1. Introduction

Various types of temperature-modulated differential scanning calorimetry (tm-DSC) are now used to study thermal properties of materials, especially of high polymers. Among them, a unique type of tm-DSC has been used for the same purpose [1,2]. In this type, heat flux-DSC (hf-DSC) is used, and the modulation is given by modulated light irradiation to the cells or the cell holders. Therefore, this type of DSC should be called photo-modulated hf-DSC (pm-hf-DSC).

The present authors have pursued theoretical approaches to understand steady state in various types of tm-DSC, such as hf-DSC and power compensation DSC by direct temperature modulation, and hence their application to measurements of complex heat capacity were also investigated [3–5]. In these apparatuses additional heat flows occur together with the main heat flows from the furnace to the sample and the reference material; they are heat loss to the environment through the thermocouple leads and by purge gas, and heat exchange between the sample and the reference material. These heat flows were considered in our previous papers [3–5].

The heat capacities existing inevitably with these heat paths have influence on the temperature oscillations by phase shift and amplitude decrement, so that these heat capacities were also taken into accounts [3–5]. In other theoretical considerations on tm-DSC, these effects are neglected [6] or considered partly [7],

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but it was one of the purpose of our previous papers to point out the amplitude decrement and the phase shift which depend on the thermal characteristics of the apparatus. Thermal contact between the cell and the cell holder is also a factor influencing the temperature oscillation, so that its effect was also considered [4,5].

Similar approach has been applied to pm-hf-DSC, and the results are reported in this paper. The feature of this type of tm-DSC is discussed on the base of the results.

2. Models

The schematic drawing of an hf-DSC is shown in Fig. 1, where the reference material is not used because of the reason described below. In this apparatus the heat is supplied to the sample through the base plate and it is expressed as Q_{Ks}. The heat path has the heat capacity, C_K and its heat transfer coefficient is K_K. Similarly, the heat, Q_{Kr}, is supplied to the reference material side through the base plate. Its thermal characteristics are the same with those of the sample side (C_K and K_K), because of the symmetry of the apparatus.

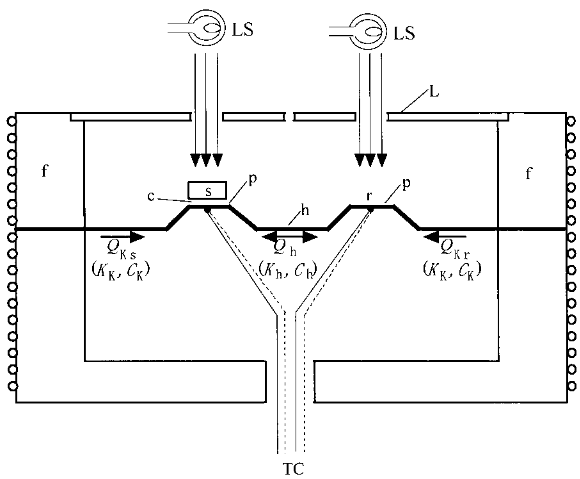

Fig. 1. Schematic drawing of pm-hf-DSC apparatus, where the light is irradiated from above. The symbols are as follows: s, sample; r, reference material side; p, cell holder plate; f, furnace; h, heat path for mutual heat exchange; L, lid of furnace; c, thermal contact, LS, light source; TC, thermocouple; K, heat transfer coefficients; C, heat capacities and Q, heat flows.

In addition to these heat flows, the mutual heat exchange occurs between the sample side and the reference material side, and it is Q_h in the figure. The characteristics of this heat path are expressed by K_h and C_h. Though it is not shown in the figure, the third heat flow occurs and it is the heat loss to the outside from the sample and the reference material side through the thermocouple leads and by the purge gas by the overall heat transfer coefficient, K_0.

The heat capacities are distributed along the heat paths, but they are approximated to be concentrated at some points for simplicity. For instance, C_K is located at the mid-point between the furnace and the sample. It is also assumed that the temperature distribution within the sample is negligibly small, and its effect will be discussed below.

Thus, one of the models used in this research (Model 1) can be expressed by electrical equivalent circuits, which are shown in Fig. 2. In the circuits light irradiation is expressed as micro-power-sources (MPS) attached to the sample and the reference material side.

One of the points we should consider for tm-DSC is thermal contact between the sample cell and the cell holder, because this is an uncontrollable experimental factor and has effect on the temperature oscillations. When we use the reference material, another uncontrollable experimental factor is introduced, i.e., thermal contact between the reference material cell and its holder plate. Therefore, the reference material should not be used to avoid unnecessary error and only the sample cell is set in the apparatus, when we take the thermal contact effect into accounts (see Fig. 1).

In relation to this, two types of pm-hf-DSC can exist. In one type the modulated light is irradiated at the upper lids of the sample cell and the reference material side from above (Fig. 1), while in the other type the light is irradiated at the rear side of the cell holder plates from below (Fig. 3). To take this thermal contact effect into accounts, two other models are made and their electrical equivalent circuits are reproduced in Figs. 4 and 5 (Models 2 and 3), respectively. In these equivalent circuits, the sample cell is separated from the cell holder, the thermocouple and so on, and a resistance between the sample cell and the cell holder represents the thermal contact. Thus, in the Model 2 the light energy is transferred to the sample

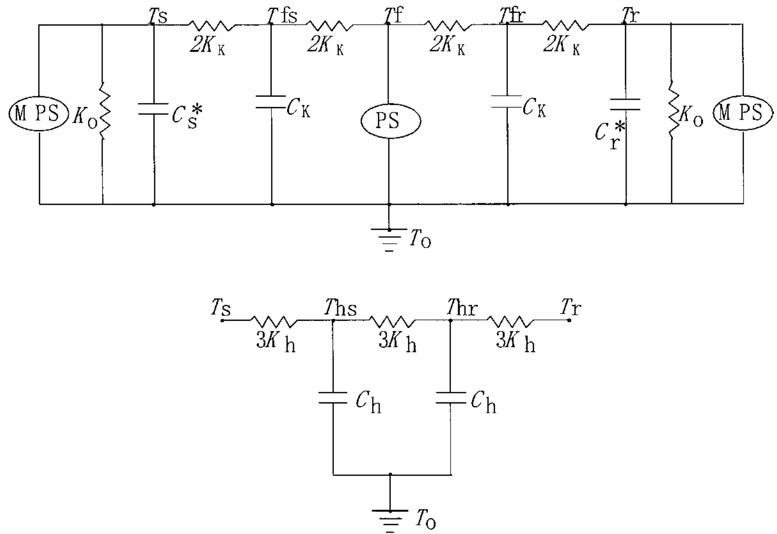

Fig. 2. Equivalent electrical circuits for photo-modulated DSC without thermal contact effect (Model 1). The main part (upper) and the additional part for mutual heat exchange (lower) are shown separately for easy recognition. PS and MPS are, respectively, the power source (the heat source) for the furnace and the micro-power source (the light source).

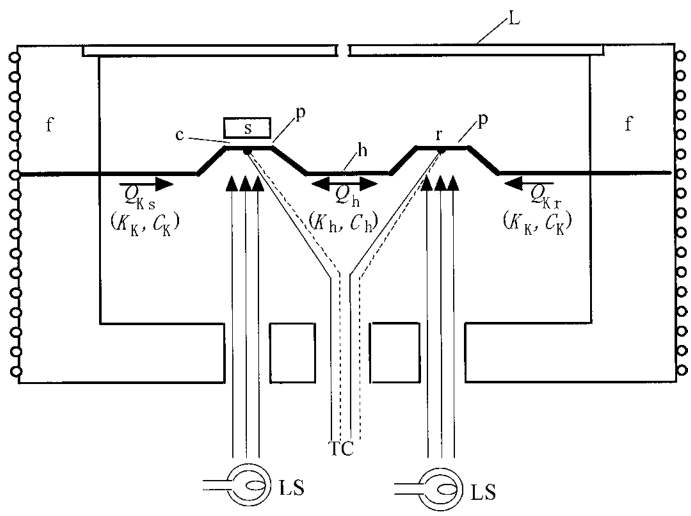

Fig. 3. Schematic drawing of pm-hf-DSC apparatus, where the light is irradiated from below. The symbols are the same as in Fig. 1.

cell holder (including the thermocouple) through the sample and the thermal contact, while in the Model 3 the light energy is supplied directly to the cell holders. Besides this geometrical difference we should notice that the temperature difference we measure is not the difference between the sample temperature and the reference side temperature, but the temperature difference between the thermocouples attached to the cell holders. The heat transfer coefficient due to this thermal contact is expressed by K_c, and it is not taken into account in the Model 1 (see Fig. 2), but it is involved in the other two models (Figs. 4 and 5).

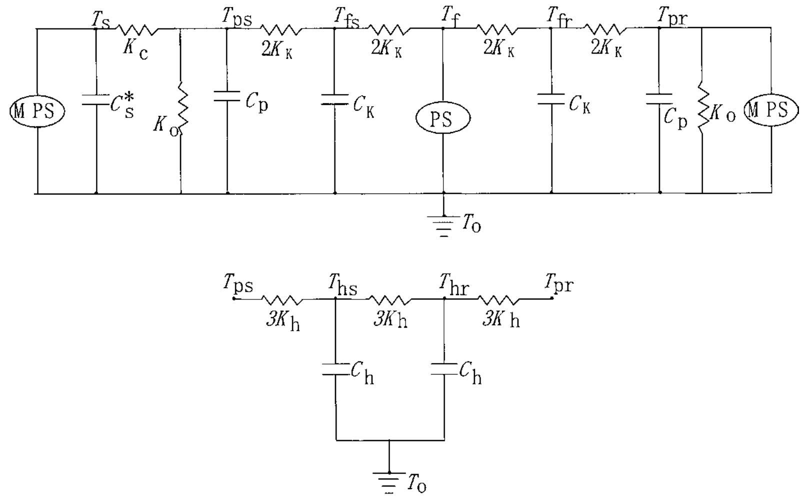

Fig. 4. Equivalent electrical circuits for photo-modulated DSC, where the light is irradiated from above and the thermal contact effect is taken into accounts (Model 2). The main part (upper) and the additional part for mutual heat exchange (lower) are shown separately for easy recognition. PS and MPS are the same as in Fig. 2.

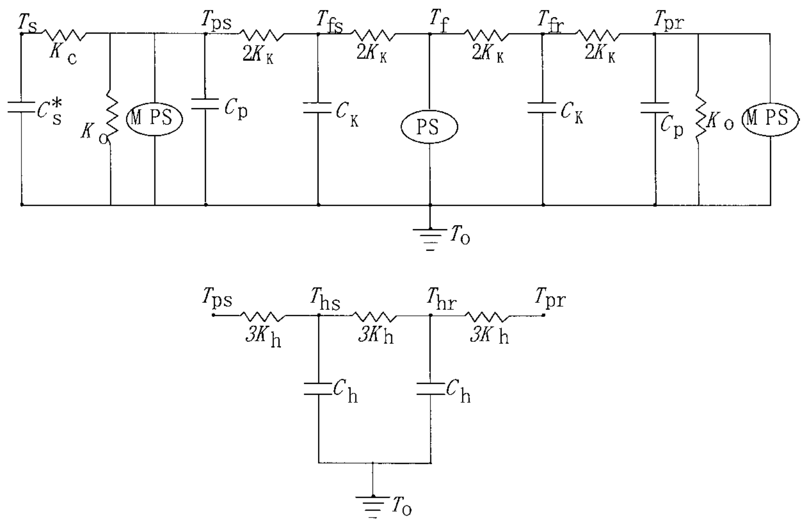

Fig. 5. Equivalent electrical circuits for photo-modulated DSC, where the light is irradiated from below and the thermal contact effect is taken into accounts (Model 3). The main part (upper) and the additional part for mutual heat exchange (lower) are shown separately for easy recognition. PS and MPS are the same as in Fig. 2.

3. Fundamental equations

3.1. Pm-DSC without thermal contact effect (Model 1)

For the steady state of the first model (Fig. 2), the fundamental equations without the thermal contact effect are as follows:

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

$$C_s^* \mathrm{d}T_s/\mathrm{d}t = 2K_K(T_{fs} - T_s) + 3K_h(T_{hs} - T_s) + K_o(T_o - T_s) + P_s^* \exp(\mathrm{i}\omega t) + P_{s0}, \tag{2}$$

$$C_h dT_{hs}/dt = 3K_h(T_s - T_{hs}) + 3K_h(T_{hr} - T_{hs}), \tag{3}$$

$$C_h dT_{hr}/dt = 3K_h(T_r - T_{hr}) + 3K_h(T_{hs} - T_{hr}), \tag{4}$$

$$C_r^* dT_r/dt = 2K_K(T_{fr} - T_r) + 3K_h(T_{hr} - T_r) + K_o(T_o - T_r) + P_r^* \exp(i\omega t) + P_{r0}, \tag{5}$$

$$C_K dT_{fr}/dt = 2K_K(T_f - T_{fr}) + 2K_K(T_r - T_{fr}), \tag{6}$$

where C, T, t, K, P^*, P_0 and ω are the heat capacity, the temperature, the time, the heat transfer coefficient, the complex amplitude of modulated power input, the constant power input and the angular frequency, respectively. It is worth noting that $P^*$and P_0 are not the light intensity, but the energy absorbed into the sample and the reference material side. The complex is introduced to express both the amplitude and the phase angle, and the asterisks mean that these quantities are complexes consisting of the real and the imaginary parts, while exp(ix) is equal to cos x + i sin x and i is the unit of imaginary numbers. The subscripts for the temperatures and the power inputs are as follows:

1. f, the furnace;
2. fs, the mid-point between the furnace and the sample;
3. s, the sample (+cell);
4. r, the reference material (+cell);
5. fr, the mid-point between the furnace and the reference material;
6. hs, a point in the heat path for mutual heat exchange;
7. hr, another similar point near the reference material, and
8. o, the environment.

The subscripts for the heat capacities and the heat transfer coefficients, K, s, r, h and o are as follows:

1. K, the heat path between the furnace and the sample or the reference material side;
2. s, the sample (+cell);
3. r, the reference material (+cell);
4. h, the heat path for the mutual heat exchange, and
5. o, the heat path to the environment.

These symbols are also shown in Fig. 2 of the equivalent electrical circuits.

The heat capacity is expressed as a complex figure, as follows:

$$C^* = C' - iC'', \tag{7}$$

where C^*, C' and C'' are 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 in this paper to investigate various possibilities of the heat capacity measurements.

3.2. Pm-DSC irradiated from above (Model 2)

To elucidate the thermal contact effect, similar but somewhat different fundamental equations are derived. For the second model (Fig. 4), where the light is irradiated on the lids of the cells from above, we have

$$C_K dT_{fs}/dt = 2K_K(T_f - T_{fs}) + 2K_K(T_{ps} - T_{fs}), \tag{8}$$

$$C_s^* dT_s/dt = K_c(T_{ps} - T_s) + P_s^* \exp(i\omega t) + P_{s0}, \tag{9}$$

$$C_p dT_{ps}/dt = 2K_K(T_{fs} - T_{ps}) + 3K_h(T_{hs} - T_{ps}) + K_o(T_o - T_{ps}) + K_c(T_s - T_{ps}), \tag{10}$$

$$C_h dT_{hs}/dt = 3K_h(T_{ps} - T_{hs}) + 3K_h(T_{hr} - T_{hs}), \tag{11}$$

$$C_h dT_{hr}/dt = 3K_h(T_{pr} - T_{hr}) + 3K_h(T_{hs} - T_{hr}), \tag{12}$$

$$C_p dT_{pr}/dt = 2K_K(T_{fr} - T_{pr}) + 3K_h(T_{hr} - T_{pr}) + K_o(T_o - T_{pr}) + P_{pr}^* \exp(i\omega t) + P_{pr0}, \tag{13}$$

$$C_K dT_{fr}/dt = 2K_K(T_f - T_{fr}) + 2K_K(T_{pr} - T_{fr}), \tag{14}$$

where the subscripts, c, p, pr and ps mean the thermal contact, the cell holder, that for the reference material and that for the sample, respectively. The reference material is not used in this case and the light is irradiated directly to the cell holder in the reference side.

3.3. Pm-DSC irradiated from below (Model 3)

For the third model (Fig. 5), where the light is irradiated at the cell holder plate from below, the fundamental equations are as follows:

$$C_\mathrm{K}\mathrm{d}T_\mathrm{fs}/\mathrm{d}t = 2K_\mathrm{K}(T_\mathrm{f}-T_\mathrm{fs}) + 2K_\mathrm{K}(T_\mathrm{ps}-T_\mathrm{fs}), \quad (15)$$

$$C_\mathrm{s}^*\mathrm{d}T_\mathrm{s}/\mathrm{d}t = K_\mathrm{c}(T_\mathrm{ps}-T_\mathrm{s}), \quad (16)$$

$$\begin{aligned} C_\mathrm{p}\mathrm{d}T_\mathrm{ps}/\mathrm{d}t = {} & 2K_\mathrm{K}(T_\mathrm{fs}-T_\mathrm{ps}) + 3K_\mathrm{h}(T_\mathrm{hs}-T_\mathrm{ps}) \\ & + K_\mathrm{o}(T_\mathrm{o}-T_\mathrm{ps}) + K_\mathrm{c}(T_\mathrm{s}-T_\mathrm{ps}) \\ & + P_\mathrm{ps}^* \exp(\mathrm{i}\omega t) + P_\mathrm{ps0}, \end{aligned} \quad (17)$$

$$C_\mathrm{h}\mathrm{d}T_\mathrm{hs}/\mathrm{d}t = 3K_\mathrm{h}(T_\mathrm{ps}-T_\mathrm{hs}) + 3K_\mathrm{h}(T_\mathrm{hr}-T_\mathrm{hs}), \quad (18)$$

$$C_\mathrm{h}\mathrm{d}T_\mathrm{hr}/\mathrm{d}t = 3K_\mathrm{h}(T_\mathrm{pr}-T_\mathrm{hr}) + 3K_\mathrm{h}(T_\mathrm{hs}-T_\mathrm{hr}), \quad (19)$$

$$\begin{aligned} C_\mathrm{p}\mathrm{d}T_\mathrm{pr}/\mathrm{d}t = {} & 2K_\mathrm{K}(T_\mathrm{fr}-T_\mathrm{pr}) + 3K_\mathrm{h}(T_\mathrm{hr}-T_\mathrm{pr}) \\ & + K_\mathrm{o}(T_\mathrm{o}-T_\mathrm{pr}) + P_\mathrm{pr}^* \exp(\mathrm{i}\omega t) \\ & + P_\mathrm{pr0}, \end{aligned} \quad (20)$$

$$C_\mathrm{K}\mathrm{d}T_\mathrm{fr}/\mathrm{d}t = 2K_\mathrm{K}(T_\mathrm{f}-T_\mathrm{fr}) + 2K_\mathrm{K}(T_\mathrm{pr}-T_\mathrm{fr}). \quad (21)$$

3.4. Operating conditions

In the pm-DSC apparatus, the furnace is controlled at a constant heating rate

$$T_\mathrm{f} = T_\mathrm{b} + \beta t, \quad (22)$$

where T_b and β are the initial temperature and the heating rate, respectively, and when we make quasi-isothermal measurements, β equals zero. Because of modulated irradiation, the other temperatures, T_i, increase linearly with oscillation in the steady state as follows:

$$T_\mathrm{i} = T_\mathrm{b} + \beta t + A_\mathrm{i}^* \exp(\mathrm{i}\omega t) - \beta'_\mathrm{i} t - B_\mathrm{i}, \quad (23)$$

where, A_i^*, β'_i and B_i are, respectively, the complex amplitude, the decrease of the heating rate due to heat loss to the environment and the constant temperature lag from the furnace temperature. The temperatures are not the complex quantities and only their real parts have physical meanings. This is the same in the equations below.

4. Derivation and solutions

4.1. Pm-DSC without thermal contact effect (Model 1)

First the case for neglecting the effect of thermal contact is dealt with. When we get differences in the fundamental equations (Eqs. (1)–(6)) between the symmetric points, we have

$$\begin{aligned} \Delta C^*\mathrm{d}T_\mathrm{s}/\mathrm{d}t + C_\mathrm{r}^*\mathrm{d}\Delta T/\mathrm{d}t = {} & 2K_\mathrm{K}\Delta T_\mathrm{f} + 3K_\mathrm{h}\Delta T_\mathrm{h} \\ & -(2K_\mathrm{K}+3K_\mathrm{h}+K_\mathrm{o})\Delta T + \Delta P^* \exp(\mathrm{i}\omega t) + \Delta P_0, \end{aligned} \quad (24)$$

$$C_\mathrm{K}\mathrm{d}\Delta T_\mathrm{f}/\mathrm{d}t = 2K_\mathrm{K}\Delta T - 4K_\mathrm{K}\Delta T_\mathrm{f}, \quad (25)$$

$$C_\mathrm{h}\mathrm{d}\Delta T_\mathrm{h}/\mathrm{d}t = 3K_\mathrm{h}\Delta T - 9K_\mathrm{h}\Delta T_\mathrm{h}, \quad (26)$$

where

$$\Delta C^* = C_\mathrm{s}^* - C_\mathrm{r}^*, \quad (27)$$

$$\Delta P^* = P_\mathrm{s}^* - P_\mathrm{r}^*, \quad (28)$$

$$\Delta P_0 = P_\mathrm{s0} - P_\mathrm{r0}, \quad (29)$$

$$\Delta T = T_\mathrm{s} - T_\mathrm{r}, \quad (30)$$

$$\Delta T_\mathrm{f} = T_\mathrm{fs} - T_\mathrm{fr}, \quad (31)$$

$$\Delta T_\mathrm{h} = T_\mathrm{hs} - T_\mathrm{hr}. \quad (32)$$

The temperature difference, ΔT, changes similarly to Eq. (9), so that we have

$$\Delta T = \Delta A^* \exp(\mathrm{i}\omega t) - \Delta\beta' t - \Delta B \quad (33)$$

and similarly for the other temperature differences between the symmetric points, ΔT_i,

$$\Delta T_\mathrm{i} = \Delta A_\mathrm{i}^* \exp(\mathrm{i}\omega t) - \Delta\beta'_\mathrm{i} t - \Delta B_\mathrm{i}, \quad (34)$$

where Δ expresses the difference between the symmetric points. Introducing Eqs. (33) and (34) into Eqs. (24)–(26) and comparing the coefficients, we have simultaneous equations and their solutions, similarly to the derivation in the previous paper [3–5].

From the terms relating with t, we get

$$\Delta\beta' = \Delta\beta'_\mathrm{i} = 0. \quad (35)$$

By using this relation we get the following equation from the terms describing the constant temperature lags:

$$\Delta C' = \{\Delta P_0 + (K_\mathrm{K} + 2K_\mathrm{h} + K_\mathrm{o})\Delta B\}/\beta, \quad (36)$$

where ΔC' is the real part of the complex heat capacity difference between the sample and the reference material. This relation is essentially the same as that for the conventional DSC, where P_{s0}, P_{r0}, P_s^* and P_r^* are all equal to zero. When the power input by the modulated light is not different between the sample and the reference material, the relation becomes exactly equal to that for the conventional DSC.

From the coefficients in the oscillating terms complex amplitude can be obtained:

$$\Delta A^* = (\Delta P^* - i\omega A_s \Delta C^*)/(S_2 + iS_1), \tag{37}$$

where S_1 and S_2 are as follows:

$$S_1/\omega = C_K/4(1+\omega^2\tau_K^2) + C_h/9(1+\omega^2\tau_h^2) + C'_r \tag{38}$$

$$S_2 = -K_K/(1+\omega^2\tau_K^2) - K_h/(1+\omega^2\tau_h^2) + (2K_K + 3K_h + K_o) + \omega C''_r. \tag{39}$$

The terms τ are given below:

$$\tau_K = C_K/4K_K, \tag{40}$$

$$\tau_h = C_h/9K_h. \tag{41}$$

When the power input is not different between the sample and the reference material,

$$\Delta P^* = 0. \tag{42}$$

Then Eq. (37) becomes

$$\Delta A^* = -i\omega A_s \Delta C^*/(S_2 + iS_1) \tag{43}$$

and this is the same equation for tm-hf-DSC [4], so that the method for heat capacity determination by tm-hf-DSC [4] can be applied to pm-hf-DSC. When the inputs by the irradiated light are different, ΔP^* should additionally be taken into accounts, as seen in Eq. (37). Therefore, the method becomes somewhat complicated. When only the sample is irradiated,

$$\Delta A^* = (P_s^* - i\omega A_s \Delta C^*)/(S_2 + iS_1). \tag{44}$$

4.2. Pm-DSC irradiated from above (Model 2)

In order to see the thermal contact effect for the Model 2 of pm-hf-DSC in which the light is irradiated on the lids of the cells (Figs. 1 and 3), the following relation is first derived by introducing Eq. (23) into Eqs. (9) and (10) for solving the other fundamental Eqs. (8–14):

$$\beta'_s = \beta'_{ps}, \tag{45}$$

$$B_s = B_{ps} + \{C_s^*(\beta - \beta'_{ps}) - P_{s0}\}/K_c, \tag{46}$$

$$A_s^* = (K_c A_{ps}^* + P_s^*)/(K_c + i\omega C_c^*). \tag{47}$$

This relation expresses the amplitude decrement and the phase shift by the thermal contact. It is then introduced into Eq. (10), and the same method of derivation explained above is applied. Thus, we have

$$\Delta B_p = \{C_s(\beta - \beta'_{ps}) - \Delta P_0\}/(K_K + 2K_h + K_o). \tag{48}$$

This is again the same as that for the conventional DSC when ΔP_0 is controlled to be zero.

From the oscillating terms we have

$$(S_2 + iS_1)\Delta A_p^* = (P_s^* - i\omega C_s^* A_{ps}^*)/(1 + i\omega\tau_c^*) - P_r^*, \tag{49}$$

where

$$S_1/\omega = C_K/4(1+\omega^2\tau_K^2) + C_h/9(1+\omega^2\tau_h^2) + C_p, \tag{50}$$

$$S_2 = -K_K/(1+\omega^2\tau_K^2) - K_h/(1+\omega^2\tau_h^2) + (2K + 3h + k), \tag{51}$$

$$\tau'_c = C'_s/K_c, \tag{52}$$

$$\tau''_c = C''_s/K_c. \tag{53}$$

For heat capacity measurement we get Eq. (49), but its practical usefulness is limited, because τ_c^* is an unknown and uncontrollable experimental factor. This point is a fundamental drawback of Model 2 compared with Model 3 as described below. If we can make the thermal contact good enough and if we neglect this factor, Eq. (49) naturally reduces to Eq. (37), but it may cause some error.

4.3. Pm-DSC irradiated from below (Model 3)

For Model 3 of pm-hf-DSC in which the light is irradiated on the cell holders from below (Figs. 3 and 5), the next equations are first derived from Eq. (16) similarly to the above:

$$\beta'_s = 0, \tag{54}$$

$$\beta C_s = K_c(B_s - B_{ps}), \tag{55}$$

$$A_s^* = A_{ps}^*(1 + \omega\tau''_c - i\omega\tau''_c)/\{(1 + \omega\tau''_c)^2 + \omega^2\tau'^2_c\}. \tag{56}$$

The amplitude decrement and the phase shift by the thermal contact shown in this equation are different from Eq. (47). Similarly to the above, it is introduced into Eq. (17) and the same method is applied. The obtained relations are shown below:

$$\beta C'_{\mathrm{s}} = (K_{\mathrm{K}} + 2K_{\mathrm{h}} + K_0)\Delta B_{\mathrm{p}} + \Delta P_0, \qquad (57)$$

$$(S_2 + \mathrm{i}S_1)\Delta A^*_{\mathrm{p}} = \Delta P^* - \mathrm{i}\omega A^*_{\mathrm{ps}} C^*_{\mathrm{s}} / \{(1 + \mathrm{i}\omega\tau^*_{\mathrm{c}}), \qquad (58)$$

where S_1 and S_2 are given in Eqs. (50) and (51).

For the phase angle difference, δ

$$\tan\delta = (R_2 C'_{\mathrm{s}} - R_1 C''_{\mathrm{s}})/(R_2 C''_{\mathrm{s}} + R_1 C'_{\mathrm{s}}), \qquad (59)$$

$$\sin\delta = (R_2 C'_{\mathrm{s}} - R_1 C''_{\mathrm{s}})/\sqrt{(C'^2_{\mathrm{c}} + C''^2_{\mathrm{s}})(R_1^2 + R_2^2)}, \qquad (60)$$

where

$$R_1 = S_2(1 + \omega\tau''_{\mathrm{c}}) - \omega S_1 \tau'_{\mathrm{c}}, \qquad (61)$$

$$R_2 = S_1(1 + \omega\tau''_{\mathrm{c}}) - \omega S_2 \tau'_{\mathrm{c}}. \qquad (62)$$

As mentioned above, Eq. (57) is essentially the same as the equation for the conventional DSC. The relation obtained from the oscillating terms, Eq. (58), is somewhat complicated, but when the power input by the light are equal to each other, the equation becomes simple and it is equal to that for tm-hf-DSC. This equation shows us an advantage of Model 3 over Model 2, in which the equalization of the light power does not bring us the simple relation such as for Model 3.

5. Discussion

Even in pm-hf-DSC the two parameters, i.e., the time constants, τ_{K} and τ_{h} originated from the apparatus, are involved together with the other time constants τ^*_{c}. Moreover, the light power inputs are both contained in the derived relations. Reflecting these situations, the relations for pm-DSC are somewhat complicated compared with those for tm-pc-DSC and tm-hf-DSC. This is caused by the facts that the phase shift occurs due to the heat capacities and the heat transfer coefficients in the heat paths, as shown by S_1 and S_2. Furthermore, the power input difference (not the light intensity difference) between the sample and the reference side has an effect to the relations used for the heat capacity measurements.

To reduce this complexity, the light power inputs for the sample and the reference side should be equal to each other. By this reason, Model 3 of pm-DSC, where the light is irradiated to the cell holder directly from below, is preferable to Model 2, considering the thermal contact effect. The situation becomes much simpler for the case that the thermal contact effect is negligible and the power input difference can be neglected, and it is quite the same as tm-hf-DSC.

As Hatta [8] pointed out before, the correction of the thermal contact effect cannot be done, when the imaginary part of the heat capacity is not negligible, because two unknown experimental factors, τ'_{c} and τ''_{c} are involved. However, when the imaginary part is negligible, sin δ is in a definite relation with τ'_{c} provided that the power input difference is zero. Therefore, the correction can be made as was postulated by Hatta, using experimentally obtained relation between sin δ and the correction factor. Another solution of this problem may be use of grease to keep good thermal contact.

As stated above, the temperature distribution in the sample is neglected in this paper. However, the thermal response of the sample is the same as that of the thermal contact, because the heat capacity and the thermal resistance are distributed in the sample. The situation in the sample is quite the same as for the thermal contact, and the temperature oscillation propagates through the combination of the heat capacity and the thermal resistance, so that the amplitude decrement and the phase shift occur similarly in the sample. Therefore, the sample has the same effect as the thermal contact, i.e., the amplitude decrement and the phase shift, especially for a thick sample. This effect was already discussed in a paper by Schenker and his co-worker [9], and it is another point to be taken into account in the actual heat capacity measurements.

Thus, we should consider three causes for the amplitude decrement and the phase shift; they are the thermal characteristics of the apparatus, the thermal contact and the sample itself. The first problem can be solved using the correction factor, $(S_2 + \mathrm{i}S_1)$, obtained by careful experiments with standard materials, such as α-alumina [4]. However, the other two depend on the operator's skill and the experimental conditions. Use of thinner sample and grease for the good thermal contact seem to be appropriate means for these problems.

One of the features of pm-DSC is in the temperature control of the furnace. It should be controlled at a constant temperature or heated at a constant rate without oscillation, as seen in Eq. (22). Therefore, modulated temperature control is not needed, and this would bring us flexibility in design of the apparatus and expand the frequency range to higher frequency. This is a potential advantage over the other types of tm-DSC [1,2].

6. Concluding remarks

1. General analytical solutions for the steady state in pm-hf-DSC have been derived, and they are useful for the complex heat capacity measurements by pm-hf-DSC.
2. The solutions for Model 2, where the light is irradiated at the sample cell from above, are much more complicated than those for Model 3, in which the light is irradiated at the cell holder plate from below. Therefore, the Model 3 is preferable to Model 2.
3. The solutions for pm-hf-DSC are more complicated than tm-hf-DSC. However, when the difference in the power input by the modulated light irradiation is equal to each other for Model 3, the equation for the complex heat capacity measurements is reduced to that for tm-hf-DSC. Moreover, pm-hf-DSC may have some other possibilities, which cannot be achieved by tm-hf-DSC.
4. The effects of the thermal characteristics of the apparatus and the thermal contact upon the amplitude decrement and the phase shift are elucidated and discussed. It is pointed out that the similar effect of the sample thickness should also be examined.

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