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Characteristic and applicability of a temperature-modulated differential scanning calorimeter for steady state measurement of heat capacity

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Abstract

Temperature-modulated calorimetry, in which an apparatus for temperature-modulated differential scanning calorimetry (DSC) is employed, has a variety of advantages in heat capacity measurement. Namely, the absolute value of heat capacity can be obtained easily, by using periodic signal we can exclude the effects of external noises and drifts, the frequency dependence of heat capacity can be measured, etc. However, it is quite different from differential scanning calorimetry when we consider the principle of its performance, although the apparatus developed for DSC is generally used for temperature-modulated calorimetry as well. In this paper, the difference between them is clarified and based upon it the possibility of the application is discussed.

Keywords: Temperature-modulated calorimetry; Temperature-modulated DSC; Heat capacity; Periodic heating; Equivalent circuit; Temperature waves

1. Introduction

Temperature-modulated calorimetry, in which a conventional differential scanning calorimeter is used has a variety of advantages.

1. Superior to light-irradiation a.c. calorimetry, the absolute value of heat capacity can be determined easily and furthermore, superior to Joule-heating a.c. calorimetry, heat capacities such as a temperature sensor, a heater, etc. do not affect the measurement.
2. In comparison with conventional DSC, the effects of external noises and drift can be easily excluded because the a.c. temperature response to periodic heating is used in analyzing the data.
3. Heat capacity can be measured as a function of frequency.

When we consider the principle of the performance of an apparatus, within framework of a naïve model the expression for obtaining heat capacity is given in common terms in both heat-flux DSC and temperature-modulated calorimetry. Namely, in heat-flux DSC, the heat capacity, C, of a sample is expressed by

$$C = \frac{K\Delta T}{\mathrm{d}T/\mathrm{d}t}, \tag{1}$$

where K is the heat transfer coefficient of the heat paths between a heater and a base plate, ΔT the temperature difference between reference and sample

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sides and dT/dt the heating rate. On the other hand, in temperature-modulated calorimetry, C is expressed by

$$C = \frac{KA_\Delta}{\omega A_S}, \tag{2}$$

where A_Δ is the amplitude of a.c. temperature difference between reference and sample sides, ω the angular frequency and A_S the amplitude of a.c. temperature of sample side. In addition, the phase difference between the a.c. temperature difference and the a.c. temperature of sample side is $\pi/2$. By comparing Eqs. (1) and (2), we find that the both expressions are essentially the same. However, the relation of Eq. (2) is not always correct. In temperature-modulated calorimetry, we have to take into account the effects of the propagation of a.c. temperature waves in the apparatus and a thermal resistance between the pan and a base plate since much quick temperature response is required different from the conventional DSC. For instance, although K is almost constant in heat-flux DSC, K is almost constant but it depends not only on temperature but also on frequency in temperature-modulated calorimetry. In the present paper, the above contributions have been considered in an apparatus when a.c. temperature wave propagation takes place. We have already proposed a method to obtain the heat capacity even when there is a thermal resistance between a pan and a base plate [1,2]. This is not discussed further in this paper.

By taking into account the above aspects, it is pointed out that temperature-modulated calorimetry is especially useful for the measurement of the heat capacity anomaly at a glass transition where even in a small change of the heat capacity we can obtain the anomaly independent of noise and drift against temperature.

2. Temperature-wave propagation in an apparatus

When we measure heat capacity by periodical heating methods, generally it is required that the thermal diffusion length is much larger than sample thickness, because the temperature in accordance with periodic heating should change uniformly over a sample. In periodic heating, both the temperature wave number and the temperature decay constant in a material are given by the same expression as

$$k = \sqrt{\frac{\omega}{2a}} = \sqrt{\frac{\omega\rho c}{2\lambda}}, \tag{3}$$

where ω is the angular frequency, a the thermal diffusivity, ρ the density, c the heat capacity and λ the thermal conductivity. Here, $1/k$ is called thermal diffusion length. As seen in Eq. (3), the magnitude of k depends not only on frequency but also on thermophysical properties of a sample.

As discussed above, the uniformity of a.c. temperature in a sample has been considered so far [3,4]. At a high frequency and/or in a thick sample, owing to the characteristic of a.c. temperature waves it is inevitable to exclude the temperature distribution in a sample. Schenker and Stäger [3] have calculated the distribution by solving the differential equation of thermal diffusion in terms of a finite element analysis and a priori expressed a sample thermally by heat capacitances and thermal resistances in the same manner as an electrical equivalent circuit. Hatta and Minakov [4] have proposed the condition to attain the proper uniformity of a.c. temperature in a sample for the heat capacity measurement based upon the exact solution. It is pointed out that in temperature-modulated calorimetry the above phenomena should be taken into account not only for a sample but also for an apparatus. Then, in the present paper attention is focussed in representing the portion in an apparatus, e.g., a heat transfer portion, a base plate, in terms of heat capacitances and thermal resistances.

To consider further, let us discuss one-dimensional a.c. temperature wave propagation. As shown in Fig. 1, plane a.c. temperature waves propagate along x-direction. The relation between a.c. temperature T and a.c.

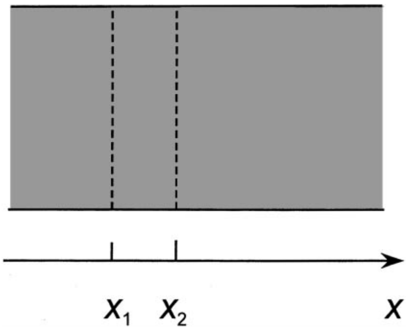

Fig. 1. One-dimensional temperature wave propagation in a bulk material.

heat flux q at $x=x_1$ and $x=x_2$ is considered. Generally, the a.c. temperature T_1 and a.c. heat flux q_1 at $x=x_1$ relate with a.c. temperature T_2 and a.c. heat flux q_2 at $x=x_2$ as follows [5]:

$$\begin{pmatrix} T_2 \\ q_2 \end{pmatrix} = \begin{pmatrix} \cosh[(1+\mathrm{i})k(x_2-x_1)] & -(\sinh[(1+\mathrm{i})k(x_2-x_1)])/((1+\mathrm{i})\lambda k) \\ -(1+\mathrm{i})\lambda k \sinh[(1+\mathrm{i})k(x_2-x_1)] & \cosh[(1+\mathrm{i})k(x_2-x_1)] \end{pmatrix} \begin{pmatrix} T_1 \\ q_1 \end{pmatrix}. \tag{4}$$

When

$$k(x_2-x_1) < 1, \tag{5}$$

each term in Eq. (4) can be expanded in terms of $k(x_2-x_1)$. Furthermore, if we take into account the first-order term with respect to $k(x_2-x_1)$, we obtain

$$\begin{pmatrix} T_2 \\ q_2 \end{pmatrix} = \begin{pmatrix} 1 & -R \\ -\mathrm{i}\omega C & 1 \end{pmatrix} \begin{pmatrix} T_1 \\ q_1 \end{pmatrix}, \tag{6}$$

where $R=(x_2-x_1)/\lambda$ and $C=\rho c(x_2-x_1)$. Then, in the form of an electrical equivalent circuit the relation might be expressed. When there is only a resistance R between x_1 and x_2, the relation between a.c. temperature T and a.c. heat flux q at $x=x_1$ and $x=x_2$ is given by

$$\begin{pmatrix} T_2 \\ q_2 \end{pmatrix} = \begin{pmatrix} 1 & -R \\ 0 & 1 \end{pmatrix} \begin{pmatrix} T_1 \\ q_1 \end{pmatrix}. \tag{7}$$

This equivalent circuit is expressed as shown in Fig. 2. On the other hand, when there is only a capacitance between x_1 and x_2, the relation between a.c. temperature T and a.c. heat flux q at $x=x_1$ and $x=x_2$ is given by

$$\begin{pmatrix} T_2 \\ q_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ -\mathrm{i}\omega C & 1 \end{pmatrix} \begin{pmatrix} T_1 \\ q_1 \end{pmatrix}. \tag{8}$$

This equivalent circuit is expressed as shown in Fig. 3.

When there is a capacitance and a resistance in order from x_1 to x_2 and vice versa, we can draw the equivalent circuit as in Fig. 4A and B, respectively. From Eqs. (7) and (8) the relation between a.c. temperature T and a.c. heat flux q at $x=x_1$ and $x=x_2$ is given by

$$\begin{aligned} \begin{pmatrix} T_2 \\ q_2 \end{pmatrix} &= \begin{pmatrix} 1 & -R \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ -\mathrm{i}\omega C & 1 \end{pmatrix} \begin{pmatrix} T_1 \\ q_1 \end{pmatrix} \\ &= \begin{pmatrix} 1+\mathrm{i}\omega CR & -R \\ -\mathrm{i}\omega C & 1 \end{pmatrix} \begin{pmatrix} T_1 \\ q_1 \end{pmatrix} \end{aligned} \tag{9}$$

for Fig. 4A. The relation for Fig. 4B is given by

$$\begin{aligned} \begin{pmatrix} T_2 \\ q_2 \end{pmatrix} &= \begin{pmatrix} 1 & 0 \\ -\mathrm{i}\omega C & 1 \end{pmatrix} \begin{pmatrix} 1 & -R \\ 0 & 1 \end{pmatrix} \begin{pmatrix} T_1 \\ q_1 \end{pmatrix} \\ &= \begin{pmatrix} 1 & -R \\ -\mathrm{i}\omega C & 1+\mathrm{i}\omega CR \end{pmatrix} \begin{pmatrix} T_1 \\ q_1 \end{pmatrix} \end{aligned} \tag{10}$$

If we ignore $\mathrm{i}\omega CR$ in diagonal components, both Eqs. (9) and (10) tend to Eq. (6). It should be pointed out that, since $k(x_2-x_1)=\sqrt{\omega CR/2}$, the condition of $\omega CR \ll 1$ is the same as the condition of Eq. (5). In one-dimensional a.c. temperature wave propagation, the equivalent circuit is shown by either Fig. 4A or B because they are equivalent under the above condition.

Based upon the above consideration, we can construct the equivalent circuit for an apparatus [6]. It is pointed out that, in a temperature-modulated calorimeter, the heat transfer coefficient K of the heat path

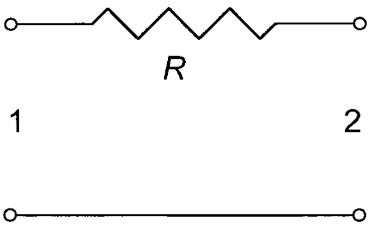

Fig. 2. Equivalent circuit when there is only a thermal resistance between x_1 and x_2.

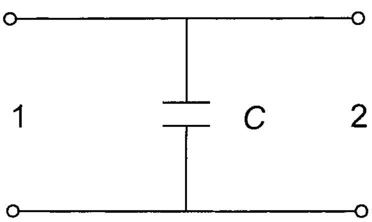

Fig. 3. Equivalent circuit when there is only a heat capacitance between x_1 and x_2.

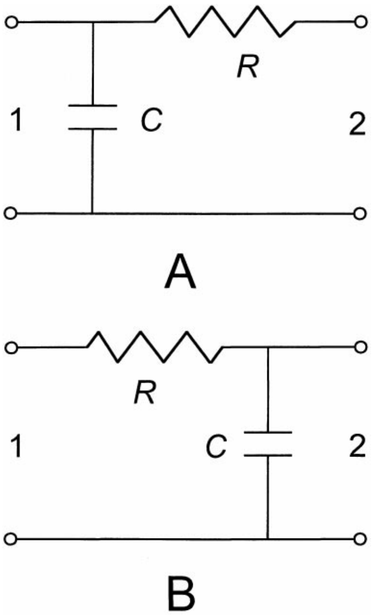

Fig. 4. (A) Equivalent circuit composed of a heat capacitance and a thermal resistance in order from x_1 to x_2. (B) Equivalent circuit composed of a thermal resistance and a heat capacitance in order from x_1 to x_2.

from the heater to the base plate, the heat transfer coefficient of the mutual heat exchange between the sample and the reference sides, the heat capacity of the base plate, etc. are no longer expressed in terms of a single component of heat capacitance and thermal resistance as in a conventional differential scanning calorimeter. Furthermore, the equivalent circuit for the total system depends on frequency as deduced from the condition of Eq. (5). For instance, in a bulk material shown in Fig. 1, when frequency increases, x_2-x_1 should be chosen by smaller distance and as a result the bulk material is expressed by connecting circuits of Fig. 4A or B in series.

The above facts indicate that Eq. (2) should be modified in temperature-modulated calorimetry, since K becomes complex and the other parts in the apparatus are also modified. As a result, the phase difference between A_Δ and A_S is no longer $\pi/2$. In fact, as shown in the previous paper [2], K and the heat capacity of the base plate depends on frequency. However, as far as the total system consists of a linear circuit, we can more or less obtain an unique relation between the heat capacity of a sample and the a.c. temperatures in an apparatus. The most significant difference in the total equivalent circuit between a temperature-modulated calorimeter and a conventional differential scanning calorimeter is that in former we have to take into account the heat capacity of the base plate [1,2,7]. Even in such a case, we can derive an improved relation between the heat capacity of a sample and the a.c. temperatures in an apparatus, if we use the information on the phases [1,2]. Furthermore, we have already shown that, even when there is the contribution of the thermal contact conductance between the sample pan and the base plate of an apparatus which is another significant contribution for temperature-modulated calorimetry, we can obtain a much improved relation [1,2].

3. Dissipation of heat from the surface of a sample

In a temperature-modulated calorimeter, the role of gas for the heat capacity measurement is not clear yet. In order to consider it, let us analyze such a system as shown in Fig. 5. The thickness d of a sample is thin enough to attain uniform temperature change in the sample, i.e., to determine the heat capacity C of the sample per unit area within accuracy of 1% $kd \leqq 0.4$ [4]. When a.c. heat flux q is applied to the front surface of a sample without heat dissipation, we obtain the a.c. temperature at the front surface as

$$T(0)=\frac{q}{\mathrm{i}\omega C}. \tag{11}$$

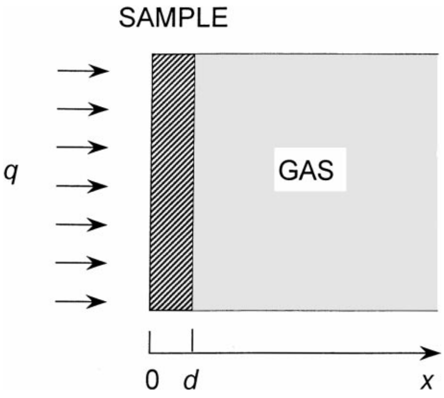

Fig. 5. Heat dissipation from the surface of a sample to surrounding gas.

On the other hand, when a part of heat dissipates from the rear surface of the sample into gas, the a.c. temperature at the front surface is given by

$$T(0) = \frac{q[\lambda k + (1+\mathrm{i})\lambda_{\mathrm{g}} k_{\mathrm{g}} k d]}{\mathrm{i}2\lambda^2 k^3 d + (1+\mathrm{i})\lambda_{\mathrm{g}} k_{\mathrm{g}} \lambda k}, \qquad (12)$$

where the suffix g indicates gas. Usually, we can put so that λk is smaller than $\lambda_{\mathrm{g}} k_{\mathrm{g}} k d$. Then, Eq. (12) is approximately rewritten as

$$\begin{aligned} T(0) &\cong \frac{q}{\mathrm{i}2\lambda k^2 d + (1+\mathrm{i})\lambda_{\mathrm{g}} k_{\mathrm{g}}} \\ &= \frac{q}{\mathrm{i}\omega(\rho c d + \sqrt{\rho_{\mathrm{g}} c_{\mathrm{g}} \lambda_{\mathrm{g}}/\omega} + \sqrt{\omega \rho_{\mathrm{g}} c_{\mathrm{g}} \lambda_{\mathrm{g}}}}. \end{aligned} \qquad (13)$$

In Eq. (13) if $\omega\rho c d$ is larger than $\sqrt{\omega \rho_{\mathrm{g}} c_{\mathrm{g}} \lambda_{\mathrm{g}}}$, it tends to Eq. (11). In such a case, we can neglect the contribution of gas. Generally, since $\sqrt{\rho_{\mathrm{g}} c_{\mathrm{g}} \lambda_{\mathrm{g}}}$ indicates thermal effusivity in gas, the sample is covered by gas thermally, and as seen in Eq. (13) the heat capacity of the sample is modified and furthermore, the apparent heat loss should be added.

4. Conclusion

In a temperature-modulated calorimeter, the characteristic of the individual portion in an apparatus is different from that for a conventional differential scanning calorimeter. The heat-transfer coefficient in a temperature-modulated calorimeter is no longer a simple heat conductance as in conventional differential scanning calorimeter. This behavior becomes much remarkable at a high frequency. Nevertheless, the system is composed of a linear circuit and therefore, once one calibrates the apparatus using a standard material, one can measure the heat capacity of a sample with a high accuracy. Furthermore, the heat loss through the surrounding gas should be carefully taken into account.

By taking into account the above aspects, we can apply the temperature-modulated calorimetry to the heat capacity measurement of a variety of materials. Especially, it is usefully applied to the measurement of the heat capacity anomaly at a glass transition where even in a small change of the heat capacity we can detect the anomaly independent of noise and drift against temperature. Furthermore, we can measure frequency dependence of the heat capacity at a glass transition.

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