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Conditions required for heat-capacity measurements using modulated-temperature calorimetry

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Abstract

Modulated-temperature calorimetry, in which the same apparatus as a standard differential scanning calorimeter is used, is a powerful method for measuring heat capacities. Precise heat capacity measurements are useful, for example, to analyze anomalous behavior at the glass transition. However, owing to the periodically-modulated temperature we have to pay attention to: (1) the thickness of the sample; (2) the thermal contact resistance between the sample and the sample pan; and (3) the thermal contact resistance between the sample pan and the base plate of the apparatus. This article will illustrate the following. The thickness of a sample should be chosen so as to satisfy uniformly-modulated temperature conditions throughout a sample, and subsequently both thermal contact resistances should be reduced so that the relaxation times caused by the thermal contact resistances are adequately small in comparison with the period of modulated temperature. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Calorimetry; Heat capacity; Modulated temperature DSC; Sample thickness; Thermal contact

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1. Introduction

Both standard differential scanning calorimetry and modulated-temperature calorimetry are common approaches for heat-capacity measurement (Reading, 1993). In comparison to standard differential scanning calorimetry, temperature-modulated calorimetry has distinct advantages in that, owing to the periodically-modulated temperature, external noise and drift can be excluded from measurement. On the other hand, for precise heat-capacity measurement we have to pay attention to the following contributions: the thickness of the sample, the thermal contact resistance between the sample and the sample pan, and the thermal contact resistance between the sample pan and the base plate of the apparatus. In previous papers, we have discussed the optimal thickness of a sample required for heat-capacity measurement (Hatta and Minakov, 1999) and have also considered the thermal contact resistances (Hatta and Muramatsu, 1996; Hatta and Katayama, 1998; Hatta and Minakov, 1999). In the present paper, the issue of the spatial uniformity of the modulated temperature will be considered, not only in the sample itself but also over a combination of the sample, the sample pan and the base plate of

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an apparatus during the heat-capacity measurement.

2. Conditions for heat-capacity measurement

2.1. Sample thickness

To perform heat-capacity measurements by periodic-modulation methods, it is generally required that the thermal diffusion length is much larger than the sample thickness because the temperature should modulate with spatial uniformity throughout the sample. The inverse of the thermal diffusion length, k, in a sample is given by

$$k=\sqrt{\frac{\omega}{2D}}=\sqrt{\frac{\omega\rho c}{2\kappa}} \tag{1}$$

where ω is the angular frequency, D is the thermal diffusivity, ρ is the density, c is the intrinsic heat capacity and κ (is the thermal conductivity. As seen in Eq. (1), the magnitude of k depends not only on the frequency but also on the thermophysical properties of the sample.

As an example, let us consider a cylindrical bulk material with thickness, L and cross-sectional area, a. The base of the sample is heated by applying heat flux per unit area of $q\exp(i\omega t)$ as illustrated in Fig. 1. The ac temperatures at the base and at the top are given, respectively, by

$$T(0)=\frac{q}{(1+i)\kappa k}\coth[(1+i)kL] \tag{2}$$

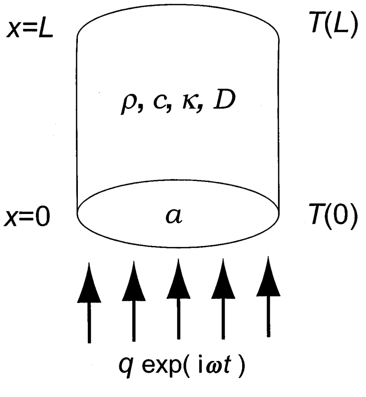

Fig. 1. A cylindrical sample whose base is heated periodically.

$$T(L)=\frac{q}{(1+i)\kappa k}\text{cosech}[(1+i)kL] \tag{3}$$

When kL is smaller than unity, we can obtain the following approximate expressions from Eq. (2) and Eq. (3), respectively:

$$T(0)=\frac{qa}{i\omega C}\left[1+i\frac{2}{3}(kL)^2+\frac{4}{45}(kL)^4\right] \tag{4}$$

$$T(L)=\frac{qa}{i\omega C}\left[1-i\frac{1}{3}(kL)^2-\frac{7}{90}(kL)^4\right] \tag{5}$$

where the heat capacity of the sample, C, is ρcLa. In order to attain spatial uniformity of the modulated temperature within 1%, the modulus of the difference between the expanded terms in Eq. (4) and Eq. (5) should be smaller than 0.01, that is

$$(kL)^2\leq 0.01$$

i.e.

$$kL\leq 0.1 \tag{6}$$

The above condition is consistent with that for heat-capacity measurement within an accuracy of 1% (Hatta and Minakov, 1999). The condition for the heat-capacity measurement is obtained from Eq. (4). Therefore, for a certain frequency and a certain material, the maximum thickness, $L^{\mathrm{T}}_{\max}$ $(=0.1/k)$, of a sample is required to achieve a uniform temperature and to perform the heat-capacity measurement, $L^{\mathrm{C}}_{\max}$ $(=0.4/k)$ is required.

For example, at 0.01 Hz in a sapphire sample

$$L^{T}_{\max}=0.2\ \text{cm}$$

$$L^{\mathrm{C}}_{\max}=1\ \text{cm}$$

and at 0.01 Hz in a polystyrene sample

$$L^{T}_{\max}=0.02\ \text{cm}$$

$$L^{\mathrm{C}}_{\max}=0.07\ \text{cm}$$

If the thickness of the sample satisfies the condition for uniform temperature, the heat capacity can be measured with sufficient accuracy. The above conditions for the thickness of a sample are related to the phase deviation from the ideal. Here, we focus on the heat-capacity measurement within an accuracy of 1% where $kL^{\mathrm{C}}_{\max}$ is 0.4 (Hatta and Minakov, 1999) and then, from Eq. (4) the maximum phase deviation φ is given by

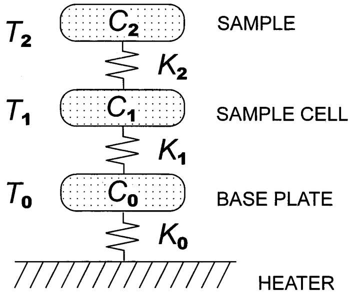

Fig. 2. A model for the sample side in a temperature-modulated calorimeter.

$2(k\ L^{\mathrm{C}}_{\mathrm{max}})/3$ rad, i.e. approximately 6°. Therefore, under the same conditions as high accuracy heat-capacity measurements can be performed from the amplitude of the ac temperature, significant phase deviation also takes place.

2.2. Thermal contact resistances

Let us consider a system composed of a thermal conductance K_0 between the heater of an apparatus and a base plate of the apparatus. The heat capacity of the base plate is C_0, the thermal contact conductance between the base plate and the sample pan is K_1, the heat capacity of the sample pan is C_1, the thermal contact conductance between the sample pan and sample is K_2 and the heat capacity of the sample is C_2 (see Fig. 2). The system indicates a typical model for the sample side of a temperature-modulated calorimeter. In this system, there is no temperature distribution within the heater, the base plate, the sample pan, and the sample. The periodically-modulated temperatures of these components are put as T_h, T_0, T_1, and T_2, respectively. It should be pointed out that for the base plate of the apparatus, even if there are sample and reference positions, C_0 can be estimated simply from the heat capacity of a disc with the radius of $L^{\mathrm{C}}_{\mathrm{max}}$ at the sample position based upon the same expression for the conditions of sample dimensions, i.e. when both positions are separated from each other by $L^{\mathrm{C}}_{\mathrm{max}}$ there is no interference thermally. In fact, when the base plate is made of constantan, at 0.01 Hz $L^{\mathrm{C}}_{\mathrm{max}}$ is about 0.6 cm. As a result, the above lumped heat capacities and thermal conductances as shown in Fig. 2 can be defined reasonably well under the condition that the spatial uniformity of the periodically-modulated temperature takes place in the sample.

Solving the energy-balance equations for the system, the following relation can been obtained:

$$T_2 = \frac{1}{1 - \omega^2 \dfrac{C_1 C_2}{K_1 K_2} + i\omega \left[\dfrac{C_1}{K_1} + \dfrac{C_2}{K_2} + \dfrac{C_2}{K_2} \right]} T_0 \tag{7}$$

In ideal conditions, T_2 should be equal to T_0, because usually the periodically-modulated temperature T_0 of the base plate is detected in the measurement and heat capacity of a sample is obtained from the periodically-modulated temperature.

When $\omega C_1/K_1 \ll 1$, Eq. (7) results in the approximation

$$T_2 = \frac{1}{1 + i\omega C_2 \left[\dfrac{1}{K_1} + \dfrac{1}{K_2} \right]} T_0 \tag{8}$$

On the other hand, when $C_2/K_2 \ll 1$, Eq. (7) results in the approximation

$$T_2 = \frac{1}{1 + \dfrac{i\omega (C_1 + C_2)}{K_1}} T_0 \tag{9}$$

Furthermore, when both $C_1/K_1 \ll 1$ and $C_2/K_2 \ll 1$, Eq. (7) results in

$$T_2 = \frac{1}{1 + i\omega \dfrac{C_2}{K_1}} T_0 \tag{10}$$

From the above consideration, the relaxation times C_2/K_2, C_1/K_1 and C_2/K_1 should be small enough to result in spatial uniformity of the modulated temperature, i.e. $T_2 = T_0$. This indicates that to obtain the ideal condition both C_1 and C_2 should be small (Boller et al., 1994) and both K_1 and K_2 should be large. Amongst these the requirement of a small C_2 value is consistent with the requirement for the sample thickness. However, the origins of the both requirements are completely different and, therefore, in the former the sample weight and in the latter the sample thickness should be small.

To deduce the quantitative condition for getting spatial uniformity of the modulated temperature, the following may be derived from Eq. (7):

$$T_2 = Ae^{-i\varphi}T_0 \tag{11}$$

$$A = \left[\left(1 - \omega^2\frac{C_1C_2}{K_1K_2}\right)^2 + \omega^2\left(\frac{C_1}{K_1} + \frac{C_2}{K_1} + \frac{C_2}{K_2}\right)^2\right]^{-1/2} \tag{12}$$

$$\varphi = \arctan\frac{\omega\left(\dfrac{C_1}{K_1} + \dfrac{C_2}{K_1} + \dfrac{C_2}{K_2}\right)}{1 - \omega^2\dfrac{C_1C_2}{K_1K_2}} \tag{13}$$

Under the condition that C_2/K_2, C_1/K_1 and C_2/K_1 are smaller than unity, Eq. (12) and Eq. (13) are expanded and then, if the correction terms down to the lowest order in Eq. (12) and Eq. (13) are taken into account, we obtain the following approximations, respectively:

$$A = 1 - \frac{1}{2}\omega^2\left(\frac{C_1^2}{K_1^2} + \frac{C_2^2}{K_1^2} + \frac{C_2^2}{K_2^2} + 2\frac{C_1C_2}{K_1^2} + 2\frac{C_2^2}{K_1K_2}\right) \tag{14}$$

$$\varphi = \omega\left[\frac{C_1}{K_1} + \frac{C_2}{K_1} + \frac{C_2}{K_2}\right] \tag{15}$$

Therefore, to keep the distribution of the amplitude of the modulated temperature within 1%, the following relation should hold

$$\omega^2\left(\frac{C_1^2}{K_1^2} + \frac{C_2^2}{K_1^2} + \frac{C_2^2}{K_2^2} + 2\frac{C_1C_2}{K_1^2} + 2\frac{C_2^2}{K_1K_2}\right) \le 0.02 \tag{16}$$

Eq. (16) indicates that ω times the sum of relaxation times should be less than 0.14. This condition results from the fact that, as seen from Eq. (15), φ becomes 8° at the maximum. As discussed before, it should be pointed out that the correction for the phase φ is marked in comparison with that for the amplitude A, because the correction terms are linear in φ and parabolic in A.

Finally, it should be stressed that, when K_2 is large enough, we can correct the contribution of K_1 by an ingenious method (Hatta and Muramatsu, 1996; Hatta and Katayama, 1998), involving only a sample pan at the sample position and no pan at the reference position. Therefore, it is important in practical terms to raise the thermal conductance K_2 for precise heat-capacity measurements. For liquid samples the requirement of K_2 is straightforward because in principle the thermal conductance K_2 is sufficiently large, while for a solid sample, glue (with a high thermal conductivity if possible) might be useful to raise the thermal conductance K_2. In this case, the heat capacity of the glue is measured first, followed by measurement of the total heat capacity of the sample and the glue, hence we obtain heat capacity of the sample from the difference.

3. Conclusions

For precise heat-capacity measurement using a temperature-modulated calorimeter, first of all it is necessary to prepare a sample with appropriate thickness so as to attain spatial uniformity of the modulated temperature. It should be noted that this does not necessarily mean using a low sample mass. Only when the sample satisfies the proposed thickness condition can we consider another relevant conditions. Subsequently, we have to raise the thermal conductance between the sample and sample pan and also the thermal conductance between the sample pan and the base plate of the apparatus. For the former, there is no significant difficulty for a liquid sample while for a solid sample the application of glue with a high thermal conductivity may be satisfactory. For the latter, even if there remains thermal conductance between the sample pan and the base plate, there is a method available to account for this contribution (Hatta and Muramatsu, 1996; Hatta and Katayama, 1998).

As discussed in this paper, the phase deviation from the ideal is remarkable when one attempts to perform heat-capacity measurements. Usually, this is partly because of the thickness of a sample and partly because of the thermal contact resistances. It is very hard to distinguish these two contributions. Therefore, it is always important to choose a sample with appropriate thickness, after which one can consider the contribution of the phase deviation as a result of the thermal contact resistances, although the correction is not simple.

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