# Some remarks on heat capacity measurements by temperature-modulated calorimetry

Ichiro Hatta[a,*], Alexandar A. Minakov[b]

[a]*Department of Applied Physics, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan*
[b]*General Physics Institute, Russian Academy of Sciences, Vavilov St. 38, 117942, Moscow, Russian Federation*

## Abstract

In temperature-modulated calorimetry, the condition in sample amount, especially thickness, required for high-accuracy heat capacity measurement should be made clear. We propose the condition of maximum thickness of a sample for measuring heat capacity within an accuracy of 1%. The other important factor for high-accuracy heat capacity measurement is thermal contact conductance between a sample and a sample pan and also that between a pan and a base plate of an apparatus. The conditions in these thermal contact conductances required for high-accuracy heat capacity measurement are discussed. Among them, if only thermal contact conductance between a pan and a base plate is significant, there is an ingenious method to measure heat capacity with high accuracy. Furthermore, if the thermal contact conductance between a pan and a base plate is infinite, we offer a simple method to obtain complex heat capacity. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

During the 5th Lähnwitzseminar on Calorimetry, a lot of stimulative discussions on heat capacity measurements using a temperature-modulated calorimetry have been made. We have learned that sometimes discussions cause some complication. This is usually the case in the beginning of the research in new fields. However, we think that it is better to draw common concept in order to be widespread over researchers who have good understanding in this method. From this viewpoint, we will try to solve some problems that are important but still not clear yet.

The problems are the proper thickness of a sample, the contribution of the thermal contact between a sample and a sample pan and also that between a sample pan and a base plate of an apparatus, the calibration of the heat capacity, and a method to obtain complex heat capacity. The similar study performed by Merzlyakov and Schick [1] had been presented in the 5th Lähnwitzseminar on Calorimetry. A part of the present paper and their paper are complement.

In the present study, we will consider the above problems and show conditions for the high-accuracy heat capacity measurements.

*Corresponding author. Tel.: +81-52-789-4466; fax: +81-52-789-3706; e-mail: hatta@nuap.nagoya-u.ac.jp

## 2. Conditions for high-accuracy heat capacity measurement

### 2.1. Sample thickness

To perform heat capacity measurements by periodic 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 be changed uniformly over a sample. In periodic heating, both the thermal wave number and the thermal decay constant in a material are given by the same expression as

$$k = \sqrt{\frac{\pi f}{D}} = \sqrt{\frac{\pi f \rho c}{\kappa}}, \tag{1}$$

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

To consider further, let us discuss the case that a cylindrical bulk material which is a model of a sample with thickness of $L$ and the circular surface, whose area is $a$ at the bottom ($x=0$), is heated by applying heat flux per unit area of $q \exp(\mathrm{i}2\pi ft)$ as illustrated in Fig. 1. The *ac* temperature at the bottom is given by [2]

$$T(0) = \frac{q}{\sqrt{2\pi f \rho c \kappa}} \exp\left[-\mathrm{i}\left(\frac{\pi}{4} + \varphi\right)\right]$$
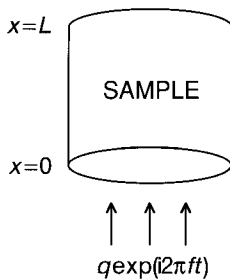$$\times \sqrt{\frac{\cosh(2kL) + \cos(2kL)}{\cosh(2kL) - \cos(2kL)}}, \tag{2}$$



Fig. 1. A cylindrical rod-like sample periodically heated at the bottom.

where the phase $\varphi$ is given by

$$\varphi = \tan^{-1} \frac{\sin(2kL)}{\sinh(2kL)}.$$

When $kL$ is smaller than unity, we can approximately obtain the following expression:

$$T(0) = \frac{qa}{\mathrm{i}2\pi f \rho cLa} \left(1 + \frac{14}{45}(kL)^4\right) \exp\left(\mathrm{i}\frac{2}{3}(kL)^2\right). \tag{4}$$

Heat capacity observed is modified by contributions of the thickness of a sample as seen in Eq. (4). As will be seen in Eq. (7), by taking into account the largest contribution to modifying the heat capacity $C$, Eq. (4) is rewritten as

$$T(0) = \frac{qa}{\mathrm{i}2\pi f \rho cLa} \left(1 + \frac{14}{45}(kL)^4\right). \tag{5}$$

Then, to determine heat capacity $C$ ($=\rho cLa$) within accuracy of 1% the following condition is required:

$$\frac{14}{45}(kL)^4 \leq 0.01, \quad \text{i.e., } kL \leq 0.4. \tag{6}$$

Therefore, the thickness of a sample required at the maximum is $0.4/k$ ($=0.4\sqrt{(\kappa/\pi f \rho c)}$). When the condition of Eq. (6) is sufficiently satisfied, $T(0)$ is expressed as

$$T(0) = \frac{Q}{\mathrm{i}2\pi fC}, \tag{7}$$

where $Q$ is $qa$.

For a disk-like sapphire sample, let us consider the condition of Eq. (6). Since thermal diffusivity is about $0.14 \text{ cm}^2 \text{ s}^{-1}$, at a period of 60 s ($f=0.017$ Hz) $k$ is about $0.6 \text{ cm}^{-1}$. Then, to measure the heat capacity within accuracy of 1% the maximum thickness $L$ should be: $L_{\max}=0.7$ cm.

Practically, when the bottom of the disk is 0.20 cm$^2$, the maximum weight is about 800 mg. As expected from Eq. (5) the apparent heat capacity measured becomes smaller when the sample weight is heavier. In connection with this fact, Boller et al. [3] have measured the dependence of apparent heat capacity on weight in sapphire samples. They have pointed out that the decrease of the apparent heat capacity is due to the low thermal conductivity of sapphire samples. However, this is not the case since their results deviate

below 100 mg, which is far lower than 800 mg. Then, the deviation of their results might be caused by the effects of thermal contact conductance between a sample and a sample pan and/or thermal contact conductance between a sample pan and a base plate as discussed below.

For a polystyrene film, the thermal diffusivity is about $0.001 \ \mathrm{cm^2 \ s^{-1}}$. Then, since $k$ is about $7 \ \mathrm{cm^{-1}}$ at a period of 60 s, the maximum thickness required for heat capacity measurement within accuracy of 1% is given as $L_{\mathrm{max}}$=0.06 cm.

Then, we will claim that before setting a sample into a sample pan a sample should be chosen so as to satisfy the condition of Eq. (6). Even if we use such a sample and get smaller heat capacity with increasing the weight of a sample, the behavior might be caused by the other factors, e.g., finite thermal contact conductance between a sample and a sample pan and/or between a sample pan and a base plate. They are considered in the following subsection.

## 2.2. Thermal contact conductance

First we consider the contribution of the thermal contact conductance $K_{\mathrm{si}}$ between a sample and a sample pan. This system is expressed in terms of a model as shown in Fig. 2. The characteristic relaxation time $\tau_{\mathrm{i}}$ of the system is given by

$$\tau_{\mathrm{i}} = \frac{C_{\mathrm{si}}}{K_{\mathrm{si}}}, \qquad (8)$$

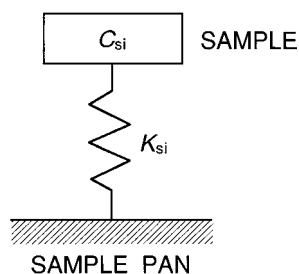where $C_{\mathrm{si}}$ is heat capacity of a sample. Therefore, to



Fig. 2. A model for thermal contact conductance between a sample and a sample pan. The conductance and the heat capacity of the sample are given by $K_{\mathrm{si}}$ and $C_{\mathrm{si}}$, respectively. The same model can be applied to that for thermal contact conductance between a sample pan and a base plate of an apparatus.

exclude the contribution of the thermal contact conductance, i.e., to attain quick response, $2\pi f \tau_{\mathrm{i}}$ should be small, i.e., the lower frequency, the smaller heat capacity (the lighter weight of a sample) and the bigger thermal contact conductance are the better. Generally, it is difficult to estimate the magnitude of $K_{\mathrm{si}}$. Then, at least the former two quantities should be chosen so as to satisfy the condition so that the contribution of $K_{\mathrm{si}}$ can be ignored.

Second we consider the contribution of the thermal contact conductance between a sample pan and a base plate of an apparatus. In this consideration we discuss further under the condition that the thermal contact conductance between a sample and a sample pan is infinite. Then, this thermal system is similar to that shown in Fig. 2, but the sample and the sample pan are replaced by a sample pan including a sample and a base plate, respectively, where the sample and the sample pan are unified thermally. Therefore, it results in the fact that the lower frequency, the smaller total heat capacity composed of a sample and a sample pan and the bigger thermal contact conductance are the better.

In both the cases, when the above relaxation times become longer than $1/2\pi f$, i. e., the weight of a sample is heavier, the measured heat capacity deviates from the true heat capacity.

## 2.3. Correction for high-accuracy heat capacity measurement

When both a sample pan and a reference pan are put on a base plate as in a standard differential scanning calorimetry, there are two uncontrollable thermal contact conductances between a pan and a base plate even if thermal contact conductance between a sample and a sample pan is infinite. Then, we have pointed out that it is much simple to use only a sample pan in the sample side where there remains only an uncontrollable parameter [4,5]. In such a setup, we have developed an ingenious method to analyze the experimental results and to obtain heat capacity with high accuracy [4,5]. In this case, a model for a thermal system of an apparatus is given as in Fig. 3, where there is a thermal contact conductance between a sample pan and a base plate, $K'$. We measure *ac* temperature of the sample side at the base plate, $T_{\mathrm{s0}}$, and the *ac* temperature
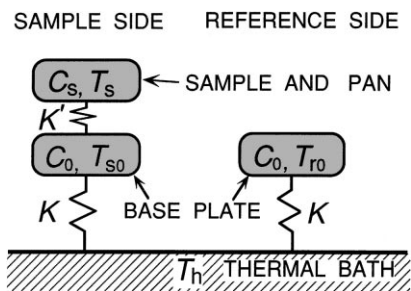
Fig. 3. A model of a temperature-modulated calorimeter. To deduce ambiguity in the measurement, only a pan containing a sample is placed on the base plate at the sample side, but no pan on the base plate at the reference side.

difference between the sample and the reference sides at the base plate, $\Delta T (= T_{r0} - T_{s0})$. These are given by the following relations:

$$T_{s0} = A_s \exp[i(2\pi f t + \varepsilon)], \tag{9}$$

$$\Delta T = A_\Delta \exp[i(2\pi f t + \delta)], \tag{10}$$

where $A_s$ and $A_\Delta$ are amplitudes and $\varepsilon$ and $\delta$ are phases. In a naïve calculation, the so-called measured heat capacity including that of a sample pan, $C_s$(measured) can be expressed as

$$C_s(\text{measured}) = \frac{K A_\Delta}{2\pi f A_s}, \tag{11}$$

where $K$ is thermal conductance between a base plate and a thermal bath. Usually the measured heat capacity does not agree with the true heat capacity in temperature-modulated calorimetry. Then, we should correct the measured heat capacity and thus corrected heat capacity is expressed as $C_s$(corrected). In the case of a model of Fig. 3, the ratio of $C_s$(measured) and $C_s$(corrected)($= C_s$) and the phase difference $\delta - \varepsilon$ are given in [4]

$$\frac{C_s(\text{measured})}{C_s(\text{corrected})}$$
$$= \frac{1}{[1 + (2\pi f \tau_s)^2]^{1/2}[1 + (2\pi f \tau_0)^2]^{1/2}}, \tag{12}$$

$$\sin(\delta - \varepsilon) = \frac{1 - (2\pi f \tau_s)(2\pi f \tau_0)}{[1 + (2\pi f \tau_s)^2]^{1/2}[1 + (2\pi f \tau_0)^2]^{1/2}}, \tag{13}$$

where two characteristic relaxation times $\tau_s$ and $\tau_0$ are

given as

$$\tau_s = \frac{C_s}{K'}, \tag{14}$$

$$\tau_0 = \frac{C_0}{K}, \tag{15}$$

where $C_0$ is the heat capacity of the base plate. In Eqs. (12) and (13), at a measuring frequency $f$, $\tau_s$ and $\tau_0$ are common parameters and furthermore $\tau_s$ depends on $C_s$ and on the other hand, $\tau_0$ is a constant. Then, by measuring the ratio of Eq. (12) and the phase difference of Eq. (13) using a standard material whose heat capacity is known, we can obtain a single relation between the ratio and the phase difference as a function of the heat capacity $C_s$. Therefore, based upon this relation we can determine the heat capacity of the unknown sample, i.e., from the measured phase difference we can obtain the ratio of the heat capacities and finally, $C_s$(corrected) is able to determined. Within the framework of the present model, it has been concluded that, even if there is an uncontrollable parameter $K'$, we can obtain heat capacity of a sample based upon a single calibration curve [4,5]. Then, it is strongly recommended to perform the heat capacity measurement without a reference pan.

Furthermore, when the relaxation time $\tau_s$ is far shorter than $1/2\pi f$, Eqs. (12) and (13) tend, respectively, to

$$\frac{C_s(\text{measured})}{C_s(\text{corrected})} = \frac{1}{[1 + (2\pi f \tau_0)^2]^{1/2}}, \tag{16}$$

$$\sin(\delta - \varepsilon) = \frac{1}{[1 + (2\pi f \tau_0)^2]^{1/2}}. \tag{17}$$

As expected from Eq. (14), the above two expressions, Eqs. (16) and (17), hold under the condition of smaller $C_s$ and/or larger $K'$ in addition to smaller $f$. The condition is similar to that pointed out in the previous Section 2.2. Furthermore, $C_s$(measured)/$C_s$(corrected) becomes apparently smaller in a thicker sample as discussed in Section 2.1. There are a lot of reasons which results in small $C_s$(measured)/$C_s$(corrected), however, we cannot distinguish them easily. Then, careful treatment in the analysis of the observed data is required.

Under the above condition of $\tau_s \ll 1/2\pi f$, the analysis is not difficult even if we put a reference pan (an empty pan) on the reference side. Because the thermal

contact conductance between the pan and the base plate at the both sides are infinite, the pan and the base plate are unified thermally. It makes possible to replace such that $C_0$ is composed of those of the sample pan and the base plate and $C_s$ is heat capacity of a sample itself. Under such circumstances, Eq. (16) is identical with those in the paper of Wunderlich et al. [6]. However, they did not take into account the contribution of the heat capacity of the base plate. We point out that in $C_0$ the heat capacity of the base plate should be included. Furthermore, it is worth to point out that, since Eqs. (16) and (17) are identical, without knowing the magnitude of $C_0$ we can determine $C_s$(corrected) from $C_s$(measured) and $\delta - \varepsilon$.

Finally, we should stress that the quantity $K$ given in Eq. (11) depends on frequency and temperature as indicated in [4]. In the strict sense, $K$ is not a constant parameter. Then, it is better to leave $K$ as a parameter which should be precedently determined using a standard sample, i.e., when we have to make a calibration curve at a frequency and at a temperature.

## 2.4. Complex heat capacity

In the case when $2\pi f \tau_s$ is neglected, i.e., $\tau_s$ is short enough, complex heat capacity, $C_s' - iC_s''$, can be easily obtained from $T_{s0}$ and $\Delta T$. Let us define

$$C_s' - iC_s'' = \sqrt{C_s'^2 + C_s''2}\exp(-i\gamma) \qquad (18)$$

We obtain the following relations:

$$\frac{C_s(\text{measured})}{\sqrt{C_s'^2 + C_s''2}} = \frac{1}{[1 + (2\pi f \tau_0)^2]^{1/2}}, \qquad (19)$$

$$\sin(\delta - \varepsilon + \gamma) = \frac{1}{[1 + (2\pi f \tau_0)^2]^{1/2}}. \qquad (20)$$

In Eqs. (19) and (20), $C_s$(measured) and $\tau_0$ are given by Eqs. (11) and (15), respectively.

Practically, the procedure of the analysis is performed as follows. We measure temperature dependence of $\delta - \varepsilon$ in a sample where heat capacity has frequency dispersion. Its temperature dependence is schematically shown in Fig. 4 and shows anomalous behavior due to the frequency dispersion. On the other hand, $\delta - \varepsilon + \gamma$ is given by Eq. (20) and therefore, its temperature dependence is normal. Outside the region
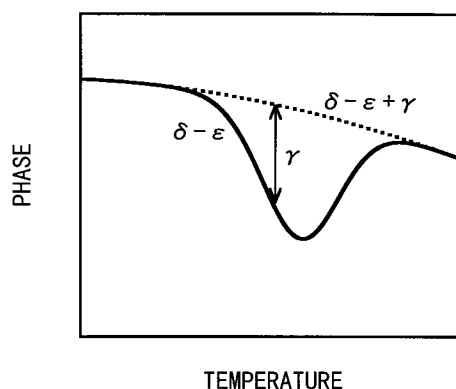


Fig. 4. Phase differences, $\delta - \varepsilon$ and $\delta - \varepsilon + \gamma$. Phase $\gamma$ is related to the frequency dispersion of heat capacity, i.e., $\delta - \varepsilon$ coincides with $\delta - \varepsilon + \gamma$ in the region of no frequency dispersion.

where the frequency dispersion of the heat capacity takes place, $\delta - \varepsilon + \gamma$ coincides with $\delta - \varepsilon$ as seen in Fig. 4. As a result, from the difference between $\delta - \varepsilon + \gamma$ and $\delta - \varepsilon$, $\gamma$ is obtained. In addition, from $C_s$(measured), $\sqrt{C_s'^2 + C_s''2}$ is obtained using Eqs. (19) and (20). Finally we obtain $C_s' - iC_s''$ using Eq. (18).

Furthermore, in the case when $2\pi f \tau_s$ cannot be neglected, i.e., $\tau_s$ is not short enough, the procedure to obtain complex heat capacity is a little complicated. In principle, we have to know $C_0$, $K$ and $K'$ in Eqs. (12) and (13) precedently using a standard sample. Based upon them, we can obtain the complex heat capacity from the measurement of $\delta - \varepsilon$ and $C_s$(measured). However, the key point in this method is that $K'$ should be determined within a smaller scatter.

## 3. Conclusions

Summing up the conclusions as follows:

1. There are several reasons that measured heat capacity deviates from the true heat capacity. To measure heat capacity within accuracy of 1% at least the thickness of a sample should be less than $0.6/k$.
2. First, a sample should be prepared so as to satisfy the above thickness. There remain the other origins. These are for instance thermal contact conductance between a sample and a sample pan and also that between a sample pan and a base plate of

an apparatus. To reduce these contributions it is important to make the response times as short as possible.

3. Heat capacity of a base plate of an apparatus should be taken into account always in temperature-modulated calorimetry. Especially it depends on frequency (or period of modulation).

4. When we can ignore thermal contact conductance between a sample pan and a base plate, i.e., the thermal contact conductance is infinite, complex heat capacity is derived in a simple method.

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