

# AC calorimetric aspect of dynamic differential scanning calorimetry<sup>1</sup>

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## Abstract

A dynamic differential scanning calorimeter (dynamic DSC) works simultaneously as a differential scanning calorimeter and an AC calorimeter, using the same apparatus with AC temperature modulation superposed on a linear temperature ramp. From the AC calorimetric (ACC) operation, we can determine the absolute value of the heat capacity by making the best of the twin-type apparatus, although the temperature resolution is a little lower than in a high precision AC calorimeter. In addition, it should be pointed out that in the ACC operation, heat capacity can be determined easily in comparison with differential scanning calorimetric (DSC) operation. Therefore, at a second order phase transition, the ACC operation is useful for obtaining linear heat capacity and furthermore, the frequency dispersion of linear heat capacity is obtainable. On the other hand, at a first order phase transition, the situation is complicated. In this case, we have to pay attention to non-linear heat capacity. The analysis of the waveform of AC temperature observed at a steady temperature might be useful to obtain evidence for the kinetic mechanism.

*Keywords:* AC calorimetry; Differential scanning calorimetry; Linear heat capacity; Non-linear heat capacity; Latent heat; Phase transition

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## 1. Introduction

Differential scanning calorimetry (DSC) is widely accepted as a useful analytical tool for thermal properties of various materials. In heat flux DSC, the temperature of, for instance, a reference material is scanned linearly against time, and the temperature difference, which is proportional to the heat flux difference between a sample and the refer-

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ence material, is measured. As a result, we can obtain the thermogram related to heat capacity for the sample. Recently, dynamic DSC has been proposed, in which AC temperature modulation is superposed on a linear temperature ramp [1]. From the AC temperature difference between the sample and the reference material, we can obtain the reversible component. By subtracting the reversible component from the thermogram obtained by the DSC operation, we finally obtain the irreversible components. However, the adequacy to classify into reversible and irreversible components should be considered very rigorously. So far, independent AC calorimetry (ACC) has been intensively developed [2]. However, consideration for the case when simultaneous measurement of DSC and ACC is performed has not been sufficiently done yet, especially from the viewpoint of ACC. In this paper, ACC operation in dynamic DSC is the focus of attention.

## 2. Analyses

Let us first discuss heat flux DSC, where the temperature of a reference cell is scanned. Heat balance on the reference side is given by

$$C_r \frac{dT_r}{dt} = K(T_h - T_r) \quad (1)$$

where  $C_r$  is the effective heat capacity of the sum of the reference material and its cell including the contribution of the surrounding materials,  $t$  is time,  $K$  is the effective coefficient of heat transfer between the reference material and a heater, and  $T_r$  and  $T_h$  are the temperatures of the reference material and the heater, respectively.

On the other hand, heat balance on the sample side is given by

$$C_s \frac{dT_s}{dt} + \Delta H_s \frac{dx}{dt} = K(T_h - T_s) \quad (2)$$

where  $C_s$  is the effective heat capacity of the sum of the sample and its cell including the contribution of the surrounding materials. In principle, except for the heat capacity of the sample, the heat capacity of the cell including the surrounding materials is the same as those on the reference side.  $K$  is the effective coefficient of heat transfer between the sample and the heater, which is also equivalent to that on the reference side.  $T_s$  is the temperature of the sample,  $\Delta H_s$  is the enthalpy due to kinetic mechanism and  $x$  is the fraction of the part of the sample transformed by the kinetic mechanism.

Next, let us consider the ACC part in the same twin-type calorimeter [3]. In the following, AC temperature  $\tilde{T}$ , AC heat flux  $\tilde{Q}$  and AC part  $\tilde{x}$  of the fraction at  $x$  include implicitly the factor of  $\exp(i\omega t)$  and then,  $d\tilde{T}/dt = i\omega \tilde{T}$ ,  $\tilde{T}/\tilde{Q}$ , etc. are independent of  $t$ . Heat balance on the reference side in this case is given by

$$\tilde{C}_r = \frac{d\tilde{T}_r}{dt} + \tilde{K}\tilde{T}_r = \tilde{Q} \quad (3)$$

where  $\tilde{C}_r$  is the effective heat capacity of the sum of the reference and its cell including the surrounding materials. It should be pointed out that generally  $\tilde{C}_r$  is smaller than the effective heat capacity of the cell including the surrounding materials in the DSC operation, because the characteristic dimension is smaller in the ACC operation than in the DSC operation.  $\tilde{T}_r$  is the AC temperature of the reference.  $\tilde{K}$  and  $\tilde{Q}$  are the effective coefficient of heat transfer from the reference material to its surroundings and AC heat flux supplied to the reference material, respectively.  $\tilde{K}$  is also different from the corresponding coefficient in the DSC operation.

Heat balance on the sample side is given by

$$\tilde{C}_s \frac{d\tilde{T}_s}{dt} + \tilde{K}\tilde{T}_s + \Delta\tilde{H}_s \frac{d\tilde{x}}{dt} = \tilde{Q} \quad (4)$$

where  $\tilde{C}_s$  is the effective heat capacity of the sum of the sample and its cell including the surrounding materials. The latter heat capacity is almost the same as that on the reference side.  $\tilde{T}_s$  is the AC temperature of the sample. In this consideration, for simplicity it is assumed that  $\tilde{K}$  and  $\tilde{Q}$  are the same as those on the reference side.  $\Delta\tilde{H}_s$  is related to the dynamic enthalpy due to the kinetic process. For instance, in a two-state change, according to the AC temperature modulation the boundary of the two states might oscillate with some phase lag and deviate from sine waveform, in which  $\tilde{x}$  indicates the AC part at the fraction of  $x$ .

First, we consider linear heat capacity due to thermal fluctuation. In this case, the terms related to  $\Delta\tilde{H}_s$  and  $\Delta\tilde{H}_r$  should be excluded from Eqs. (2) and (4), respectively. From Eqs. (1) and (2) without the third term on the left-hand side of Eq. (2), we obtain

$$\Delta T = \left( -\frac{dT_r/dt}{K} \right) \cdot \Delta C_s \quad (5)$$

where  $\Delta T = T_s - T_r$  and  $\Delta C_s = C_s - C_r$ . In ideal heat flux DSC, the temperature scan rate,  $dT_r/dt$ , is constant. Then, from the measurement of  $\Delta T$  as a function of time, we can obtain the temperature dependence of  $\Delta C_s = C_s - C_r$ , i.e. the temperature dependence of the linear heat capacity of the sample. It is worth noticing that the linear heat capacity anomaly due to thermal fluctuation at second-order phase transition is included in  $\Delta C_s$ , i.e. generally it shows critical behavior. This indicates that such linear heat capacity in samples is not always temperature independent.

From Eqs.(3) and (4), we can derive  $\Delta\tilde{T}$  an angular frequency  $\omega$  under a certain condition as [3]

$$\Delta\tilde{T} = \left[ -\frac{i\omega\tilde{Q}}{(i\omega\tilde{C}_r + \tilde{K})^2} \right] \cdot \Delta\tilde{C}_s \quad (6)$$

where  $\Delta\tilde{T} = \tilde{T}_s - \tilde{T}_r$  and  $\Delta\tilde{C}_s = \tilde{C}_s - \tilde{C}_r$ . As seen in Eq. (6),  $\Delta\tilde{T}$  is proportional to  $\Delta\tilde{C}_s$ . Then we obtain the linear heat capacity,  $\Delta\tilde{C}_s$ . This is in fact linear heat capacity at

an angular frequency  $\omega$ . Generally, at second order phase transition we can expect the frequency dispersion of the linear heat capacity due to thermal fluctuation.

In the practical measurement to obtain  $\Delta \tilde{C}_s$ , we first have to calibrate the factor of the square brackets in Eq. (6). Since  $\tilde{Q}$ ,  $\tilde{C}_r$  and  $\tilde{K}$  are generally frequency dependent, the factor should be determined at a measuring frequency. In the above theoretical consideration, we assumed that the temperature oscillated uniformly over the sample, i.e. the angular frequency should be lower than a certain frequency given by the inverse of the internal relaxation time [2]. Furthermore, the calibration should be done in the temperature range where the measurement will be performed, because  $\tilde{C}_r$  and  $\tilde{K}$  are temperature dependent.

At a first order phase transition, the terms concerned with  $\Delta H_s$  and  $\Delta \tilde{H}_s$  should be taken into account in the analysis. In fact, the kinetics of the phase boundary becomes significant. In such a case, the application of dynamic DSC results in a complicated response. When we wish to know the kinetic mechanism, the ACC operation should be carried out at a proper steady temperature. Furthermore, to estimate the latent heat at the first-order phase transition from the result obtained by dynamic DSC, we have to pay attention to the fact that the contribution of the latent heat is included not only in the irreversible component but also in the reversible component.

### 3. Conclusion

Some experimental trials in differential AC calorimetry have been conducted [4,5], where  $\tilde{K}$  of Eq. (6) has been ignored. However, it should be stressed that, in the simultaneous measurement of DSC and ACC, we can no longer ignore  $\tilde{K}$  as given in Eq. (6). Nevertheless, by employing a differential ACC we can easily obtain the absolute value of the linear heat capacity of a sample without knowing the details of  $\tilde{K}$ . As pointed out in Section 2, the so-called reversible component of the heat capacity due to thermal fluctuation should be called linear heat capacity. At second-order phase transition, we can obtain linear heat capacity and furthermore, its frequency dispersion. On the other hand, we need to pay special attention in the analysis of first-order phase transition.

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