

## *Instrumentation*

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# **SIMULATION OF TEMPERATURE-MODULATED DSC OF TRANSITIONS REPRESENTED BY ABRUPT CHANGES IN HEAT CAPACITY**

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## **Abstract**

Computer simulations have been applied to elucidate the response of a sample to temperature-modulated differential scanning calorimetry (tm-DSC) during transitions. Two cases have been simulated; a latent heat without supercooling (represented by an abrupt heat capacity pulse with perfect reversibility) and a latent heat with perfect supercooling or large hysteresis (an abrupt heat capacity change without reversibility, i.e. the change in heat capacity is seen on heating, but not on cooling). Because the simulation was applied to these well-characterized phenomena, the results are useful to reveal actual sample thermal responses during transitions. The non-reversible component was observed in both cases and has no distinct difference. Higher harmonics due to non-linearity of the transitions were also observed. Furthermore, by inspecting thermal response of the sample and the essential feature of tm-DSC, a new method of data analysis has been devised.

**Keywords:** computer simulation, dynamic DSC (temperature modulated DSC), enthalpy-temperature plots, supercooling, transition

## **Introduction**

Temperature-modulated differential scanning calorimetry (tm-DSC) has drawn much interest since its initial publication [1, 2], because something new is seen in this technique. In the technique, oscillating thermal responses of the sample and reference material are recorded while undergoing a linearly increasing temperature-change with superimposed sinusoidal temperature modulation, and their difference

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is separated into an in-phase response and the other component. This technique, however, is applicable only to transitions occurring over a certain temperature range, to kinetic processes and to heat capacity measurements, because several cycles of oscillation are needed in the mathematical treatment to separate the thermal response into the two components by Fourier transformation.

This new technique has mainly been applied to polymers because of the above-mentioned reason, and obtained results have been discussed in relation to the underlying physical processes. However, in polymers these processes are very complicated depending on the thermal history of the sample and have not yet been thoroughly investigated. On the other hand, there are only few applications to simple transitions of low-molecular mass substances of well known nature [3], since this technique is not applicable to sharp transitions.

Therefore, we do not have an exact basis for the discussion of these, and the physical meaning of the responses in a transition region has not yet been clarified. Because these processes become non-linear, as previously pointed out [4], mathematical analytical methods can not be applied, and we present in this paper simulation for two typical physical phenomena; (1) a reversible abrupt heat capacity change (latent heat without any supercooling) (case 1) and (2) a non-reversible abrupt heat capacity change (latent heat with perfect supercooling or hysteresis) (case 2). Two types of simulations are made for each case (example 1 and example 2). These simulations correspond to well characterized phenomena and are useful for discussing real results by tm-DSC. They are also useful to understand the real heat flow in an apparatus. These simulations are discussed in this report in relation to the nature of the transitions, and a new method to elucidate the nature of the transitions has been proposed.

## Simulation method

The simulation method adopted in this report is a finite difference method, and it was fully described in our previous report [5] together with two models of heat flux DSC (hf-DSC) [6]. The two models are patterned after commercial DSC equipments; in model A the sample is connected with the reference material, so that there is a mutual heat exchange between them, while in model B the sample is connected with the reference material only via the common heat source, and there is, therefore, no mutual heat exchange. In both models the heat source temperature is controlled at a constant heating rate with modulation of a constant amplitude and a constant frequency.

The two examples of simulations are summarized in Table 1. For case 1 an abrupt pulse of heat capacity is representing the transition; the heat capacity of the sample,  $C_s$ , increases from  $C_{p1}$  to  $C_{p2}$  in the transition range from  $T_i$  to  $T_e$  and decreases to the initial value above the transition temperature, the heat of transition corresponding to the pulse. Namely,

$$C_s = C_{p1} \quad \text{for } T_s < T_i \text{ and } T_s > T_e \quad (1)$$

and

$$C_s = C_{p2} \quad \text{for } T_i < T_s < T_e \quad (2)$$

where  $T_s$  is the sample temperature. In this transition, the process is assumed to be heat-transfer controlled so that rate of transition is fixed by the amount of heat supplied [4, 7, 8], and the heat supply is proportional to the temperature difference between the heat source and the sample, since the heat flows only by conduction [4, 7, 8].

For case 2, the heat capacity increases abruptly during the transition similar to case 1 [Eqs (1) and (2)], but the part of the sample that has changed to the high temperature form changes its heat capacity on cooling to the initial heat capacity,  $C_{p1}$ , because of non-reversibility of the transition. Thus, the heat capacity during the transition for  $T_i < T_s < T_e$  in heating mode is given by;

$$C_s = C_{p2} \quad \text{for } T_s = T_m < T_e \quad (3)$$

and

$$C_s = C_{p1} \quad \text{for } T_s < T_m \text{ and } T_s > T_e \quad (4)$$

where  $T_m$  is the maximum temperature to which the sample has been heated. In the cooling mode, in contrast, the heat capacity is always:

$$C_s = C_{p1} \quad (5)$$

For example 1 the thermophysical properties of the sample, such as the heat capacity, the latent heat and the transition temperature, are patterned after pure indium (Table 1), though real indium melts at a constant temperature and its melt supercools usually by few degrees. Because this transition is completed within a narrow temperature range, a small amplitude and high frequency were applied. Similarly, for example 2 the thermophysical properties of the sample were patterned after irreversibly changing polyethylene.

**Table 1** Thermophysical properties and operational parameters of the simulated samples

Example	Ex. 1	Ex. 2
1) Thermophysical properties of simulated samples		
Steady state heat capacity ( $C_{p1}$ ) ( $J K^{-1}$ )	0.24	2.45
Increased heat capacity ( $C_{p2}$ ) ( $J K^{-1}$ )	145.24	36.58
Duration ( $T_i/K - T_e/K$ )	429.3–429.5	392–398
2) Operation		
Amplitude/K	0.2	0.2
Period/s	30	30
Angular frequency/ $s^{-1}$	0.21	0.21
(Frequency/Hz	0.033	0.033)
Heating rate/ $K \text{ min}^{-1}$	0.2	1

## Results and discussion

The simulated sample response of case 1 for example 1 with model A are reproduced in Fig. 1. Similar results were also obtained with model B and for case 2. It should be noted that the sample temperature remains almost constant during the transition. In example 1 the temperature of the heat source increases continuously above the sample temperature so that the sample does not show a cooling in the transition region except the very beginning. The operational parameters, such as the heating rate, the amplitude and the frequency, influence the sample-temperature response. In Fig. 1b), the temperature of the reference material is shown, and a distortion of the oscillation is seen due to the mutual heat exchange in model A, but the distortion is not found in model B because of missing heat exchange.

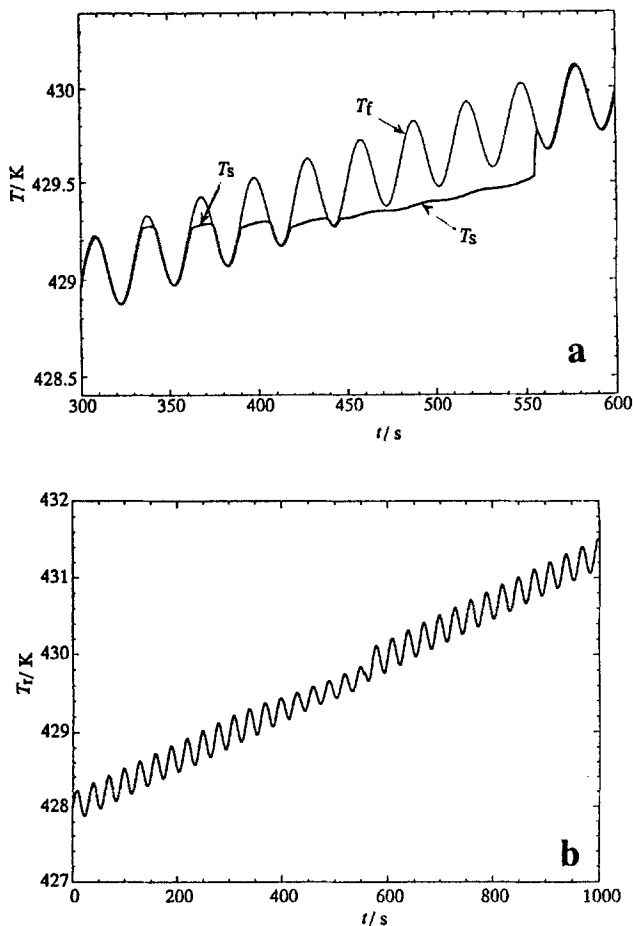


Fig. 1 Temperature change of sample,  $T_s$ , reference material,  $T_r$ , and heat source,  $T_f$ , of case 1 for example 1 with model A (reversible transition). a) sample and heat source temperatures, b) reference material temperature

Fourier transformation was applied to these responses and the obtained results are shown in Figs 2 and 3. The "total heat flow",  $dq/dt$ , results from integrating the temperature difference between sample and reference and the "reversible heat flow" is calculated by integrating the in-phase component of the difference, the "non-reversible" component being the difference between the two. Similar results were obtained by the other model [1, 2].

The purpose of this research is to elucidate the effect of reversibility of the transitions, so that a comparison was made between the two cases. Comparing the figures, distinctive differences between reversible and non-reversible transitions are not found, and this is also true for the other model. In both cases non-reversible components are seen. In example 2 the constant, non-reversible component seems to be caused by the high constant heat capacity, which causes the phase shift and hence the out-of phase component [6].

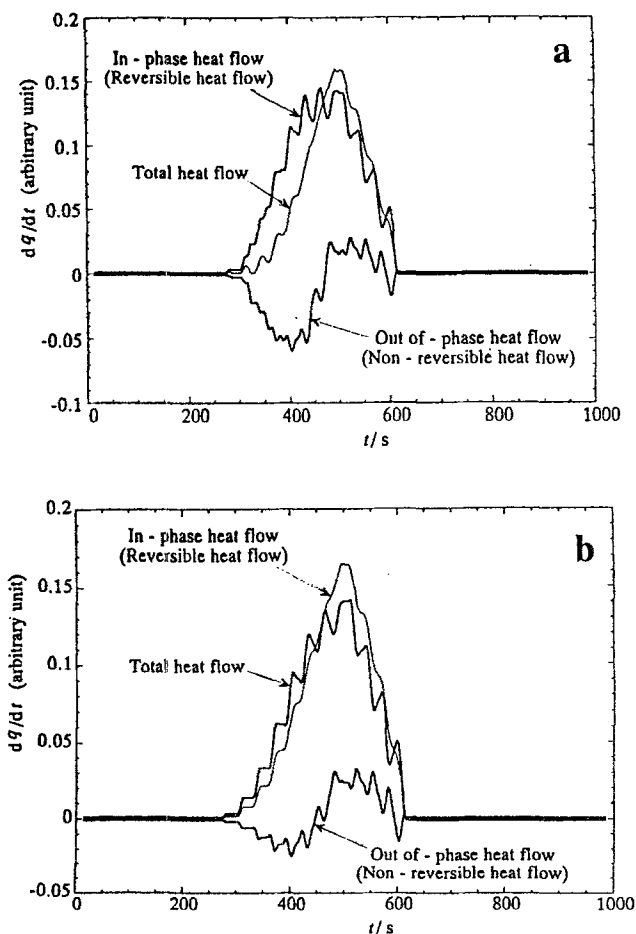


Fig. 2 "Reversible heat flow" and "non-reversible heat flow" for example 1 by model A. a) case 1, b) case 2. Integration for Fourier transformation was made for 4 cycles

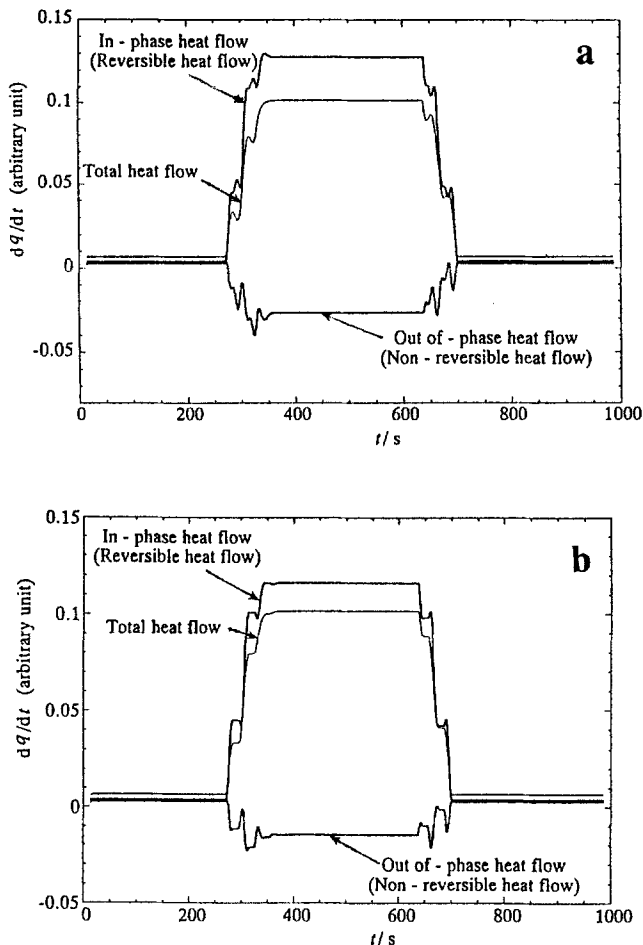


Fig. 3 "Reversible heat flow" and "non-reversible heat flow" for example 2 by model B. a) case 1, b) case 2. Integration for Fourier transformation was made for 2 cycles

Because the abrupt heat capacity changes are typical non-linear processes, higher harmonics exist. The second harmonics were, thus, calculated by integrating the component of double frequency, and are shown in Figs 4 and 5. The second harmonics of the out-of-phase component were also found. In examples 1, higher harmonics exist over the whole transition range. On the other hand, in example 2 of case 1 the higher harmonics exist only in the beginning and at the end, while they exist during the whole transition in the case 2 caused by distorted oscillation due to the super-cooling. Comparing these figures, the time interval of non-linearity caused by the sharp increase of heat capacity is about 100 s.

A unique point of tm-DSC is the superposed temperature modulation, and there are two aspects to its application.

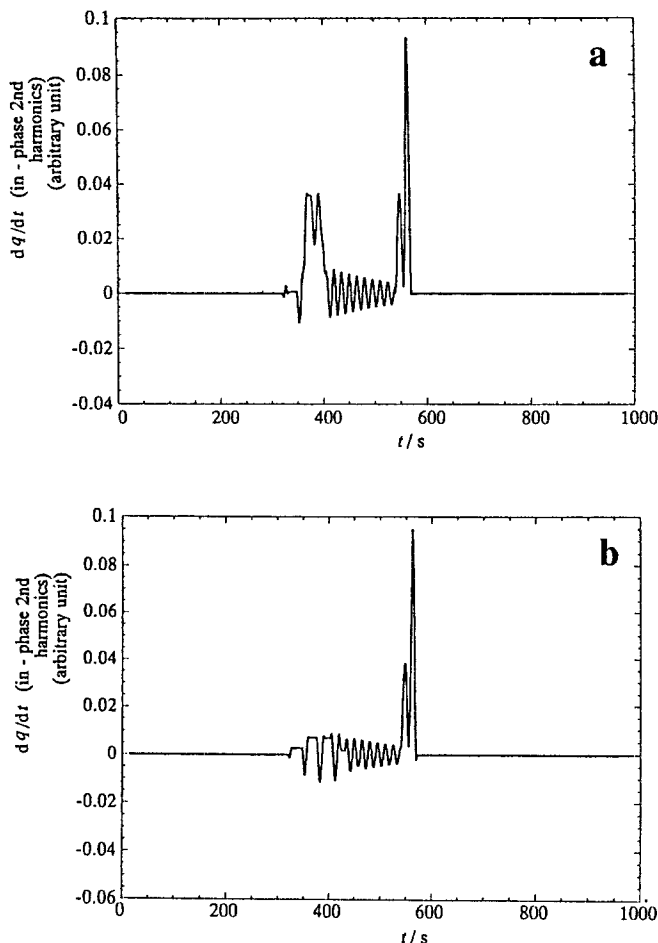


Fig. 4 In-phase second harmonics in example 1 with model A. a) case 1, b) case 2. Integration for Fourier transformation was made for 2 cycles

One is to use the sample thermal response to this modulation, and its use for heat capacity measurements [6, 9, 10]. Because linearity exists and the dynamic steady state is established in this case (or quasi-linearity and quasi-steady state) [5, 6], the situation is the same as in other modulated thermal analysis, such as dynamic thermomechanometry and dynamic thermoelectrometry, in which modulation, such as strain-modulation, stress-modulation and voltage-modulation, is superposed on a linear temperature change. The modulated quantities can then be treated independently of the temperature, and hence, the sample properties can be measured, such as moduli and dielectric properties. In tm-DSC the thermal response of the sample to temperature modulation can be separated by deconvolution because of linearity or quasi-linearity, and the heat capacity can be estimated.

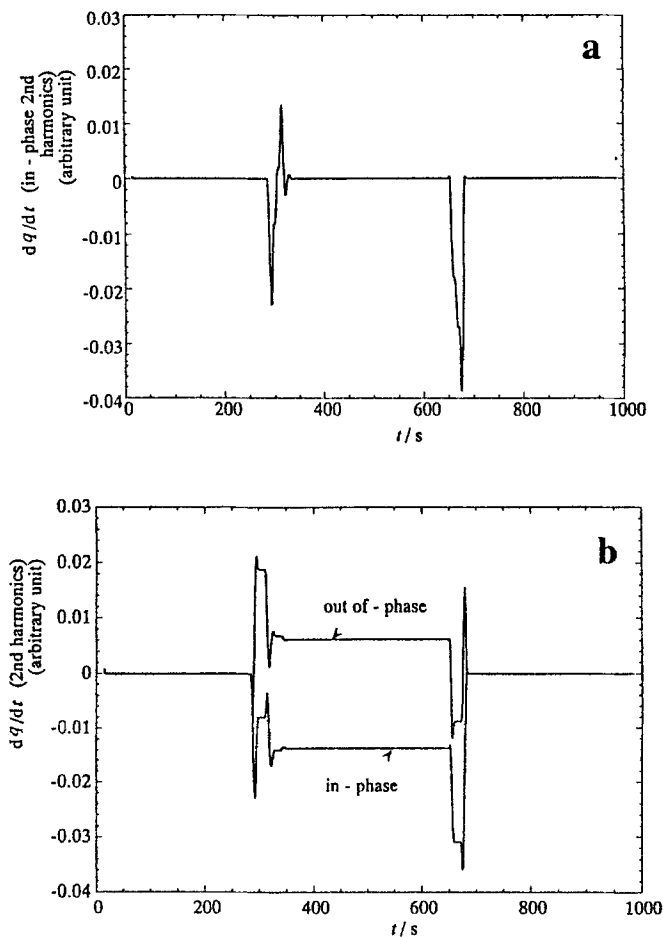


Fig. 5 Second harmonics in example 2 with model A. a) In-phase harmonics of case 1, b) case 2. Integration for Fourier transformation was made for 2 cycles

The other is the possibility of alternative observation of the sample thermal behavior in the heating and cooling mode (e.g., supercooling). This is useful for observation of the nature of the transition.

Considering this point, the authors propose plotting of the time integral of the above-mentioned temperature differences vs. the sample temperature in order to detect irreversibility, because the integrals are related to heat absorbed by or evolved from the sample and, hence, to the enthalpy. For observation of exothermic processes, the nature of the processes is revealed by the fact that the sample temperature increases (or, at least, does not decrease) while the time integral of the temperature differences decreases. When the temperature differences are multiplied by the heat-transfer coefficient and integrated, the quantities obtained are approximately equal to the heat, on assumption that the profile of the temperature distribution within and



around the sample at the beginning of integration is the same as that at the end of the integration [8, 11], because a small part of the heat is also used to change the temperature profile due to the modulation.

During the transitions, the heat is the sum of heat absorbed by or evolved from the sample and the heat transferred to the environment and the reference material. In the case of the temperature difference between the sample and the reference material, the heat is equal to the heat absorbed by or evolved from the sample for model B, provided that the reference material of an empty pan is thermally symmetric to the sample. For model A the mutual heat exchange should be taken into account. Takahashi proposed before a similar method of estimating enthalpy by conventional static DSC [12].

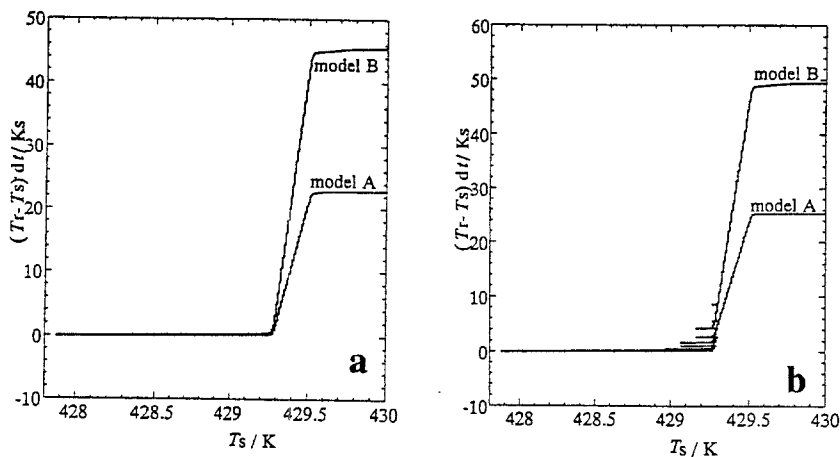


Fig. 6 Time integral of temperature differences for example 1. a) case 1, b) case 2

The integration has been made for the above simulated cases, and results are shown in Figs 6 and 7. As clearly seen, the supercooling is detected as spikes in the plots. Trace of the plot in the figure of the integral vs. the sample temperature is useful to reveal the nature of transition.

## Concluding remarks

In ac calorimetry or isothermal operation of tm-DSC, temperature modulation is applied to the sample and the sample thermal response to the modulation can be detected simply. However, in standard tm-DSC the modulation is superposed upon a linear temperature change, and during the transitions the thermal response of the sample to the modulation can not be observed separately. This causes complications and the sample thermal behavior can not be observed clearly. In this sense tm-DSC is not a dynamic operation of ac calorimetry, and the situation in tm-DSC is different from other modulated thermal analyses, such as dynamic thermomechanometry and dynamic thermoelectrometry.

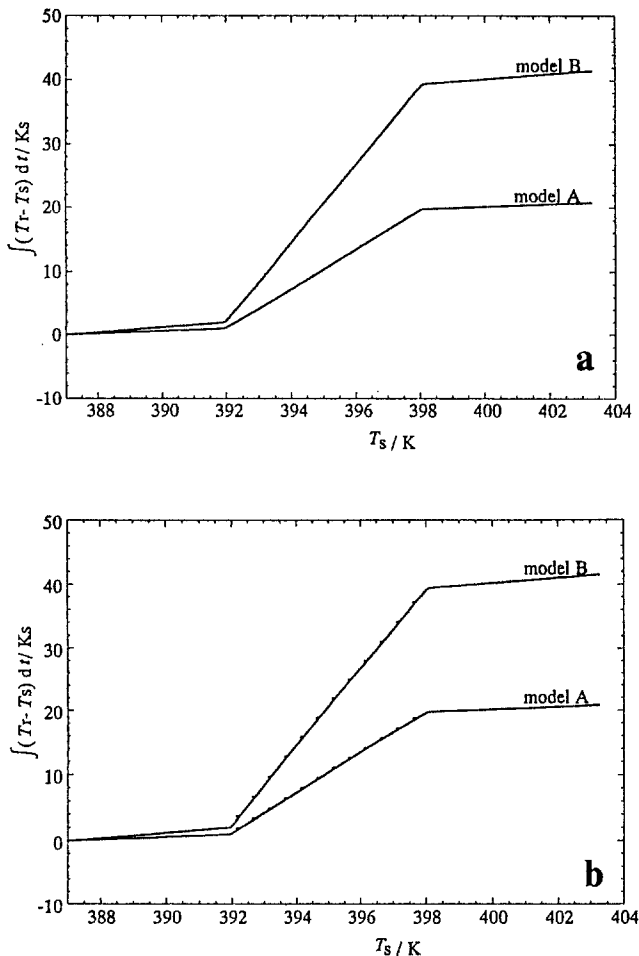


Fig. 7 Time integral of temperature differences for example 2. a) case 1, b) case 2

In tm-DSC of transitions with latent heats, the temperature modulation is not independent of the linearly changing temperature, and separation (or deconvolution) of the sample thermal response to the modulation can not be made, because of the non-linearity of the process observed [4]. On the other hand, separation of the sample thermal response to the modulation from that to the linearly changing temperature can be made in heat capacity measurements without latent heat, because the observed process is linear or quasi-linear and the steady state or quasi-steady state is established [5, 6].

Quasi-linearity holds and quasi-steady state is established even in a glass transition without relaxation [5, 6], while it does not hold in the transitions discussed in this paper. Questions are raised about the boundary between quasi-linearity and

non-linearity and the extent to which quasi-steady state differs from steady state. These are remaining problem to be solved.

Instead, another aspect of tm-DSC, i.e., the alternative observation in cooling and heating modes can be useful, and the time integrals of the above-mentioned temperature differences are informative. The trace of plot of the integral vs. the sample temperature reveals the nature of the transition.

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