

Linearity and non-linearity in DSC: A critique on modulated DSC [☆]

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Abstract

Recently a new interesting technique, modulated differential scanning calorimetry (MDSC), was published. This technique is based on Fourier transformation, and its sound applicability depends on linearity in thermal processes, because the Fourier transformation is based on linearity or the superposition principle. If a process under observation is a non-linear process, the physical meaning of the Fourier transformation should be closely examined. The DSC output signals of some processes, such as melting and reaction, have been revealed to be non-linear. Therefore, differentiation of linearity from non-linearity in DSC thermal responses is very important for modulated DSC, and they are discussed in this paper. In this discussion, methods to analyze oscillating output signals are also proposed.

Keywords: Deconvolution; DSC; Dynamic DSC; Linearity; MDSC

Introduction

Recently a new technique of heat-flux differential scanning calorimetry, hf-DSC, was set forth [1,2]. In this new technique, temperature oscillation is added to linear heating, and oscillating thermal response in the form of the temperature difference is recorded. The thermal response is analyzed by Fourier transformation, and the

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response in phase with the temperature oscillation is thought to be caused by reversible change or equilibrium change in the sample, while the response out of phase with the temperature oscillation is postulated to be non-reversible change [1,2]. Because the Fourier transformation is applied to the response, it is implicitly assumed that linearity, or the superposition principle, holds in the response.

However, this is not always clear, and non-linear responses have been observed in DSC results [3]. In order to elucidate the applicability of this very interesting technique, it is essential to differentiate linear from non-linear response in hf-DSC. What can be done and what cannot be done by this technique? The answer to this question is strictly connected with the linearity and non-linearity of the process. In order to obtain the correct answer, thermal responses, such as the baseline, peak area and peak shape, are considered theoretically and their linearities are examined by experimental facts. It is elucidated that linearity holds for the baseline and peak area, but thermal response by sample transformation is a non-linear process, so the physical meaning of observation of the transformation behavior by this technique is not clear. However, the thermal response by electrical heating, instead of the sample transformation, is a linear process. These theoretical considerations are described in detail, and methods to analyze oscillating thermal response are proposed in this paper.

2. Linearity

First of all, the mathematical and physical meaning of linearity and non-linearity should be made clear in relation to DSC. Linearity can be expressed by the equations

$$f(x + y) = f(x) + f(y) \quad (1)$$

$$f(ax) = af(x) \quad (2)$$

For DSC, x and y express quantities to be measured and the function expresses its output signal. Eq. (1) is the basis of the superposition principle and Eq. (2) indicates proportionality for quantitative measurement.

Hitherto, two contradictory postulations have been made. Tateno [4] postulated the applicability of a linear theory of measurement, and he deconvoluted DTA curves to reaction rate curves by using a transfer function of the DTA apparatus. The transfer function corresponds to $f(u)$ for a pulsive u in Eq. (1), and the deconvolution is a procedure for obtaining $x + y + \dots$, which occurs consecutively, from the observed $f(x + y + \dots)$ by using the transfer function. This procedure of deconvolution was made on the basis of linearity or the superposition principle. However, O'Neill [5] analyzed the heat transfer in power compensation DSC (pc-DSC) and postulated that transformation of the sample, such as melting, proceeds by a heat-transfer-controlling mechanism.

These two contradictory postulates are expressed schematically in Fig. 1. According to the linear theory of measurement, the output signal is deformed by

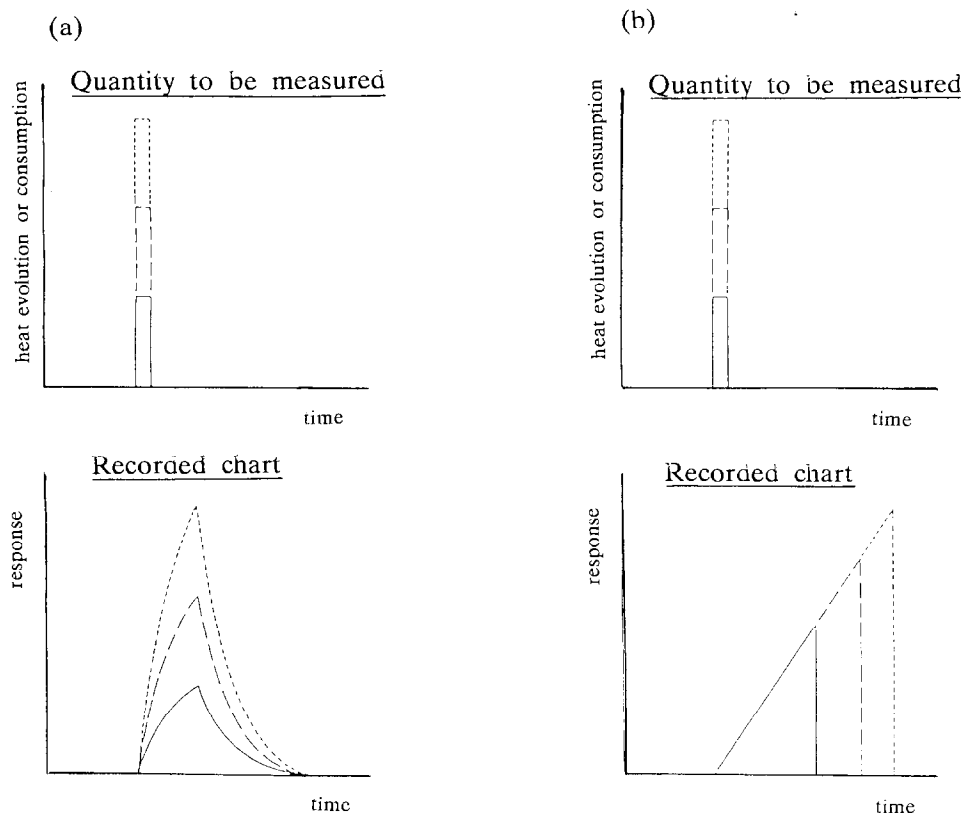


Fig. 1. Schematic expressions of (a) linear theory of measurement and (b) heat-transfer-controlling mechanism. Reproduced from Ref. [3] with permission.

the transfer function as shown in Fig. 1a, and the peak height is proportional to the quantity to be measured. For example, the DSC peak height of melting of a pure sample should be proportional to the sample mass, if linearity holds in a melting process.

However, O'Neill's postulate [5] can be expressed as in Fig. 1b. The heat is transferred by temperature gradient and the sample temperature is kept constant during the transformation, while the temperature of the heat source is controlled to increase linearly. Therefore, the temperature gradient also increases linearly and the rate of transformation is controlled by this linearly increasing temperature gradient, through which the heat is supplied. Thus the additional energy input due to the transformation is increased linearly in pc-DSC, and the additional temperature difference is similarly increased linearly in hf-DSC [3]. The same peak shape can be obtained by both types of DSC, because the heat transfer mechanism is the same [3]. Non-linearity is implicitly postulated by this heat transfer mechanism due to the constant sample temperature during the transformation.

3. Experimental facts and theoretical considerations

Experimental verification was made by one of the present authors [3]. With a pc-DSC, indium melting peaks were observed by changing the sample mass, and the results are reproduced in Fig. 2. Similar results were also obtained using DTA of a micro-sample. From these results we can conclude that the above heat-transfer-controlled melting proceeds in both types of DSC, and it can be concluded that the sample temperature is kept approximately constant during the melting. Thus, the temperature distribution within the sample can be neglected during the melting.

However, a linear process was also observed with an hf-DSC [3]. Pulsive electrical heating was made by inserting an electrical heater into the sample cell, and some peaks were obtained by changing the current and duration. They were compared in relation with the current, and the peak height was proportional to the current. A peak of long duration was compared with a peak synthesized by superposition of successive peaks of short duration, and excellent agreement was obtained between them. In other words, by adding $f(x)$ and $f(y)$ we can get $f(x + y)$, and this synthesized $f(x + y)$ is in excellent agreement with the $f(x + y)$ observed for $x + y$. Thus it was concluded that linearity holds in the case of electrical heating.

Similar results were obtained by using peaks obtained by infrared irradiation of the sample pan of a pc-DSC [3]. Thus linearity holds in both types of DSC, when

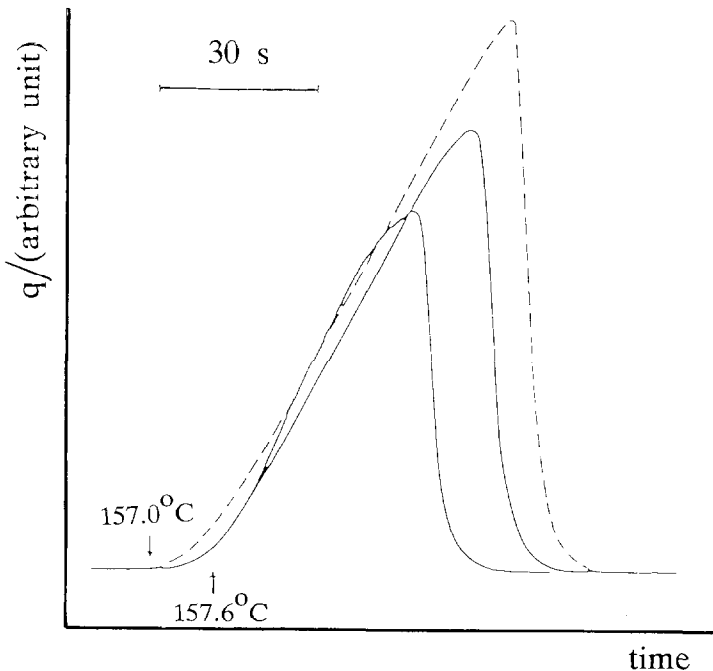


Fig. 2. DSC curves of melting for high-purity indium. The broken line is for remelting. Reproduced from Ref. [3] with permission.

heat evolves or absorbs independently of the sample temperature. In this case the evolved or absorbed heat is consumed by the sample temperature change.

For the baseline, it is clear that linearity holds, because linearity has been used in heat capacity measurements by using the baseline shift. From a theoretical viewpoint, the temperature distribution in an hf-DSC apparatus was analyzed in detail for sample cells of cylindrical symmetry [6] and for sample cells of general geometry [7]. In the dynamic steady state at a constant heating rate, the temperature of every part around the sample and the reference material is increased linearly, so that the temperature gradient at any point is proportional to the heating rate and it is also proportional to the heat capacity of the part to which the heat is supplied from the particular point.

Similarly, linearity holds in the peak area, because proportionality has been used in measurements of transformation heats. The linearity in this case was also theoretically considered for sample cells of cylindrical symmetry [6] and for sample cells of general geometry [7]. The following fundamental equation for heat conduction holds for the additional temperature, T' , due to a sample transformation in an hf-DSC apparatus

$$\lambda \nabla T = c\rho \frac{dT'}{dt} + \frac{d\Delta H}{dt} \quad (3)$$

where ∇ , λ , c , ρ , t and ΔH are respectively a Laplacian operator, the thermal conductivity, the heat capacity, the density, the time and the transformation heat. By integration from the beginning of the peak to its end, we get the following equation for any point [7]

$$\lambda \int T' dt = \Delta H \quad (4)$$

where the thermophysical properties of the sample, i.e., c and ρ , are assumed to be constant during the transformation, and the integral on the left side corresponds to the peak area. Thus the integral equation for the peak area is mathematically equivalent to the equation for temperature distribution in the steady state, and linearity holds for the peak area, as it holds for the baseline.

4. Concluding remarks

As seen in the above discussion, linearity holds for a baseline and peak area. Therefore, modulated DSC can be applied to heat capacity measurements, but applicability of this technique to melting behavior observation is not certainly proved. For this application, further considerations using a theoretical approach are necessary.

For theoretical consideration of the baseline, an analytical approach can be applied. In this approach, it can be assumed that the temperature distribution within the sample is negligibly small, though linearity holds for the case of detectable temperature distribution in the sample. Therefore, a fundamental equa-

tion for DTA derived by Vold [8] can be used and the temperature oscillation is introduced into the equation. Thus, the relation of a baseline with experimental parameters, such as heat transfer coefficients, heating rate, sample mass, etc., can be derived as an analytical solution.

For examination of modulated DSC results on sample transformation, the above analytical approach cannot be applied, but computer simulation seems to be a powerful tool. For this approach another assumption can be introduced, i.e., constant temperature of the sample during the transformation.

These approaches will give us valuable suggestions, and we will report them in the near future.

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