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Heat capacity measurements by dynamic differential scanning calorimetry

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Abstract

Dynamic differential scanning calorimetry (d-DSC) has attracted much attention, and it was postulated that high-precision heat capacity measurements can be made by this technique. However, its applicability, accuracy and precision have not yet been made clear. Because it is based on Fourier transformation, it can be applied to linear thermal responses. The dynamic steady state and the base line, from which the heat capacity is estimated, demonstrate a linear response in DSC, so that the dynamic steady state has been theoretically considered by analytical methods, and analytical solutions have been derived for the dynamic steady state and hence for the heat capacity measurement. For further examination, numerical solutions have also been obtained by taking account of other factors, which may potentially influence the measurements. In conclusion, a few points should be considered in the high-accuracy heat capacity measurements, because some factors, which have not been considered before, affect the dynamic steady state or the base line. Furthermore comparison has been made between d-DSC and conventional DSC in this research.

Keywords: DSC base line; Dynamic DSC (temperature modulated DSC); Heat capacity measurement

1. Introduction

In conventional heat flux differential scanning calorimeter (hf-DSC), a sample and thermally inert reference material, such as alpha-alumina or an empty pan, are heated

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or cooled at a constant rate, and the temperature difference between them is recorded against the time or temperature. Transformation of the sample can be detected as a peak in the record. In dynamic differential scanning calorimetry (d-DSC), temperature oscillation is superposed on this constant rate heating in hf-DSC. Thermal response in the form of temperature difference is separated into out-of-phase response and in-phase response by Fourier transformation, and the out-of-phase response is asserted to be the non-reversible change in the sample, while the in-phase response is thought to be the reversible or equilibrium change [1, 2]. Since its publication [1,2], this technique has attracted much attention because something new is seen in d-DSC curves. However a thorough examination of this new technique has not yet been made and this is necessary before its full potential is established.

Linearity in the thermal response is implicitly assumed in the separation of the in-phase response from the out-of-phase response, because Fourier transformation is applied. But this is not clearcut. The present authors have elucidated that in DSC, both hf-DSC and power compensation DSC, there are linear responses, such as the steady state, i.e., the base line, and non-linear responses, such as the sample transformation behavior, i.e., the peak shape [3, 4]. It was also made clear that the sample temperature can be assumed constant during the transition [3, 4]. Therefore, a simple mathematical treatment can be applied to the dynamic steady state and an analytical solution can be obtained, although it cannot be applied to non-linear responses. Analytical and numerical solutions are described and heat capacity measurements by d-DSC are theoretically considered in this report.

It was postulated [5, 6] that heat capacity measurement can be made more precisely by d-DSC than by conventional hf-DSC [7], but the conclusion of the present theoretical considerations is not so optimistic. There are a few points to be taken into account in order to make accurate heat capacity measurements by d-DSC and a marked advantage of d-DSC over conventional DSC has not been found for heat capacity measurements.

2. Model and fundamental equations

In 1949, Vold published an excellent paper on the theoretical considerations of differential thermal analysis (DTA) [8]. Because hf-DSC is a variety of DTA, her theory can be used in the present considerations. However, other factors should be taken into account. They are the heat capacity of the heat paths from the heat source to the sample and from the heat source to the reference material, because heat capacity has a role in shifting the phase of oscillation.

Thus two equations are derived for heat flow from the source to the midpoint of the heat path, and for heat flow from the midpoint to the sample. The heat capacity of the heat path material is distributed along the path, but in the simple equation below it is concentrated at the midpoint for simplicity, as follows

$$C_{fs} dT_{fs}/dt = K(T_f - T_{fs}) + K(T_s - T_{fs}) \quad (1)$$

$$C_s dT_s/dt + \Delta H dx/dt = K(T_{fs} - T_s) + k(T_o - T_s) + h(T_f - T_s) \quad (2)$$

where C , T , t , ΔH and dx/dt are the heat capacity, temperature, time, heat of sample transformation and its rate, respectively. The subscripts s, f, fs and o denote the sample, heat source, midpoint between the sample and heat source, and the environment, respectively; an K , k and h are the heat transfer coefficients between the indicated temperatures.

Similarly for the reference material

$$C_{fr} dT_{fr}/dt = K(T_f - T_{fr}) + K(T_r - T_{fr}) \quad (3)$$

$$C_r dT_r/dt = K(T_{fr} - T_r) + k(T_o - T_r) + h(T_s - T_r) \quad (4)$$

where the subscripts r and fr are the reference material and the midpoint between the reference material and the heat source.

The above equations can be expressed as an equivalent electrical circuit, as shown in Fig. 1, in which the mutual heat exchange between the sample and the reference material is not shown. In one commercial apparatus, this heat exchange does not occur, because the sample and the reference material are connected not directly but through the common heat source, while in another commercial apparatus it does exist due to a direct connection.

Before solving these equations, we should make clear the other assumptions implicitly included in the equations and the equivalent circuit.

First, the heat transfer coefficients are common for the sample side and the reference material side. It is implicitly assumed that the apparatus is made symmetrically, and that the sample and reference material are set in the same surroundings.

Second, the temperature distributions within the sample and reference material are neglected, and this does not deviate much from the real temperature distribution in hf-DSC for micro-amounts of sample, as discussed in our previous papers [3, 4].

Third, it is assumed that the heat transfers only by conduction, because it is proportional to the temperature difference between the sources and the sinks in the above four equations. In other words, convection and radiation should be negligibly small in the apparatus. This assumption is thought to be real in hf-DSC because of the

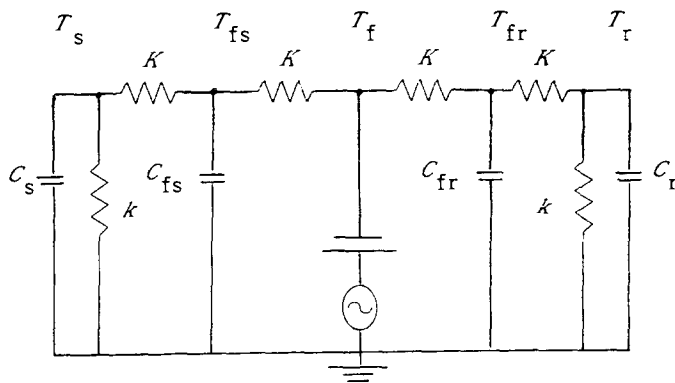


Fig. 1. Equivalent circuit of hf-DSC.

following facts. In DTA, the temperature difference measured is the difference between the temperature gradient from the heat source to the sample and that to the reference material, because the temperature distribution in the heat source is small. Especially in hf-DSC, the gradients measured are those occurring outside the sample and reference material. If the heat flows only by conduction, the gradients are proportional to the heat fluxes. Thus, the peak area is proportional to the heat of sample transformation, and in hf-DSC the proportionality coefficient is not dependent on the sample but is a characteristic of the apparatus [9]. This proportionality in hf-DSC is evidence for the fact that the heat flows only by conduction.

In d-DSC the heat source temperature changes at a constant rate, ϕ , with oscillation of the amplitude, A_t , and frequency, ω .

Therefore

$$T_t = T_b + \phi t + A_t \exp(i \omega t) \quad (5)$$

where T_b and i are the initial temperature and the unit of an imaginary number, respectively and $\exp(ix)$ equals $(\cos x + i \sin x)$ (Euler's formula). Because the temperatures of the sample and the reference material follow the above temperature change with time lags and phase shifts in the steady state ($\Delta H = 0$)

$$T_s = T_b + \phi t + A_s^* \exp(i \omega t) - B_s \quad (6)$$

$$T_{ts} = T_b + \phi t + A_{ts}^* \exp(i \omega t) - B_{ts} \quad (7)$$

$$T_r = T_b + \phi t + A_r^* \exp(i \omega t) - B_r \quad (8)$$

and

$$T_{tr} = T_b + \phi t + A_{tr}^* \exp(i \omega t) - B_{tr} \quad (9)$$

where the B 's are the constant temperature lags and the A^* 's are complexes expressing the amplitudes and phase shifts. Only the real parts in these terms have physical meanings, and both the real and imaginary parts of the complex amplitudes, A^* 's, are related to the amplitude and the phase shift.

3. Analytical solution on dynamic steady state

Substituting Eqs. (5), (6), (7), (8) and (9) into the starting Eqs. (1), (2), (3) and (4), and comparing the coefficients, we have the following simultaneous equations.

For the non-oscillating terms

$$\phi C_{ts} = K(2B_{ts} - B_s) \quad (10)$$

$$\phi C_s = K(B_s - B_{ts}) + k(B_s - \phi t) + h(B_s - B_r) \quad (11)$$

$$\phi C_{tr} = K(2B_{tr} - B_r) \quad (12)$$

and

$$\phi C_r = K(B_r - B_{tr}) + k(B_r - \phi t) + h(B_r - B_s) \quad (13)$$

because $T_o = T_b$.

For the real parts of the oscillating terms

$$-\omega C_{fs} A_{f_{si}} = K(A_f + A_{sr} - 2A_{f_{sr}}) \quad (14)$$

$$-\omega C_s A_{si} = K(A_{f_{sr}} - A_{sr}) - kA_{sr} + h(A_{rr} - A_{sr}) \quad (15)$$

$$-\omega C_{fr} A_{f_{ri}} = K(A_f + A_{rr} - 2A_{f_{rr}}) \quad (16)$$

and

$$-\omega C_r A_{ri} = K(A_{f_{rr}} - A_{rr}) - kA_{rr} + h(A_{sr} - A_{rr}) \quad (17)$$

where the last subscripts of the amplitudes, r and i, indicate the real and the imaginary parts of the amplitudes, respectively.

For the imaginary parts of oscillating terms

$$\omega C_{fs} A_{f_{sr}} = K(A_{si} - 2A_{f_{si}}) \quad (18)$$

$$\omega C_s A_{sr} = K(A_{f_{si}} - A_{si}) - kA_{si} + h(A_{ri} - A_{si}) \quad (19)$$

$$\omega C_{fr} A_{f_{rr}} = K(A_{ri} - 2A_{f_{ri}}) \quad (20)$$

and

$$\omega C_r A_{rr} = K(A_{f_{ri}} - A_{ri}) - kA_{ri} + h(A_{si} - A_{ri}) \quad (21)$$

For conventional hf-DSC, the oscillating terms are equal to zero, and only Eqs. (10), (11), (12) and (13) hold. Because $(B_s - B_r)$ is the temperature difference in the steady state, it is the base line measured by conventional hf-DSC, and we have

$$B_s - B_r = \phi(C_s - C_r)/(K/2 + k + 2h) \quad (22)$$

on assumption that the apparatus is made symmetrically and $C_{fs} = C_{fr}$. It is worth noting that Vold [8] derived an equation equivalent to this but with some correction terms due to assymetry of the apparatus. (Note that $K/2$ is equal to the heat transfer coefficient between the heat source and the sample or the reference material.) This is the very basis for the principle of heat capacity measurements by conventional hf-DSC. It should also be noted that the heat capacities of the heat paths have no effect on the heat capacity measurement by this method.

By combining Eqs. (14) and (15) we have

$$-\omega(2C_s A_{si} + C_{fs} A_{f_{si}}) = K(A_f - A_{sr}) - 2kA_{sr} + 2h(A_{rr} - A_{sr}) \quad (23)$$

Similarly, from Eqs. (16) and (17)

$$-\omega(2C_r A_{ri} + C_{fr} A_{f_{ri}}) = K(A_f - A_{rr}) - 2kA_{rr} + 2h(A_{sr} - A_{rr}) \quad (24)$$

By combining Eqs. (18) and (19), we get

$$-\omega(2C_s A_{sr} + C_{fs} A_{f_{sr}}) = KA_{si} + 2kA_{si} - 2h(A_{ri} - A_{si}) \quad (25)$$

By the same procedure from Eqs. (20) and (21)

$$-\omega(2C_r A_{rr} + C_{fr} A_{f_{rr}}) = KA_{ri} + 2kA_{ri} - 2h(A_{si} - A_{ri}) \quad (26)$$

General analytical solutions for the above simultaneous equations of the oscillating terms cannot be obtained. To obtain them, the direct mutual heat exchange between the sample and the reference material and the heat capacities of the heat paths must be neglected, namely

$$h = 0$$

and

$$C_{fs} = C_{fr} = 0$$

Thus we have the following solutions

$$A_{sr} = \frac{(K/2)(K/2 + k)A_f}{\omega^2 C_s^2 + (K/2 + k)^2} \quad (27)$$

$$A_{rr} = \frac{(k/2)(K/2 + k)A_f}{\omega^2 C_r^2 + (K/2 + k)^2} \quad (28)$$

$$A_{si} = -\frac{(K/2)\omega C_s A_f}{\omega^2 C_s^2 + (K/2 + k)^2} \quad (29)$$

and

$$A_{ri} = -\frac{(K/2)\omega C_r A_f}{\omega^2 C_r^2 + (K/2 + k)^2} \quad (30)$$

For the heat capacity measurement, a few relations can be derived from the above solutions, as follows

$$C_s^2 = \{K/2(K/2 + k)A_f - (K/2 + k)^2 A_{sr}\} \omega^2 A_{sr} \quad (31)$$

$$A_{si}/A_{sr} = -\omega C_s/(K/2 + k) \quad (32)$$

or

$$C_s = A_{si}(K/2 + k)/\omega A_{sr} \quad (32')$$

and

$$\frac{A_{si}}{A_{sr}} - \frac{A_{ri}}{A_{rr}} = -\frac{\omega(C_s - C_r)}{(K/2 + k)} \quad (33)$$

In the latter three equations, Eqs. (32), (32') and (33), the A_r/A_i terms are the tangents of the phase shift angle from the heat source.

These four equations cannot be directly applied to the output of the commercial d-DSC, because the temperature difference between the sample and the reference material, not between the sample and the heat source, is measured. The amplitude, A_d , and the tangent of the phase difference, $\tan \delta$, recorded in the commercial d-DSC are as follows

$$A_d^2 = A_{dr}^2 + A_{di}^2 = (A_{sr} - A_{rr})^2 + (A_{si} - A_{ri})^2 \quad (34)$$

$$\tan \delta = (A_{si} - A_{ri})/(A_{sr} - A_{rr}) \quad (35)$$

It should be noted that though the dynamic steady state dealt with in this report is a completely reversible process, the out-of-phase component exists in the response. Therefore the out-of-phase response does not directly correspond to a non-reversible process or to a non-equilibrium process.

Taking into account the complexity of Eqs. (27), (28), (29) and (30), Eqs. (34) and (35) are very complicated and inappropriate for heat capacity measurement, as they are. In the papers by Wunderlich and his coworkers [5, 6], similar but simple relations for the temperature difference are derived as follows, neglecting the heat transfer coefficient to the environment (k), the mutual heat exchange (h) and the heat capacities of the heat paths (C_{fs} and C_{fr}), together with further approximation

$$C_s = KA_{dr}/(2\omega A_{sr}) \quad (36)$$

Therefore, the applicability of the d-DSC, in which the temperature difference between the sample and the reference material is measured, is not clear, and it will be discussed later in this report by numerical solution of the above simultaneous equations.

Thus, Eqs. (31), (32) and (32') are simple and useful. Instead of measuring and using the temperature difference between the sample and the reference material, the temperatures of the sample and the heat source should be measured and compared with each other to estimate the necessary quantities to use these relations.

By comparing Eq. (22) with Eqs. (31), (32), (33) and (36) a unique feature of d-DSC is made clear: the heating rate, ϕ is contained in Eq. (22), but in the latter equations the frequency is involved. Thus high sensitivity is achieved by high frequency in d-DSC without sacrifice of the temperature resolution, although high sensitivity is achieved by high heating rate in conventional DSC *with* sacrifice of the temperature resolution [9].

4. Numerical solution of simultaneous equations

As clearly shown above, the effects of the mutual heat exchange and the heat capacity of the heat path should be taken into account in examining heat capacity measurement by d-DSC. For this purpose, a matrix method (see Appendix) has been applied to obtain numerical solutions.

In the above starting equations, for simplicity, the sample and reference material are related to the heat path without the heat capacity. Even so, the analytical solution cannot be obtained. For the matrix method, there is no such restriction, so that modification was introduced to the simple starting equations, Eqs. (1)–(4). The modification was made by considering heat capacity in the path for the mutual heat exchange. This path was divided into four parts of thermal resistance, and the heat capacity of the path was divided into three and attached to the three connections of these four resistances, as shown in Fig. 2 and the equations in the Appendix.

Two models of DSC apparatus were examined by this method. One is an apparatus with the direct mutual heat exchange (Model A) and the model is equivalent to the circuit in Fig. 1 with addition of the circuit in Fig. 2. The other is an apparatus without the mutual heat exchange (Model B), which is equivalent to the circuit in Fig. 1. The parameters of the apparatus, such as K , k , C_{fs} , etc. are determined for both by

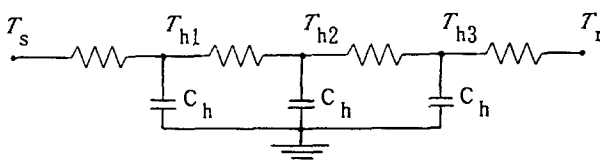


Fig. 2. Equivalent circuit of mutual heat exchange between sample and reference material for numerical solution by the matrix method.

estimating them from the design and the materials of the actual commercial apparatus, and they are tabulated in Table 1.

The operating conditions are also given in Table 1. The modulating amplitude and the heating rate are both somewhat larger than usual, but they have little effect on the results, for the following reasons. The process is linear, therefore the amplitudes of the thermal responses are proportional to the modulating amplitude, and the heat capacity is assumed constant, so that its temperature change is zero and independent on the heating rate.

The result of these numerical solutions are shown in Table 2, where the amplitudes and the base lines are tabulated for four cases of the sample heat capacity. These are used for estimating errors in heat capacity measurement methods by d-DSC.

In actual heat capacity measurements, the coefficients, $K/2$ and/or $(K/2 + k)$, characteristics for the apparatus, are first estimated as a function of the temperature by using

Table 1
Parameters for numerical solution
(1) Apparatus

	Model A	Model B
$K/mW K^{-1}$	73.6	73.6
$k/mW K^{-1}$	0.348	0.348
$h/mW K^{-1}$	36.8	0
$C_{fs}/mJ K^{-1}$	6.61	6.61
$C_{fr}/mJ K^{-1}$	6.61	6.61
$C_{h1}/mJ K^{-1}$	5.81	0
$C_{h2}/mJ K^{-1}$	6.61	0
$C_{h3}/mJ K^{-1}$	5.81	0

(2) Operation

Amplitude	4 K
Period	60 s
Angular frequency	$0.1047 s^{-1}$
(Frequency)	0.01667 Hz
Heating rate	$5 K min^{-1}$
C_r (empty pan)	$24.21 mJ K^{-1}$

Table 2
Results of complex amplitudes and temperature lags by the matrix method

$C_s/\text{mJ K}^{-1}$	A_{sr}/K	A_{si}/K	A_{rr}/K	A_{ri}/K	B_s/mK	B_r/mK
Model A						
20	3.96	-0.29	3.97	-0.24	58.3	47.1
50	3.94	-0.42	3.96	-0.28	83.6	55.5
70	3.92	-0.50	3.95	-0.30	100.4	61.1
100	3.89	-0.62	3.94	-0.34	125.7	69.5
Model B						
20	3.96	-0.27	3.96	-0.16	53.3	30.9
50	3.93	-0.43	3.96	-0.16	86.9	30.9
70	3.91	-0.54	3.96	-0.16	109.4	30.9
100	3.86	-0.70	3.96	-0.16	143.0	30.9

standard material, such as synthetic sapphire, and then the heat capacity of the sample is estimated by using the coefficients and the measured amplitudes and/or the tangent for the sample by using Eq. (33) or Eq. (36). This procedure was followed using the obtained results in Table 2, and errors in the heat capacity calculated are listed in Table 3. Because the temperature is uniform within the sample cell, the only thermophysical property that has an influence on the temperature oscillations is the heat capacity. Therefore, the results of different sample heat capacity are shown in these tables.

As seen in Table 2, the sample temperature oscillates independently of the reference material temperature for model B, while the interference is clearly shown between these two temperatures for model A. This is the effect of the mutual heat exchange. However, the errors in Table 3, which are systematic errors or deviations from the true values due to the apparatus and the equation used, are less for model A than for model B when Eq. (36) is used. The approximation included in Eq. (36) may compensate the effect of the mutual heat exchange.

The accuracy shown in Table 3 is fairly high, and for the case of using Eq. (33) (or Eq. (32')) and the apparatus without the mutual heat exchange, the accuracy is satisfactorily high. For the method using Eq. (22) and the base line with a conventional hf-DSC, accuracy is extremely good without error in this calculation, because the heat flow to the environment and the mutual heat exchange are taken into account in Eq. (22) and numerical solutions are obtained from the same model equations. However, in actual measurements, thermal disturbance from the outside might cause some error (low precision or low reproducibility) in the base line of the conventional DSC, while in d-DSC this disturbance cannot cause errors, because only the response of the same frequency as the modulating oscillation is analysed for the measurements. To take advantage of this, it is necessary to use a sample and standard material of equal heat capacity for both types of apparatus. For all methods and apparatus, constancy of K , k and h is important, and good thermal contact between the sample cell bottom and the cell holder is essential in the practical procedure in order to achieve high precision, i.e., high reproducibility [10].

Table 3
Results of error percentage in heat capacity measurements by the matrix method

$C_s(\text{sample})/\text{mJ K}^{-1}$	$C_s(\text{standard})/\text{mJ K}^{-1}$			
	20	50	70	100
(1) Eq. (36)				
Model A				
20	0.000	0.24	0.46	0.87
50	-0.24	0.000	0.21	0.62
70	-0.46	-0.22	0.000	0.41
100	-0.87	-0.62	-0.41	0.000
Model B				
20	0.000	0.36	0.70	1.36
50	-0.36	0.000	0.34	0.99
70	-0.70	-0.34	0.000	0.65
100	-1.34	-0.98	-0.65	0.000
(2) Eq. (33) by present authors				
Model A				
20	0.000	-0.26	-0.46	-0.82
50	0.26	0.000	-0.21	-0.57
70	0.47	0.21	0.000	-0.36
100	0.83	0.57	0.36	0.000
Model B				
20	0.000	-0.01	-0.02	-0.03
50	0.01	0.000	-0.01	-0.02
70	0.02	0.01	0.000	-0.01
100	0.03	0.02	0.01	0.000

5. Improvement of d-DSC apparatus

As clearly seen above, unfavorable factors exist in the present apparatus, such as the mutual heat exchange and the heat loss to the environment, and these unfavorable factors can be made negligible in designing a new apparatus. Specifically, the sample cell holder should be connected with the reference material cell holder through the common heat source, and the thermocouples to measure the temperatures of the sample and the reference material should be connected to the amplifier through the heat source with enough thermal contact with it. Furthermore, temperature oscillation with modulated light may be one possible way to minimize the effect of the heat capacities of the heat paths. However, the theory for this type of d-DSC is different from the present theoretical considerations, because the starting equations are different [11].

As seen above, the output signal should also be re-examined. The fundamental and essential signals to be recorded are the temperatures of the sample and the heat source, not the temperature difference between the sample and the reference material. Furthermore, the role of the reference material in d-DSC is less important than in conventional DSC. In the original DSC, the temperature difference was recorded with a strip chart recorder, but nowadays the temperatures can be recorded with a computer and

necessary quantities can be calculated. Therefore the above-mentioned improvement can easily be done.

6. Concluding remarks

From the above theoretical considerations, the following points have been made clear.

(1) The mutual heat exchange between the sample and the reference material and the heat capacities of the heat paths have influence on the temperature oscillation of the sample and the reference material.

(2) The heat flow to the environment complicates the relations used in the heat capacity measurements, because $K/2$ and $(K/2 + k)$ are both involved in the equation, provided that the temperature difference between the sample and the reference material is measured. However, this heat flow and the above mutual heat exchange do not have such an undesirable effect on heat capacity measurement by conventional DSC.

(3) For heat capacity measurement, the apparatus without direct mutual heat exchange is preferable for high accuracy (deviation from the true value), and it is desirable to decrease the heat flow to the environment. The temperature difference, not between the sample and the reference material, but between the sample and the heat source should be recorded, and for this temperature difference a much simpler relation can be derived which is much more useful for heat capacity measurements. Thus the role of the reference material is only to detect unfavourable thermal disturbance to the measurements in d-DSC.

(4) A specimen of the same heat capacity as that of the standard material seems desirable, because reproducible oscillation would be observed, even if the above-mentioned apparatus is used. However, the situation is still very complicated and thus there is no clear advantage of d-DSC over conventional DSC as far as heat capacity measurements and accuracy are concerned, while improvement in the precision (reproducibility) may be expected for d-DSC by filtering only the oscillating response of the definite modulating frequency.

(5) In accordance with our research strategy [4], we are carrying out research on DSC curves for temperature-dependent heat capacities and transitions by simulation, and the results will be submitted to the journal in the near future.

Appendix A. Matrix method

Fundamental equations similar to Eqs. (1)–(4) can be expressed for the modified model as follows

$$C_{fs} dT_{fs}/dt = K(T_f - T_{fs}) + K(T_s - T_{fs}) \quad (A1)$$

$$C_s dT_s/dt = K(T_{fs} - T_s) + k(T_o - T_s) + 4h(T_{h1} - T_s) \quad (A2)$$

$$C_{h1} dT_{h1}/dt = 4h(T_s - T_{h1}) + 4h(T_{h2} - T_{h1}) \quad (A3)$$

$$C_{h2} dT_{h2}/dt = 4h(T_{h1} - T_{h2}) + 4h(T_{h3} - T_{h2}) \quad (A4)$$

$$C_{h3} dT_{h3}/dt = 4h(T_{h2} - T_{h3}) + 4h(T_r - T_{h3}) \quad (\text{A5})$$

$$C_r dT_r/dt = K(T_{fr} - T_r) + k(T_o - T_r) + 4h(T_{h3} - T_r) \quad (\text{A6})$$

$$C_{fr} dT_{fr}/dt = K(T_f - T_{fr}) + K(T_r - T_{fr}) \quad (\text{A7})$$

where the subscripts h1, h2 and h3 denote the divided heat capacities and the temperatures of the mutual heat exchange path from the sample side to the reference material side, respectively. The heat of sample transformation is eliminated, because the dynamic steady state is dealt with. These equations are rewritten as follows

$$C dT/dt = K T + F + T_o \quad (\text{A8})$$

where

$$C = \begin{pmatrix} C_{fs} & & & & & & \\ & C_s & & & & & \\ & & C_{h1} & & & & \\ & & & C_{h2} & & & \\ & & & & C_{h3} & & \\ & 0 & & & & C_r & \\ & & & & & & C_{fr} \end{pmatrix} \quad (\text{A9})$$

$$F = \begin{pmatrix} K T_r \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ K T_r \end{pmatrix} \quad (\text{A10})$$

$$T = \begin{pmatrix} T_{fs} \\ T_s \\ T_{h1} \\ T_{h2} \\ T_{h3} \\ T_r \\ T_{fr} \end{pmatrix} \quad (\text{A11})$$

$$T_o = \begin{pmatrix} 0 \\ k T_o \\ 0 \\ 0 \\ 0 \\ k T_o \\ 0 \end{pmatrix} \quad (\text{A12})$$

and

$$\mathbf{K} = \begin{pmatrix} -2K, & K, & 0, & 0, & 0, & 0, & 0 \\ K, & -(K+4h+k), & 4h, & 0, & 0, & 0, & 0 \\ 0, & 4h, & -8h, & 4h, & 0, & 0, & 0 \\ 0, & 0, & 4h, & -8h, & 4h, & 0, & 0 \\ 0, & 0, & 0, & 4h, & -8h, & 4h, & 0 \\ 0, & 0, & 0, & 0, & 4h, & -(2K+4h+k), & K \\ 0, & 0, & 0, & 0, & 0, & K, & -2K \end{pmatrix} \quad (\text{A13})$$

The heat source temperature is given as Eq. (5). Therefore, the complex amplitudes are given by the next matrix equation

$$\mathbf{K} \begin{pmatrix} \omega C_{fs} \\ \omega C_s \\ \omega C_{h1} \\ \omega C_{h2} \\ \omega C_{h3} \\ 0 \\ \omega C_r \\ \omega C_{fr} \\ -\omega C_{fs} \\ -\omega C_s \\ -\omega C_{h1} \\ -\omega C_{h2} \\ -\omega C_{h3} \\ 0 \\ -\omega C_r \\ -\omega C_{fr} \end{pmatrix} = \begin{pmatrix} A_{fs} \\ A_{sr} \\ A_{h1r} \\ A_{h2r} \\ A_{h3r} \\ A_{rr} \\ A_{fr} \\ A_{fsi} \\ A_{si} \\ A_{h1i} \\ A_{h2i} \\ A_{h3i} \\ A_{ri} \\ A_{fri} \end{pmatrix} = \begin{pmatrix} -K A_f \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -K A_f \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad (\text{A14})$$

This equation was solved numerically with a computer using the parameters in Table 1, and the results are shown in Tables 2 and 3.

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