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OPTIMIZATION OF EXPERIMENTAL PARAMETERS IN TMDSC

The influence of non-linear and non-stationary thermal response

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Abstract

To treat data from temperature modulated differential scanning calorimetry (TMDSC) in terms of complex or reversing heat capacity firstly one should pay attention that the response is linear and stationary because this is a prerequisite for data evaluation. The reason for non-linear and non-stationary thermal response is discussed and its influence on complex (reversing) heat capacity determination is shown. The criterion for linear and stationary response is proposed. This allows to choose correct experimental conditions for any complex heat capacity measurement. In the case when these conditions can not be fulfilled because of experimental restrictions one can estimate the influence of non-linearity and non-stationarity on measured value of complex or reversing heat capacity.

Keywords: complex heat capacity, non-linearity, non-linear thermal response, non-stationarity, reversing heat capacity, TMDSC

Introduction

Dynamic susceptibilities characterising material properties are derived under linear and stationary response approach. Among such values is complex heat capacity c_p^* given by the ratio between vector amplitudes of measured heat-flow rate and heating rate (time derivative of temperature) [1, 2]. Under linear response doubling the perturbation amplitude (e.g. temperature) leads to doubling the response amplitude (e.g. heat-flow) so that at given temperature and time the value of c_p^* depends only on frequency. Stationary conditions assume that system properties do not change during one modulation period so that the value of c_p^* is well defined.

However for dynamic calorimetric measurements, especially in the vicinity of transitions, the response of the system is often non-linear. In this case the value of c_p^* depends not only on frequency but also on perturbation. There is no generally accepted criterion for linear thermal response. One can argue [3] that in calorimetric measurements external perturbation is $\delta T/T$ and except for phenomena occurring at

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low-temperatures $\delta T/T$ is usually small and one can utilise the linear response theory. Sometimes one says, referring to TMDSC measurements, that one should use temperature perturbation as small as possible [4, 5], but at the same time underlying scanning rate should be so low, that changes in mean temperature during one modulation period are smaller than amplitude of temperature modulation [6, 7]. These conditions, being rather qualitative, depend a lot on sample in question and can considerably restrict the range of possible experiments if one wish to get linear response. Therefore it is of importance to evaluate quantitatively the non-linear part of the thermal response and its influence on measured data.

On the other hand thermal response is often non-stationary especially when mean temperature is scanned through transition regions with high scanning rate or during quasi-isothermal measurement of fast irreversible processes. Then system properties change a lot during one modulation period independently on perturbation. Under such conditions heat capacity c_p^* can not be determined unambiguous.

As shown in [8] the response of a DSC apparatus in time domain can be represented as the convolution product of the perturbation with the corresponding Green's functions. Consequently, the response of the DSC can be considered as linear. In TMDSC linearity can be checked in the frequency domain i.e. by looking at higher harmonics in the response under harmonic perturbation [5]. Before considering non-linear and/or non-stationary thermal response one should know linearity limitations of the instrument itself. Under conditions that sample response is linear, e.g. in the molten state, non-linearity (higher harmonics) comes only from the instrument. In this way under applied range of temperature perturbation one can determine an accuracy limit of a given instrument due to harmonic distortions. This has been done on the example of a Perkin Elmer DSC 2. For 4 mg sample and modulation period of 100 s apparatus distortions are smaller than 1% for heating rate amplitudes A_q in the range 2 K min^{-1}$\leq A_q \leq$60 K min^{-1} which corresponds to temperature amplitudes 0.5 K min^{-1}$\leq A_T \leq$15 K min^{-1} [9]. At larger amplitudes uncertainties come from non-linear behaviour of the apparatus and at lower amplitudes – from low signal-to-noise ratio.

In the following we chose the value of 1% as a realistic accuracy limit and compare this value to uncertainties in c_p^* determination due to non-linear and non-stationary thermal response of the sample. Other sources for systematic errors in c_p^* determination like calibration problems are not discussed here.

Experimental

The TMDSC experiments were performed with a Perkin Elmer Pyris-1 DSC and a modified computer controlled Perkin Elmer DSC-2. To perform temperature modulated measurements with the DSC-2 a sinusoidal voltage was added to the temperature control unit. The DSC's are temperature calibrated for heating rate zero by indium and lead according to the GEFTA recommendation [10]. The calibration was checked in TMDSC mode with the smectic A to nematic transition of 8OCB [11].

The linear aliphatic polylactone polycaprolactone (PCL), with structure $[(CH_2)_5COO]$– used in the experiments is a commercial sample synthesized by Aldrich Chemie with a molecular mass average M_W=55700 g mol^{-1}. More details about the sample are reported in [12]. The poly(ether ether ketone) (PEEK), with structure $[O(C_6H_4)–CO–C_6H_4–O–C_6H_4]$– is available from ICI, trade name Victrex 381G. In contrary to PEEK PCL shows a very narrow melting range. The effects in the glass transition region were studied for a polystyrene (PS), BASF 168N and a poly(vinyl acetate) (PVAc).

Non-linearity in TMDSC measurements

An example of non-linear behaviour is shown in Fig. 1 for the glass transition of PVAc. As one can see the value of c_p^* depends on applied temperature amplitude.

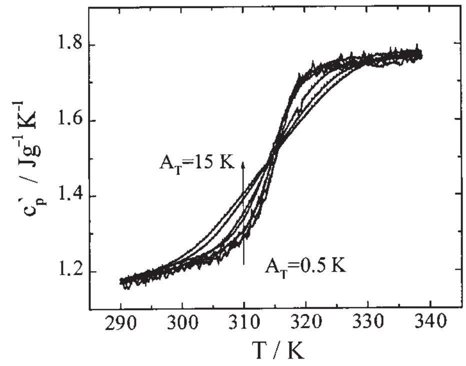

Fig. 1 Real part of specific heat capacity c_p^* obtained from first harmonic of measured heat-flow rate for different temperature amplitudes as a function of temperature. PVAc; underlying heating rate q_o= –0.25 K min^{-1}, frequency of temperature modulation ω=0.03 rad s^{-1}

For amplitude dependent part of c_p^* one can write in first approximation:

$$\Delta c_p^* \approx \frac{dc_p^*}{dA_T} A_T \tag{1}$$

where A_T is temperature amplitude and dc_p^*/dA_T is temperature amplitude derivative of complex heat capacity. If relative changes of complex heat capacity is in the same order or smaller than chosen accuracy limit η, i.e.

$$\frac{\Delta c_p^*}{c_p^*} \approx \frac{1}{c_p^*}\frac{dc_p^*}{dA_T} A_T \leq \eta \tag{2}$$

then within experimental uncertainties one can consider the response as linear. For the example shown in Fig. 1 c_p^* at 310 K changes from 1.3 to 1.42 J g^{-1} K^{-1} during increasing temperature amplitude from 0.5 to 15 K, therefore $\mathrm{d}c_\mathrm{p}^*/\mathrm{d}A_\mathrm{T}\approx 0.12/15=0.008$ J g^{-1} K^{-2}. Taking for c_p^* at 310 K the value under linear response ($c_\mathrm{p}^*=1.3$ J g^{-1} K^{-1}) and for accuracy limit $\eta\approx 0.01$ Eq. (2) yield $A_\mathrm{T}\leq 1.6$ K. Thus, for A_T smaller than 1.6 K response becomes linear and one gets a correct value for c_p^*. Within experimental uncertainties the c_p^*-profiles coincide for the two smallest temperature amplitudes as can be seen in Fig. 1.

Non-linearity for $A_\mathrm{T}>1.6$ K in the previous example is mainly caused by temperature dependence of c_p^* at glass transition [13]. Under large temperature amplitude system goes out of the transition region that leads finally to smearing of $c_\mathrm{p}^*(T)$ profile. Another reason for non-linearity can be seen in temperature modulated scan measurements in the melting region of polymers when a large heating rate perturbation is combined with an underlying heating rate q_0. Part of the sample which has been melted during heating cycle ($q(t)>0$) can not be crystallised during cooling cycle ($q(t)<0$) because crystallisation and melting rates of polymers are quite different [14]. This affects the asymmetry in the heat-flow rate and therefore the heat-flow amplitude and the c_p^* value obtained. Such heating rate amplitude dependence of the modulus of c_p^* and of the phase angle is shown in Figs 2 and 3, respectively, on example of PEEK (Victrex 381G).

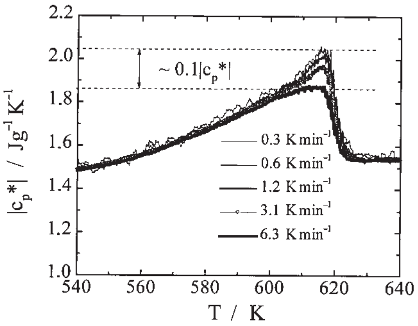

Fig. 2 Modulus of specific heat capacity c_p^* *vs.* temperature at different amplitudes of modulated heating rate A_q for temperature modulated scan measurements in the melting region of PEEK. Perkin Elmer DSC 2, $m_\mathrm{s}=26$ mg, $q_\mathrm{o}=2$ K min^{-1}, $t_\mathrm{p}=1$ min, sinusoidal temperature oscillations

Note that under given experimental conditions temperature amplitudes were not higher than 1 K – with such amplitudes system stays always within the transition region, except the very end of melting. In this example there is heating rate amplitude dependence but no temperature amplitude dependence of c_p^*.

Analogous to Eq. (1) for heating rate amplitude dependent part of c_p^* one can write in first approximation:

$$\Delta c_\mathrm{p}^* \approx \frac{\mathrm{d}c_\mathrm{p}^*}{\mathrm{d}A_\mathrm{q}} A_\mathrm{q} \tag{3}$$

where $\mathrm{d}c_\mathrm{p}^*/\mathrm{d}A_\mathrm{q}$ is heating rate amplitude derivative of complex specific heat capacity. If relative changes of complex heat capacity in the same order or smaller than chosen accuracy limit η, i.e.

$$\frac{\Delta c_\mathrm{p}^*}{c_\mathrm{p}^*}\approx\frac{1}{c_\mathrm{p}^*}\frac{\mathrm{d}c_\mathrm{p}^*}{\mathrm{d}A_\mathrm{q}}A_\mathrm{q}\leq\eta \tag{4}$$

then one can consider the response as linear.

The same way as it has been done for glass transition example one can estimate by Eq. (4) acceptable range of heating rate amplitudes for the case shown in Fig. 2. The value of c_p^* at 615 K changes for about 10% (1.87 to 2.04 J g^{-1} K^{-1}) during increasing of heating rate amplitude from 0.3 to 6.3 K min^{-1}. Therefore one should apply a heating rate amplitude $A_q\leq0.6$ K min^{-1} to keep these changes in c_p^* smaller than 1%. As one can see in Figs 2 and 3 calculated modulus of c_p^* as well as phase angle within experimental uncertainties coincides at $A_q=0.3$ and 0.6 K min^{-1}. In this case heating only condition, $A_q<q_o$, used to examine irreversible melting [15], would be not enough to meet conditions of linearity, Eq. (4), because of the influence of re-crystallisation and re-organisation.

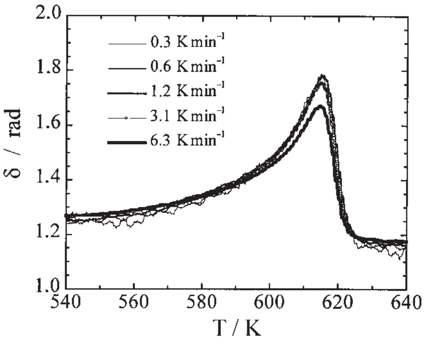

Fig. 3 Phase angle δ between heat-flow rate and heating rate *vs.* temperature at different amplitudes of modulated heating rate A_q for temperature modulated scan measurements in the melting region of PEEK. Perkin Elmer DSC 2, m_s=26 mg, q_0=2 K min^{-1}, t_p=1 min, sinusoidal temperature oscillations

Non-stationarity in TMDSC measurements

In this section it is assumed that conditions of linearity, Eqs (2, 4), are fulfilled. Under stationary conditions it is enough to calculate at given frequency only one value of complex specific heat capacity c_p^*. However, system properties can change with time independently on perturbation, e.g. due to overall crystallisation or chemical reactions, degradation with time and so on. Under such conditions the value of complex specific heat capacity depends on time, $c_\mathrm{p}^*(t)$. In this case one assigns to given time t the mean value of c_p^* over one modulation period t_p. Relative changes of value over one modulation period are given by:

$$\frac{\Delta c_\mathrm{p}^*}{c_\mathrm{p}^*}\approx t_\mathrm{t}\frac{1}{c_\mathrm{p}^*}\frac{\mathrm{d}c_\mathrm{p}^*}{\mathrm{d}t} \tag{5}$$

where $\mathrm{d}c_\mathrm{p}^*/\mathrm{d}t$ denotes the rate of change of the c_p^* value (time derivative of $c_\mathrm{p}^*(t)$). In temperature modulated scan measurements, in addition to possible changes with time, system properties can also change due to scanning of the mean temperature. Since mean temperature is connected with time as $\langle T\rangle=T_0+q_0(t-t_0)$, where T_o and t_o denote starting temperature and time, respectively, formally one can rewrite Eq. (5) as:

$$\frac{\Delta c_\mathrm{p}^*}{c_\mathrm{p}^*}\approx q_0 t_\mathrm{p}\frac{1}{c_\mathrm{p}^*}\frac{\mathrm{d}c_\mathrm{p}^*}{\langle T\rangle} \tag{6}$$

where now $\mathrm{d}c_\mathrm{p}^*/\mathrm{d}\langle T\rangle$ denotes temperature derivative of $c_\mathrm{p}^*(T)$. If c_p^* depends both on time and on temperature, $c_\mathrm{p}^*=c_\mathrm{p}^*(t,T)$, then $\mathrm{d}c_\mathrm{p}^*/\mathrm{d}\langle T\rangle$ is different for different underlying heating rates q_0. The point here is not the separation of time and temperature evolution of c_p^* (that can be done by measuring with different underlying heating rates), but uncertainties of determination due to such evolution. From Eqs (5, 6) one can write the condition of stationarity as:

$$\frac{\Delta c_\mathrm{p}^*}{c_\mathrm{p}^*}\approx t_\mathrm{p}\frac{1}{c_\mathrm{p}^*}\frac{\mathrm{d}c_\mathrm{p}^*}{\mathrm{d}t}\leq\eta \tag{7}$$

or

$$\frac{\Delta c_\mathrm{p}^*}{c_\mathrm{p}^*}\approx q_0 t_\mathrm{p}\frac{1}{c_\mathrm{p}^*}\frac{\mathrm{d}c_\mathrm{p}^*}{\mathrm{d}\langle T\rangle}\leq\eta \tag{8}$$

where again η denotes the chosen accuracy limit.

At given rate of system evolution $\mathrm{d}c_\mathrm{p}^*/\mathrm{d}t$ one should use only such modulation periods t_p that stationary condition, Eq. (7), is fulfilled. Figure 4 shows the results from quasi-isothermal ($q_0=0$) TMDSC measurement in the melting region of a semi-crystalline polymer. In such measurements the relaxation of the system does not depend on given temperature perturbation [16]. One can see by eye that at shorter modulation period heat-flow rate is more or less symmetric and one can consider c_p^* value and its relaxation with time. On the contrary at large period c_p^* value is very arbitrary at the beginning of the relaxation. For the first 20 min heat-flow amplitude and therefore c_p^* decreases by a factor of two, $(1/c_\mathrm{p}^*)\cdot(\mathrm{d}c_\mathrm{p}^*/\mathrm{d}t)\approx1/20\ \mathrm{min}^{-1}$. Then according to Eq. (7) modulation period in this case should be smaller than 0.2 min=12 s to keep uncertainties smaller than 1%. For 2.5 min period there is an error of about 13% in determination of c_p^* value at the first 20 min of the experiment.

Consider another example of non-stationary response when system properties change with mean-temperature during scanning. The value of c_p^* at glass transition region strongly depends on temperature, $\mathrm{d}c_\mathrm{p}^*/\mathrm{d}\langle T\rangle\neq0$. Under high scanning rate and large periods even one modulation can cover the whole transition region. Then in such measurements the value of c_p^* near the transition will be ambiguous. Figure 5 shows c_p^* at glass transition at different underlying cooling rates. According to Eq. (6) at given modulation period uncertainties from non-stationarity increase with increasing underlying scanning rate. As a result one can see with increasing scanning rate gradual deviations of c_p^* curve from the correct value (obtained at the lowest q_0). These deviations become very large at q_0=8 K min^{-1}. As one can estimate between 370 and 380 K c_p^* changes for about 0.3 J g^{-1} K^{-1}, so that $\mathrm{d}c_p^*/\mathrm{d}\langle T\rangle \approx 0.03$ J g^{-1} K^{-2}, and at 375 K $c_p^* \approx 1.65$ J g^{-1} K^{-1}. By Eq. (8) one can obtain for modulation period of 2 min that $q_0 \leq 0.3$ K min^{-1}. The c_p^* curve taken at q_0=0.2 K min^{-1} meets this requirement. Note that in this example conditions of linearity are also fulfilled.

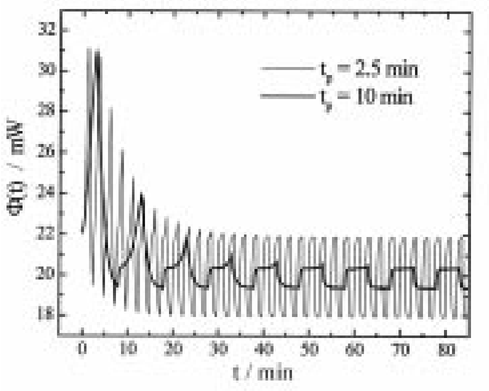

Fig. 4 Heat-flow rate (without empty pan correction) in quasi-isothermal melting of PCL for two different modulation periods. Mean temperature T_0=335 K was reached by heating the sample from semi-crystalline state. Perkin Elmer Pyris 1, m_s=76 mg, A_T=0.5 K, saw-tooth temperature oscillations

In general, if modulation period is given and stationarity condition is not fulfilled then one should try to decrease the rate of system changes if possible, e.g. by decreasing underlying scanning rate q_0 or by choosing another mean temperature for measurement of crystallisation to slow down crystallisation rate.

Higher harmonics

In previous sections we analysed influence of non-linear and non-stationary response on c_p^* determination by varying experimental parameters. Another way to check this influence for given experimental parameters is to look at higher harmonics of the heat-flow response. Under harmonic temperature perturbations higher harmonics in the heat flow rate will give the measure of non-linearity and non-stationarity of the response. Then a systematic error in determination of first harmonic of the heat-flow (and therefore error in c_p^* determination) can be estimated as

$$\frac{\Delta c_p^*}{c_p^*} = \frac{\Delta h_1}{h_1} \approx \frac{\sum\limits_{n>1} h_n}{h_1} \tag{9}$$

where h_n denotes amplitude of n^{th} harmonic of heat-flow rate.

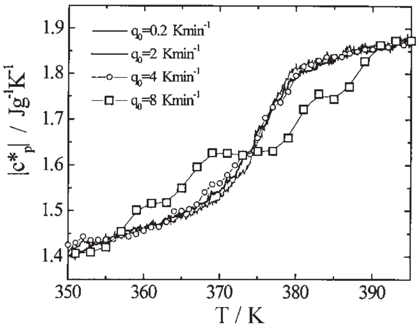

Fig. 5 Modulus of specific heat capacity at glass transition region of PS *vs.* temperature for different underlying cooling rates q_0. Perkin Elmer Pyris 1, m_s=23.62 mg, A_T=0.5 K, t_p=2 min

Under non-linear response in melting region shown in Figs 2 and 3, asymmetry in heat flow rate results higher harmonics after Fourier transform. Figure 6 shows the maximum value of the normalised amplitudes of second and third harmonics of measured heat-flow rate for the same measurements as in Figs 2 and 3. With decreasing perturbation amplitude higher harmonics due to non-linear response should trend to zero value, but in fact they almost do not change at the two lowest heating rate amplitudes. This is partly due to some apparatus harmonic distortions (like noise) and due to contribution from non-stationarity (next figure). Important point here is that about 10% of higher harmonics at A_q=6.3 K min^{-1} (Fig. 6) coming from non-linearity results the same 10% decrease of measured modulus of c_p^* and in a decrease of the phase angle, as already shown in Figs 2 and 3. One can also see gradual decrease of higher harmonics with decreasing heating rate amplitude that means that heating only conditions do not qualitatively change general tendency.

Non-stationary response will result also some higher harmonics even under linear response. The last case is represented in Fig. 7 on an example of TMDSC measurements in melting region of PEEK. Non-stationarity in this case is caused by strong temperature dependence of c_p^* at the end of melting region, as one can see in Fig. 2. Heating rate amplitude is very low so that the response is linear, but still one can detect some higher harmonics. As already mentioned under given modulation period one should decrease underlying scanning rate to decrease non-stationarity. One can see, that amplitude of second harmonic decreases gradually with decreasing scanning rate, i.e. with decreasing of non-stationarity. Combining Eqs (9) and (8) one can notice, that the value for higher harmonics should linear increase with increasing underlying scanning rate. This is in a good agreement with measured data, shown in Fig. 7. The value of h_2 deviates from a straight line only at the highest scanning rate q_0=8 K min^{-1} because Eq. (8), like all others, was derived under assumption of small changes of c_p^* (linear approximation).

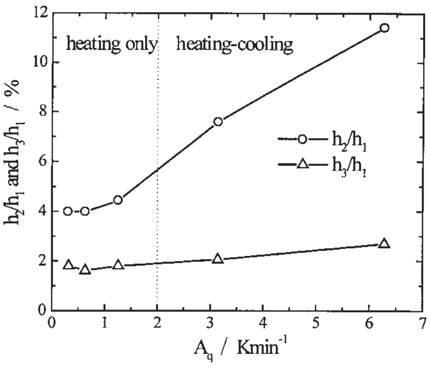

Fig. 6 Maximum value of normalised amplitude of second, h_2, and third, h_3, harmonics of heat-flow rate *vs.* amplitude of modulated heating rate, A_q, for temperature modulated scan measurements in the melting region of PEEK. Perkin Elmer DSC 2, m_s=26 mg, q_0=2 K min^{-1}, t_p=1 min, sinusoidal temperature oscillations

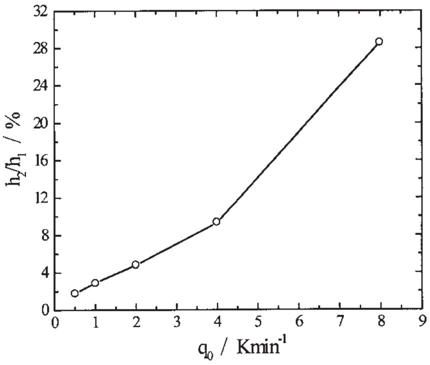

Fig. 7 Maximum value of normalised amplitude of second harmonic h_2 *vs.* underlying heating rate q_0 for temperature modulated scan measurement in the melting region of PEEK. Perkin Elmer DSC Pyris 1, m_s=16 mg, t_p=1 min, A_q=0.2 K min^{-1}, saw-tooth temperature oscillations

Discussion

One of the interesting application of TMDSC is heat capacity spectroscopy – measuring complex heat capacity c_p^* at different frequencies. Varying modulation frequency one has to vary either temperature amplitude or heating rate amplitude or both of them. Then one automatically changes influence of non-linearity or/and influence of non-stationarity on c_p^* determination, Eqs (4, 6) and Eqs (7, 8), respectively. Because of these non-linearity and non-stationarity one can obtain frequency dependence of measured complex heat capacity which is far from real kinetics of the transition under investigation.

In general one can use two ways to check linear response – to vary the amplitude of perturbation or to look at higher harmonics on the heat-flow response under harmonic perturbation. In first case it takes more than one measurement. To check stationary conditions one can vary the rate of system evolution or can look at higher harmonics. Again first way takes more than one measurement and sometimes it is impossible to change the rate of system evolution. Therefore we propose to check linearity and stationarity of every c_p^* measurements by looking at higher harmonics of the measured heat-flow rate under harmonic perturbation. Then one can estimate uncertainties in c_p^* determination by Eq. (9). (Frequently used saw-tooth temperature profile already contains spectrum with odd harmonics. In this case one should take under considerations only even harmonics, as it has been done on the example in Fig. 7.) To select the range of experimental parameters (temperature amplitude A_T, heating rate amplitude A_q, modulation period t_p, underlying scanning rate q_0) under desirable experimental accuracy η, one should use conditions given in Eqs (4, 6–8).

Conclusions

Before considering the value of complex (or reversing) heat capacity at given measurement one should always check whether the thermal response is linear. To do that under harmonic perturbation one can look at higher harmonics of the response (of the periodic heat-flow rate in case of TMDSC). There are two reasons of presence of higher harmonics: non-linearity and non-stationarity. Both of them influence the value of first harmonic and therefore influence accuracy of complex (or reversing) heat capacity determination. One can not say in advance which perturbation is supposed to be large and which is small. The range of acceptable perturbation amplitude depends on sample in question and is given by conditions of linearity, Eqs (4, 6). The same holds for stationarity: acceptable range of modulation periods and underlying heating rates depends on how fast sample heat capacity changes with time and/or with temperature and is given by conditions of stationarity, Eqs (7, 8). If certain accuracy is required then one should simultaneously meet conditions of linearity and stationarity.

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