Complex heat capacity measurements by TMDSC
Part 1. Influence of non-linear 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 one should know heat transfer and apparatus influences on experimental results. On the other hand one should pay attention that the response is linear because this is a prerequisite for data evaluation. The reason for non-linear thermal response is discussed and its influence on complex heat capacity determination is shown. The criterion for linear response is proposed. This allows to choose correct experimental conditions for any complex heat capacity measurements. In the case when these conditions cannot be fulfilled because of experimental restrictions one can estimate the influence of non-linear response on measured value of complex or reversing heat capacity. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Besides other dynamic calorimetric methods like AC [1–3] and 3ω [4,5], temperature modulated differential scanning calorimetry (TMDSC), introduced by Reading and co-workers [6] as an extension of the conventional DSC, gives a possibility to measure complex heat capacity[1] [7,8]. It is well understood however, that the value for complex heat capacity $c_p(\omega)$ being given by the ratio between vector amplitudes of measured heat flow rate and heating rate should be corrected for heat transfer effects. This will be discussed in detail in part 2 of this paper [9]. But

another and more general point is that the response of the system should be linear if one wants to treat data in terms of complex heat capacity. Often for dynamic calorimetric measurements, especially in the vicinity of phase transitions, the response of the system is non-linear, i.e. doubling the perturbation amplitude (e.g. temperature) does not necessarily lead to doubling the response amplitude (e.g. heat flow). In this case the value of $c_p(\omega)$ depends not only on frequency but also on perturbation amplitude. There is no generally accepted criterion for linear thermal response. One can argue [10] that in calorimetric measurements external perturbation is $\delta T/T$ and except for phenomena occurring at low temperatures $\delta T/T$ is usually small and one can utilize the linear response theory. Sometimes one says, referring to TMDSC measurements, that one should use temperature perturbation as small as possible [11,12], but at the same time under-

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[1]Note that the term complex heat capacity always includes the so called reversible heat capacity which equals the modulus of complex heat capacity.

lying scanning rate should be so low, that changes in mean temperature during one modulation period is smaller than amplitude of temperature modulation [13,14]. These conditions, being rather qualitative, depend a lot on sample in question. On the other hand they can considerably restrict the range of possible experiments if one wish to get linear response. Therefore it is of the importance to evaluate quantitatively non-linear part of the thermal response and its influence on measured data.

In the following paper we examine the influence of non-linear thermal response on measured values of complex heat capacity and propose some criteria for linearity of TMDSC measurements. It is assumed that experimental uncertainty of $c_p(\omega)$ determination comes from non-linear response only. Heat flow and temperature calibration is beyond the scope of the paper.

2. TMDSC data treatment

The response $\varepsilon(t)$ of a system to an external perturbation $\sigma(t)$ can be written as

$$\varepsilon(t) = \hat{K}(t_0, t)\,\sigma(t),\tag{1}$$

where $\hat{K}(t_0, t)$[2] is an operator which transforms a set of functions $\sigma(t)$ to a set of functions $\varepsilon(t)$ and where $t \in [t_0, \infty)$. (One can include in $\hat{K}(t_0, t)$ history dependence by making $t_0 \to -\infty$) In dynamic calorimetric measurements from physical point of view temperature $T(t)$ serves as a driving force and heat $Q(t)$ is measured as a response, or vice versa [10]. Because of construction principle TMDSC, as well as DSC, measures time derivative of the heat and on the other hand temperature change serves as a driving force. Then formally one can consider heating rate, $q(t) \equiv \dot{T}(t)$, as the external perturbation and heat flow rate, $\Phi(t) \equiv \dot{Q}(t)$, as the response. Since $q(t)$ is only derivative of temperature it represents possible temperature–time program only to some arbitrary constant. Then operator $\hat{K}(t_0, t)$ can depend on starting temperature $T_0 = T(t_0)$ so that Eq. (1) becomes

$$\Phi(t) = \hat{K}(T_0, t_0, t)\,q(t).\tag{2}$$

Consider farther, the set of experiments with the same starting temperature T_0. If $\hat{K}(t_0, t)$ is linear and stationary (see Eq. (8)), then one can rewrite Eq. (2) as convolution product in time space,

$$\Phi(t) = C(t) * q(t),\tag{3}$$

where $C(t)* = \hat{K}(t)$. Applying next the Fourier transform, $F[f](\omega) = (f(t), e^{i(\omega, t)})$, one can resolve convolution product as [15]

$$F[\Phi] = F[C * q] = F[C]\,F[q],\tag{4}$$

where $F[C]$ is a function of angular frequency ω, which can be calculated as

$$F[C](\omega) = \frac{F[\Phi](\omega)}{F[q](\omega)} = m\,c_{\mathrm{eff}}(\omega).\tag{5a}$$

This ratio one can treat as an effective or apparent frequency dependent heat capacity $m\,c_{\mathrm{eff}}(\omega)$, where m is sample mass. Assumption of linear and stationary response is used here to represent operator equation, Eq. (2), as simple ratio in frequency domain, Eq. (5a). How to get the correct value of sample complex heat capacity from this ratio is described in [9].

In TMDSC measurements one can consider the following values: $t_p = 2\pi/\omega$ – modulation period, $A_\Phi \equiv |F[\Phi](\omega)|$ – heat flow amplitude, $A_q \equiv |F[q](\omega)|$ - heating rate amplitude, $A_T \equiv |F[T](\omega)| = A_q/\omega$ – amplitude of temperature oscillations, $\arg\{F[\Phi](\omega)\} - \arg\{F[q](\omega)\} = \arg\{F[C]\}(\omega)$ – phase shift between $q(t)$ and $\Phi(t)$. In addition to periodic part of $q(t)$ and of $\Phi(t)$ one can consider also mean values over one period: q_0 – underlying heating rate, $\Phi_{\mathrm{underlying}}$ – underlying heat flow, $\langle T \rangle = T_0 + q_0(t - t_0)$ – mean temperature. In DSC measurements total heat capacity is determined as:

$$m\,c_p(q_0) = \frac{\Phi_{\mathrm{underlying}}}{q_0}.\tag{5b}$$

Farther, unless another specifies, we will discuss only effective specific heat capacity at given frequency, $c_p(\omega)$, determined by Eq. (5a) not by Eq. (5b), i.e. $c_p(\omega) \equiv c_{\mathrm{eff}}(\omega)$.

3. Non-linear response

For general case of non-linear response one can separate the response into linear, quadratic, cubic, etc.

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[2] Upper index ^ stands for operators.

parts so that Eq. (1) becomes:

$$\varepsilon(t) = \hat{K}\sigma(t) = \hat{K}_1\sigma(t) + \hat{K}_2\sigma(t) + \hat{K}_3\sigma(t) + \cdots \tag{6}$$

where $\hat{K}_1$ is a linear operator $\hat{K}_1\alpha\sigma(t) = \alpha\,\hat{K}_1\sigma(t)$ for any complex number α, and analogous $\hat{K}_n\alpha\sigma(t) = \alpha^n\,\hat{K}_n\sigma(t)$. The presence of higher order terms ($n>1$) in the response will be called non-linearity. Even if the perturbation $\sigma(t)$ is pure sinusoidal function, non-linearity results some higher harmonics in the response $\varepsilon(t)$. At any given perturbation $\sigma(t)$ one can choose such small perturbations $\alpha\sigma(t)$, where $|\hat{\alpha}| \ll 1$ (or more correctly $|\alpha| \ll \min\limits_{n>1}\{\sqrt[n-1]{|K_1\sigma(t)|/|K_n\sigma(t)|}\}$, that higher order terms become negligible in comparison with linear one:

$$\varepsilon(t) = \hat{K}\alpha\sigma(t) = \alpha\,\hat{K}_1 + \alpha^2\,\hat{K}_2\sigma(t) \\ + \alpha^3\,\hat{K}_3\sigma(t) + \cdots \cong \alpha\,\hat{K}_1\sigma(t). \tag{7}$$

The same happens with higher harmonics: they become negligible in comparison with first one. Then one can consider the response as linear.

However, it can be possible that at any small perturbation there are appreciable higher harmonics in the response. Response can become inharmonic under any small harmonic perturbation when system properties change with time independently of perturbation. In this case operator describing the response is non-stationary. Remember that operator $\hat{K}(t_0, t)$ is stationary then the following condition is fulfilled for any time shift t_1 and any perturbation $\sigma(t)$:

$$\hat{K}(t_0, t)\sigma(t) = \hat{K}(t_0 + t_1, t + t_1)\sigma(t) \\ = \hat{K}(t - t_0)\sigma(t), \tag{8}$$

where t_0 denotes the starting point of experiment, so that $t \in [t_0, \infty)$. Then for non-stationary operator one can write:

$$\hat{K}(t_0 + t_1, t + t_1) = \hat{\Delta}(t_0, t_1)\,\hat{K}(t_0, t), \tag{9}$$

where operator $\hat{\Delta}(t_0, t_1)$ describes evolution of the system properties with time. In real systems such changes are continuous, that means $\hat{\Delta}(t_0, t_1)f(t) \to f(t)$ at $t_1 \to 0$ for any function $f(t)$ (or equivalently $\hat{\Delta}(t_0, t_1) \to \hat{I}$ at $t_1 \to 0$, where $\hat{I}$ is unity operator). Then one can write in first approximation for small t_1:

$$\hat{\Delta}(t_0, t_1) \cong t_1\,\hat{\dot{\Delta}}(t_0) + \hat{I}, \tag{10}$$

where $\hat{\dot{\Delta}}(t_0) = \lim_{t_1 \to 0}(\hat{\Delta}(t_0, t_1) - \hat{I})/t_1$ is an operator describing the rate of system evolution. Under harmonic perturbation during one period t_p changes for $\hat{\Delta}(t_0, t_p) \cong t_p\,\hat{\dot{\Delta}}(t_0) + \hat{I}$, for examples see Figs. 9 and 10. This leads to inharmonic response and as a result to the appearance of higher harmonics and to the uncertainty in determination of first harmonic:

$$\frac{\delta h_1}{h_1} \approx t_p|\hat{\dot{\Delta}}(t_0)|, \tag{11}$$

where h_1 in shorter form denotes first harmonic of the response $\varepsilon(t)$, $h_1 \equiv F[\varepsilon](\omega)$. One can see from Eq. (11) that the smaller the period of perturbations and/or the rate of system evolution the smaller is the influence of non-stationarity.

Schematically representation of the conditions of linearity/non-linearity and stationarity/non-stationarity is shown in Fig. 1, where response $\varepsilon(t)$ to some step perturbation $\sigma(t) = \alpha\,\Theta(t - t_i)$ is plotted. One can see that under condition of linearity increasing of perturbation leads to proportional increasing of the response that is not the case under non-linear conditions. Under stationary condition correlation between the perturbation and the response is invariant to the time shift. Under non-stationary conditions this correlation depends on absolute starting time. Both responses stationary and non-stationary can be linear or non-linear. And both linear and non-linear responses can be stationary or non-stationary. In frequency domain both
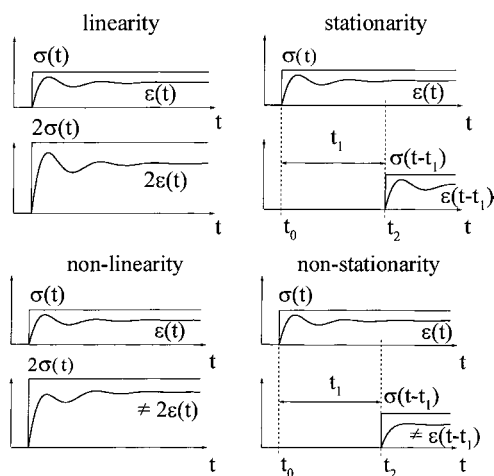

Fig. 1. Schematically representation of the conditions of linearity/non-linearity and stationarity/non-stationarity.

non-linearity and non-stationarity lead to the appearance of higher harmonics and to the uncertainty in determination of the first harmonics.

4. Linearity of the apparatus

Before proceeding to experimental sections one should say a few words about linearity of the equipment. The linearity of DSC has been proved in the sense that response can be represented as convolution product of perturbation with Green's functions [16]. In TMDSC linearity can be checked in the frequency domain i.e. by looking at higher harmonics in the response under harmonic perturbation. Under conditions that sample response is linear, e.g. in the molten state, non-linearity (higher harmonics) comes only from the instrument. Fig. 2 shows the result from such measurement where the amplitude of second harmonic $h_2 \equiv F[\Phi](2\omega)$ of the measured heat flow $\Phi(t)$ is plotted versus modulated heating rate amplitude $A_q = \omega A_T$. Note that heat flow at given temperature modulation amplitude A_T is proportional to the angular frequency ω. Therefore, analogous plots over A_T would be different at different frequencies. One can see that by decreasing the amplitude of heating rate perturbation the amplitude of second harmonic decreases proportionally to A_q^2 but never becomes less than
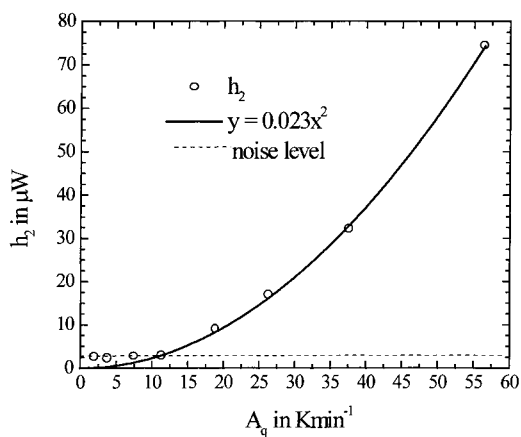
Fig. 3. Normalized amplitude of second harmonic h_2 (open circles) and third harmonic h_3 (open triangle) versus heating rate amplitude A_q. First four points of second harmonic are fitted by hyperbola (solid line). The same experimental conditions as in Fig. 2.

$\sim 3\,\mu W$. This is the noise level of the instrument. Such a noise contains wide spectrum (in principle "white" noise) therefore there is the same lower limit ($\sim 3\,\mu W$) for any harmonics. Now if one looks at normalized value of higher harmonics, Fig. 3, one can see what happens: decreasing of heating rate amplitude decreases the non-linearity only to some extend then noise starts to dominate. In Fig. 3 this corresponds to the amplitude A_q=11 k/min. Under smaller amplitudes signal-to-noise ratio decreases – this would not improve the accuracy of heat capacity determination. From such figures one can estimate instrument contribution to the non-linearity for given experimental conditions. Harmonic distortion of the apparatus η can be considered about 1% under heating rate amplitude in the range 2 K min^{-1}≤A_q≤60 K min^{-1}. This value $\eta \approx 0.01$ one can take as an accuracy limit of the dynamic heat capacity measurements. Measuring heavier sample, i.e. larger sample heat capacity, one can increase signal-to-noise ratio and improve lower limit of heating rate. Making larger temperature difference between block and ovens (for power compensated DSC) one can increase higher limit of heating rate amplitude, because then there will be less problems with fast cooling during cooling cycle of modulation. And last remark: higher harmonics can be smaller than that shown in Fig. 3 at extreme high frequencies for TMDSC, let us say at t_p<20 s, then higher frequency

Fig. 2. Amplitude of second harmonic h_2 (open circles) versus heating rate amplitude A_q. Quadratic fit function (solid line) and noise level (dashed line) are also shown. Polystyrene sample of mass m_s=4.435 mg was measured by PE DSC-2 in the melt (T_0=400 K), t_p=100 s, sinusoidal temperature oscillation.
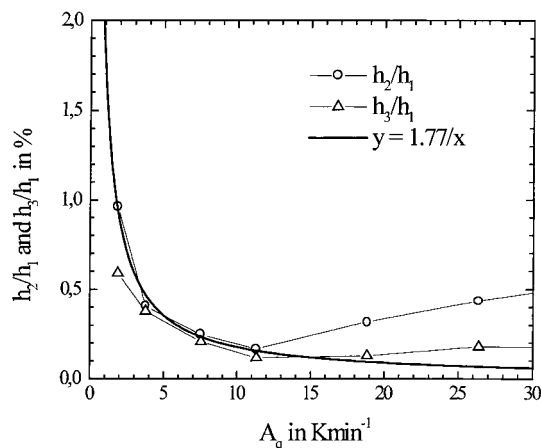
part of heat flow spectrum is damped by heat transfer problems and by low-pass filters of the electronics.

Applying saw-tooth temperature oscillation (i.e. meander-shape heating rate profile) heat flow already has some odd harmonics. This is a small disadvantage of saw-tooth modulation in comparison with sinusoidal one when one wants to compare spectra to see non-linear response. But nevertheless by looking at even harmonics one can check such type of non-linear response which results asymmetry of the heat flow profile.

5. Non-linearity in TMDSC measurements

Consider an example of reversible melting during every modulation period, as shown in Fig. 4. Calculated amplitude of heat flow A_Φ is higher than the heat flow due to phonon heat capacity (i.e. the heat flow outside the melting and crystallization region) because it contains a large contribution from the melting and crystallization enthalpy. One can double the temperature amplitude at a given modulation frequency, i.e. double the heating rate amplitude, but would get the same response in the first harmonic of the heat flow since the melting and crystallization areas do not change. Then the calculated value of the complex heat capacity would be almost half of the initial one. One can take a half of the heating rate amplitude and would get almost double value of complex heat
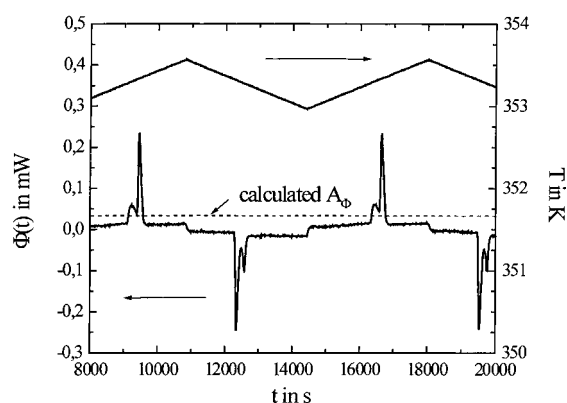

Fig. 4. Measured heat flow for the nematic-isotropic phase transition (during heating) and isotropic-nematic phase transition (during cooling) of 8OCB by using a quasi-isothermal saw-tooth temperature modulation [17].

capacity. It is clear that in this case one has non-linearity – too large perturbation. Note that under linear response heat capacity does not depend on modulation amplitude (whether temperature or heating rate). Non-linearity here is caused by strong temperature dependence of excess heat capacity at the transition. In first approximation with small step in temperature ΔT one can write for changes in total specific heat capacity:

$$\Delta c_p \approx \frac{\mathrm{d}c_p}{\mathrm{d}T}\Delta T. \tag{12}$$

If there are some time dependent processes in the transition then temperature derivative of heat capacity $\mathrm{d}c_p/\mathrm{d}T$ depends on given heating rate q_0. One can rewrite Eq. (12) for temperature modulated measurement at given frequency as:

$$\Delta c_p(\omega) \approx \frac{\mathrm{d}c_p(\omega)}{\mathrm{d}T(\omega)}A_T, \tag{13}$$

where now step in temperature is temperature amplitude A_T and $\mathrm{d}c_p(\omega)/\mathrm{d}T(\omega)$ is temperature amplitude derivative of complex heat capacity. If relative changes of complex heat capacity in the same order or smaller than harmonic distortion of the apparatus η, i.e.

$$\frac{\Delta c_p(\omega)}{c_p(\omega)} \approx \frac{1}{c_p(\omega)}\frac{\mathrm{d}c_p(\omega)}{\mathrm{d}T(\omega)}A_T \leq \eta, \tag{14}$$

then within the experimental uncertainties one can consider the response as linear. For the case shown in Fig. 3 one would reach conditions of linearity maybe only in millikelvin range of temperature amplitudes A_T. Only then one can speak about complex heat capacity at nematic–isotropic transition.

Another example of non-linearity can be seen in temperature modulated scan measurement in melting region of polymers. Since crystallization and melting rates of polymers are quite different [18] large part of the sample which has been melted during heating cycle ($q(t) > 0$) cannot be crystallized during cooling cycle ($q(t) < 0$). This leads to asymmetry in the heat flow rate, as shown in Fig. 5 (thin line). By choosing smaller heating rate perturbation on top of underlying heating rate q_0 one can get symmetric response (thick lines in the figure). Asymmetry in heat flow rate results higher harmonics after Fourier transform. Fig. 6 shows the normalized values for second and third
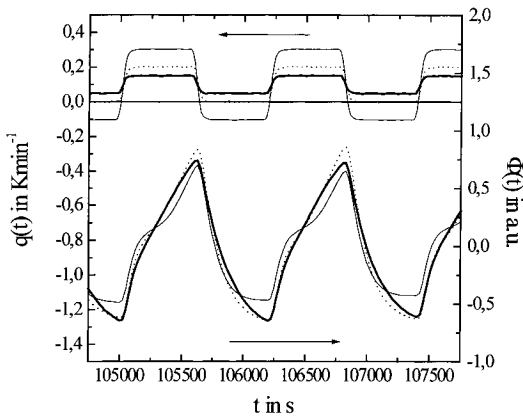
Fig. 5. TMDSC scan measurement in melting region of poly(ether-etherketone) (PEEK Victrex 381G). Different heat flow rate curves $\Phi(t)$ (multiplied by some factors for better comparison) correspond to different heating rate profiles $q(t)$: thin line – heating-cooling; dotted line – heating-isotherm; thick line – heating only. Setaram DSC 141, m_s=169 mg, q_0=0.1 K min^{-1}, t_p=20 min, saw-tooth temperature oscillations.

Fig. 7. Modulus of specific heat capacity $c_p(\omega)$ versus temperature at different 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.

harmonics of measured heat flow rate in analogous TMDSC measurements. Important point here is not non-linear part itself but its influence on first harmonic determination. Results for the first harmonic normalized by Eq. (5a) from the same experiment are presented in Figs. 7 and Fig. 8. One can see that 10% of higher harmonics at modulated heating rate amplitude A_q=6.3 K min^{-1} (see Fig. 6) results 10% decrease of
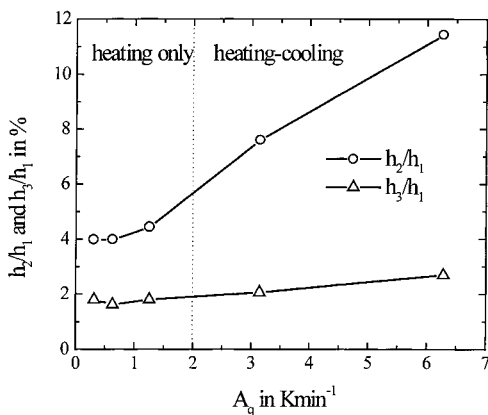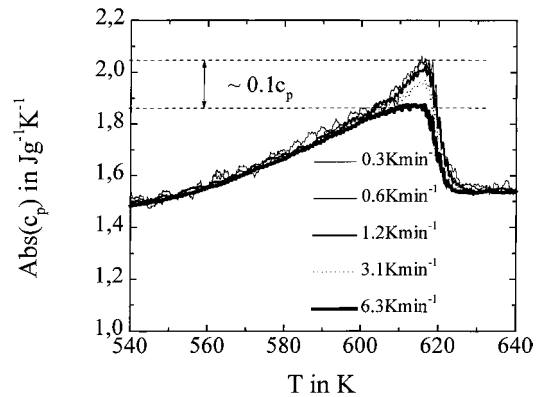
measured modulus of $c_p(\omega)$ and also decrease of argument of $c_p(\omega)$. In this case to avoid asymmetry in the heat flow rate first one should eliminate crystallization by choosing heating only condition so that $A_q=\omega A_T<q_0$ i.e.

$$q(t) = q_0 + \text{Re}\left(A_q e^{-i\omega t}\right) > 0, \tag{15}$$

where q_0 is a constant underlying heating rate. If during melting some re-crystallization or re-organization happen, that is also slower than melting, total
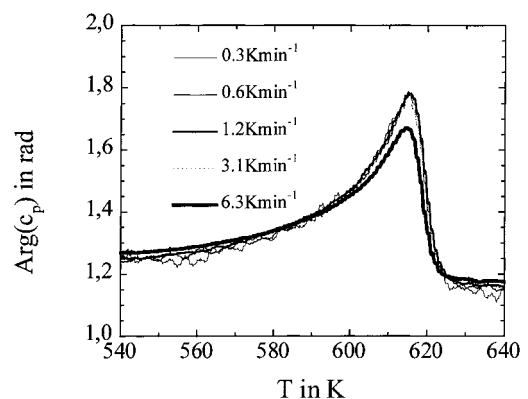

Fig. 6. Normalized amplitude of second, h_2, and third, h_3, harmonics versus amplitude of modulated heating rate, A_q, for temperature modulated scan measurements in the melting region of PEEK. Perkin-Elmer DSC 2, m_s=26 mg, q_0=2 K min^{-1}, t_p=1 min, sinusoidal temperature oscillations.

Fig. 8. Argument of $c_p(\omega)$ versus temperature at different 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.

specific heat capacity determined by common DSC run will be different for different underlying heating rates q_1 and q_2: $c_p(q_1) \neq c_p(q_2)$. Since $\Phi(t) = m\, c_p\, q(t)$ (m is sample mass) for underlying heat flow rate $\Phi(t) = \Phi_{underlying}$ and underlying heating rate $q(t) = q_0$ one can write from Eq. (2):

$$\hat{K}\alpha q(t) \neq \alpha \hat{K} q(t), \tag{16}$$

where $q(t) = q_1$, $\alpha = q_2/q_1$. Eq. (16) holds not only for constant underlying heating rate but also for periodic heating rates $q(t)$ and $\alpha\, q(t)$. Then analogous to Eq. (13) after Fourier transform at given frequency non-linear part equals

$$\Delta c_p(\omega) \approx \frac{\mathrm{d}c_p(\omega)}{\mathrm{d}q(\omega)} A_q, \tag{17}$$

where $\mathrm{d}c_p(\omega)/\mathrm{d}q(\omega)$ is the heating rate amplitude derivative of complex specific heat capacity. In that case heating only condition, Eq. (15), can be not enough to get linearity. But one can choose such a small perturbation amplitude A_q that

$$\frac{\Delta c_p(\omega)}{c_p(\omega)} \approx \frac{1}{c_p(\omega)} \frac{\mathrm{d}c_p(\omega)}{\mathrm{d}q(\omega)} A_q \leq \eta, \tag{18}$$

where η denotes given experimental accuracy (harmonic distortion of the apparatus). Under such conditions one reaches linearity. In Figs. 6–8 heating only condition corresponds to $A_q < 2$ K min^{-1}, but linearity is reached at $A_q \leq 0.6$ K min^{-1}, there amplitude of second harmonic does not depend on A_q. Calculated modulus of c_p as well as phase angle coincides at $A_q = 0.3$ K min^{-1} and 0.6 K min^{-1}. The remaining higher harmonics here are caused by non-stationarity (see next section).

6. Non-stationarity in TMDSC measurements

In this section assume that conditions of linearity, Eqs. (14) and (18), are fulfilled. Under stationary conditions, Eq. (8), it is enough to calculate at given frequency only one value of complex specific heat capacity $c_p(\omega)$. However system properties can change with time independently on perturbation, e.g. due to overall crystallization or chemical reactions, evaporation of the sample, apparatus drift with time and so on. Under such conditions the value of complex specific heat capacity depends on time, $c_p(\omega) = c_p(\omega, t)$. In this case one assigns to given time t the mean value of $c_p(\omega)$ over one modulation period t_p. Then the uncertainty in determination of $c_p(\omega)$, according to Eq. (11), is

$$\frac{\Delta c_p(\omega)}{c_p(\omega)} \approx t_p \frac{1}{c_p(\omega)} \frac{\mathrm{d}c_p(\omega)}{\mathrm{d}t}. \tag{19}$$

In addition to possible changes with time system properties can also change due to scanning of the mean temperature in temperature modulated scan measurements. Since mean temperature is connected with time as $\langle T \rangle = T_0 + q_0(t - t_0)$ formally one can rewrite Eq. (19) as:

$$\frac{\Delta c_p(\omega)}{c_p(\omega)} \approx q_0\, t_p \frac{1}{c_p(\omega)} \frac{\mathrm{d}c_p(\omega)}{\mathrm{d}\langle T \rangle}. \tag{20}$$

If $c_p(\omega)$ depends both on time and on temperature, $c_p(\omega) = c_p(\omega, t, T)$, then $\mathrm{d}c_p(\omega)/\mathrm{d}\langle T \rangle$ is different for different underlying heating rate q_0. The point here is not the separation of time and temperature evolution of $c_p(\omega)$ (that can be done by measuring with different underlying heating rates), but uncertainties of $c_p(\omega)$ determination due to such evolution. From Eqs. (19) and (20) one can write the condition of stationarity as:

$$\frac{\Delta c_p(\omega)}{c_p(\omega)} \approx t_p \frac{1}{c_p(\omega)} \frac{\mathrm{d}c_p(\omega)}{\mathrm{d}t} \leq \eta \tag{21}$$

or

$$\frac{\Delta c_p(\omega)}{c_p(\omega)} \approx q_0\, t_p \frac{1}{c_p(\omega)} \frac{\mathrm{d}c_p(\omega)}{\mathrm{d}\langle T \rangle} \leq \eta, \tag{22}$$

where again η denotes given experimental accuracy (harmonic distortion of the apparatus). At given rate of system evolution $\mathrm{d}c_p(\omega)/\mathrm{d}t$ one should use only such modulation periods t_p that stationary condition, Eq. (21), is fulfilled. Fig. 9 shows the results from quasi-isothermal ($q_0 = 0$) TMDSC measurement in melting region of semi-crystalline polymer. In such measurements the relaxation of the system does not depend on given temperature perturbation [19]. One can see by eye that at shorter modulation period heat flow rate is more or less symmetric and one can speak about $c_p(\omega)$ and its relaxation with time. On the contrary at large period the value of $c_p(\omega)$ at the beginning of the relaxation is very arbitrary.

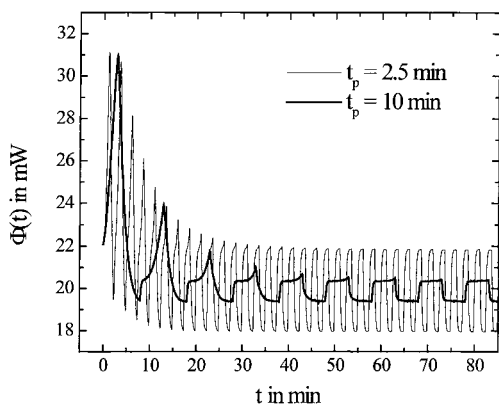If modulation period is given and stationarity condition is not fulfilled then one should try to decrease

Fig. 9. Heat flow rate (without empty pan correction) in quasi-isothermal melting of poly(ε-caprolactone) 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.

Fig. 11. Normalized amplitude of second harmonic h_2 versus 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.

rate of system changes if acceptable, e.g. by choosing higher mean temperature for measurement of crystallization from the melt to slow down crystallization rate. At scan measurements one should decrease underlying heating rate q_0. The last case is represented in Figs. 10 and 11 where results from TMDSC measurements in melting region of PEEK are shown. Fig. 10 shows evolution of $c_p(\omega)$ with temperature (note again, that such temperature dependence can
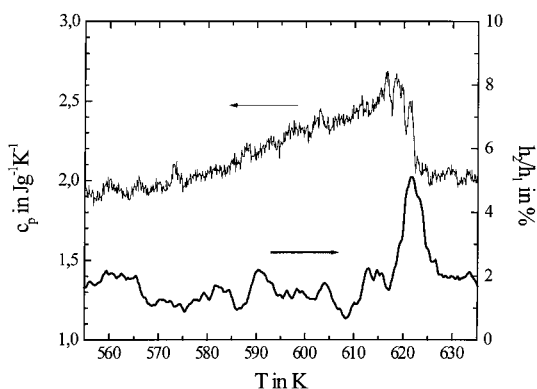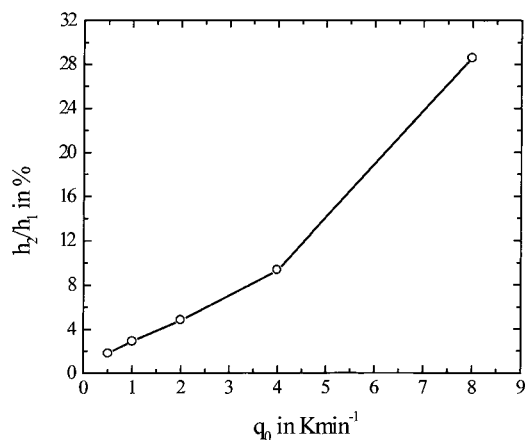

Fig. 10. Modulus of complex specific heat capacity $c_p(\omega)$ and normalized amplitude of second harmonic h_2 versus temperature for temperature modulated scan measurement in the melting region of PEEK. Perkin-Elmer DSC Pyris 1, m_s=1616 mg, q_0=2 K min^{-1}, t_p=1 min, A_q=0.2 K min^{-1}, saw-tooth temperature oscillations.

contain partly time dependence, with cannot be separated from one scan measurement) and normalized value of second harmonic h_2. At 630 K the sample is already in the molten state that means linear sample response. Then under this experimental conditions harmonic distortion of the apparatus $\eta\approx2\%$. Conditions of linearity, Eq. (18), are fulfilled. But around 620 K there are relatively large changes in $c_p(\omega)$, i.e. large $dc_p(\omega)/d\langle T\rangle$. This non-stationarity results the peak of 5% in the second harmonic. Fig. 11 shows the height of this peak versus underlying heating rate q_0. According to Eq. (22) there should be linear dependence of non-stationarity on underlying heating rate. This one can see in the figure for $q_0\leq4$ K min^{-1}. The last point, q_0=8 K min^{-1}, deviates from straight line due to approximation made in Eq. (11) for small modulation periods or small rate of system evolution. At q_0=8 K min^{-1} second harmonic reached the value of 30% (so there is an error of 30% in determination of first harmonic). Under such conditions one can use the smallest possible temperature modulations but still have 30% of harmonic distortion, because the reason of that is not a large perturbation but non-stationarity. Then to eliminate non-linear part one should decrease underlying heating rate. At q_0=0.5 K min^{-1} second harmonic equals only 2% of the first. At the same time harmonic distortion of the apparatus $\eta\approx2\%$ – condition of stationarity, Eq. (22), is fulfilled.

7. Discussion

In previous sections we discussed mainly the second harmonic as the measure of non-linear response. Of course one should consider all higher harmonics. Regardless of the reason non-linear response causes a systematic error in determination of first harmonic, which can be written as

$$\frac{\Delta h_1}{h_1} \approx \frac{\sum_{n>1} h_n}{h_1}, \tag{23}$$

where h_n denotes nth harmonic. However, in some dynamic calorimeters from construction reasons it could be difficult to apply such check of linear response. E.g. in 3ω method measured signal always has spectrum with odds harmonics even at linear thermal response from the sample.

One cannot say in advance which perturbation is supposed to be large and which is small. For example in Fig. 3 the best linearity was at heating rate amplitude A_q=11 K min^{-1} that corresponds to temperature amplitude A_T=3 K. In the other measurement, Fig. 4, to get linear response one should use temperature perturbation in millikelvin range to stay within the transition. The range of acceptable perturbation amplitude depends on sample in question and is given by conditions of linearity, Eqs. (14) and (18).

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. For example at t_p=1 min underlying heating rate could be 0.5 K min^{-1} for PEEK sample, see Fig. 11, to meet conditions of stationarity, but it should be much smaller for PCL sample, which has much narrower melting peak and therefore much larger $c_p(\omega)$ changes with temperature. The range of acceptable periods and underlying heating rates is given by the conditions of stationarity, Eqs. (21) and (22).

In extremely cases of non-linear response, like shown in Fig. 4, one can see with the naked eye that calculated value of complex (reversing) heat capacity would be meaningless. But this becomes visible only because the data first were recorded in time domain and then recalculated in frequency domain. In this experiment measuring only first harmonic (i.e. calculated heat flow amplitude) one could not realize high non-linearity of the response.

One of the interesting application of TMDSC is heat capacity spectroscopy – measuring complex heat capacity $c_p(\omega)$ at different frequencies. Varying modulation frequency one should vary whether temperature amplitude or heating rate amplitude or both of them. Then one changes influence of non-linearity on $c_p(\omega)$ determination, see Eqs. (13) and (17). One also changes influence of non-stationarity on $c_p(\omega)$ determination, see Eqs. (19) and (20). And that is the most important point: paying no attention on non-linear part of the response or being fully aware that the response is linear one could obtain very interesting frequency dependence of complex heat capacity which arose mainly from non-linearity or non-stationarity and is far from real kinetics of the transition.

One can use another way to check linear response – to vary the amplitude of perturbation. But firstly: this way one could not estimate non-stationarity; secondly: one need at least two measurements. Moreover in AC and 3ω methods, where periodic heat flow serves as a perturbation, changes in perturbation amplitude assume some possible changes in mean temperature or in temperature gradient in the sample. This should be taken into account especially in transition region – the results can be different at different power input only due to difference in mean temperature, but not due to non-linearity.

8. Conclusion

Before speaking about 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 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. If certain accuracy is required then one should simultaneously meet conditions of linearity and stationarity.

Acknowledgements

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