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Temperature-modulated DSC using higher harmonics of the Fourier transform[1]

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Abstract

In this paper, experiments with temperature-modulated calorimetry are described in which use is made of multiple modulation frequencies for the evaluation of the heat capacity. The different harmonics of the Fourier series of the heat-flow rate and heating rate of a single sawtooth-modulation experiment were deconvoluted to extract data pertaining to different frequencies. In the normally employed temperature-modulated differential scanning calorimetry (TMDSC), one uses only the first harmonic of the Fourier series. In such a typical TMDSC experiment with a period of less than about 150 s, one needs to correct the measurements by extrapolation to zero frequency, utilizing data taken at different frequencies. It is shown that the extrapolation of the heat capacity from the amplitudes of the first and higher harmonics of the Fourier-transforms of heat-flow rate and heating rate permits the evaluation of the correct heat capacity from a single experiment. The number of harmonics which can be used for the correction depends on the chosen period of the sawtooth. In case of the power-compensation calorimeter employed in this study, the upper limit of frequency of the highest harmonic is about $2\pi/10$ rad s^{-1} (0.1 Hz), i.e., for modulation with a period of 120 s, up to the eleventh harmonic can be utilized, although the amplitude (and precision) decreases for the higher harmonics. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction and theoretical details

Heat capacity can be determined by standard differential scanning calorimetry (DSC) as well as temperature-modulated differential scanning calorimetry (TMDSC). Both methods require the measurement of the well-calibrated heat-flow rate into the sample as response to the temperature change of the sample which is forced by the heating program. In the standard DSC the programmed temperature is a linear ramp over a rather large temperature interval (typically 50–100 K) with a heating rate of 5–40 K min^{-1} [1]. In TMDSC, the programmed temperature is produced by superposition of a constant heating rate and a temperature-modulation [2]. The common modulations are sinusoidal or sawtooth-like. The simultaneous use of multiple modulation frequencies was proposed already at the outset of TMDSC [3], but as far as we are aware of, has not yet been routinely applied to TMDSC. In the present paper we show that it is possible to deconvolute a centro-symmetric saw-

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tooth modulation into its various, sinusoidal Fourier components to obtain simultaneous information on the sample response to modulation with different frequencies. The advantages of using the sawtooth-modulation for the generation of a multiple frequency response of the sample are its ease of precise generation and its well-known Fourier series which contains only odd, sinusoidal harmonics. The disadvantage is the decrease of the harmonics in amplitude with frequency. It will be shown in a subsequent paper, however, that the latter problem can be removed by the construction of a specially designed, complex sawtooth. For a temperature-modulation about the temperature T_0, one obtains, for example

$$T(t) - T_0 = \frac{8A}{\pi^2} \times \left[\sin\omega t - \frac{1}{9}\sin 3\omega t + \frac{1}{25}\sin 5\omega t - \cdots\right], \quad (1)$$

where A is the modulation amplitude; ω, the frequency in rad s^{-1}; and t, the time.

The heat capacity can be calculated from the heat-flow rate caused by the underlying heating rate $\langle q\rangle$, as well as by the modulated heating rate. Both methods give the same results in absence of any latent heat that disturbs the steady state, and in absence of a slow response of the sample, as in the glass-transition region. An advantage of the use of TMDSC compared to the standard DSC is that the experiment can be performed quasi-isothermally, and errors due to baseline or instrumental drifts are largely eliminated if the periodic part of the response is used for the calculation [4].

The calculation of the heat capacity, C_p, from quasi-isothermally performed TMDSC requires the evaluation of the amplitudes of the modulated heat-flow rate, $A_{HF}(\nu)$, and the modulated sample temperature, $A_{T_s}(\nu)$, which both are approximated by the first Fourier component (ν=1) of the corresponding Fourier series, illustrated by Eq. (1)[5]

$$C_p = \frac{A_{HF}(\nu)}{A_{T_s}(\nu)}\frac{1}{\nu\omega}K(\omega). \quad (2)$$

The dimensionless correction function $K(\omega)$ in Eq. (2) derives from the necessity to correct the fitted amplitude of the heat-flow rate for errors due to the different equilibration behaviors of the sample and reference calorimeters caused by the sample heat capacity [6,7]. It should be noted that a separate calibration of the heat-flow rate must be done, as usual, by comparison with a measurement of a calibrant, such as sapphire. Both measurement and calibration run must, naturally, also be baseline-corrected. In power-compensated DSC, the correction function $K(\omega)$ can either be determined by using the measured phase shift between heating rate and heat-flow rate [6], or by using a correction function similar in form as was originally derived for the TA Instruments heat-flux calorimeter [8]

$$K(\omega) = \sqrt{1+\tau^2\omega^2}, \quad (3)$$

where τ is a time-constant, dependent on the instrument design. A more complicated expression was derived recently for the Mettler–Toledo heat-flux DSC, which is not controlled at the sample temperature sensor, but rather at the heating block [9]. The time constant τ in Eq. (3) can be obtained by plotting the inverse of the squared, uncorrected heat capacity (Eq. (2) with K=1) versus the square of the frequency [7]. The intercept of the plot at ω^2=0 is directly the inverse of the squared, corrected heat capacity if the heat-flow rate was calibrated. Thus, several measurements at different frequencies are necessary to assure a statistically significant precision in the linear regression and extrapolation to ω^2=0.

The application of Eq. (2) implies that the measured heat-flow rate is linearly related to the temperature change and that the superposition principle holds [10,11]. Linearity of the response requires an instrument which responds linearly in the sum of all distortions of the output signal, which in case of the Perkin-Elmer DSC has been proven and represented by the Green's function (apparatus function) [12]. Furthermore, the measured thermal event must respond in its output, the heat-flow rate, linearly to the modulation, a fact proven for heat-capacity measurements, but still in debate for many specific irreversible thermal events like melting or crystallization. The consequence of a linear connection between the input signal, A_{T_s}, and the output signal, A_{HF}, is the exact correspondence of the first harmonic approximation of the heating rate to the first harmonic approximation of the heat-flow rate. In case of a perfect sinusoidal oscillation of the heating rate only the first harmonic of the heat-flow rate exists, and in case of a centro-symmetric sawtooth-modulation, all even harmonics are eliminated and higher harmonics of the heating rate and heat-flow rate have the same fractional deviation from the first harmonic, as shown in Eq. (1).

In the present paper, we will analyze the higher harmonics of the Fourier representation of the heating rate and heat-flow rate and check their applicability to calculate heat capacities at different frequencies out of one data set. It is self-understood that the same method of deconvolution of the higher harmonics can be applied to assess the frequency dependence of the apparent heat capacity, as it is found, for example, in the glass-transition region. The goal of the present analysis is to test the use of heat-capacity data from higher harmonics in order to correct the frequency-dependence and to obtain a true value of C_p with a single measurement as suggested by Eqs. (2) and (3).

2. Experimental

For the investigation a PYRIS-1 system with a liquid nitrogen accessory, both from Perkin-Elmer Corp., were used. The temperature signal was calibrated by the onset of the melting temperatures of indium and cyclohexane at a heating rate of 10 K min^{-1}, and the heat-flow rate was calibrated by the heat of fusion of indium. No further correction to the quasi-isothermal mode of measurement was made. The furnace was purged with helium at a flow rate of 20 ml min^{-1}. The time, sample temperature, heat-flow rate (after subtraction of a baseline run), and program temperature were saved as ASCII data and externally processed with our own software [13]. Experiments were performed quasi-isothermally with a sawtooth-modulated program temperature. The programmed temperature-amplitude was 1 K and the period was varied from 30 to 120 s.

The materials used in this study were sapphire in form of a disk (22.14 mg), a standard, atactic polystyrene, provided as powder (ca. 12 mg) and a poly(ethylene-*co*-octene), shaped into a film (ca. 8 mg). The poly(ethylene-*co*-octene) (24 wt% 1-octene, 78.000 g mol^{-1}) was part of a more extensive investigation of the phase structure of the polymer and the study of the reversible polymer melting and crystallization which is particularly apparent in these poorly-crystallized copolymers. Detailed information about this research can be found in Refs. [14,15].

3. Results and discussion

Fig. 1 shows the typical raw data (open squares) of (a) the sample-temperature and (b) the heat-flow rate of a measurement on poly(ethylene-*co*-octene) at 374 K with an amplitude of 1.0 K and a period of 120 s. The illustrated part of the experiment corresponds exactly to one period. The figure also includes the first, third, fifth, seventh, and ninth harmonic of the corresponding Fourier series. The higher harmonics can easily be recognized by their increasing frequency. As expected from Eq. (1), the even-numbered harmonics do not appear. In case of the heat-flow rate, the amplitude decreases less with the number of the harmonic than does the amplitude of the sample temperature. Furthermore, the deviation of the amplitude of the first harmonic from the true experimental values (□), is ca. +25%, the deviation between true and the fitted heating rates is ca. +20%. This type of deviation is frequency-dependent and caused by the different approaches to steady state of the heat-flow rate and heating rate or sample temperature [7]. These deviations directly affect the calculated heat capacity in Eq. (2) when no corrections are applied.

Fig. 2 contains a plot of the uncorrected heat capacities versus the modulation period, calculated with Eq. (2) with $K(\omega)$ set equal to one. The filled squares correspond to the measurement with a period of 120 s, shown in Fig. 1. The five points at the periods 120, 120/3, 120/5, 120/7 and 120/9 s are the heat capacities calculated using the amplitudes of the different harmonics of the same measurement (ν=1, 3, 5, 7 and 9, respectively). Additional data are obtained by variation of the period p to 60, 40, and 30 s and calculation of the various heat capacities of the corresponding harmonics. The dashed line at c_p=2.43 J g^{-1} K^{-1} is the expected specific heat capacity of the amorphous poly(ethylene-*co*-octene) in the liquid state, as calculated from the ATHAS data base which contains information on the constituent homopolymers [16].

Fig. 3 represents the reciprocal of the squared, uncorrected specific heat capacities versus the square of the frequency, which should give a linear relationship if Eq. (3) holds. The overall data show a distinct

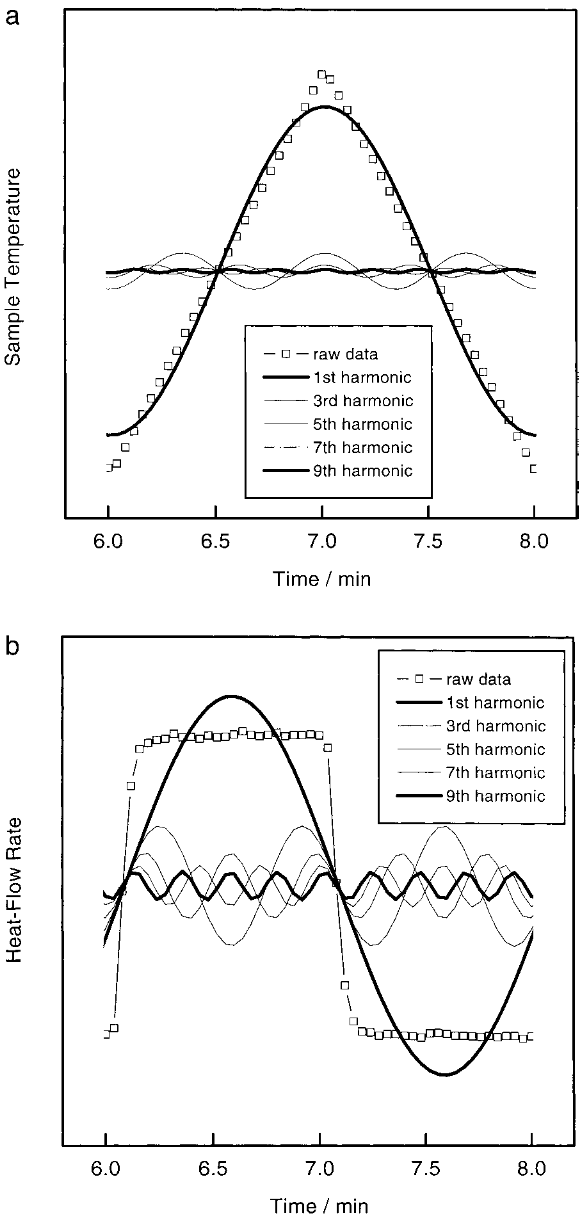

Fig. 1. (a) Sample temperature as a function of time. Raw data and different harmonics of the corresponding Fourier series shown in Eq. (1) [poly(ethylene-*co*-octene)]. (b) The heat-flow rates as a function of time corresponding to the sample temperatures shown in (a). Raw data and different harmonics of the corresponding Fourier series shown in Eq. (1) [poly(ethylene-*co*-octene)].

non-linearity, but at sufficiently low frequencies, indeed, the data are linear. This is seen in more detail in the plot of the insert which has an enlarged scale.

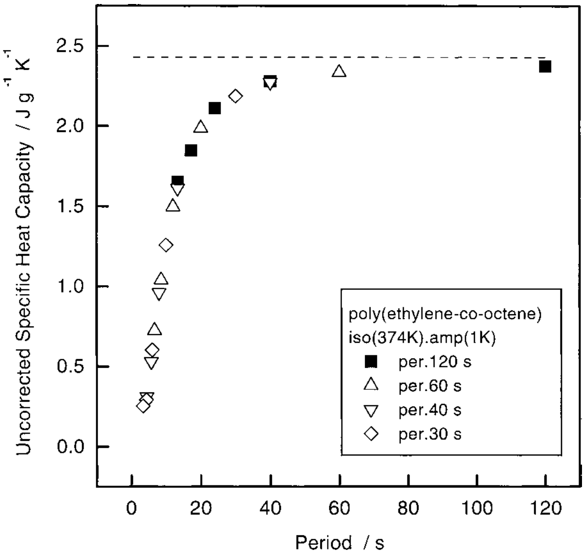

Fig. 2. Uncorrected specific heat capacity of poly(ethylene-*co*-octene) as function of the modulation period.

The lower limit of a modulation period that fits the linear relationship might be taken at 10–15 s (0.395–0.175 of the abscissa of the figure, respectively). When the period is larger than this limit, the experimental data can be included in the correction method using

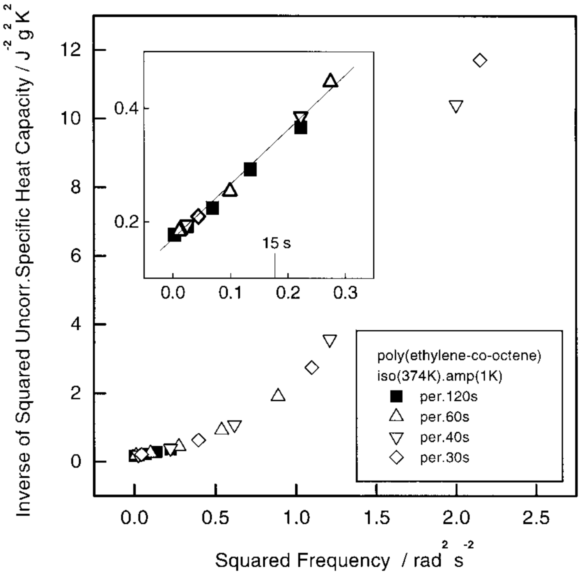

Fig. 3. Plot of the inverse of the squared, uncorrected specific heat capacity as a function of the squared frequency (data of Fig. 2).

Eq. (3). This lower limit of the modulation period varies to some degree with the experimental conditions, such as sample mass, thermal conductivity of the material, sample geometry, etc.

Of special importance is the fact that the specific heat capacities calculated from the higher harmonics fit exactly the same relation as those calculated from the first harmonics taken from separate experiments of modulations in the frequency range of the higher harmonics. As in Fig. 2, the filled squares in Fig. 3 derive from the same measurement with the sawtooth period of 120 s. The first to the ninth harmonic of the corresponding Fourier series all yield the same corrected specific heat capacity. The same is true for the first to the fifth harmonic of the sawtooth with a period of 60 s, the first and third harmonic for the 40 s sawtooth, and the first harmonic of the sawtooth with a period of 30 s. The higher harmonics than the just listed ones increasingly deviate from the straight line, but still follow a common functional relationship.

The result of Fig. 3 is verified by measurements on sapphire, displayed in Fig. 4, and also on sapphire and polystyrene, analyzed with a Perkin-Elmer DSC 7 as used in [7], purged with nitrogen and cooled with an intracooler. The latter data are not shown. The sapphire data in Fig. 4 are obtained using the same experimental conditions as for the measurement of poly(ethylene-*co*-octene), i.e., the quasi-isothermal modulation temperature was 374 K, the amplitude 1.0 K, and the sawtooth periods were 120, 60 and 40 s. At sufficiently low frequencies the heat capacities calculated from any of the harmonics fit, again, the same linear relationship when using Eqs. (2) and (3).

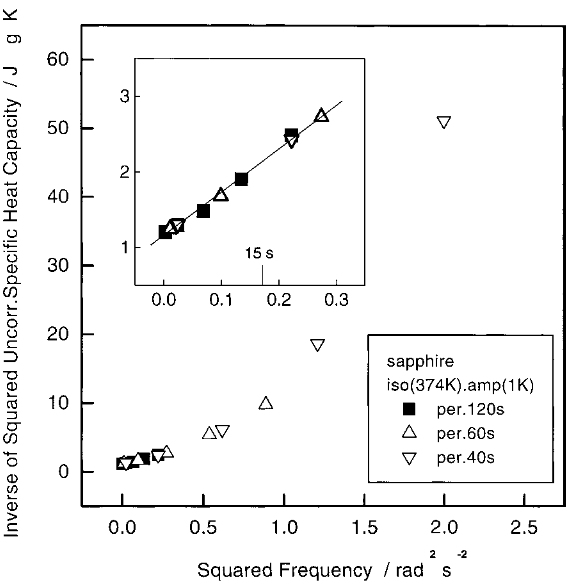

Fig. 4. Plot of the inverse of the squared, uncorrected specific heat capacity as a function of the squared frequency for sapphire.

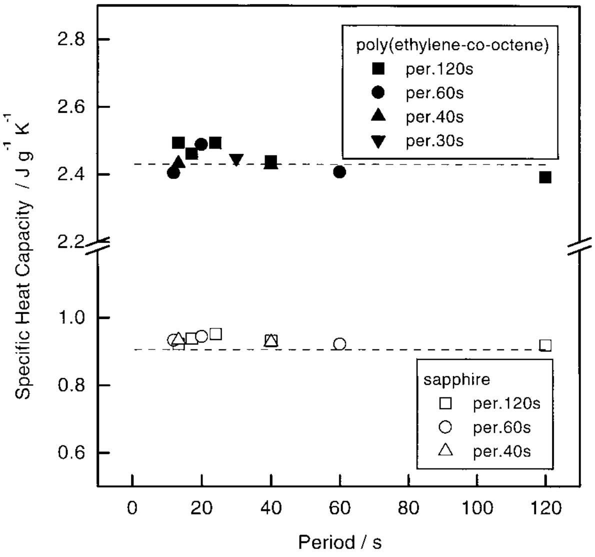

Fig. 5. Corrected specific heat capacity of the measurements shown in Figs. 2–4.

In Fig. 5 a plot is given for the corrected specific heat capacities from the data shown in Figs. 2–4. The time constant τ for the correction according to Eq. (3) was calculated including all data points at periods larger than 10 s. The time constants are 2.40 and 2.24 s for poly(ethylene-*co*-octene) and sapphire, respectively.

It is not the scope of this study to judge the accuracy of the presented approach to determine heat capacities by quasi-isothermal, sawtooth-modulated DSC. Since the amplitudes of the higher harmonics decrease in their absolute value, it is obvious that the statistical significance of the data decreases. A single measurement of sufficiently long period can, however, establish the slope to extrapolate to frequency zero and to obtain the corrected heat capacity. The reasons for the preference of using higher harmonics in the determination of the heat capacity than separate experiments with different frequencies are (a) the savings of time in generating reasonable data sets, and (b) the exact correspondence of the sample geometry and history which is of particular importance for samples that are not in equilibrium, as is common for polymeric materials. The extrapolation to zero frequency and the establishment of the critical frequency up to which Eq. (3) is valid could easily be included in a computer program for data evaluation and lead to improved heat capacity measurements. At present we also work on modifying the sawtooth by manipulating the amplitudes of the higher harmonics, so that four to five harmonics with almost equal amplitudes are generated by one complex sawtooth. The feasibility of the concept has been proven, and a description of the application of this special sawtooth for all major types of temperature-modulated calorimeters is in preparation.

This type of simultaneous TMDSC at various frequencies is of particular importance for the assurance of identical thermal history, as is imperative for the study of the frequency-dependence of the change of the apparent heat capacity in the glass-transition region. The required data would in this case involve the deviation of the apparent heat capacity from Eqs. (2) and (3) in the frequency range where no deviation is expected, as is known from the behavior of the sample outside the transition region.

4. Summary

The presented data show that higher harmonics of the Fourier series of the heat-flow rate and heating rate can be used to produce correct heat capacities with the Perkin-Elmer power-compensation DSC. The amplitudes of the higher harmonics can be corrected according to a model derived earlier if the period of the corresponding harmonic is not lower than 10–15 s. Furthermore, the calculations prove that the linear behavior of the instrument is not destroyed by insertion of the sample into the system. The described method offers, in addition, the possibility of automation by including the presented analysis into every measurement to yield higher quality heat-capacity data. Finally, the proposed method should be of value to establish the frequency dependence of the apparent heat capacity in the study of time-dependent processes.

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