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Temperature modulated differential scanning calorimetry – extension to high and low frequencies

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ABSTRACT

Common temperature modulated DSCs are limited in the accessible frequency range to about 0.1–0.001 Hz. We describe an extension of this frequency range towards lower and higher frequencies by using conventional DSCs (without TMDSC option). By applying steps in the temperature-time profile a simultaneous multi frequency analysis of the heating rate and the heat flow rate response yields heat capacity data over about 2 orders of magnitude in frequency from one single measurement. Based on this step response analysis we show on the example of a Calvet calorimeter, Setaram BT 2.15, an extension down to 10^{-5} Hz and on the example of a chip calorimeter, Mettler Toledo Flash DSC 1, an extension up to 150 Hz. Details of the experimental procedures are provided and the influence of sample size on the obtained data and general limitations, particularly regarding temperature assignment, are discussed. A relaxation map is used to combine all calorimetric data and to compare them with dielectric data.

1. Introduction

Due to progress in the field of novel materials, an urgent need in investigating their properties emerges. Calorimetry gives an opportunity to measure heat capacity of those materials to obtain information about phase transitions and their kinetics. One way to make calorimetric experiments is increasing or decreasing the temperature at constant rate, e.g. differential scanning calorimeter (DSC). Another common way to perform precise heat capacity measurements is by stepwise increasing temperature employing adiabatic calorimetry [1–4]. It is a classical method for heat capacity determination, usually at low temperatures. The large samples and precise adiabatic control results in high accuracy in heat capacity. A third common way to determine heat capacity and its relaxation behavior is AC-calorimetry when temperature of the sample is periodically oscillating [5–11]. In alternating current (AC) calorimeters oscillating heat is provided to the sample and as the response the oscillating temperature is registered. The frequency of the resulting temperature oscillation can often be linked to the dynamics of the molecular processes under study. The relation $\omega_{\max}\ \tau_{\alpha}=1$ is valid at the dynamic glass transition for the maximum of the frequency dependent imaginary part of complex heat capacity, where $\omega = 2\pi f$ is angular frequency of the perturbation and τ_{α} is primary structural relaxation time. For cooling at constant cooling rate the relation between cooling rate and corresponding relaxation time is not as easy obtained [12–14]. For the glass transition at a cooling rate of 10 K min^{-1} it is common to assign $\tau(T_g)$ ~100 s [15].

Another periodic perturbation is applied in the so-called temperature modulated differential scanning calorimetry (TMDSC). In TMDSC the programmed temperature-time profile contains an oscillating part. The system response to such temperature-time profile is a periodic heat flow. The temperature-time profile can be any periodic function. If it is a sinusoidal function then we have a single frequency response. In case of non-harmonic temperature-time profiles, higher harmonics will be generated and can be analyzed. Consequently, in one measurement many frequencies can be applied [16–21].

Here, we follow the simultaneous multi-frequency approach based on a step response as suggested by Merzlyakov [17,18] in order to extend the frequency range of common DSC apparatuses (10^{-3}–10^{-1} Hz) towards higher and lower frequencies. The step response TMDSC technique is not limited to specific DSC devices with particular software options. DSC devices such as the fast chip based Mettler Toledo Flash DSC 1 or the slow Setaram Calvet calorimeter BT 2.15, which do not have any temperature modulation technique built in can be used as well.

The limiting factor in assessing higher frequencies is not only sample size, but addenda heat capacity, the contribution of the measuring cell to the system heat capacity and the resulting time

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constants [22]. The Flash DSC 1 chip has a much smaller measuring cell compared to a conventional DSC and with that, the addenda heat capacity is reduced by a factor of about 10^6 (2 J/K, PerkinElmer Pyris 1; 2 μJ/K Mettler Toledo Flash DSC 1). With the Flash DSC 1 the accessible frequency range for calorimetric measurements is extended to higher frequencies (10^{-1}–10^2 Hz) as shown below.

At lower frequencies, larger sample masses are needed to yield reasonable signal to noise ratios in the heat flow signals. The large volume measuring cells of the Calvet calorimeters from Setaram allow an extension of the frequency range down to 10^{-6} Hz. Finally, a frequency range from 10^{-6} Hz to 10^2 Hz is available with TMDSC utilizing conventional DSC apparatuses from different manufactures. Combining this with advanced AC-calorimetric techniques broadens the frequency range for heat capacity spectroscopy up to 10^6 Hz, covering in total 12 orders of magnitude in frequency [23,24].

The paper is structured in the following way. First, an overview of conventional TMDSC and the extension to multi-frequency TMDSC is given. The experimental part starts with examples of the used temperature-time profiles and the obtained heat flow rates. Then the way is proposed for temperature calibration for the Flash DSC 1 in TMDSC mode. At the end of the experimental part sample preparation will be discussed. The result chapter shows measured curves and limitations in the dynamics of the measuring systems. Finally the obtained results are combined in a relaxation map and discussed.

2. Temperature modulated differential scanning calorimetry (TMDSC) in a wide frequency range

2.1. Basic considerations

The understanding that heat capacity can be time dependent and consequently frequency dependent was not always clear [25,26]. The first hint for such dependency came from the measurements of ultrasound propagation in gases [27]. Time dependency occurs when heat is not simultaneously distributed into all degrees of freedom in the sample, e.g. translational first and rotational later. The sample's fast degrees of freedom are directly, thermally, coupled to the measured temperature. The change of temperature or heat in the sample becomes time dependent if heat is later distributed to slow degrees of freedom and as a result, time and frequency dependencies occur [26]. Consequently, also heat capacity becomes a complex function with frequency dependent magnitude and phase. The frequency dependent heat capacity can be compared to admittance in dielectric spectroscopy, and can be similarly treated [28].

Direct time dependent enthalpy measurements in single component systems, not undergoing a phase transition, are not too often reported. One of the examples is the isothermal temperature drift measurement in adiabatic calorimeters in the glass transition range, e.g. Suga [29,30] and references there in. A direct measurement of the heat flow rate during annealing a polymer sample below the glass transition was described in [31,32].

Examples of such time dependent heat flow rate measurements at very different time scales are shown in Fig. 1 for a Setaram Calvet calorimeter BT 2.15 and in Fig. 2 for a Mettler Toledo Flash DSC1. After a programmed step in temperature the resulting sample temperature, (a), the corresponding heating rate and the heat flow rate (b) are shown. An upward temperature step is programmed in Fig. 1 and a downward step in Fig. 2. The heat flow rate curves for both instruments are shown for two temperatures in and outside the glass transition range of 5-phenyl-4-ether (5PPE), respectively.

For both instruments, the smearing of the temperature step and consequently the heating rate profile due to instrumental time constants are seen. In the BT 2.15 the decay of the heat flow rate in the glassy state follows closely the heating rate profile since no relaxation process occur on the time scale of the instrument. In the Flash DSC 1 at least one significant additional time constant exists between the thermometer and the sample as seen from the significant longer relaxation of the heat flow rate in the glassy state compared to the cooling rate decay. For both instruments the much longer decay of the heat flow rate due to the relaxation in the glass transition range is seen in the blue curves. Note the different time scales. From such heat flow rate and heating rate curves the heat capacity spectrum is available from Eq. (2) below as described by Merzlyakov and Schick [33].

2.2. Conventional TMDSC

Differential scanning calorimetry (DSC) is widely used in many fields, e.g. physics, chemistry, material science. It is commonly accepted as a standard tool for the investigation of phase transitions, chemical reactions and to determine heat capacity in short time with reasonable accuracy. The theory of DSC is well established [34,35]. Temperature modulation is an extension to DSC. The first who performed such measurements was Gobrecht et. al [36]. They used a PerkinElmer DSC-1B with additional mechanical parts to produce a sinusoidal temperature modulation.

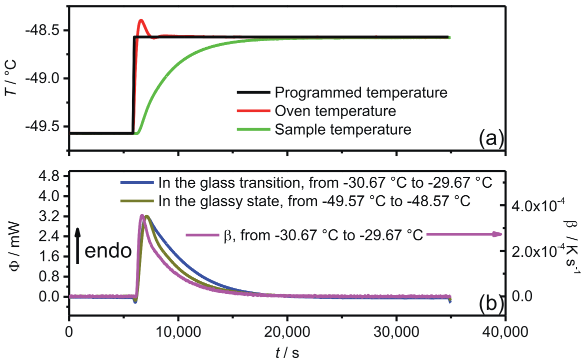

Fig. 1. Programmed upward temperature step of 1 K at heating rate 0.5 K min^{-1} (ca. 10^{-2} K s^{-1}) in a Setaram Calvet calorimeter BT 2.15. (a) Programmed temperature (black), oven temperature (red) and measured sample temperature (green), (b) heating rate (magenta, right axis) and heat flow rate in the glass transition region (blue) and in the glassy state (dark yellow, left axis). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

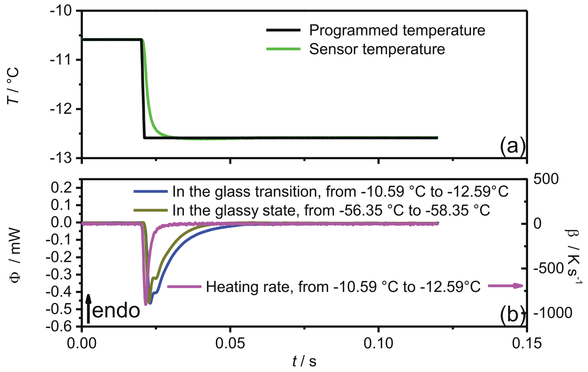

Fig. 2. Programmed downward temperature step of 2 K at cooling rate 2000 K s^{-1} in a Mettler Toledo Flash DSC 1 calorimeter. (a) Temperature program (black) and measured sensor temperature (green), (b) heating rate (magenta, right axis) and heat flow rate in the glass transition region (blue) and in the glassy state (dark yellow, left axis). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)