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Dynamic behaviour of power-compensated differential scanning calorimeters.
Part 3. The influence of material properties (an error evaluation) ☆

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Abstract

Falsification (smearing) of measured DSC curves is caused by heat conduction phenomena from the DSC and from the sample itself. In a previous paper in this series, an algorithm is given to desmear measured heat flow-rate curves on the basis of the theory of linear response. In the case of a sample with low thermal conductivity and small changes of the material properties, the Green's function can be estimated from the measured curve itself. These conditions are valid for the glass transition process of polymers and one can obtain the Green's function for desmearing the DSC curves of this process from the glassy state or from the liquid state respectively. But every change of material properties during the thermal event causes an error in the desmearing procedure. This error can be evaluated from a model calculation.

Keywords: DSC; Error evaluation; Glass transition; Model; Smearing

1. Introduction

In calorimetric investigations by means of the dynamic DSC method, the thermodynamic functions of the sample the (the change of enthalpy $(\mathrm{d}H/\mathrm{d}t)(T)$,

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the heat capacity $C_p(T)$) are not identical to the measured curves. Systematic errors are caused by the falsification (smearing) of the measured curve due to heat transfer relaxation processes inside the sample and also in the DSC furnace.

In the first of this series of papers [1], it was shown that in a discussion of smearing, one has to distinguish between

(i) transitions with large changes of material properties, e.g. first-order phase transitions;
(ii) transitions without latent heat and with small changes of material properties in substances with low thermal conductivity, e.g. the glass transition in polymers.

In this paper we restrict ourselves to the second case. The aim is to evaluate the maximum error of our result if we desmear a measured curve with the aid of the "step-response Green's function" [1] which can easily be obtained from the response of the measured heat flow rate curve on switching on and off the heating power (starting and stopping the dynamic operation mode).

A simple algorithm to correct the error of smearing in the case of a simple one-furnace calorimeter was introduced elsewhere [2]. These studies were improved in Part 2 of this series of papers [3] for a real two-furnace power-compensated DSC.

This correction was made with the aid of the theory of linear response. Thus the measured heat flow rate $\Phi_{\mathrm{out}}(t)$ is the convolution product of the Green's function $G(t)$ with the true heat flow rate $\Phi_{\mathrm{in}}(t)$, which is connected to the process within the sample

$$\Phi_{\mathrm{out}}(t) = \int_0^t G(t-\tau)\Phi_{\mathrm{in}}(\tau)\,\mathrm{d}\tau \tag{1a}$$

or abbreviated

$$\Phi_{\mathrm{out}}(t) = G(t) * \Phi_{\mathrm{in}}(t) \tag{1b}$$

where Φ_{in} is the unsmeared heat flow rate, i.e. the heat flow rate into an ideal, infinitely thin, ideally thermally coupled sample in an ideal heat-conducting DSC. The Green's function $G(t)$ includes the transfer characteristics of both the DSC and of the sample.

There are two reasons for the smearing of the signal from the sample. One is the finite heat resistance between sample and heater; the other is the temperature profile within the sample. Due to the temperature profile, the thermal event does not take place in the whole sample at one moment, but at different times in different regions of the sample.

The temperature profile builds up after switching from isothermal conditions to temperature scan, and it vanished again when the heating rate changes to zero at the end of the scan.

During a run with constant heating rate and in the absence of any thermal event, i.e. no change of material properties, there is a parabolic-shaped temperature profile within the sample which does not change with temperature but is shifted along the temperature axis [4].

Switching the scan rate β on or off results in a step-like change of the heat flow rate Φ_{in} into the measuring system because $\Phi_{\mathrm{in}} = C_p\beta$, where C_p is the heat capacity of the sample and β the heating rate. Thus the step-response Green's function G_{sr} of the sample–DSC system can be extracted from the relaxation behaviour of the measured curve at the start or at the end of the scan. It includes both the smearing due to heat transport and the developing of the temperature profile inside the sample.

The exact desmearing of measured curves, including thermal events, by solution of the convolution integral (Eq. (1)) is also possible if

(i) the Green's function is determined from the switch behaviour of the sample in question; and

(ii) the material properties (specific heat capacity c_p, density ρ, and thermal conductivity λ) do not change, and the heat resistance between sample and heater also remains constant.

In reality, every thermal event within the sample is coupled to changes of material properties which cause a change of the temperature profile [4]. This leads to an additional falsification of the measured signal and a faulty result if we desmear the measured curve with the step-response Green's function. We shall discuss this and evaluate the error in question in the case of a glass transition. The evaluation will be made by means of model calculations. The changes of material properties during glass transition are rather small and well known.

As we have little knowledge about the change in the coefficient of heat transfer to the sample at the glass transition, i.e. the thermal contact between pan and sample in the glassy state and the liquid state respectively, this effect will not be considered in the following calculations.

2. Description of the model

As described above, the step-response Green's function to desmear a DSC curve can be extracted from both the switch-on and switch-off behaviour of the measured curve. To determine it, the measured heat flow rate curve must be deconvoluted with a characteristic step-like function $S(t)$. The result is the searched Green's function $G_{sr}(t)$. The characteristic function is

$$S(t) = \Theta(t - t_0)c_p(T(t))\beta m_s \tag{2}$$

where Θ is the so-called step function which switches from zero to one at t_0, c_p the specific heat capacity, m_s the sample mass, and β the scan rate. If $G_{sr}(t)$ is estimated from the switch-on step, the temperature dependence of c_p (slope) must be considered in $S(t)$, in contrast to the switch-off step leading to isothermal conditions (horizontal line).

The Green's function obtained in this way is only valid for the material properties at the time of switching. In the case of heating curves, the properties in question are those of the glass at switch-on and those of the liquid at switch-off. As the material properties change during the glass transition, none of these Green's functions is exactly valid for desmearing this region of the curve.

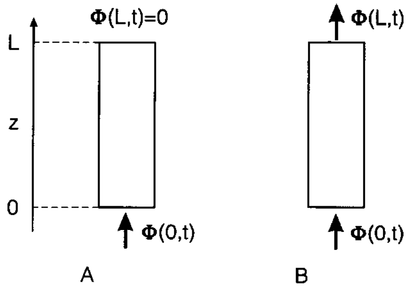

Fig. 1. One-dimensional model of a homogeneous heat conductor of thickness L (Φ, heat flow rate). A, adiabatically isolated on the top; B, with a thermal event at the top.

To determine how large this error can be, we compare the curve of a hypothetical glass transition with that obtained if we smear the model function with the step-response Green's function of the liquid state (from the switch-off) and then desmear it with the Green's function of the glassy state (from switch-on). There are reasons to believe that this comparison yields the maximum error, as the glass transition properties fall between the glassy and liquid ones and the true desmeared curve must be in between that desmeared with the switch-on Green's function and that desmeared with the switch-off Green's function.

The model we use is one-dimensional.

The sample is approximated by a homogeneous heat conducting rod of length L. During a temperature scan with heating rate β, there is a constant heat flow rate $\Phi = mc_p\beta$ into the bottom of the sample. In the absence of any thermal event, the heat conductor is throught to be adiabatically isolated at the top (Fig. 1) [4].

In reality during a scan, the sample is indeed heated from all sides leading to the adiabatically isolated range being somewhere inside the sample [5]. Such a real sample may be described approximately as a connection of two one-dimensional heat conductors.

The evaluation is calculated for a model polystyrene whose properties are given in Table 1.

Table 1
Material properties of the model polystyrene

Property	Glassy state	Liquid state	Remarks
$c_p/(\mathrm{J\ g^{-1}\ K^{-1}})$	1.6	2.0	Own measurement
$\lambda/(\mathrm{W\ mK^{-1}})$	0.11	0.12	Approximated from values at 50 and 100°C [6]
$\rho/(\mathrm{g\ cm^{-3}})$	1.036	1.026	Approximated from values in Ref. [7]
$\alpha/(\mathrm{s\ mm^{-2}})$	15.07	17.09	Calculated from values above

3. Error estimation

3.1. The temperature profile change

For the one-dimensional model sample (Fig. 1), the temperature profile reads

$$T(z,t) = T_0 + \beta t - \alpha\beta L z\left(1 - \frac{z}{2L}\right) + \frac{16\alpha L^2}{\pi^3}\beta \sum_{n=0}^{\infty} \frac{\sin\left(\frac{2n+1}{2}\pi\frac{z}{L}\right)}{(2n+1)^3} e^{-x_n^2 t} \tag{3}$$

with

$$x_n^2 = \frac{(2n+1)^2\pi^2}{4\alpha L^2} \quad \text{and} \quad \alpha = \frac{\rho c_p}{\lambda}$$

(ρ is density, c_p specific heat capacity, and λ thermal conductivity), assuming constant scan rate β and no thermal event, with T_0 being the start temperature of the scan [4].

After relaxation of the switching-on processes, the third term disappears and a parabolic temperature profile is developed inside the sample

$$T(z,t) = T_0 + \beta t - \alpha\beta L z\left(1 - \frac{z}{2L}\right) \tag{4}$$

In Fig. 2 the calculated temperature profiles of the glassy state and of the liquid state are shown for the case of the hypothetical polystyrene sample with a thickness of 1 mm at a heating rate of 20 K min^{-1}.

The temperature difference between the bottom and adiabatically isolated top of the sample is 2.5 K in the glassy state. It increases during the glass transition by

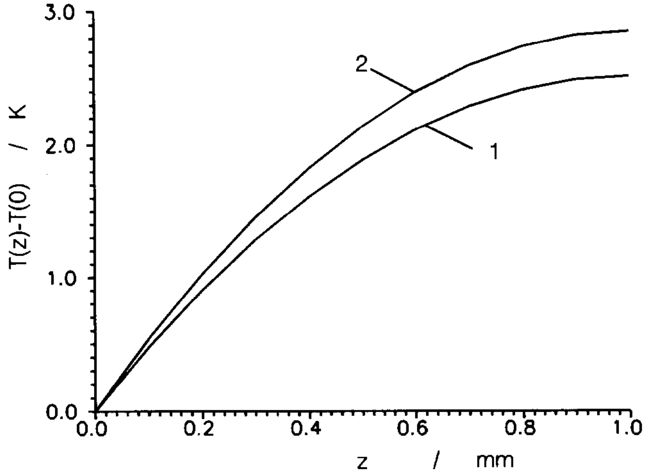

Fig. 2. Calculated temperature profiles of a 1 mm thick polystyrene sample (adiabatically isolated on the top), heating rate $\beta = 20$ K min^{-1}: curve 1, glassy state; curve 2, liquid state.

0.3–2.8 K in the liquid state. The reason for this is the change of the material property α.

In reality, during the glass transition, profile 1 slowly turns into profile 2. For simplicity, an abrupt change is used in our calculation, representing the worst case for error estimation.

This change of α can be simulated by switching on an additional heat flow (as from a thermal event). This heat flow rate Φ_0 is thought to derive exclusively from the top of the sample (Fig. 1) to obtain the maximal length of the heat conduction paths and, thus, the maximal additional smearing.

It changes the temperature profile from that of the glassy state to the larger profile of the liquid state, only if Φ_0 leaves the sample at the top. Φ_0 is evaluated from Fourier's law

$$\Phi_0 = -\frac{\lambda A \Delta T}{z} \tag{5}$$

where A and ΔT denote the cross sectional area and the temperature difference in question. The heat flow rate into a 20 mg sample at a heating rate of 20 K min^{-1} is about 0.8 mW.

With an additional heat flow rate Φ on the top of the sample, the temperature profile [4] changes to

$$\begin{aligned} T(z,t) &= T_0 + \beta t - \alpha\beta L z\left(1 - \frac{z}{2L}\right) \\ &\quad - \frac{2}{mc}\sum_{n=0}^{\infty} \cos\left((2n+1)\frac{\pi}{2}\left(1 - \frac{z}{L}\right)\right)\int_0^t \mathrm{e}^{-x_n^2(t-t')}\Phi(L,t')\,\mathrm{d}t' \end{aligned} \tag{6}$$

To obtain the temperature profile for our case, $\Phi(t)$ has to be substituted by the step function of intensity Φ_0 at time $t = 0$ and $z = L$. From Eq. (6) we obtain

$$\begin{aligned} T(z,t) &= T_0 + \beta t - \alpha z L \beta\left(1 - \frac{z}{2L}\right) - \frac{\Phi_0 z}{\lambda A} \\ &\quad + \frac{8\Phi L}{\pi^2 \lambda A}\sum_{n=0}^{\infty} \frac{\cos\left(\frac{\pi}{2}(2n+1)\left(1 - \frac{z}{L}\right)\right)}{(2n+1)^2}\mathrm{e}^{-x_n^2 t} \end{aligned} \tag{7}$$

In Fig. 3, the stationary temperature profile (after such a time that the last term of Eq. (7) vanishes) is shown in addition to those of Fig. 2.

It can be seen that the temperature profile of the liquid state and that of the glassy state with a constant additional heat flow rate of $\Phi_0 = 0.8$ mW from the top are nearly the same in our approximation. This result is the basis of the following simulation of the glass transition, with a thermal event on the top of the sample (with the heat flow leaving the sample) and the sample bulk serving for heat transport only (without additional transition).

Both a step-function

$$\Phi(L,t) = \Phi_0 \Theta(t) \tag{8}$$

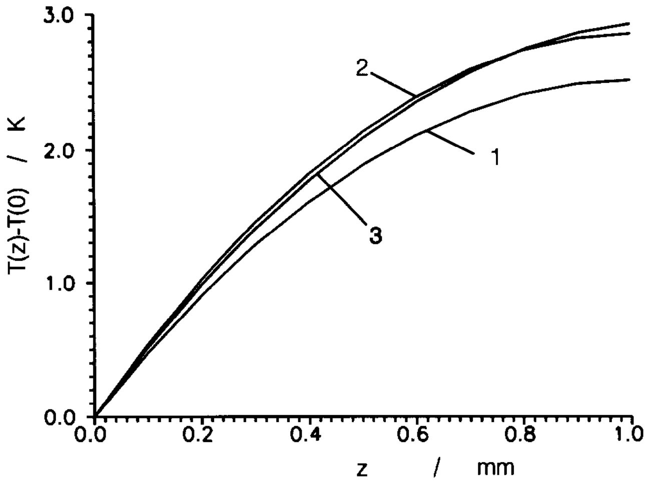

Fig. 3. Calculated temperature profiles of 1 mm thick polystyrene sample, heating rate $\beta = 20$ K min^{-1}. Curves 1 and 2, from Fig. 2. Curve 3, in glassy state (same as 1) but with an additional constant heat flow rate of 0.8 mW out of the top of the sample.

and a ramp

$$\Phi(L,t) = \begin{cases} 0 & \text{if } t < 0 \\ \dfrac{\Phi_0 \beta}{\Delta T} t & \text{if } 0 \leq t < \dfrac{\Delta T}{\beta} \\ \Phi_0 & \text{if } t \geq \dfrac{\Delta T}{\beta} \end{cases} \tag{9}$$

are used as model functions to simulate the real heat flow of a glass transition (Fig. 4). In the second case, the maximal heat flow out of the sample is obtained after the rise time $\Delta T/\beta$, where ΔT characterizes the width of the glass transition interval.

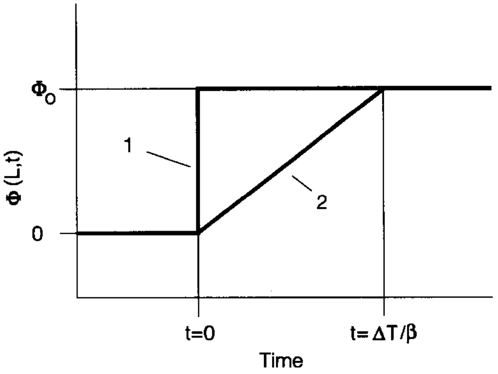

Fig. 4. Representation of the functions $\Phi(L,t)$, the additional heat flow rate out of the top of the sample to simulate a glass transition: 1, step function; 2, ramp function.

For times larger than the rise time, the additional heat flow is assumed to be constant.

In the following, the temperature profile will be estimated for both model functions. The thermal event is taken to start at $t = 0$, a time large enough after the scan switch-on (start of measurement) to obtain stationary conditions. Eq. (6) then describes the temperature profile after the thermal event $\Phi(L,t)$.

The solution for a step function Φ (Eq. (8)) is given by Eq. (7).

If $\Phi(L,t)$ is a ramp function, two different time intervals must be considered to solve the convolution integral in Eq. (6):

(i) for time $t < \Delta T/\beta$ we get

$$\begin{aligned}\int_0^t \mathrm{e}^{-x_n^2(t-t')}\Phi(t')\,\mathrm{d}t' &= \frac{\Phi_0\beta}{\Delta T}\,\mathrm{e}^{-x_n^2 t}\int_0^t t'\mathrm{e}^{x_n^2 t'}\,\mathrm{d}t' \\ &= \frac{\Phi_0\beta}{\Delta T x_n^2}\left(t - \frac{1}{x_n^2}(1 - e^{-x_n^2 t})\right)\end{aligned} \tag{10}$$

(ii) for time $t \geq \Delta t/\beta$ we get

$$\begin{aligned}\int_0^t \mathrm{e}^{-x_n^2(t-t')}\Phi(t')\,\mathrm{d}t' &= \Phi_0\mathrm{e}^{-x_n^2 t}\left(\frac{\beta}{\Delta T}\int_0^{\Delta T/\beta} t'\mathrm{e}^{x_n^2 t'}\,\mathrm{d}t' + \int_{\Delta T/\beta}^{\infty} \mathrm{e}^{x_n^2 t'}\,\mathrm{d}t'\right) \\ &= \Phi_0\mathrm{e}^{-x_n^2 t}\frac{\beta}{\Delta T x_n^4}\left(\mathrm{e}^{x_n^2 \Delta T/\beta}\left(x_n^2\frac{\Delta T}{\beta} - 1\right) + 1\right) \\ &\quad + \frac{\Phi_0\mathrm{e}^{-x_n^2 t}}{x_n^2}(\mathrm{e}^{x_n^2 t} - \mathrm{e}^{x_n^2 \Delta T/\beta}) \\ &= \frac{\Phi_0}{x_n^2}\left(1 - \frac{\beta}{\Delta T x_n^2}(\mathrm{e}^{-x_n^2(t-\Delta T/\beta)} - \mathrm{e}^{-x_n^2 t})\right)\end{aligned} \tag{11}$$

With this result the temperature profile of our model can be calculated

$$T(z,t) = \begin{cases} T_0 + \beta t - \alpha\beta L z\left(1 - \dfrac{z}{2L}\right) - \dfrac{8\Phi_0 L\beta}{\pi^2 A\lambda\Delta T} \\ \quad \times \displaystyle\sum_{n=0}^{\infty}\frac{\cos\left((2n+1)\frac{\pi}{2}\left(1 - \frac{z}{L}\right)\right)}{(2n+1)^2}\left(t - \frac{1}{x_n^2}(1 - \mathrm{e}^{-x_n^2 t})\right) & \text{if } 0 \leq t < \dfrac{\Delta T}{\beta} \\ T_0 + \beta t - \alpha\beta L z\left(1 - \dfrac{z}{2L}\right) - \dfrac{8\Phi_0 L\beta}{\pi^2 A\lambda\Delta T} \\ \quad \times \displaystyle\sum_{n=0}^{\infty}\frac{\cos\left((2n+1)\frac{\pi}{2}\left(1 - \frac{z}{L}\right)\right)}{(2n+1)^2}\left(\frac{\Delta T}{\beta} - \frac{1}{x_n^2}(\mathrm{e}^{-x_n^2(t-\Delta T/\beta)} - \mathrm{e}^{-x_n^2 t})\right) & \text{if } t \geq \dfrac{\Delta T}{\beta} \end{cases} \tag{12}$$

3.2. The measured signal

In the considered model, the heat flow rate at the bottom of the sample is that which would be measured with the DSC. This heat flow rate can be estimated by inserting the calculated temperature profile into Fourier's law

$$\Phi(0,t) = -\lambda A \frac{\partial T(0,t)}{\partial z} \tag{13}$$

In the first case, the thermal event is represented by a step function

$$\Phi(0,t) = mc\beta + \Phi_0 - \Phi_0 \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \mathrm{e}^{-x_n^2 t} \tag{14}$$

In the second case of $\Phi(L,t)$ being a ramp function, the solution is

$$\Phi(0,t) = \begin{cases} mc\beta + \dfrac{\Phi_0 \beta}{\pi \Delta T} t - \dfrac{\Phi_0 \alpha \beta L^2}{2\Delta T} \left(1 - \dfrac{32}{\pi^3} \displaystyle\sum_{n=0}^{\infty} \dfrac{(-1)^n}{(2n+1)^3} \mathrm{e}^{-x_n^2 t}\right) & \text{if } 0 \leq t < \dfrac{\Delta T}{\beta} \\ mc\beta + \Phi_0 - \dfrac{16 \Phi_0 \alpha \beta L^2}{\pi^3 \Delta T} \displaystyle\sum_{n=0}^{\infty} \dfrac{(-1)^n}{(2n+1)^3} \left(\mathrm{e}^{-x_n^2 (t - \Delta T/\beta)} - \mathrm{e}^{-x_n^2 t}\right) & \text{if } t \geq \dfrac{\Delta T}{\beta} \end{cases} \tag{15}$$

In Eqs. (14) and (15), the first term of the sum describes the steady state heat flow rate for linear heating without any thermal event. The second term is the heat flow rate which is switched on at the top of the sample (to simulate a thermal event). The smearing due to the heat transport inside the sample is given by the third term. This term vanishes for large times (steady state).

For a model sample (polystyrene) with a thickness of 1 mm, the heat flow rate into the bottom of the sample can be calculated both with the aid of Eq. (14) or, better, with Eq. (15). This additional heat flow rate caused by the simulated thermal event of $\Phi(L,t)$, is plotted in Fig. 5 for ramp widths of $\Delta T = 0$, 5, 10, and 20 K respectively. The heating rate is always 20 K min^{-1}.

Similar heat flow rates into a sample with a reduced thickness of half a millimeter are shown in Fig. 6. This case equals a sample of 1 mm thickness thought to be identically heated both from the bottom and the top of the pan. An adiabatic layer thus arises in the middle of the sample. In this layer, the described thermal event to simulate a glass transition will now take place. This case is closer to reality than the former one. But in reality the power through the lid of the pan is always smaller than the power through the bottom, leading to an adiabatic layer at about 2/3 of the thickness of the sample [5]. To estimate the maximum error, the first case should be considered. The results for a reduced thickness of the sample are given for the sake of comparison.

From Figs. 5 and 6, a "glass transition time" can be estimated. This is the time when the measured heat flow rate curve reaches one half of the step height. (Usually the "glass rate temperature" is that temperature at which the heat capacity change is half of the total change.) Comparing the true ramp change with the

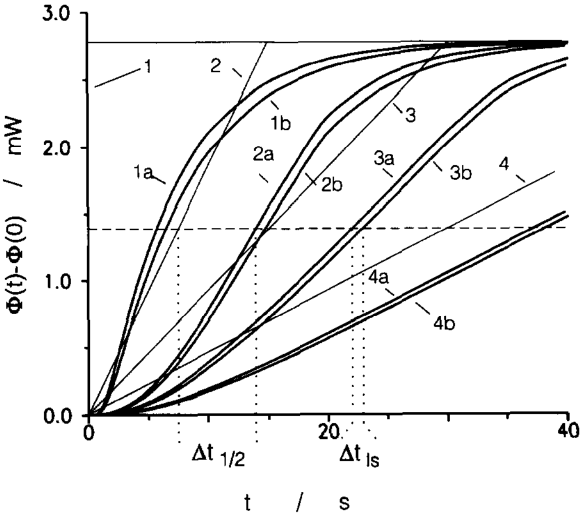

Fig. 5. The calculated additional heat flow rates $\Phi(0,t)$ on the bottom of the sample (thick lines), caused by a hypothetical additional heat flow $\Phi(L,t)$ (thermal event) on the top of the sample (thin lines). Ramp width: curve 1, $\Delta T = 0$ K; curve 2, $\Delta T = 5$ K; curve 3, $\Delta T = 10$ K; curve 4, $\Delta T = 20$ K (heating rate $\beta = 20$ K min^{-1}). Curves (a) are calculated with the material properties of the glassy state and curves (b) with those of the liquid state.

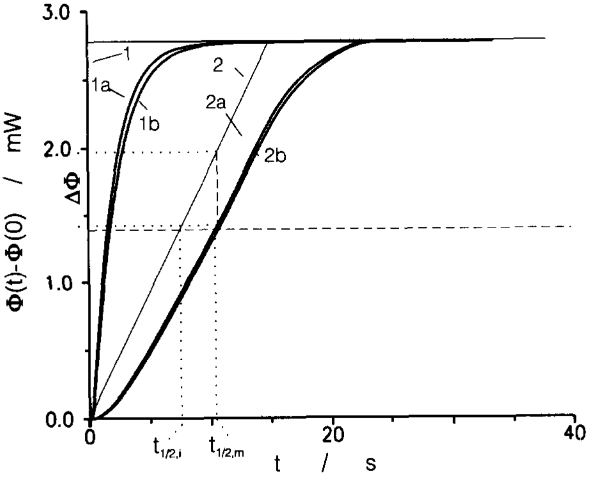

Fig. 6. Curves from Fig. 5 but calculated for a sample of half thickness: curve 1, $\Delta T = 0$ K; curve 2, $\Delta T = 5$ K; $T_{1/2} = t_{1/2}\beta$.

calculated curves, we find that the smearing effect is smaller in the glassy state than in the liquid state.

The time difference Δt_{ls} of 0.75 s corresponds (at a heating rate of 20 K min^{-1} (see Fig. 5)) to a temperature difference of the "glass transition temperature" of

Table 2
Difference between the half-step temperatures, $\Delta T_{1/2} = T_{1/2,\mathrm{m}} - T_{1/2,\mathrm{i}}$, of measured and "true" curves in the glassy state ($\Delta T_{1/2}$ in the liquid state is 0.25 K higher)

Sample thickness	Width of transition ramp $\Delta T/\mathrm{K}$	Calculated error $\Delta T_{1/2}/\mathrm{K}$
1 mm	0	1.73
	5	2.23
	10	2.50
	20	2.50
0.5 mm	0	0.47
	5	0.60

0.25 K. In the case of the reduced effective thickness (Fig. 6) this difference is only 0.07 K.

If we compare the calculated "measured curve" with the real one (the ramp in question) at half-step-height, we find smearing times $\Delta t_{1/2}$ which depend on experimental parameters (width of ramp, sample thickness, heating rate; see Figs. 5 and 6). From these times, the respective temperature differences $\Delta T_{1/2}$ can be calculated. Table 2 presents the results for the cases of Figs. 5 and 6. This $\Delta T_{1/2}$ represents the error of the dynamic determination of the glass transition temperature in the case of our model polystyrene sample. As can be seen, this error is mostly determined by the general smearing effect of thermal conductivity of the sample, where the change of the material properties has an influence, which is one order of magnitude smaller.

With increasing width of the ramp, we calculate a larger $\Delta T_{1/2}$. For better interpretation of this result we discuss the difference between the "true signal" $\Phi(L,t)$ and the corresponding "measured signal" $\Phi(0,t)$. In the case of $t < \Delta T/\beta$ (the time when the steady state value of the heat flow rate Φ_0 has not yet been reached, see Fig. 4), this difference $\Delta\Phi$ can be calculated from Eqs. (9) and (15) to be

$$\Delta\Phi(t) = \frac{\Phi_0 \alpha \beta L^2}{2\Delta T}\left(1 - \frac{32}{\pi^3}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)^3}\mathrm{e}^{-x_n^2 t}\right) \tag{16}$$

After disappearance of the relaxation term (which is only relevant at the very beginning of the time interval in question), a constant, time-independent difference of this heat flow rate remains (see Fig. 6)

$$\Delta\Phi(t) = \frac{\Phi_0 \alpha \beta L^2}{2\Delta T} \tag{17}$$

As, in the example, the real heat flow rate at the top $\Phi(L,t)$ increases linearly with a slope (Fig. 4)

$$\frac{\Delta\Phi}{\Delta t} = \frac{\Phi_0 \beta}{\Delta T}$$

the delay in time between $\Phi(0,t)$ and $\Phi(L,t)$ (with observance of Eq. (17)) reads

$$\Delta t = \frac{\alpha L^2}{2} \tag{18}$$

From this we calculate the difference in the half-step temperatures using the definition of the heating rate $\beta = \Delta T/\Delta t$

$$\Delta T_{1/2} = T_{1/2,\mathrm{m}} - T_{1/2,\mathrm{i}} = \frac{\alpha L^2}{2}\beta \tag{19}$$

As can be seen, the temperature error of the measurement, which is caused by the smearing effect of the sample, is, apart from the heating rate, dependent on the sample properties. This temperature error is independent of the slope of Φ.

The temperature error according to Eq. (19) arises after the disappearance of the relaxation term. For the model sample in question, these temperature errors are 2.51 and 2.85 K for the glassy state and the liquid state respectively (at half-sample thickness, they reduce to 0.63 and 0.71 K).

3.3. The step-response Green's function

In this section the maximum error of faulty desmearing caused by the change of the material quantity α during glass transition will be estimated.

As mentioned above, the necessary Green's function can be determined from the response of the heat flow rate curve on switching on or off the temperature scan (the step-response Green's function G_{sr}). In the first case, $G_{\mathrm{sr}}(t)$ contains the heat transport properties of the glass. In the other case, it includes the corresponding properties of the liquid.

For a discussion of the maximum error estimation, the smeared measured signal due to a hypothetical thermal event in the liquid state will be desmeared by means of the Green's function of the glassy state.

The change of the heat flow rate at the bottom of the sample, which is caused by an additional heat flow rate $\Phi(L,t)$ at the top of the sample, reads in Laplace space [2]

$$\phi(0,s) = \frac{1}{\cosh\sqrt{\alpha s}L}\,\phi(L,s) \tag{20}$$

where s corresponds to time t and the convolution product transforms into a simple multiplication, the fraction being the Green's function in Laplace space.

If the true heat flow rate of a thermal event is smeared by the Green's function of the liquid state and desmeared by means of the step-response Green's function of the glassy state, then we get (at a worst case) the (incorrect) heat flow rate

$$\phi_{\mathrm{d}}(0,s) = \frac{\cosh\sqrt{\alpha_1 s}L}{\cosh\sqrt{\alpha_2 s}L}\,\phi(L,s) \tag{21}$$

where α_1 and α_2 are the reciprocal thermal diffusivities of the glassy and the liquid state, respectively. This equation describes in Laplace space the connection between the real event at the top of the sample $\phi(L,s)$ and the wrongly desmeared heat flow rate curve at the bottom of the sample $\phi_{\mathrm{d}}(0,s)$. The fraction determines the Green's function which causes this error in Laplace space (it should be unity in an error-free case).

The corresponding Green's function in time space is calculated by means of an inverse Laplace transformation from Eq. (21)

$$G_{\mathrm{d}}(t) = \mathscr{L}^{-1}\left(\frac{\cosh\sqrt{\alpha_1 s}L}{\cosh\sqrt{\alpha_2 s}L}\right) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} \frac{\cosh\sqrt{\alpha_1 s}L}{\cosh\sqrt{\alpha_2 s}L}\,\mathrm{e}^{st}\,\mathrm{d}s \tag{22}$$

The complex integral in Eq. (22) is evaluated by determining the residuals of the integrand. In time space we get

$$G_{\mathrm{d}}(t) = \frac{\pi}{\alpha_2 L^2}\sum_{n=0}^{n}(-1)^n(2n+1)\cos\left(\pi\frac{2n+1}{2}\sqrt{\frac{\alpha_1}{\alpha_2}}\right)\mathrm{e}^{-x_n^2 t} \tag{23}$$

And the incorrect desmeared heat flow rate curve $\Phi_{\mathrm{d}}(0,t)$ can be determined by convolution of the hypothetical heat flow rate due to a thermal event $\Phi(L,t)$ with the incorrect Green's function $G_{\mathrm{d}}(t)$

$$\Phi_{\mathrm{d}}(t) = \Phi_{\mathrm{d}}(0,t) = \int_0^t G_{\mathrm{d}}(t-t')\Phi(L,t')\,\mathrm{d}t' \tag{24}$$

Inserting Eqs. (14) and (15) into Eq. (24) we get:

(i) for a step-like thermal event

$$\Phi_{\mathrm{d}}(t) = mc\beta + \Phi_0\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\cos\left(\sqrt{\frac{\alpha_1}{\alpha_2}}\frac{2n+1}{2}\pi\right)\left(1-\mathrm{e}^{-x_n^2 t}\right) \tag{25}$$

and

(ii) with a ramp-like event (of the width ΔT)

$$\Phi_{\mathrm{d}}(t) = \begin{cases} mc\beta + \dfrac{4\Phi_0\beta}{\pi\Delta T}\displaystyle\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\cos\left(\sqrt{\frac{\alpha_1}{\alpha_2}}\frac{2n+1}{2}\pi\right) \\ \quad\times\left(t-\dfrac{4\alpha_2L^2}{(2n+1)^2\pi^2}\left(1-\mathrm{e}^{-x_n^2 t}\right)\right) & \text{if } 0 \le t < \dfrac{\Delta T}{\beta} \\ mc\beta + \dfrac{4\Phi_0\beta}{\pi\Delta T}\displaystyle\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\cos\left(\sqrt{\frac{\alpha_1}{\alpha_2}}\frac{2n+1}{2}\pi\right) \\ \quad\times\left(\dfrac{\Delta T}{\beta}-\dfrac{4\alpha_2L^2}{(2n+1)^2\pi^2}\left(\mathrm{e}^{-x_n^2(t-\Delta T/\beta)}-\mathrm{e}^{-x_n^2 t}\right)\right) & \text{if } t \ge \dfrac{\Delta T}{\beta} \end{cases} \tag{26}$$

The results from Eqs. (25) and (26) are shown in Figs. 7 and 8.

A measure for the error of the determined glass transition temperature from the faulty desmeared measured curve is the difference in the half-step temperatures $T_{1/2}$

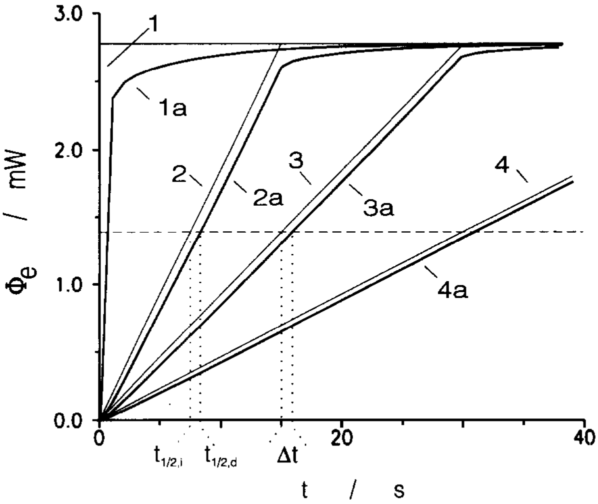

Fig. 7. Simulated thermal event of different ramp width (thin lines) and calculated corresponding desmeared heat flow rates, curves (a), where the measured heat flow rate curve from the liquid model polystyrene has been desmeared with the aid of the step-response Green's function of the glassy state. Ramp width: curve 1, $\Delta T = 0$ K; curve 2, $\Delta T = 5$ K; curve 3, $\Delta T = 10$ K; curve 4, $\Delta T = 20$ K.

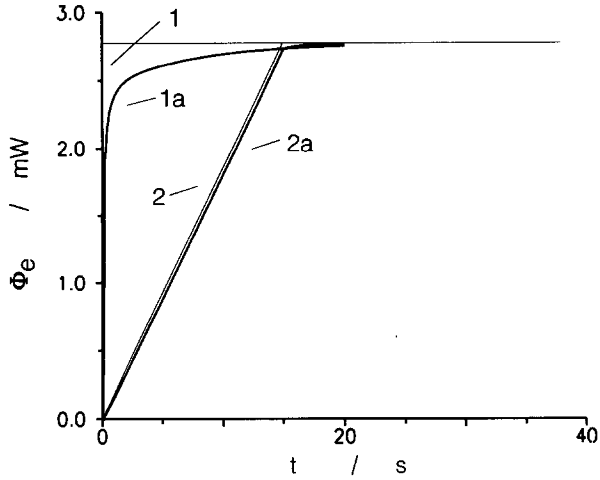

Fig. 8. Curves as in Fig. 7 but at reduced sample thickness, $T_{1/2} = t_{1/2}\beta$.

between the input heat flow rate $\Phi(L,t)$ and the above calculated incorrect heat flow rate $\Phi_d(t)$. These differences are presented in Table 3.

As can be seen, the errors in $T_{1/2}$ after desmearing by means of an incorrect step-response Green's function equal the differences between the half-step temperatures of the smeared curve from the glassy state and from the liquid state (Fig. 5).

Table 3
Differences between half-step temperature $T_{1/2}$ of the input heat flow rate ($\Phi(L,t)$) and that of the desmeared heat flow rate ($\Phi_d(t)$), $\Delta T_{1/2} = T_{1/2,d} - T_{1/2,i}$

Sample thickness	Width of transition ramp ΔT/K	Calculated error $\Delta T_{1/2}$/K
1 mm	0	0.16
	5	0.23
	10	0.25
	20	0.25
0.5 mm	0	0.03
	5	0.06

The maximum temperature error of the desmeared curves, when neglecting the change of Green's function due to the material properties during glass transition, is thus about 0.25 K. This error is about one order of magnitude lower than the total temperature error if we do not desmear the measured curves (Fig. 5).

As our model is only a rough upper-limit approximation (rather unfavorable concerning heat transport), smaller values can be expected in reality (like the results for reduced sample thickness).

Comparison of Fig. 5 with Fig. 7, and Fig. 6 with Fig. 8 shows that the heat flow rate curves desmeared with the aid α_n of a slightly incorrect step-response Green's function yield, however, a better approximation of the real thermal event than the measured curves do.

4. Conclusions

Faultless desmearing (deconvolution) of measured curves is only possible if the Green's function is determined with the sample being in place and having the same material properties as during the measurement.

We have shown by model calculations that in the case of small changes of material properties (as during a glass transition), the error of using the Green's function determined with one set of material properties for desmearing a curve measured with the other set of material properties is within the order of magnitude of the measuring error.

As a result, it should be possible to desmear a glass transition curve with either the Green's function obtained with the sample in the glassy state or that obtained with the sample in the liquid state.

These two (somewhat different) Green's functions can easily be determined from the step-response behaviour on switching on and off the heating or cooling from isothermal model.

Thus the "step-response Green's function" can be used to desmear measured curves, if the material properties do not change more than in the case of glass transitions. These theoretical evaluations will be proved experimentally in the next paper of this series.

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