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Influence of the heat conductivity of the sample on DSC curves and its correction

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Abstract

Heat conduction in DSC and sample as well as heat transfers cause a falsification (smearing) of the measured heat flux in DSC measuremts. Therefore transition phenomenons (peaks and steps) in DSC-curves are measured broader and shifted along the temperature scale. A method is shown which allows a correction of the "smeared" DSC-curves on the base of linear response in the case of badly heat conducting samples. The necessary Green's function can be received from the smeared curve without additional measurement.

1. INTRODUCTION

In analyzing DSC measurements beside transition temperatures often the exact shape of peaks or c_p step changes (glass transition) are of interest [1,2]. From the DSC-curves it isn't possible to get these informations directly. Therefore various algorithms have been developed which allow e.g. the corrections of temperature of transition peaks [3,4]. These methods can be used successfully in measuring small samples with good heat conductivity. Because in scanning operation there is no significant temperature gradient inside the sample. In the case of substances with low heat conductivity a temperature gradient inside the sample cannot be neglected. In measuring polymers with heating rates of 10 K/min there appear temperature gradients of up to 2 K inside the sample [5]. In DSC-curves of this substances the peak and step transitions are measured to broad and transitions temperatures are shifted to higher values. Temperatures and transitions shapes depend on the

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geometry of the sample.

Such systematic errors cannot be avoided by variation of experimental conditions. For the analysis od DSC-curves it is necessary to use algorithms in which the "smearing" of the curves by heat conductivity of the sample as well as influences of the measuring device are taken into consideration.

With aid of methods of the theory of linear response the smearing effect can be described with a Green's function. The problem is to develop an algorithm for estimation of this function, where sample and measuring device are considered as one system. In order to investigate the cause of smearing the following cases are distinguished:

(i) real measuring device and ideal sample

(ii) ideal measuring device and real sample with heat transfer between device and sample

(iii) real system of sample and measuring device.

In each of this cases it is assumed that the interactions between the measuring system and surroundings do not change during the measurement. These assumption is fulfilled in the case of a sufficient small temperature range.

2. DESCRIPTION OF TRANSFER BEHAVIOR OF SAMPLE AND MEASURING DEVICE

The DSC measures the heat flux which is necessary to change the temperature of a sample at a constant scanning rate. In the idealized case the course temperature of the sample is always equal to the program temperature. Assuming that the energy produced by the heater is transferred into the sample without any losses and relaxation and that there is no temperature gradient inside the sample, the registered heating power is equal to the heat flux calculated from the equation:

$$\Phi(t) = m_s c_p(T)\beta + m_s q_t. \tag{1}$$

with m_s being the mass of the sample, c_p the spezifical heat capacity, β the temperature scanning rate, and q_t the energy of transition (in the case of a first order phase transition). The measured heat flux $\Phi(t)$ is caused by the temperature gradient between heater and sample.

In real measurements the measured signal is considerably different from the expected one from equation 1, a smearing of the heat flux is produced by the heat conducting system DSC - sample.

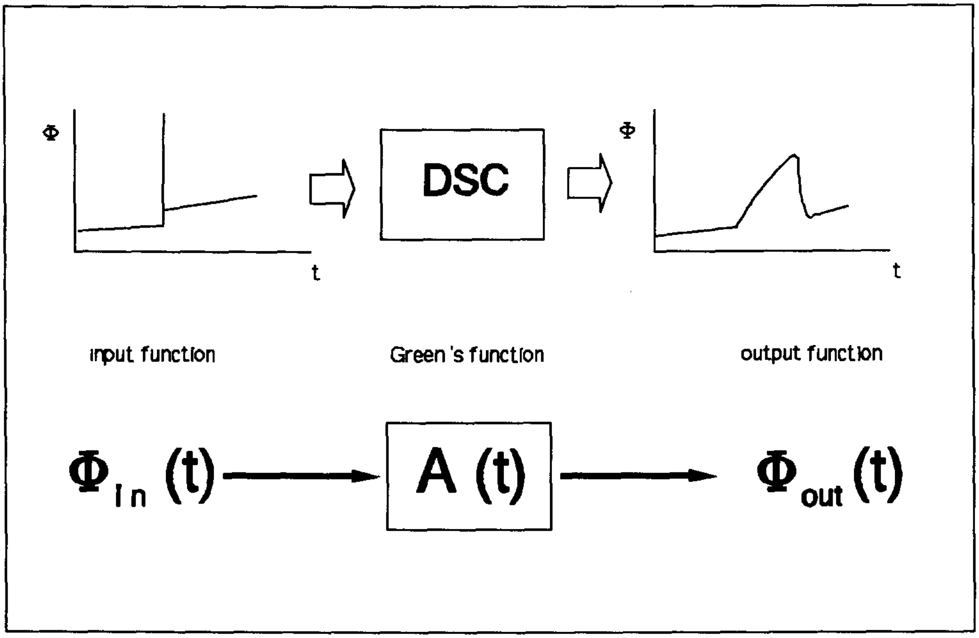

Figure 1. Connection of input function and output function in a DSC in the case of a first order phase transition

In figure 1 the connection is shown schematically. The input function $\Phi_{in}(t)$ is calculated according to equ. 1. The DSC-curve is the output function belonging to it.

Reasons for the difference between input and output function arises from the heat transfer paths between heater and sample, and inside the sample as well, and from the electronics.

Considering the temperature range small enough the DSC can be described as a linear system. The transfer behavior of the measuring device is then described by the Green's function A(t).

The connection between input function $\Phi_{in}(t)$ and output function $\Phi_{out}(t)$ is given by the convolution integral:

$$\phi_{out}(t) = A(t) * \phi_{in}(t) \tag{2a}$$

that is:

$$\phi_{out}(t) = \int_0^t A(t-\tau)\phi_{in}(\tau)\, d\tau . \tag{2b}$$

Thus, if the Green's function is known the input function can be calculated from Φ_{out}. A(t) is the answer of the device on a Dirac impulse input function.

In this paper an algorithm for determination of this specific Green's function is presented for the case of badly head conducting samples, under the assumption of only small changes of such the properties as heat conductivity λ, heat capacity c_p, and density ρ for the transitions in question.

This assumption is usually fulfilled in case of transitions without enthalpy step changes (e.g. glass transition, and second order transition).

3. THE INFLUENCE OF THE MEASURING DEVICE AND THE SAMPLE ON THE SMEARING

To simplify the investigations we consider only the half of the twin calorimeter, which contains the sample. The influence of the reference side is neglected [6]

3.1. Smearing in the case of ideal sample

To begin with, for easier description of smearing problems the contribution of the sample shall be abstracted from. A model that corresponds to these conditions is a DSC with a infinite thin sample in it.

A heat resistance between DSC and sample is neglected. Then the falsification of the measured curve is caused through the heat transport inside the DSC and the following electronics.

In the literature there have been described different procedures for estimation of the

Green's function A(t) [3].

Always the Green's function must be estimated in a separate experiment. These methods are useful to desmear measured curves of samples, which are close to the considered model, e.g. melting curves of thin indium samples.

If the heat conduction of the sample and heat transfer between DSC and sample cannot be neglected, these procedures fail, because the sample specific transfer properties are not referred to. Hence it is necessary to estimate the Green's function for each sample separate.

3.2. Smearing in the case of a real sample in an ideal calorimeter

Only the sample is the cause of smearing in this case. In the considered model the sample has a low heat conductivity. The calorimeter is assumed to be ideal, that is there is no smearing of the signals through the measuring device.

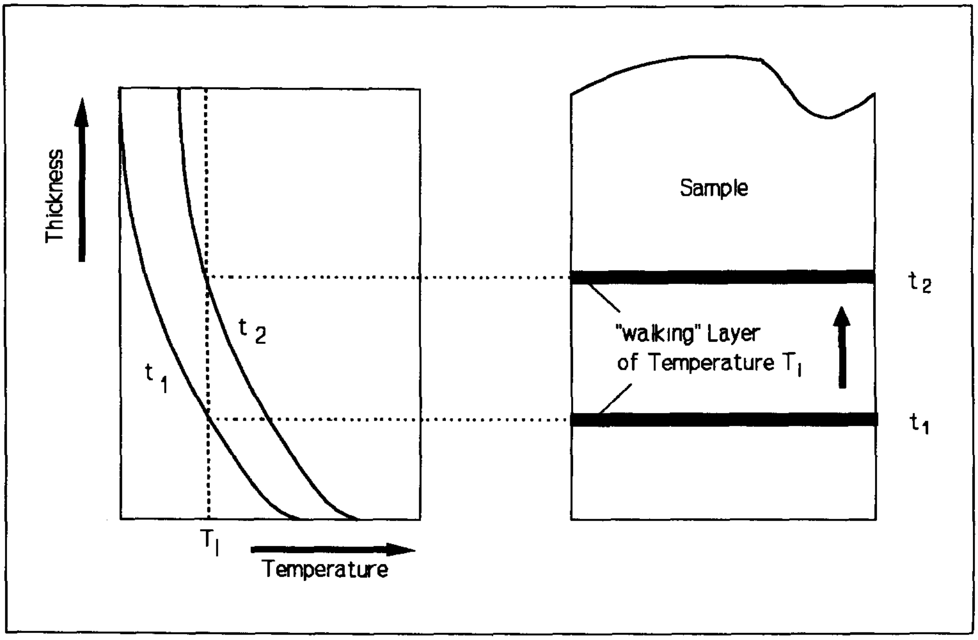

Figure 2. Scheme of the temperature profile and a "walking" layer of temperature T_l inside the sample at two times (t_2>t_1)

Only the heat transfer between DSC and sample and within the sample are taken into account.

In samples with bad heat conductivity at a temperature scan with constant rate a temperature gradient is build up within the sample which, after reaching of stationary conditions, doesn't change anymore [7]. When a transition takes place thus the whole volume will not carry out this transition at the same time. According to the temperature profile there are regions which start earlier and other which start later with the transition. For illustration this circumstances shall be described by a discrete model of a "walking" layer. The transition in question takes place in one layer. In this model a layer is the region of the sample which correspond to the same thermodynamical state.In figure 2 the model is shown schematically.

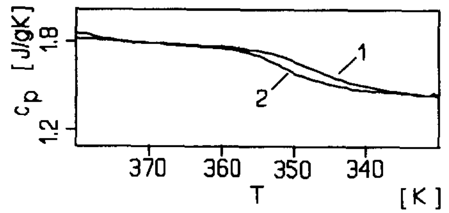

Figure 3. Glass transition of PVC foils of different thickness
(cooling rate: -20 K/min,
m_s: 1...2.396 mg; 2...49.948 mg)

In figure 3 the smearing effect of the "walking" layers on the measured signal is represented for the case of a glass transition.

With increasing mass a larger temperature gradient is built up due to the longer path of heat flow which leads to an increase of the measured glass temperature and to a broader measured glass transition range.

At first the smearing of the measured heat flux of one layer shall be described. When a transformation takes place in this layer the enthalpy changes and induces a heat flux Φ^l_{in}. This heat flux follows from equ. 1 when m_s is replaced by the mass of the layer m^l. The heat flux of a sample without temperature gradient (this is a infinite thin sample) may be calculated from the heat flux of the layer with the highest temperature by

$$\Phi_{in}(t)=\Phi_{in}^{l_{max}}(t)\ \frac{m_s}{m^l}. \tag{3}$$

$\Phi^l_{in}(t)$ is a not smeared heat flux. This heat flux corresponds to the input function due to the theory of linear response.

Because of the heat flow paths in the sample and the heat transfer between DSC and sample the heat flux Φ^l_{in} will be smeared.

The output function $\Phi^l_{out}(t)$ is therefore the convolution integral of $\Phi^l_{in}(t)$ with the Green's function of the sample for this layer $A^l_s(t)$

$$\Phi^s_{out}(t) = A^l_s(t) * \Phi^l_{in}(t). \tag{4}$$

In this model $\Phi^l_{out}(t)$ of the sample is identical with the input function of the calorimeter.

Because of the different long heat flow paths inside the sample a different Green's function $A^l_s(t)$ must be attached to each layer.

In a sample however several layers contribute to the measured signal simultaneously. During a transition in a sample layers produce in different distances from the DSC at different times a signal $\Phi^l_{in,i}(t)$. The path of heat flow to each layer is different as well. That's why there is a specific Green's function $A^l_{s,i}(t)$ for each layer.

Since the signal transfer is carried out with the help of heat conduction, the signals of the single layers and the specific Green's functions are linear superpositionable [8]. We get for all i layers of the sample (i=1,2,3,...):

$$\Phi^s_{out}(t) = \sum_l A^l_{s,l}(t) * \Phi^l_{in,l}(t). \tag{5}$$

Generally a three dimensional temperature profile is built up in the sample. Therefore the masses of the layers and by that the magnitude of the corresponding heat fluxes will be different.

If the input function of the layers is normalized do to the layer mass in question than they distinguish only in a temporal shift: $\Delta t_i = t_i - t_0$. This time difference corresponds to the time which is necessary until the layers have the same temperature as the bottom layer of the sample had at the time t_0. Thus the specificated Green's function of one layer is given by

$$\Phi_{in}(t) = \frac{m^l}{m_s}(\delta(t-\Delta t_l) * \Phi^l_{in,l}(t)). \tag{6}$$

$\Phi_{in}(t)$ is identical for all layers and corresponds to the heat flux into an ideal sample without temperature profile.

Then eq. 4 can be written in the following form:

$$\Phi_{out}(t) = \Phi_{in}(t) * \sum_{i} \frac{m_i^l}{m_s} \left(A_{s,i}^l(t) * \delta(t-\Delta t_i)\right). \tag{7}$$

Where neither the mass of a single layers m_i^l nor the time difference Δt_i can be received from the experiment.

The Green's function of the whole sample is then:

$$A_s(t) = \sum_{i} \frac{m_i^l}{m_s} \left(A_{s,i}^l(t) * \delta(t-\Delta t_i)\right). \tag{8}$$

3.3. The smearing of measuring curves in a real system

In a real measuring system a smearing of the input function by the calorimeter and by the sample as well is found. In figure 4 this case is shown graphicly.

The input function is first smeared by the sample with the Green's function $A_s(t)$. The output function of this is simultaneously the input function of the calorimeter. After a smearing with the Green's function $A_{DSC}(t)$ the DSC-curve as the resulting output function of the total measuring system is received. The output function is then:

$$\Phi_{out}(t) = A_{DSC}(t) * \left(A_s(t) * \Phi_{in}(t)\right). \tag{9}$$

Due to the commutativity and associativity of the convolution operation the total Green's function is the convolution of the Green's function of the measuring device with the Green's function of the sample:

$$A(t) = A_{DSC}(t) * A_s(t) \tag{10}$$

It can be seen that due to the influence of the sample on the smearing the Green's function must be determined for each sample separately.

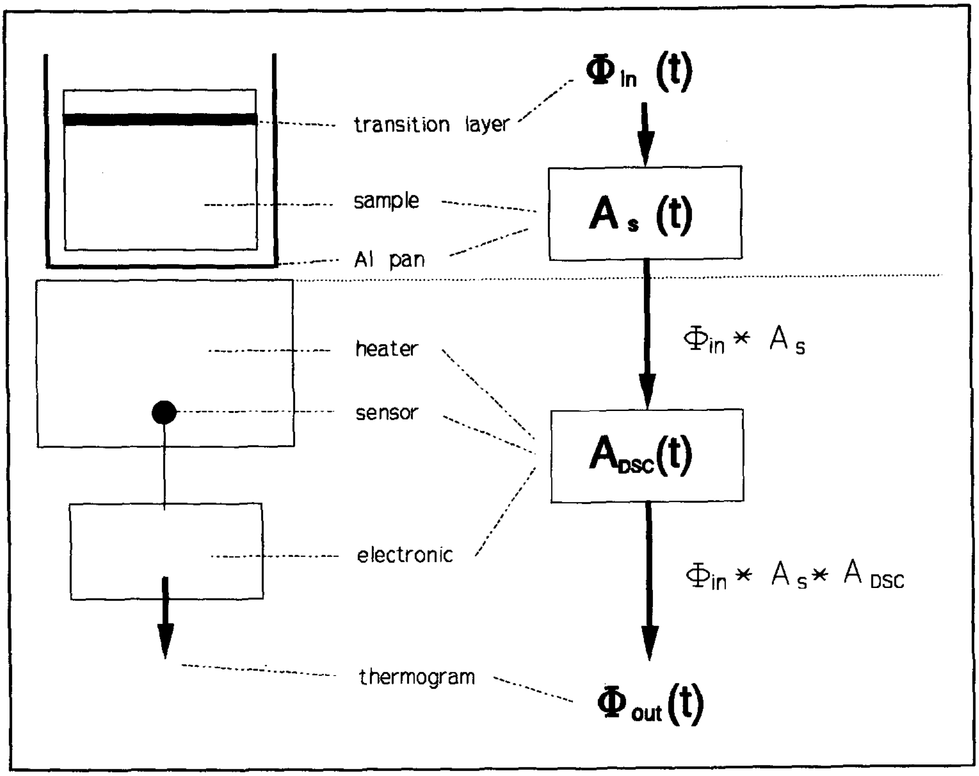

Figure 4. Origin of a Signal in a real calorimeter - sample - arrangement in the case of a single layer transition

4. ESTIMATION OF THE GREEN'S FUNCTION

The basically necessary problem in the desmearing consists in the determination of the Green's function. From eq. 2 follows, that it is possible to receive A(t) by solving the convolution integral if the input and output functions are known. The input function must be an as exact as possible defined signal of a single layer of the sample.

To determine A(t) such conditions have to be fulfilled, that "walking" layers can arise in the sample, which behave similar to those of the transition to be measured.

To simulate this condition often sharp heat pulses are used. The measured heat flux then corresponds to the Green's function.

One possibility is the thermal stimulation of the sample with a light flash [9]. The determination of A(t) is never the less connected to a rather large expenditure of devices. Furthermore the thermal conditions (and therefore the temperature profile) in the sample are incompatible to those of the scanning run of the DSC. In scanning mode the heat flow to the sample doesn't come from one side only. If the heat conductivity of aluminum of the sample pan is larger than that of the sample then heat flux into the sample will take place along the whole surface of the sample.

A better possibility to produce a definite input function can be derived from eq. 1. If the sample temperature is sufficiently far away from the transition temperature eq. 1 can be simplified to

$$\Phi(t) = m_s c_p(T)\beta . \tag{11}$$

It can be realized that a step like change of the temperature scanning rate β produces a definite input function $\Phi_{in}(t)$.

A requirement is the constance of c_p or possibility to extrapolate $c_p(T)$ from the measured curve. One way for producing a nearly step like change of β is the change from isothermal operation to scanning mode, as is the case at the beginning and at the end of each measurement.

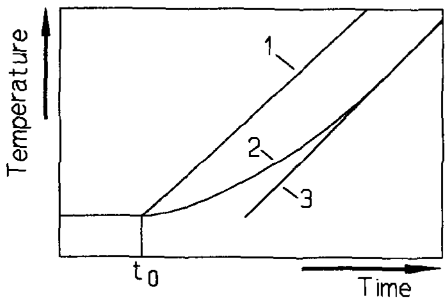

Figure 5. Temperature slop in the range of starting time of temperature scan t_0; 1- program temperature, 2- measuring temperature, 3- temperature slope in steady state

In following the behavior of the system DSC - sample arrangement at the switch on of the heating scan is investigated more exactly. The results can be used without restriction for all switch processes of the scanning rate β.

At the change from isothermal mode to a temperature scan of the calorimeter a faded bend in the curve is registered (s. figure 3).

At switching on, a temperature profile inside the sample is built up, which change the temperature in time retaining it's form and shape rather constant [7]. Thus "walking" layers inside the sample are formed.

The temperature gradient is driving force for the heat flux from the heater. The input function is given by eq. 11.

The smearing of the input function at scan rate change can be seen in the actual heating rate of the sample which, after switching on the temperature scan until steady state, is lower than the program heating rate (s. figure 5). The Green's function belonging to it is $A_{step}(t)$. Thereby a difference between sample and program temperature arises.

Now the case is considered, that the temperature profile doesn't change during a transition. Then $A_{step}(t)$ is equal to $A(t)$.

This assumption is valid for such transitions where heat capacity, density, and heat conductivity changes rather small and no transition enthalpies appear, as for instance at the glass transition and second order phase transition.

From the switch-on signal of the temperature scan the Green's function of the DSC with sample can be received by solving the convolution integral

$$\Phi_{out}(t) = \int_0^t S(t-\tau)\, A(\tau)\, d\tau . \tag{12}$$

S(t) is the input function due to the switching of the scan rate. For a DSC with a ideal step function in the scan rate S(t) reads:

$$S(t) = \theta(t-t_0) \cdot c_p(T) \cdot \beta_{pro} \cdot m_s . \tag{13}$$

$\theta(t-t_0)$ is the step function, β_{pro} the program heating rate , and t_0 the time of switching on the scan mode.

If the step like change of program scanning rate cannot be realized in a calorimeter the real change of actual program temperature voltage must be used for S(t).

If the transfer function is estimated from the switch off behavior, the temperature dependent change of c_p can be neglected. In that case also the heat transfer between heater and sample are in better agreement with the reality of transitions.

In this case for S(t) the normalized program voltage scan after switching off the dynamic operation is used.

With the Green's function obtained the convolution integral

$$\Phi_{out}(t) = \int_0^t A(t-\tau)\Phi_{in}(\tau)d\tau \tag{14}$$

can be solved for $\Phi_{in}(t)$. $\Phi_{in}(t)$ is the heat flux into the ideal sample without temperature gradient.

The Green's function depends indeed on temperature as well and should be determined near the transition temperature. It may be necessary for that reason to do this in a second run.

5. EXPERIMENTAL RESULTS

PVC samples with a mass of 2.396 mg and 49.948 mg have been measured in the temperature range from 450 K to 320 K with a cooling rate of -20 K/min. The measurements were carried out with a Perkin Elmer DSC-2. The DSC-curves are shown in fig. 6.

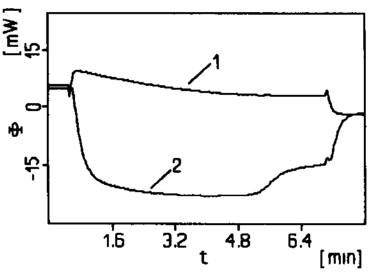

Figure 6. DSC-curves of PVC (cooling rate: -20 K/min;
1: m_s=2.396 mg; 2: m_s=49.948 mg)

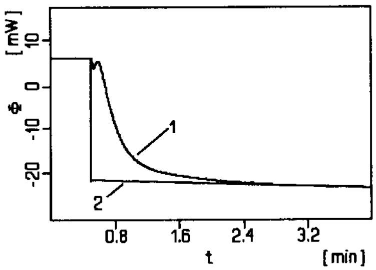

Figure 7. DSC-curve at step in switching on the temperature scan: 1;
step function S(t) at eq. 13: 2;
m_s=49,948 mg

In the $c_p(T)$-curves belonging to them (cf. fig.3) the glass transition is recognizable. Glass transition temperature and width of the glass transition $\Delta T = T_u - T_l$ depend on the mass of the sample (compare Table 1). T_l and T_u are that temperatures at which 16%

or 84% of the step high Δc_p are reached.Differences between the step heights are caused by the larger measuring uncertainty (noise) in the case of the smaller sample.

For determination of the Green's function the step of switching on the cooling scan has been used. For estimation of the function S(t) due to equ. 13 a linear extrapolation from the steady state to t_0 was carried out (s. fig. 7). In the considered temperature range (40 K) the temperature dependence of c_p can be assumed to be linear.

The calculation of the Green's function from the measured curve and the step function according to equ. 12 was performed by solving the integral equation in the given time range after discretisation and following regularization according to Tikhonov [10,11]. The numeric algorithm is described elsewhere [12].

In figure 8 the calculated Green's functions are shown. It is recognizable that these function disappear more quickly in the case of smaller samples. The smearing of DSC-curve is less because of the lower influence of the heat conductivity of the sample. (The Green's function of a non-smeared curve is the Dirac function.)

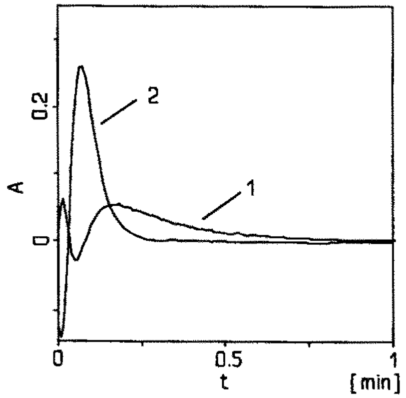

Figure 8. Green's function;
1: m_s=49.948 mg; 2: m_s=2.396 mg

The desmearing of the DSC-curve was carried out according to equ. 14 with the help of the named numeric algorithm.

For determination of the $c_p(T)$ curve a base line correction with a similar desmeared base line was used. The glass transition region of the desmeared curve is presented in figure 9. The appropriate values are listed in table 1.

The glass transition temperatures of both desmeared curves are recognizable to be in good agreement. Differences in the width of the glass transitions may point to a "overcompensation" in the desmearing of the heavy sample leading to a more narrow glass transition region. The reason of the overcompensation may lie in the large asymmetry between sample and reference during this measurement [6].

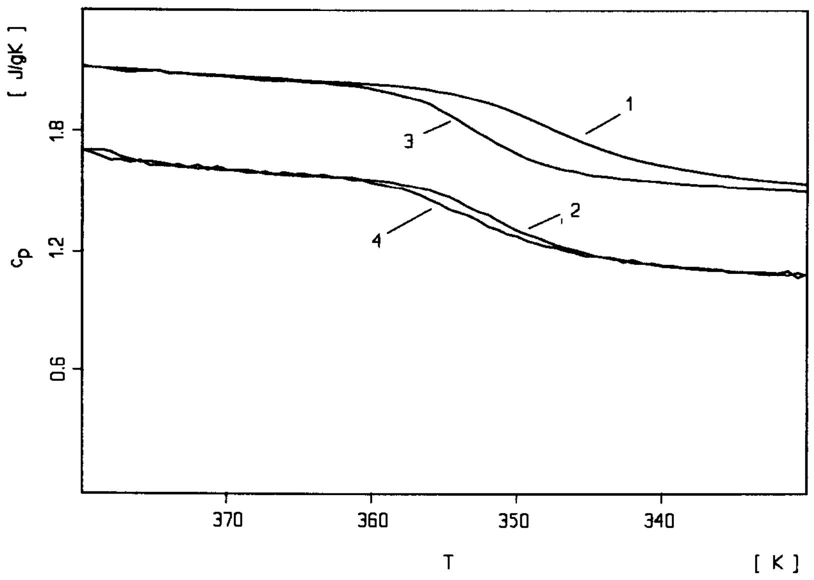

Figure 9. Measured (1,2) and desmeared (3,4) curves of the glass transition of PVC sample with different mass (1,3: m_s=49.948 mg and 2,4: m_s=2.396 mg); the curves 2 and 4 are shifted down by 0.45 J/gK

Table 1
Characteristic dates for the glass transition of the measured and desmeared DSC-curves of figure 9

		measured		desmeared	
m_s	[mg]	2.396	49.948	2.396	49.948
T_l	[K]	354.9	352.0	356.8	356.2
T_g	[K]	350.9	346.9	352.8	352.7
T_u	[K]	345.4	340.4	347.8	348.1
ΔT	[K]	9.5	11.6	9.0	8.1
Δc_p	[J/gK]	0.364	0.381	0.362	0.384

Summarizing it can be noticed, that with help of the represented method falsification (smearing) of the measured curve by reasons of heat conducton in sample and DSC can be corrected. The differences between the curves of a very light and very heavy sample are much less after the desmearing than they were in the measured curve. Cause of the remainding differences after desmearing is the simple calorimeter model used, in which the influence of the reference sample on the measured signal is neglected.

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