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Dynamic behaviour of power compensated differential scanning calorimeters.
Part 1. DSC as a linear system [1]

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Abstract

The power compensated differential scanning calorimetry (DSC) can be considered as a linear system to a first approximation. Thus the theory of linear response is applicable to describe the apparatus. An outline of this mathematical tool is given. It is shown how the apparatus and the sample and their thermal connection influence the output signal, and how to obtain the true heat flow from the measured curve with the aid of the Green's function of the apparatus and of the sample.

INTRODUCTION

Because the transport of heat needs time and the locations of the sample and of the probe are not identical, we always get a measured heat flow-time curve which essentially deviates from the true heat production or consumption rate of the sample. This holds especially in the case of dynamic calorimeters such as the differential scanning calorimeter (DSC) with a rather fast rate of temperature change. If the apparatus in question has a linear behaviour, it is in principle possible to calculate the true heat flow rate from the measured one. This procedure is often called "desmearing" in the literature. The tools for desmearing originate from the theory of linear response (TLR). For heat flux DSC the transport of heat to the sample is predominantly by heat conduction, which is indeed a linear process. Consequently desmearing of heat-flux DSC curves should be possible and has often been suggested in the literature; see, for example, refs. 1, 2.

Nevertheless a complete theory is not yet at hand. In the case of power compensated DSC the situation is complicated by the compensation

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control circuitry. It cannot be taken for granted that this active heat transport system follows linear response.

The aim of this series of papers is to explain the behaviour of power compensated DSC from a transmission theoretical point of view. In this paper we want to present the fundamental problems and the method in question. In further papers we intend to deal with the following: description of a power compensated DSC with the aid of TLR, including the influence of the control circuits and discussion of the Green's functions in question; discussion of the influence of material properties and their change during measurement on linearity of the power compensated DSC; experimental results on the influence of small changes of material properties on the measured curve; experimental verification of the theory of power compensated DSC in the case of glass transition measurements of polystyrene.

THE SMEARING PROCESS

In any dynamically working (i.e. temperature changing) apparatus there is non-homogeneous temperature distribution. Existing gradients cause heat flows. However enforced heat flows (e.g. by transitions within the sample) cause temperature gradients and thus change the temperature field. This is true for the measuring assembly and also for the sample. Depending on the temperature gradient in question, the transport of heat needs time while the temperature program of the dynamic calorimeter proceeds. As the temperature of the probe is enforced by the compensating controller to be nearly the set value of the temperature programme, the measured heat flow rate is that from the heaters, necessary to scan the probe temperature as desired. Obviously this is not the desired heat flow rate to the sample, measured as a function of sample temperature. The falsification (smearing) of the latter thus depends both on the properties of the heat transport path of the apparatus and on the sample properties.

The desmearing procedure thus has to be done in such a way that both influences will be removed. The influence of the sample on the measured curve is caused by the lag of the sample temperature related to the programme temperature and of course by the temperature profile within the sample. Both depend on sample properties (mass, thermal conductivity, surface coefficient of heat transfer, etc.) and on heating rate.

Furthermore we have to distinguish between desmearing in the following cases:

(i) steady state heating of a substance (with thermal effects), at which the lag and the profile of sample temperature do not change during the run;

(ii) heating of a sample with weak changes of capacity during the run yielding a weak change of the temperature profile and the lag (e.g. glass transition evaluation);

(iii) heating of a sample with first order transition during the run, which heavily influences the temperature-profile inside the sample. The temperature stops (at transitional temperature) in that layer where the transition takes place and the layer of transition slowly travels through the sample. With it the temperature profile and the smearing change continuously.

All these cases need different desmearing procedures, which can either be done one after the other or (in special cases) in one step at the same time.

POWER COMPENSATED DSC AS A LINEAR APPARATUS

In heat flux DSC transport of heat occurs mostly by conduction. This process can be described quantitatively by the heat conduction equation, which is a linear differential equation.

$$\frac{\partial^2 T}{\partial r^2}=\frac{\rho c_p}{\lambda}\cdot\frac{\partial T}{\partial t}$$

and

$$\frac{\mathrm{d}Q}{\mathrm{d}t}=\Phi=-A\cdot\lambda\cdot\frac{\partial T}{\partial r}$$

with

$$\frac{\partial^2 T}{\partial r^2}=\frac{\partial^2 T}{\partial x^2}+\frac{\partial^2 T}{\partial y^2}+\frac{\partial^2 T}{\partial z^2}$$

If it is supposed that the heat conductivity λ, density ρ and specific heat capacity c_p are nearly independent of temperature, transport of heat by conduction is a linear process and can be evaluated with the aid of TLR. However, heat transport by convection and radiation are non-linear processes. If these participate in calorimetric heat exchange, the linear behaviour is correspondingly disturbed. The DSC has to be designed so as to transport the heat to the sample by pure heat conduction rather than by other (consequently non-linear) processes. For heat flux DSC this demand is usually fulfilled in a first approximation, and thus this apparatus can be considered as a linear one.

In the case of power compensated DSC, sample and reference heaters are separated from each other and controlled by feedback amplifiers, usually with the aid of a proportional controller. Control and feedback systems used are linear equipment (TLR has been developed to describe such systems). The heat produced by the heater is than transported to the sample mainly by heat conduction. The sample or reference of the power compensated DSC is thus a interconnection of linear links. As every connection of linear devices remains linear likewise, the power compensated DSC should also be a linear system [3], but this conclusion can only be drawn if the twin arrangement is built very symmetrically. The problem is the highly non-linear connection of the sample and reference furnace to the isoperibol surroundings. Here the heat transport takes place principally by convection and radiation because of the large temperature differences between the furnaces and the cooling block. This non-linearity can only be neglected if it is strictly equal on both sample and reference side and thus vanishes in the differential signal. The power compensated DSC is as linear as it is symmetrically constructed.

Larger samples can influence the linearity as there are also heat transport processes within the sample. If the material properties (λ, ρ, c_p) change by an appreciable amount, the heat transport through the sample (e.g. due to a change of the temperature profile) is a non-linear process. Especially this is the case during phase transitions of the sample. In other words, a melting peak, for instance, is not allowed to be desmeared by deconvolution procedures, as the TLR cannot be applied. Besides this there will be no problems, in particular if the sample is rather small and the properties do not change greatly.

To sum up, the power compensated DSC operates as a linear combination of essentially linear links and is thus a linear apparatus in a first approximation. Consequently the TLR is in principal an adequate tool to describe its behaviour.

THEORY OF LINEAR RESPONSE AND ITS METHOD

An apparatus with linear behaviour can be considered as a black box. No knowledge about the internal construction is necessary to describe the output of the device on certain input events.

The background of this description is from TLR, which originates from the need to understand the transmitting properties of a rather complex line network. The outcome of this theory is that the output of any linear apparatus can be described as the convolution product of the input with the so called "Green's function" or "apparatus function" of that apparatus, or in mathematical terms

$$F_{\mathrm{out}}(t) = \int_{-\infty}^{\infty} F_{\mathrm{in}}(t') \cdot G(t-t')\,\mathrm{d}t' \equiv F_{\mathrm{in}}(t) * G(t) = G(t) * F_{\mathrm{in}}(t) \tag{1}$$

$F_{\mathrm{in}}(t)$ and $F_{\mathrm{out}}(t)$ being the input and output function respectively of the device in question with $G(t)$ as Green's function. In practice the time scale is chosen so that both $F(t)$ and $G(t)$ are zero for negative times.

The Green's function can easily be obtained, as it is the response of the apparatus to an impulse-like event. The output function following a step-like event (such as input function) is the integral of Green's function, as the following is valid:

$$\int_0^\infty F_{\text{out}}(t)\,\mathrm{d}t = \int_0^\infty F_{\text{in}}(t) * G(t)\,\mathrm{d}t = G(t) * \int_0^\infty F_{\text{in}}(t)\,\mathrm{d}t = F_{\text{in}}(t) * \int_0^\infty G(t)\,\mathrm{d}t \quad (2a)$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}F_{\text{out}}(t) = \frac{\mathrm{d}}{\mathrm{d}t}(F_{\text{in}}(t) * G(t)) = G(t) * \frac{\mathrm{d}}{\mathrm{d}t}F_{\text{in}}(t) = F_{\text{in}}(t) * \frac{\mathrm{d}}{\mathrm{d}t}G(t) \quad (2b)$$

Furthermore we have the distributive law

$$F_{\text{out}} = F_{\text{out1}} + F_{\text{out2}} = F_{\text{in1}} * G + F_{\text{in2}} * G = (F_{\text{in1}} + F_{\text{in2}}) * G \quad (3)$$

For an input function being a product of two functions the respective output function reads

$$F_{\text{out}} = (F_{\text{in1}} \cdot F_{\text{in2}}) * G \quad (4)$$

To calculate the behaviour of a network of different linear devices we need to calculate the Green's function from those of the components, and it is helpful to know that the Green's function of two devices connected in series is the convolution product of both Green's functions, whereas the Green's function of two parallel connected devices is the sum of those of the components. With this rule the Green's function of any network can be calculated if one has knowledge about the impulse (or step) response of the components.

Often it is easier to calculate the rather complicated integral equations (or equivalent differential equations) in Laplace- or Fourier-space [4]. One of the advantages is that the convolution product (eqn. (1)) transforms to a simple product in Fourier space (and vice versa).

The integral transforms named are, in the case of functions non-zero only for $t > 0$ defined as
Fourier transformation

$$\mathscr{F}(F(t)) = f(\omega) = \sqrt{\frac{1}{2\pi}}\int_0^\infty F(t)\mathrm{e}^{-\mathrm{i}\omega t}\,\mathrm{d}t \quad (5)$$

with $f(\omega)$ being a complex function of frequency ω.
Laplace transformation

$$\mathscr{L}(F(t)) = f(s) = \int_0^\infty F(t)\mathrm{e}^{-st}\,\mathrm{d}t \quad (6)$$

with $f(s)$ being a complex function of complex s.

Besides the factor in front of the integral, the Fourier transformation is a special Laplace transformation with $s = \mathrm{i}\omega$. The description of an apparatus with the aid of the Green's function in time space, or with its Fourier (or Laplace) transformed (the so called transfer function) in frequency space,

TABLE 1

Some useful rules and correspondences in TLR

Operation	Function in time space	Function in Laplace space
Summation	$c_1F_1(t)+c_2F_2(t)$	$c_1f_1(s)-c_2f_2(s)$
Product	$F_1(t)\cdot F_2(t)$	$f_1(s)*f_2(s)$
Convolution	$F_1(t)*F_2(t)$	$f_1(s)\cdot f_2(s)$
Integration	$\int F(\tau)\,\mathrm{d}\tau$	$1/s\cdot f(s)$
Differentiation	$\mathrm{d}/\mathrm{d}tF(t)$	$s\cdot f(s)-f(+0)$
Differentiation in Laplace space	$-t\cdot F(t)$	$\mathrm{d}/\mathrm{d}sf(s)$
Shift to the right	$F(t-t_0)$ [$t_0>0$; $F(t<0)=0$]	$\exp(-t_0s)f(s)$
Serial connection	$F_1(t)*F_2(t)$	$f_1(s)\cdot f_2(s)$
Parallel connection	$F_1(t)+F_2(t)$	$f_1(s)-f_2(s)$
Feedback via F_2		$f_1(s)/(1\pm f_1(s)f_2(s))$
Dirac function	$\delta(t)$	1
	$\delta(t-t_0)$	$\exp(-t_0s)$
Step function	$\Theta(t)$	$1/s$
	$\Theta(t-t_0)$	$1/s\exp(-t_0s)$
Exponential	$\exp(\alpha t)$	$1/(s-\alpha)$
	$t\cdot\exp(\alpha t)$	$1/(s-\alpha)^2$
	$1-\exp(-t/T)$	$1/(s\cdot(1+Ts))$
Trigonometric	$\cos(\omega t)$	$s/(s^2+\omega^2)$
	$\sin(\omega t)$	$\omega/(s^2+\omega^2)$
Hyperbolic	$\sinh(at)$	$a/(s^2-a^2)$
	$\cosh(at)$	$s/(s^2-a^2)$

is absolutely equivalent. Equation (1) reads in Fourier space

$$f_{\text{out}}(\omega)=f_{\text{in}}(\omega)\cdot g(\omega)$$

or in Laplace space

$$f_{\text{out}}(s)=f_{\text{in}}(s)\cdot g(s)$$

The convolution product transforms into a common product in both cases. It may be helpful to use Table 1 for translation of elementary functions.

APPLICATION OF THE THEORY OF LINEAR RESPONSE ON POWER COMPENSATED DSC

As shown above the power compensated DSC is a linear system to a first approximation. Thus the theory of linear response can be applied and we obtain from eqn. (1)

$$\Phi_{\text{out}}(t)=\Phi_{\text{in}}(t)*G(t) \tag{7}$$

where Φ_{out} is the measured heat flow rate, Φ_{in} the true heat production or consumption rate of the sample and $G(t)$ the Green's function of the total arrangement. As the apparatus and the sample are connected in series the total Green's function is the convolution product of that from the DSC and that from the sample.

$$G(t) = G_{\mathrm{DSC}}(t) * G_s(t) \tag{8}$$

The Green's function of the power compensated DSC will be studied in detail in Part II of this series [5]. Here we will have a look at the influence of the sample on its Green's function.

Unfortunately the Green's function of the sample is not as well defined as that from the apparatus, for it changes from sample to sample and with certain events (e.g. a transition). In the case of steady state conditions a stable temperature profile develops within the sample, such that every part of the sample raises its temperature with the heating rate β in question [6]

$$T(r, t) = T_{\mathrm{st}} + \beta \cdot t - \frac{\partial T}{\partial r} \cdot r \tag{9}$$

where T_{st} is the starting temperature, r the distance and $\partial T/\partial r$ the temperature gradient within the sample.

The sample is thought of as being subdivided into very small elements having a mass of m_i with a specific heat capacity $c_p(T)$. Then the heat flow rate into the element i, to heat it at a rate of β, reads

$$\Phi_i(T) = m_i \cdot c_p(T) \cdot \beta \tag{10}$$

As described above the heat transport may be considered as a linear phenomenon. Thus the signal transfer by heat conduction may be described with the aid of TLR, and the portion of the heat flow from the border of the DSC furnace to the element i of the sample reads

$$\Phi_{0,i}(T_0(t)) = \Phi_i(T_i(t)) * G_i(t) = m_i \cdot c_p(T_i(t)) \cdot \beta * G(t) \tag{11}$$

The left term of the equation is that part of the heat flow rate out of the furnace, which later flows as Φ_i into the element i.

The element i comes up to the furnace temperature later. The quantitative connection is given by eqn. (9) and the corresponding time delay of the element i in position at r_i reads

$$\tau_i = \frac{1}{\beta} \cdot \frac{\partial T}{\partial r} \cdot r_i$$

From eqn. (11) it follows that

$$\Phi_{0,i}(T_0(t)) = m_i \cdot c_p(T_i(t - \tau_i)) \cdot \beta * G_i(t)$$

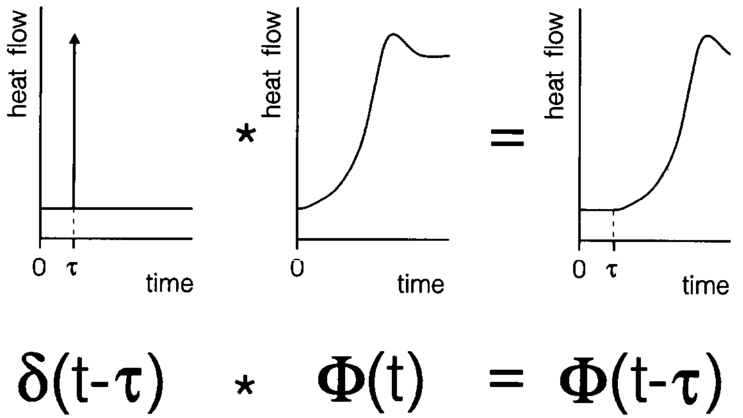

Fig. 1. The convolution of a function $\Phi(t)$ and a Dirac pulse with a delay τ as a "shift to the right" in time space.

or because of the connections demonstrated in Fig. 1 (for time shift behaviour see Table 1)

$$\Phi_{0,i}(T_0(t)) = m_i \cdot c_p(T_i(t)) \cdot \beta * \delta(t - \tau_i) * G_i(t) \tag{12}$$

To obtain the total heat flow of the furnace, we have to summarize eqn. (12) after expanding with m and collecting constant quantities

$$\begin{aligned} \Phi_{\text{out}}(T(t)) &= \sum_i \Phi_{0,i}(T_0(t)) \\ &= m \cdot C_p(T(t)) \cdot \beta * \sum_i \frac{m_i}{m} \cdot (\delta(t - \tau_i) * G_i(t)) \end{aligned} \tag{13}$$

If the subdivision of the sample is thought to be infinitesimally small, the sum becomes an integral and eqn. (13) reads

$$\Phi_{\text{out}}(T(t)) = m \cdot C_p(T(t)) \cdot \beta * \int_V (\delta(t - \tau_{\text{d}V}) * G_{\text{d}V}(t)) \frac{\text{d}V}{V} \tag{14}$$

As $m \cdot c_p(T(t)) \cdot \beta$ is the input function of a sample heated with a rate of β, we obtain from eqn. (14) the Green's function of an ideal coupled sample

$$G_{\text{s,id}}(t) = \int_V (\delta(t - \tau_{\text{d}V}) * G_{\text{d}V}(t)) \frac{\text{d}V}{V}$$

In reality the coupling of the sample to the DSC is not ideal and we have to include the Green's function of heat transfer G_{Tr}. We get the total Green's function of the real sample as a convolution product (because of the serial connection)

$$G_{\text{s}} = G_{\text{Tr}} * G_{\text{s,id}}$$

and the total Green's function of the arrangement (DSC and sample) reads

$$G(t) = G_{\mathrm{DSC}}(t) * G_{\mathrm{Tr}}(t) * \int_V (\delta(t - \tau_{\mathrm{d}V}) * G_{\mathrm{d}V}(t)) \frac{\mathrm{d}V}{V} \tag{15}$$

This equation shows that the Green's function of the sample depends on sample parameters and also on the heat transfer behaviour. Thus it changes from one experiment to the other, and with it the signal transmitting properties of the equipment. In serious situations the sample parameters, and with them the Green's function, can change greatly during one experiment.

DETERMINATION OF THE GREEN'S FUNCTION OF DSC

From TLR we learned that the Green's function on the one hand is the impulse answer and on the other hand the differentiated step answer of the arrangement in question. As a result there are two ways to determine it in the case of DSC: (i) measuring the response of the DSC according to a heat impulse inside the sample; (ii) differentiating the measured response of the DSC according to a step-like event within the sample. Both methods are used in practice. The impulse like event can be realized through the energy of a light flash absorbed by the sample pan (e.g. in a photocalorimeter) [7] or through the heat released during the sudden solidification of a heavily undercooled pure substance (mostly a metal sample) [8].

In the latter case there is a grave problem in determination of the exact moment of solidification, because of the unknown undercooling. As a consequence the beginning of the Green's function is unknown and may be shifted along the time axis. As a result the deconvoluted curve is not exactly fixed on the timescale, and thus the attached temperature is not the true one.

Another way of realization is to position a small resistor in place of the sample, and to produce a heat pulse with the aid of a current impulse. In the latter case the sample and heat transfer conditions have obviously been changed, and thus the corresponding part of the Green's function has changed, and is not measured correctly. The same is true for the other two realizations, but to a minor extent.

The method (ii) can be realized without this disadvantage. The input heat flow rate (within the sample) reads (eqn. (10))

$$\Phi_{\mathrm{in}} = mc_p\beta$$

Starting and ending a DSC run always implies the switching of the heating rate from zero to a constant value and vice versa. As a result the input heat flow Φ_{in} changes in a step-like manner and the measured heat flow ($\Phi_{\mathrm{out,step}}(t)$) caused by this event is the step response of the apparatus including the sample and its thermal coupling of the DSC [9].

Differentiating this function yields the Green's function written in eqn. (15)

$$G(t) = \frac{\mathrm{d}}{\mathrm{d}t} \Phi_{\mathrm{out,step}}$$

Switching the heating rate on and off can be done as often as necessary during every run at any temperature and we can easily obtain the true Green's function at any moment of the experiment. This step response Green's function (G_{sr}) contains both the influence of the apparatus and of the sample and its connection.

CONCLUSIONS

The power compensated DSC is, in a first approximation, a linear system if it is constructed very symmetrically. Thus the theory of linear response is to be applied for theoretical description. The Green's function of the complex measuring equipment depends on the DSC apparatus, and also on the sample and its thermal connection.

Changing sample parameters also change the Green's function. Large changes of sample parameters (e.g. during phase transition) disturb linearity. As a consequence a desmearing of transition or reaction peaks with the aid of TLS is not possible.

Otherwise desmearing by deconvolution is allowed. The Green's function can be deduced from the response of the equipment on impulse-like, or step-like, events. The former method is usually not possible without changes of the sample or other intervention into the measurement, whereas the step response can be obtained from the heat flow signal after switching on and off the heating rate without any disturbances of the apparatus.

In the next paper in this series [5], further details of the theory of power compensated DSC will be given. The following papers will show the influences of sample parameters and represent experimental verification of the theory.

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