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The analysis of temperature modulated DSC measurements by means of the linear response theory

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Abstract

A consistent description of temperature modulated differential scanning calorimeter (TM–DSC) curves based on irreversible thermodynamics is presented within the scope of the validity of the linear response approximation. Both time-independent and time-dependent processes are included. For time-dependent (linear) processes, the heat flow rate is connected to the convolution integral. This results in a generalized heat capacity which is frequency dependent and, on principle, a complex function of it.

Keywords: Heat capacity; Linear response; Temperature modulated DSC.

1. Introduction

In 1992, conventional DSC was extended with temperature modulation (TM–DSC) by Reading and coworkers [1–4]. With the introduction of this technique, DSC was available for new applications. In our opinion, the extension of the experimental parameters with the frequency is especially important.

The new technique consists of the superposition of the conventional temperature program of a DSC with a periodical temperature change and the measurement of the resulting heat flow rate. For data evaluation, two different procedures are known: separation of the "reversing" and "non- reversing" components [1], and the determination of "storage" and "loss" heat capacity [5,6]. At present, problems exist due to the interpretation of some results. The reason for this is that up until now, there has been no self-consistent theory for the evaluation of the measured curves, that is based on the

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general principles of thermodynamics. A first attempt is published in Ref. [5], but a direct connection to the laws of thermodynamics is lacking and the representation is relatively general. This may have led to some misunderstandings [7]. Here we will give a more detailed representaion of the theoretical background of TM–DSC measurements. However, we have to distinguish between time-dependent and time-independent processes or transitions of the sample and, in addition, those that react to rather small periodical temperature changes and those where the influence is so small that it cannot be measured. The latter are often processes which are thermally activated, but take place far from equilibrium. As a result, we are able to describe essential experimental results from both conventional DSC and TM–DSC measurements.

2. Theoretical background

In the case of TM–DSC, the sample response, i.e. the heat flow rate, is measured after a periodical stimulation, i.e. a temperature change. Such measurements are especially interesting if the measured process is time dependent and the characterstic intrinsic time τ is of the same order of magnitude as the period t_p (with $\tau \approx t_p/2\pi$) of the temperature change. To get the maximum amount of information, the measurements should be carried out in as wide as possible frequency and temperature ranges. The influence of heat transfer (as one time-dependent phenomenon) must not be neglected; consequently heat transfer effects require a special procedure of correction and calibration which has been published elsewhere [8,9]. For simplification, we shall concentrate here on the thermal events of the sample. The measured curves are, strictly speaking, regarded as having been corrected due to heat transfer influences (desmeared).

This attempt at a consistent description of the measured curves is based on general principles of thermodynamics. The definition of new ideas or concepts shall, if possible, be avoided. A general theory of TM–DSC must be non-linear, and thus very complex. A more simple approximation is a linear theory. Special cases of this are the time-independent approach (reversible thermodynamics) and the "classical" description of time-dependent processes (kinetics) in conventional DSCs. In this paper we focus on the linear case.

2.1. TM–DSC and reversible thermodynamics

Reversible thermodynamics is, by definition, not able to describe time-dependent processes. It characterizes any system by thermodynamic potentials, which are functions of temperature, pressure and the other variables of state. None of these quantities is thought to be a function of time, and all the processes are assumed to be very slow. In this case the second law of thermodynamics reads

$$\mathrm{d}S = \frac{\delta Q}{T} \tag{1}$$

where $\mathrm{d}S$ is the entropy change and δQ the exchanged heat.

With the degree of reaction α (as an additional variable), the total differential of enthalpy reads

$$\mathrm{d}H = \left(\frac{\partial H}{\partial p}\right)_{T,\alpha} \mathrm{d}p + \left(\frac{\partial H}{\partial T}\right)_{p,\alpha} \mathrm{d}T + \left(\frac{\partial H}{\partial \alpha}\right)_{p,T} \mathrm{d}\alpha \tag{2}$$

If we formally define a generalized (isobaric) heat capacity C as

$$C(T) = \left(\frac{\mathrm{d}H}{\mathrm{d}T}\right)_p \tag{3}$$

we get from Eq.(2) at constant pressure

$$C(T) = C_p(T) + H_r \frac{\mathrm{d}\alpha}{\mathrm{d}T} \tag{4}$$

where C_p is the usual heat capacity at constant pressure and H_r the partial enthalpy of reaction (which is practically temperature-independent.). We prefer this representation, because in DSC practice the result of a measurement is often normalized to values in units of a specific heat capacity (J g^{-1} K^{-1}). The measured enthalpy change then reads

$$\mathrm{d}H = C(T)\mathrm{d}T + H_r \mathrm{d}\alpha(T) \tag{5}$$

This equation is valid for temperature changes $\mathrm{d}T(t)$ too, if the reaction is so fast that the system is always in equilibrium in relation to the temperature change; in other words, the measured signal is in phase with $\mathrm{d}T(t)$. For DSC, this means that there must not be any smearing of the measured signal by heat transport and reaction kinetics.

Under these circumstances, the heat flow rate into the sample, i.e. the DSC curve with the empty pan curve subtracted, is

$$\Phi(T(t)) = \frac{\mathrm{d}H}{\mathrm{d}t} = C(T)\beta(t) = \left(C_p(T) + H_r \frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\beta(t) = C_p(T)\beta(t) + \Phi_r(T(t)) \tag{6}$$

where Φ_r is the heat flow of the reaction

$$\Phi_r = H_r \frac{\mathrm{d}\alpha}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t} \tag{7}$$

and β is the rate of temperature change

$$\beta(t) = \frac{\mathrm{d}T}{\mathrm{d}t} \tag{8}$$

which in the case of TM–DSC reads

$$\beta(t) = \beta_0 + \omega_0 T_a \cos \omega_0 t \tag{9}$$

with β_0 the underlying heating rate, T_a the temperature amplitude and $\omega_0 = 2\pi/t_p = 2\pi f_0$ (f_0 the frequency, t_p the period).

Inserting Eq. (9) into Eq. (6) gives the TM–DSC curve for such processes. The result depends on the temperature dependence of α, which may be written as

$$\alpha(T) = \alpha_0 + a_\alpha T + b_\alpha T^2 + \ldots \tag{10}$$

If the temperature interval of the modulation ($T - T_a$ to $T + T_a$) is small enough, we start from the linear approximation of Eq. (9) and neglect the change in Φ_r for the periodic part of the signal (T_a can always be chosen so small that $a_\alpha T_a \approx 0$). Then it follows from Eq. (6) that

$$\Phi(t) = (C_p(T_u)\beta_0 + \Phi_r(T_u)) + C_p(T_u)\omega_0 T_a \cos \omega_0 t \tag{11}$$

with $T_u = T_0 + \beta_0 t$.

We emphasize that this equation is only valid for sufficiently small temperature amplitudes T_a. The terms in parentheses reproduce the conventional DSC curve. The additional periodic component of the signal is in phase with the temperature change rate β.

In the case of larger temperature amplitudes, the product $a_\alpha T_a$ can not be neglected and we get

$$\Phi(t) = (C_p(T_u)\beta_0 + \Phi_r(T_u)) + (C_p(T_u) + H_r a_\alpha)\omega_0 T_a \cos(\omega_0 t) \tag{12}$$

For even larger temperature amplitudes T_a, the quadratic term in Eq. (10) must also be included

$$\begin{aligned}\Phi(t) = {} & (C_p(T_u)\beta_0 + \Phi_r(T_u)) + (C_p(T_u) + H_r a_\alpha)\omega_0 T_a \cos(\omega_0 t) \\ & + H_r b_\alpha \omega_0 T_a^2 \sin(2\omega_0 t)\end{aligned} \tag{13}$$

In this case, higher harmonics appear in the periodic component of the measured signal. Eqs. (12) or (13) are valid even for small temperature amplitudes and large underlying heating rates where the relevant temperature interval becomes ($T - T_a$ to $T + T_a + \beta_0 t_p$).

From this consideration it follows that the measurements should be carried out under conditions such that Eq. (11) is valid, only in this case C_p can be determined from the periodic part, and an easy separation of the underlaying part into the C_p component and the reaction enthalpy is possible. This is true for sufficiently low temperature amplitudes and thermal events which do not explicitly depend on time. In this case all properties determined from the periodic component are frequency-independent. Phase shifts, if found in measurements, cannot be interpreted within the scope of this approach.

The separation of the measured signal into reaction heat flow and underlying C_p change is possible in a similar way for those time-dependent (kinetically hindered) reactions which have a weak temperature dependence. The influence of the underlying heating rate and the temperature amplitude of the periodic part on the measured curve are the same as above. One example for such a reaction is the "cold crystallization" of PET [10]. Even in this case we find non-linear distortions in the measured signal if we use too large a temperature amplitude or too large as underlying heating rate [11].

However, frequency-dependent processes, e.g. the glass transition [11,12] and the melting of polymers, as first experimental results suggest [11,13], can not be interpreted in this manner. For this type of time-dependent function, we must use another approach.

2.2 TM-DSC signal in the case of time-dependent processes

If the kinetics of the reaction cannot be neglected, the process is explicitly time-dependent and the properties used to describe such processes are function of time. The theoretical background for this is irreversible thermodynamics rather than equilibrium thermodynamics. We shall discuss linear processes below; from the theoretical point of view, these are the simplest time-dependent processes. (This includes such processes, which although not linear, can be linearized under special conditions.) The results presented in Section 2.1 are then a special case of this description.

2.2.1. On the thermodynamics of time-dependent processes

The discussion of linear time-dependent processes is presented in detail in textbooks of irreversible thermodynamics [14–16].

A time-dependent process is always a non-equilibrium process. The second law of thermodynamics in this case reads

$$\mathrm{d}S > \frac{\delta Q}{T} \quad \text{with} \quad \mathrm{d}S = \mathrm{d_e}S + \mathrm{d_i}S \tag{14}$$

where $\mathrm{d_e}S$ is the entropy change of the system due to exchange of heat and $\mathrm{d_i}S$ the additional internal entropy change due to the irreversible processes. For a description of $\mathrm{d}_i S$ we have to introduce a time-dependent macroscopic variable $\zeta(t)$ which describes the distance of the system from equilibrium as an additional internal degree of freedom [16]. The total differential of enthalpy in this case reads

$$\mathrm{d}H = \left(\frac{\partial H}{\partial p}\right)_{T,\zeta} \mathrm{d}p + \left(\frac{\partial H}{\partial T}\right)_{p,\zeta} \mathrm{d}T + \left(\frac{\partial H}{\partial \zeta}\right)_{T,p} \mathrm{d}\zeta(t) \tag{15}$$

The variable α (degree of reaction) of thermally activated reactions may be formally treated as one ζ and the equilibrium reaction of Section 2.1 is then a special case of no time dependence.).The generalized heat capacity C at constant pressure (cf. Eq. (3) is now

$$\left(\frac{\mathrm{d}H}{\mathrm{d}T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_{p,\zeta} + \left(\frac{\partial H}{\partial \zeta}\right)_{p,T} \left(\frac{\mathrm{d}\zeta(t)}{\mathrm{d}T}\right)_p \tag{16}$$

which can be written as

$$C(T,t) = C_{\mathrm{st}}(T) + C_{\mathrm{dyn}}(T,t) \tag{17}$$

The toal heat capacity is the sum of a static (time-independent) heat capacity, C_{st}, at a certain ζ, and a dynamic (time-dependent)heat capacity, C_{dyn}. The latter corresponds to the heat flow of the process of the system from a non-equilibrium to an equilibrium state (characterized by the change in ζ).

In the case of processes far from the equilibrium, $\zeta(t)$is barely influenced by small temperature changes $\mathrm{d}T$ (from the periodic component) and the description of Section 2.1 may be used. The new additional variable $\zeta(t)$ provides special theories for the process in question, e.g. a special theory for the transition (or reaction), or a free volume theory for the glass transition. If several independent processes occur in the sample, we have one additional variable $\zeta_n(t)$ for each process

$$C_{\mathrm{dyn}}(T,t)=\sum_n\left(\frac{\partial H}{\partial \zeta_n}\right)_{p,T,\zeta_{n\neq m}}\left(\frac{\mathrm{d}\zeta_n}{\mathrm{d}T}\right)_{p,\zeta_{n\neq m}} \tag{18}$$

A special situation occurs if two processes take place, one close to and the other far from equilibrium; C_{dyn} reads

$$C_{\mathrm{dyn}}(t)=C_d(t)+\Delta_\zeta\frac{\mathrm{d}\zeta(t)}{\mathrm{d}T} \tag{19}$$

where C_{d} is the time-dependent part of the dynamic heat capacity describing the linear process (close to equilibrium) and the second term describes the far-from-equilibrium reaction characterized by $\zeta(t)$ and Δ_ζ with

$$\Delta_\zeta=\left(\frac{\partial H}{\partial \zeta}\right)_{p,T} \tag{20}$$

This quantity is assumed to be independent of small temperature changes and does not react on temperature modulation, to a first approximation.

First we look at linear processes close to equilibrium characterized by C_d. In this case the dynamic heat capacity reads

$$C_{\mathrm{dyn}}=C_{\mathrm{d}} \tag{21}$$

For such processes, the time course of the enthalpy change depends on the time the sample has been at another temperature T_l before. To explain the connection, we describe the reaction of the system on small step-like temperature changes ΔT for a quasi-isothermal process. If such a temperature change occurs at the moment t_0, the enthalpy change may be written as

$$\Delta H(t,T)=C_{\mathrm{st}}(T)\Theta(t-t_0)\Delta T+C_{\mathrm{d}}(t-t_0)\Theta(t\text{-}t_0)\Delta T \tag{22}$$

where Θ is the "step function". If a step change is repeated at every $t_n=t_0+n\Delta t$ ($n=0,1,2,\ldots$), the respective enthalpy change depends on the time the sample was at the previous temperature and the total change is the superposition of all the individual responses

$$\Delta H(t)=\sum_n(C_{\mathrm{st}}(T)+C_{\mathrm{d}}(t-t_n))\Delta T\Theta(t-t_n)=\sum_n C(T,t-t_n)\Delta T(t_n) \tag{23}$$

Integration and approaching $\Delta t\to 0$ yields the convolution integral

$$\int_0^t\Delta H(t)\mathrm{d}t=\lim_{\Delta t\to 0}\sum_n C(T,t-t_n)\Delta T(t_n)\Delta t=\int_0^t C(T,t-t')\Delta T(t')\mathrm{d}t' \tag{24}$$

Fom that it follows that

$$\Delta H(T,t)=\frac{\mathrm{d}}{\mathrm{d}t}\int_0^t C(T,t-t')\Delta T(t')\mathrm{d}t' \tag{25}$$

This relationship is valid for non-isothermal experiments as well.

Only in the case of time-independent processes or processes that do not react on temperature modulation, does the convolution integral transform into the usual product corresponding to Eq. (5). If processes far from equilibrium are included, the total generalized heat capacity reads (Eqs. (17), (19))

$$C = C_{\mathrm{st}} + C_{\mathrm{dyn}} = C_{\mathrm{st}} + C_{\mathrm{d}} + \Delta_\zeta \frac{\mathrm{d}\zeta}{\mathrm{d}T} \tag{26}$$

and Eq. (25) may be written

$$\begin{aligned}\Delta H(t) &= \int_0^t C(t-t')\beta(t')\mathrm{d}t' = C_{\mathrm{st}}(T)\Delta T(t) + \int_0^t C_{\mathrm{dyn}}(t-t')\beta(t')\mathrm{d}t' \\ &= C_{\mathrm{st}}(T)\Delta T(t) + \int_0^t \dot{C}(t-t')\Delta T(t')\mathrm{d}t'\end{aligned} \tag{27}$$

where $\dot{C}_{\mathrm{dyn}}$ is the same as $\dot{C}$, because $\dot{C}_{\mathrm{st}} = 0$. (The dots denote the first derivation with time). For the heat flow

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \Phi(t) = C_{\mathrm{st}}(T)\beta(t) + \int_0^t \dot{C}(t-t')\beta(t')\mathrm{d}t' \tag{28}$$

If the $\zeta(t)$ function is not influenced by the small modulation temperature change ΔT, or if the process in question is much slower or faster than $\Delta T(t)$, the respective term can be integrated separately and we get

$$\Phi(t) = C_{\mathrm{st}}(T)\beta(t) + \Phi_\zeta(t) + \int_0^t \dot{C}_{\mathrm{d}}(t-t')\beta(t')\mathrm{d}t' \tag{29}$$

where Φ_ζ is that part of the heat flow rate which is caused by the process characterized by ζ but not influenced by the small temperature modulation

$$\Phi\zeta(t) = \Delta_\zeta \frac{\mathrm{d}\zeta(t)}{\mathrm{d}t} \tag{30}$$

The first two terms of Eq. (29) correspond to the result in the case of equilibrium (Eq. (6)) but are now also valid for slow irreversible processes far from equilibrium. This part of Eq. (29) is described in Refs. [1–4,7]. The third term must be included for all other (linear) time-dependent processes.

2.2.2. The underlying component of the TM–DSC curves

The underlying part of the signal results from inserting the corresponding part of the temperature program

$$T_u(t) = T_0 + \beta_0\, t \tag{31}$$

into Eq. (27), or the constant heating rate β_0 into Eq. (28)

$$\begin{aligned}\Phi_{\mathrm{u}}(t, T) &= C_{\mathrm{st}}(T)\beta_0 + \Phi_\zeta(t, T) + C_{\mathrm{d}}(t, T)\beta_0 \\ &= \left(C_{\mathrm{st}}(T) + \Delta_\zeta \frac{\mathrm{d}\zeta(t, T)}{\mathrm{d}T} + C_{\mathrm{d}}(t, T)\right)\beta_0 = C(t, T)\beta_0\end{aligned} \tag{32}$$

The result of Eq. (32), where the underlying heat flow rate is described as the product of a generalized heat capacity and the underlying heating rate, is only formal. For known functions of $\zeta(T, t)$ and $C_d(T, t)$, the generalized heat capacity depends on the scanning rate β_0

$$\Phi_u(t) = C_\beta(t, T)\beta_0 \tag{33}$$

This is well known from chemical reactions, glass transition, recrystallization or melting which gives different results at different scanning rates (disregarding the additional effects due to the thermal inertia). Eq. (33) describes, of course, conventional DSC curves as well.

2.2.3. The periodic component of the TM-DSC curves

In the case of TM-DSC, the constant heating rate is superimposed with a periodic temperature change. The periodic part is

$$T_p(t) = T_a \sin \omega_0 t \tag{34}$$

with T_a the temperature amplitude and ω_0 the angular frequency. For the corresponding part of the heating rate, it follows that

$$\beta_p(t) = \omega_0 T_a \cos \omega_0 t \tag{35}$$

For not too large scanning rates β_0, the measured signal Φ can be separated into the underlying component Φ_u (corresponding to the conventional DSC signal) and the periodic component Φ_p. The underlying component Φ_u is given in Eqs. (32) and (33). To calculate the periodic component Φ_p, β_p of Eq. (35) has to be inserted instead of β into Eq. (28)

$$\Phi_p(t) = C_{st}\beta_p(t) + \int_0^t \dot{C}(t - t')\beta_p(t')\mathrm{d}t' \tag{36}$$

To solve the convolution integral in this equation, it is useful to apply the Fourier transform

$$\Phi(\omega) = \mathscr{F}(\Phi(t)) \equiv \int_0^\infty \Phi(t)\mathrm{e}^{-i\omega t}\mathrm{d}t \tag{37}$$

$$\Phi(t) = \mathscr{F}^{-1}(\Phi(\omega)) \equiv \frac{1}{2\pi}\int_0^\infty \Phi(\omega)\mathrm{e}^{i\omega t}\mathrm{d}\omega \tag{38}$$

The convolution integral transforms into a simple product in Fourier space. As Φ_ζ(cf. Eq. (30)) is usually very weakly influenced by a small temperature amplitude, it makes no contribution to the periodic component of the signal (cf. Section 2.1) and Eq. (36) reads, in Fourier space

$$\Phi_p(\omega) = C_{st}(T)\beta_p(\omega) = C_d(\omega)\beta_p(\omega) \tag{39}$$

The dynamic part of the heat capacity $C_d(\omega)$ is defined by

$$C_d(\omega) = \int_0^\infty \dot{C}_d(t)e^{-i\omega t}dt \tag{40}$$

Because $C_d(t)$, by definition, is a real function, $C_d(\omega)$ must be complex

$$C_d(\omega) = C'_d(\omega) - iC''_d(\omega) \tag{41}$$

(The unusual negative definition of the imaginary part follows from the principle of causality: the reaction of the system on any temperature change can only occur later in time.)

Inserting Eqs. (35) and (41) into Eq. (39) yields for the periodic component

$$\begin{aligned}\Phi_p(\omega) &= \omega_0 T_a((C'_d(\omega) - iC''(\omega))\pi\delta(\omega-\omega_0) + C_{st}(T)\pi\delta(\omega-\omega_0))\\ &= \omega_0 T_a(\pi\delta(\omega-\omega_0)(C'_d(\omega_0) + C_{st}(T)) - i\pi\delta(\omega-\omega_0)C''(\omega_0))\\ &= \omega_0 T_a(\pi\delta(\omega-\omega_0)C'(\omega_0) - i\pi\delta(\omega-\omega_0)C''(\omega_0))\end{aligned} \tag{42}$$

where $\delta(\omega-\omega_0)$ is the Dirac function. The heat capacity $C(\omega)$ is thus

$$C(\omega) = C'(\omega) - iC''(\omega) = (C_{st} + C'_d(\omega)) - iC''_d(\omega) \tag{43}$$

We designate the real part C' as "storage heat capacity" and the imaginary part C'' as "loss heat capacity". As can be seen, time-dependent processes contribute to the imaginary part. The Fourier retransform yields the measured periodic component

$$\begin{aligned}\Phi_p(t) &= \omega_0 T_a(C'(\omega_0)\cos\omega_0 t - C''(\omega_0)\sin\omega_0 t)\\ &= \omega_0 T_a|C(\omega_0)|\cos(\omega_0 t - \varphi)\end{aligned} \tag{44}$$

The modulus of the compex heat capacity reads

$$|C(\omega, T)| = \sqrt{C'(\omega, T)^2 + C''(\omega, T)^2} \tag{45}$$

One result of this calculation is that the amplitude of the periodic component is a function of the frequency. This is in agreement with experimental results from the glass transition process and polymer melting [12–14].

The complete measured signal is the sum of Eqs. (28) and (44). The storage heat capacity C' and the loss heat capacity C'' can be determined from it. In Section 2.1, we discussed the time-independent heat capacity C. This propery contains information related to the degrees of freedom of the molecular motions. This information is included in the real part C' of the complex heat capacity in the case of time-dependent processes. It may be frequency-dependent. To interpret the loss heat capacity C'', we have to discuss the generalized work of dissipation W_{diss} which is connected to the entropy change d_iS (Eq. (14))

$$dW_{diss} = T d_iS \tag{46}$$

It can be shown that

$$W_{diss}(\omega_0) = \pi T_a C''(\omega_0) \tag{47}$$

So the loss heat capacity is proportional to the work of dissipation and thus connected to the entropy production d_iS. In the case of glass transition, for example, this entropy change is connected to the influence of the specific cooperative movements in the liquid on the heat flow at the given temperature and frequency (see Refs. [5,12]). Finally, we consider the toal measuring signal of an TM–DSC. With the underlying component from Eq. (33) and the periodic component from Eq. (44), for the total heat flow rate we get

$$\begin{aligned}\Phi(t) &= ((C_{\mathrm{st}}(T) + C_{\mathrm{d}}(T_{\mathrm{u}}, t, \beta_0))\beta_0 + \Phi_\zeta(T_{\mathrm{u}}, t, \beta_0)) \\ &\quad + \omega_0 T_{\mathrm{a}} |C(T_{\mathrm{u}}, \omega_0)| \cos(\omega_0 t - \varphi(T_{\mathrm{u}}, \omega_0)) \\ &= C_\beta \beta_0 + \omega_0 T_{\mathrm{a}} |C| \cos(\omega_0 t - \varphi) \qquad (48)\end{aligned}$$

Time-dependent reactions far from equilibrium influence only the underlying component. The static heat capacity in the conventional DSC curve which is usually covered with the reaction enthalpy can be estimated from the periodic component. If the result is frequency-independent, it can be used as a baseline for the reaction peak in the underlying component. Cold crystallization and curing reactions are examples for such reactions. The essential phenomena of such processes, however, have already been described in Eqs. (11)–(13). It is possible to calculate the shift of the peak temperature with respect to the underlying scanning rate of such reactions.

3. Conclusion

A description of TM–DSC curves by means of thermodynamics is advantageous for a more certain interpretation of the experimental results. The introduction of additional internal variables is necessary. Knowledge of a concrete theory for the investigated thermal event and thus the ζ function makes an experimental check of this theory possible.

Furthermore, we can show that by using reversible thermodynamics for the description of the measured curves, experimental results, as the influence of the temperature amplitude on the measured curve in the cold crystallization region [10,11] or nonlinearities in the transition region [17], can be described. Temperature-dependent functions are, however, necessary to understand the separation of the measured curve into the conventional heat capacity and a part connected with the reaction enthalpy change. If the reactions, however, are frequency-dependent, the investigated results are only describable by means of (time-dependent) irreversible thermodynamics. The simplest way to succeed is to use the linear response theory. In this case the enthalpy change can be described as the convolution integral of the generalized heat capacity and the temperature change rate. The behaviour of the sample is reflected in the storage heat capacity C' and the loss heat capacity C''. The latter is connected to the entropy production in the system. This approach is valid for the calculation of both the conventional DSC and the TM–DSC signal. The description of time-independent reactions is a special case of this linear response approach.

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